This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

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

A Method of Cobalt Ion Concentration from Dilute Aqueous Solutions

Elisavet Amanatidou[a]; Mariana N. Stefanut[b]; Adrian Grozav[b]
[a] TECHNOLOGICAL EDUCATION INSTITUTE KILA KOZANIS, GREECE [b] INSTITUTE FOR CHEMICAL AND TECHNOLOGICAL SCIENCES BOCSEI NO. 6, TIMISOARA

To cite this Article Amanatidou, Elisavet , Stefanut, Mariana N. and Grozav, Adrian(1996) 'A Method of Cobalt Ion Concentration from Dilute Aqueous Solutions', Separation Science and Technology, 31: 5, 655 — 664

To link to this Article: DOI: 10.1080/01496399608000710

URL: http://dx.doi.org/10.1080/01496399608000710

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, 31(5), pp. 655–664, 1996

A Method of Cobalt Ion Concentration from Dilute Aqueous Solutions

ELISAVET AMANATIDOU
TECHNOLOGICAL EDUCATION INSTITUTE
KILA KOZANIS, 50100, GREECE

MARIANA N. STEFANUT and ADRIAN GROZAV
INSTITUTE FOR CHEMICAL AND TECHNOLOGICAL SCIENCES
BOCSEI NO. 6, 1900 TIMISOARA, ROMANIA

ABSTRACT

The liquid membrane technique is very useful for metal ions recovery from dilute solutions. Co^{2+} ions can be removed and concentrated from wastewaters with an emulsion liquid membrane. The paper describes the permeation of Co^{2+} using naphthenic acids as the carrier and kerosene as the membrane material. The inner phase is a HCl 3.162×10^{-4} solution. The extraction yield is more than 96%.

INTRODUCTION

Metal ion concentration from wastewater by classic solvent extraction involves in one or more steps the double process of extraction–reextraction. Contaminants at levels of only hundreds of parts per million can be concentrated by using an emulsion liquid membrane. This technique is widely applied in the metallurgic industry (1, 2), the alkaline and alkaline earth metal industry (3, 4), as well as in the treatment of radioactive wastewater (5, 6).

Metal ion separation by emulsion liquid membranes may be achieved by a carrier which reversibly reacts with the permeating species to form an intermediate able to diffuse across the membrane. The metal ions are released into the internal phase, and the free carrier returns to the external interface and restarts the cycle.

For instance, in liquid-phase oxidation processes for obtaining phenol, cyclohexanol, acetic acid, terephthalic acid, phthalic anhydride, etc. in the presence of Co^{2+} and Mn^{2+} salts as catalysts, wastewater containing Co^{2+} and Mn^{2+} results.

Application of the liquid membrane process for the recovery and concentration of Co^{2+} leads to some promising results.

EXPERIMENTAL

Reagents Used

The material tested as a membrane was kerosene with C_{11}–C_{13}. Solutions of various concentrations of nitric acid, hydrochloric acid, sulfuric acid, EDTA (Reactivul, Bucharest) and PEG (polyethylene glycol with an average molecular weight of 20,000, Fluka) have been used as internal phases. The emulsifier was Span 80 (Fluka).

The experimentally tested carriers were analytically pure reagents such as: phosphoric acid esters (D2EHPA and PC 88A, Merck), pyridine (Fluka), stearic acid (Merck), silicone oil (Merck), acetyl acetone (Merck), and naphthenic acids from crude oil (some characteristics are presented in Table 1).

$CoCl_2$ solutions of 625 and 300 mg/L concentration were used as the source phase for the study of Co^{2+} transport across the membrane. The source phase pH was adjusted with 0.1 N NaOH solution.

Analyses

Metallic ions permeation was followed by determination of the residual Co^{2+} concentration after liquid membrane treatment. Analyses been performed with a Carl Zeiss Jena flame spectrophotometer AAS-1. The water content of the broken membrane was determined by Karl Fischer titration.

TABLE 1
Characteristics of Naphthenic Acids (HX)

Characteristics	Value
Composition	Alkanoic acids Alkyl cyclopentanoic acids Alkyl cyclohexanoic acids
Density, kg/m^3	826
Viscosity, N·s/m^2	725.79×10^{-3}
Acid value, mg KOH/g	243.06
Saponification equivalent, mg KOH/g	247.13

Primary Emulsion

The primary emulsions were prepared in a discontinuous system using some thermostatic cells and a pallet stirrer RW 47 (Carl Zeiss Jena) with a continuously adjustable rotation speed, ranging from 100 to 1300 rpm.

The primary emulsion composition was kerosene, 25 cm^3; carrier, 25 cm^3; Span 80, 1–5 wt%; internal phase, 50 cm^3; and internal phase/organic phase ratio, 1/1 v/v. All experiments were done at 20 ± 2°C and a stirrer speed of 1200 rpm.

Multiple Emulsion

When a primary emulsion was dispersed into the Co^{2+} solution by stirring at 200–300 rpm, a multiple w/o/w emulsion was obtained which had droplets of 7–50 μm diameter (7, 8).

RESULTS AND DISCUSSION

The terms used for expressing the results have the following meanings: pH_i = inner phase initial pH value; pH_e = source phase initial pH value; η = extraction yield, %, expressed as

$$\eta = \frac{c_i - c_f}{c_i} \times 100$$

where c_i = initial concentration of the Co^{2+} solution, mg/L

c_f = final concentration of the Co^{2+} solution after treatment, mg/L

The experiments show that by choosing different internal phases (proton donor or proton nondonor), Co^{2+} transport occurs only by the "countertransport" mechanism (Table 2, Fig. 1):

$$\downarrow Co^{2+} + \underset{\text{dimer form}}{(HX)_2} \rightleftharpoons CoX_2 + 2H^+$$

The driving force of "countertransport" is the difference between pH_i and pH_e.

Experiments were carried out for pH_i values ranging from 1 to 5.5 and for pH_e values ranging from 7 to 10. Though a maximum yield is expected for the maximum pH_e–pH_i difference, practical results show that for pH_i ranging from 1 to 3 the membrane does not withstand the treatment conditions (the membrane swells or breaks). For more dilute solutions (300 mg/L Co^{2+}), high yields were obtained for pH_i ranging from 3 to 5.5 and pH_e = 10 (Fig. 2).

TABLE 2
Carrier Selection (pH_i 3.5, pH_e 10)

Carrier[a]	Intermediate form	Initial concentration of Co^{2+} (mg/L)	Final concentration of Co^{2+} (mg/L)	η (%)	Remarks
Naphthenic acid	Salt	625	25	96	Cheap
D2EHPA	Salt		385	38.4	Expensive, toxic
PC 88A	Salt		480	23.2	Expensive, toxic
Pyridine	Complex		315	49.6	Expensive, toxic
Acetyl acetone	Complex		500	20	Expensive
Silicone oil	Complex		550	12	Expensive
Stearic acid	Salt		550	12	—

[a] D2EHPA = di(2-ethylhexyl)phosphate. PC 88A = 2-ethylhexylphosphonic acid.

Different carriers were tested, and the cheapest, the most nontoxic, and the most satisfactory of them were naphthenic acids (Table 2).

Some authors have shown that a hexa-aqueous Co^{2+} complex is kinetically inert and its extraction from the aqueous to the organic phase is

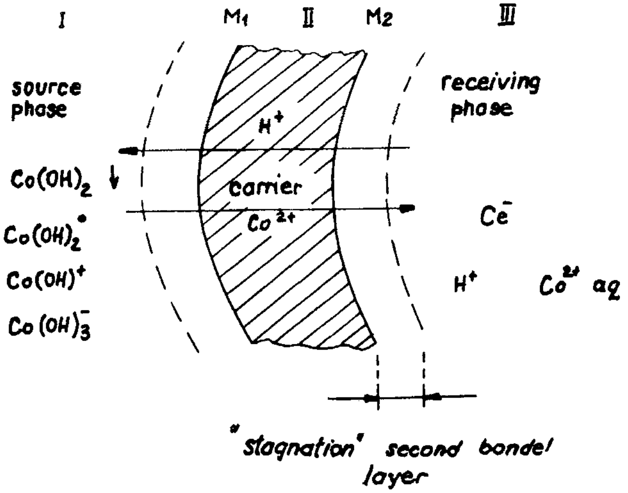

FIG. 1 Liquid membrane.

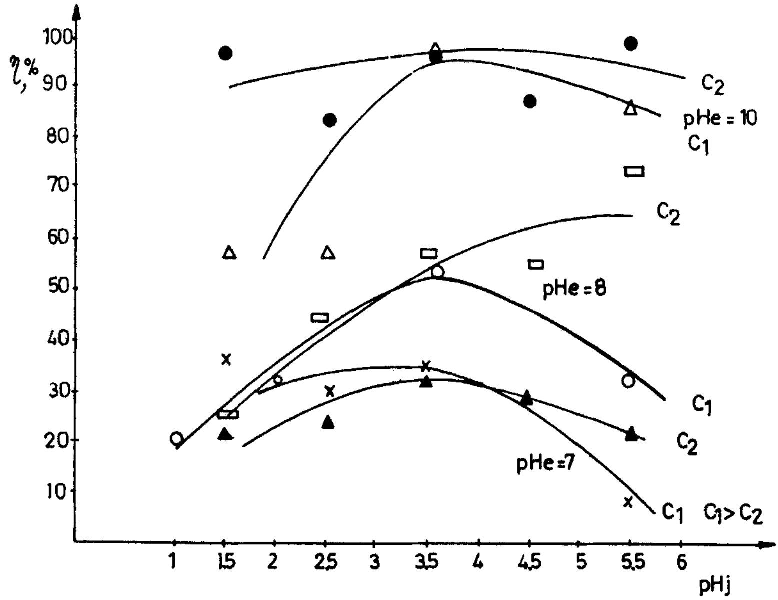

FIG. 2 Removal of Co^{2+} ions. $c_1 = 625$ mg Co^{2+}/L. $c_2 - 300$ mg Co^{2+}/L. (×) Removal of cobalt ions from concentrated solutions (c_1) at pH_e 7. (▲) Removal of cobalt ions from diluted solutions (c_2) at pH_e 7. (○) Removal of cobalt ions from concentrated solutions (c_1) at pH_e 8. (□) Removal of cobalt ions from diluted solutions (c_2) at pH_e 8. (△) Removal of cobalt ions from concentrated solutions (c_1) at pH_e 10. (●) Removal of cobalt ions from diluted solutions (c_2) at pH_e 10.

limited or stopped by a slow release of water molecules (9–11), but the addition of an organic ligand such as propionate, acetate, salicylate, formate or succinate enhances the rate of the extraction process by replacing the water molecules with ligand molecules (11).

For this work the hexa-aqueous Co^{2+} complexes were modified by adding NaOH solution. In this case the ligand was an inorganic one, $[OH]^-$. The external phase contained the complexes $Co(OH)^+$, $Co(OH)_2^0$, $Co(OH)_3^-$, and $Co(OH)_2\downarrow$:

$$Co(OH)_2\downarrow \rightleftarrows Co^{2+} + 2HO^-, \qquad pK_S = 15.7 \tag{1}$$

$$CoOH^+ \rightleftarrows Co^{2+} + HO^-, \qquad pK_1 = 4.4 \tag{2}$$

$$Co(OH)_2^0 \rightleftarrows Co^{2+} + 2HO^-, \qquad pK_{1,2} = 4.6 \tag{3}$$

$$Co(OH)_3^- \rightleftarrows Co^{2+} + 3HO^-, \qquad pK_{1,2,3} = 10.5 \tag{4}$$

From

$$K_S \cong [\mathrm{Co}^{2+}][\mathrm{OH}^-]^2 \tag{5}$$

one can note:

$$\mathrm{pCo}^{2+} = 15.7 - 2\mathrm{pOH} \tag{6}$$

$$\mathrm{pCo}^{2+} = 2\mathrm{pH} - 12.3 \tag{7}$$

From Equilibrium (2), one obtains:

$$K_1 = \frac{[\mathrm{Co}^{2+}][\mathrm{HO}^-]}{[\mathrm{CoOH}^+]} = \frac{[\mathrm{Co}^{2+}][\mathrm{HO}^-]^2}{[\mathrm{CoOH}^+][\mathrm{HO}^-]} \tag{8}$$

$$K_1 = \frac{K_S}{[\mathrm{CoOH}^+][\mathrm{HO}^-]} \tag{9}$$

$$[\mathrm{CoOH}^+] = \frac{K_S}{K_1 \cdot [\mathrm{HO}^-]} \tag{10}$$

$$\begin{gathered} \mathrm{pCoOH}^+ = \mathrm{p}K_S - \mathrm{p}K_1 - \mathrm{pOH} \\ \mathrm{pCoOH}^+ = 15.7 - 4.4 - 14 + \mathrm{pH} \\ \downarrow \mathrm{pCoOH}^+ = \mathrm{pH} - 2.7 \end{gathered} \tag{11}$$

From Equilibrium (3):

$$K_{1,2} = \frac{[\mathrm{Co}^{2+}][\mathrm{HO}^-]^2}{[\mathrm{Co(OH)}_2^0]} = \frac{K_S}{[\mathrm{Co(OH)}_2^0]} \tag{12}$$

$$\begin{gathered} \mathrm{pCo(OH)}_2^0 = \mathrm{p}K_S - \mathrm{p}K_{1,2} \\ \mathrm{pCo(OH)}_2^0 = 11.2 \end{gathered} \tag{13}$$

From Equilibrium (4):

$$K_{1,2,3} = \frac{[\mathrm{Co}^{2+}][\mathrm{HO}^-]^3}{[\mathrm{Co(OH)}_3^-]} = \frac{K_S \cdot [\mathrm{HO}^-]}{[\mathrm{Co(OH)}_3^-]} \tag{14}$$

$$\mathrm{pCo(OH)}_3^- = \mathrm{p}K_S - \mathrm{p}K_{1,2,3} + \mathrm{pOH} \tag{15}$$

$$\mathrm{pCo(OH)}_3^- = 19.2 - \mathrm{pH} \tag{16}$$

The concentration lines of Co^{2+} species vs pH are (Fig. 3):

$$\mathrm{pCo}^{2+} = 2\mathrm{pH} - 12.3$$

$$\mathrm{pCoOH} = \mathrm{pH} - 2.7$$

$$\mathrm{pCo(OH)}_2^0 = \text{constant}$$

$$\mathrm{pCo(OH)}_3^- = 19.2 - \mathrm{pH}$$

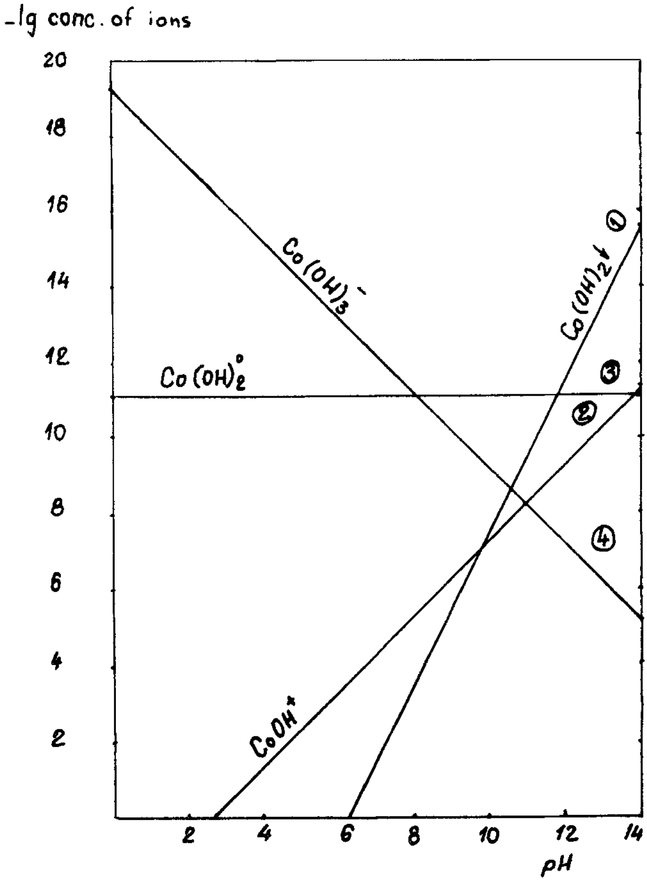

FIG. 3 Concentration of Co^{2+} species.

At pH_e 10, the values $pCo^{2+} = 7.7$, $pCoOH^+ = 7.3$, $pCo(OH)_2^0 = 11.1$, and $pCo(OH)_3^- = 9.2$ show that the $[Co^{2+}]$ and $[CoOH^+]$ concentrations are the highest in the system.

The Co^{2+} ions are hydrated by six water molecules and exhibit both an octahedral configuration and a dissipated charge in a large volume. The $Co(OH)^+$ complex has a tetrahedral structure and has a directed charge. This complex reacts with naphthenic acids and releases Co^{2+} ions.

The Co^{2+} ions are retained by the membrane, the HO^- ions are consumed by protons, and Equilibrium (1) shifts completely to $Co(OH)_2$ solubilization.

The exhausted liquid membranes were broken up by an electric field. A cylindrical cell (12) with an inner vertical insulated electrode and an outer one (coating the cell) was used; the alternating voltage (U) applied to the system ranges from 3000 to 5000 V and the frequency of the system (ν) ranges from 500 to 2000 Hz.

The breaking-up process was visually observed by a change of the H/H_0 ratio versus time (H = the level of the separated aqueous layer, H_0 = the entire height of the emulsion layer). Experimental data show that liquid membranes containing Co^{2+} ions can be easily but not completely ($H/H_0 = 0.6$) broken-up at 4000–5000 V and 500–1000 Hz (Fig. 4).

The experimental data fit a nonlinear regression program—SIMPLEX optimization by a IBM/PC/XT computer:

$$H/H_0 = b_1 + b_2e^{-b_3t} \tag{17}$$

where H = the level of separated aqueous layer, mm
H_0 = the entire height of the emulsion layer at the initial time, mm
t = time, seconds
b_1, b_2, b_3 = parameters determinated by nonlinear regression

Relation (17) shows that by plotting the experimental data for $t = 0$, one can extrapolate the time-lag of the breaking-up process. Note that the breaking-up process occurs very successfully at low frequencies and high voltages.

For values $U < 3000$ V, the process does not occur, and at $U = 5000$ V the frequency values are less important (Fig. 4).

After break-up the organic phase has about 0.8–1.5% water (detected by Karl Fischer titration), and about 40% of the Co^{2+} ions have been removed from the source phase (calculated from the balance between the source and receiving phase). In order to recycle the liquid membrane, it is necessary to "wash" it with a dilute HCl solution.

The concentration of naphthenic acids is higher than the stoichiometric value because this favors a more rapid removal of Co^{2+} and increases the viscosity and the stability of the membrane. Diffusion across the membrane is not rate limiting in the transfer process. The release of Co^{2+} at the M_2 interface is achieved by a chemical process (it is obvious that HCl is much stronger than the naphthenic acids), but the HCl concentration of the receiving phase is lower than the stoichiometric one ($pH_i = 3.5$, e.g., $[H^+] = 3.2 \times 10^{-4}$ mol/L). Tests for $pH_i = 1$, $pH_i = 2$, and $pH_i = 3$ (higher or equal concentration compared to the stoichiometric one) were made, but the results for the transport yield, membrane swelling, and membrane break-up fluctuated.

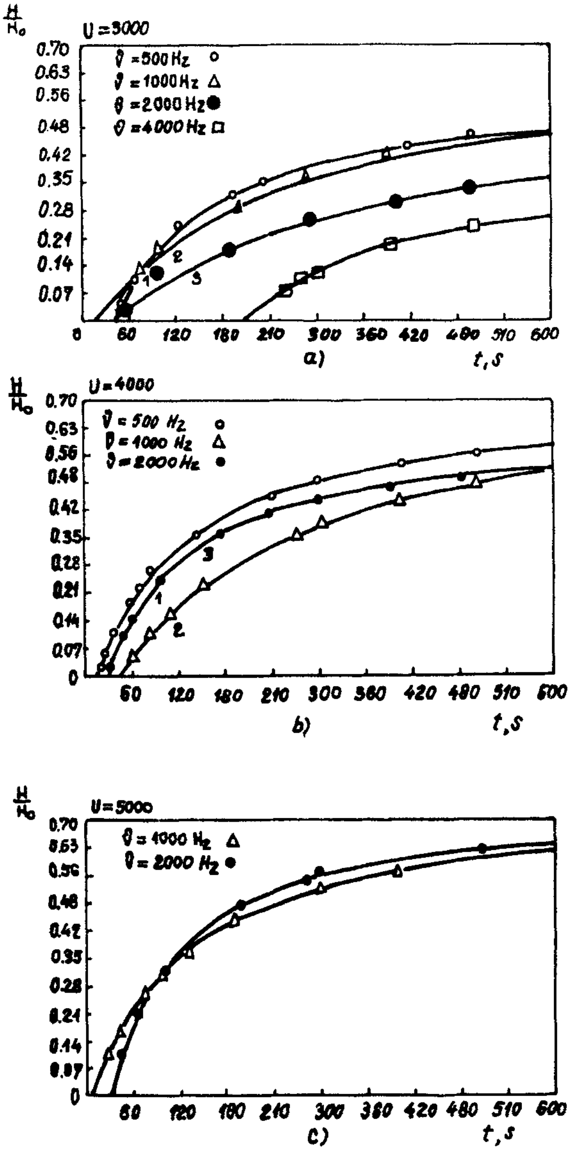

FIG. 4 Breaking-up process: (a) U = 3000 V, (b) U = 4000 V, (c) U = 5000 V.

The inner phase (pH_i = 5.5–6) after break-up contains 175 mg Co^{2+}/L, a lower value than what is stoichiometrically possible. The inner area M_2 is much larger than the outer one (there are many small encapsulated water droplets) and the unusually low concentration of metallic ions on the inner phase compared with the other species studied leads to the assumption that in the second bonded layer a "stagnation diffusion process" occurs.

That means that the large metallic ions are hexa-aqueous hydrated and that the aqueous Cl^- ions slowly diffuse into the receiving phase, and this can be the rate-determining step. This phenomenon is called "concentration polarization" in the literature (13).

CONCLUSION

The recovery and concentration of Co^{2+} ions by the emulsion liquid membrane process represents an advanced method of wastewater cleaning and may be carried out with good results at pH_i 3.5 and pH_e 10. The exhausted membrane was broken up by an alternating electric field at 4000–5000 V and 500–1000 Hz. The organic phase must be "washed" with dilute HCl solution before it is recycled.

REFERENCES

1. R. P. Cahn and N. N. Li, US Patent 4,086,163 (1978).
2. R. J. Marr, H. Lackner, and H. J. Bart, European Patent Appl., 891,126,656 (1989).
3. J. D. Lumbo, I. I. Christensen, and R. M. Izatt, *J. Chem. Educ.*, *57*, 227 (1980).
4. S. Yoshida and S. Hayano, *J. Am. Chem. Soc.*, *108*, 3903 (1986).
5. H. C. Hayworth, W. S. Ho, and W. A. J. Burno, *Sep. Sci. Technol.*, *18*(6), 493 (1983).
6. R. Chiarizia and E. P. Horwitz, *Solv. Extr. Ion. Exch.* *8*(1), 65 (1990).
7. E. Amanatidou, R. Vladea, M. Stefanut, and V. Dalea, *Chem. Chron.*, *N.S.*, *23*(1), 25 (1994).
8. E. Amanatidou, R. Vladea, M. Stefanut, and I. Naggy, *Ibid.*, *23*(1), 63 (1994).
9. P. R. Subbazaman, Sr. M. Cordes, and H. Freiser, *Anal. Chem.*, *41*(3), 1878 (1967).
10. H. Eccles, G. J. Lawson, and D. J. Rawlence, *Proceedings of the International Solvent Extraction Conference, ISES 77*, CIM Special, Vol. 21, 1979.
11. Z. M. Gu, D. T. Watson, and N. N. Li, *Ligand Accelerated Liquid Membrane Extraction of Metal Ions*, Personal Communication, 1984.
12. A. Kriechbaumer and R. Marr, *Chem.-Ing.-Tech.*, *55*(9), 700 (1983).
13. R. Rautenbach and R. Albrecht, *Membrane Processes*, Wiley, New York, 1989, p. 112.

Received by editor April 10, 1995
Revision received July 17, 1995