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

# Rare Earth Metal Extraction by Liquid Surfactant Membranes Containing a Calixarene Carboxylate Derivative: Permeation Acceleration Effect of Sodium Ions

Tatsuya Oshima; Takahiko Kakoi; Fikiko Kubota; Keisuke Ohto; Masahiro Goto; Fumiyuki Nakashio

**To cite this Article** Oshima, Tatsuya , Kakoi, Takahiko , Kubota, Fikiko , Ohto, Keisuke , Goto, Masahiro and Nakashio, Fumiyuki(1998) 'Rare Earth Metal Extraction by Liquid Surfactant Membranes Containing a Calixarene Carboxylate Derivative: Permeation Acceleration Effect of Sodium Ions', Separation Science and Technology, 33: 13, 1905 — 1917
**To link to this Article: DOI:** 10.1080/01496399808545036
**URL:** http://dx.doi.org/10.1080/01496399808545036

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, 33(13), pp. 1905–1917, 1998

# Rare Earth Metal Extraction by Liquid Surfactant Membranes Containing a Calixarene Carboxylate Derivative: Permeation Acceleration Effect of Sodium Ions

TATSUYA OSHIMA, TAKAHIKO KAKOI, FUKIKO KUBOTA, KEISUKE OHTO,* and MASAHIRO GOTO†
DEPARTMENT OF CHEMICAL SCIENCE & TECHNOLOGY
GRADUATE SCHOOL OF ENGINEERING
KYUSHU UNIVERSITY
HAKOZAKI, FUKUOKA 812-8581, JAPAN

FUMIYUKI NAKASHIO
DEPARTMENT OF INDUSTRIAL CHEMISTRY
KUMAMOTO INSTITUTE OF TECHNOLOGY
IKEDA, KUMAMOTO 860-0082, JAPAN

Downloaded At: 11:19 25 January 2011

## ABSTRACT

Calixarene carboxylate derivatives were used as a mobile carrier for rare earth permeation in a liquid surfactant membrane (LSM) system. The effect of alkali metal ions on the extraction behavior of rare earth metals in both liquid–liquid extraction and LSM systems has been studied. The addition of sodium ions considerably enhanced the extraction ability of rare earth metals in the extraction equilibrium. Furthermore, the presence of alkali metal ions in the material solution affected the rate of rare earth permeation in LSMs. The most accelerative transport of rare earth metals by LSMs was achieved by the addition of sodium ions. This acceleration effect of sodium ions was predominant in a tetracarboxylate calixarene whose cavity size just fits the ionic diameter of sodium ions. The sodium-loaded calix[4]arene derivative showed good performance as an effective mobile carrier for rare earth metals in the presence of sodium ions.

* Present address: Department of Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjo, Saga 840, Japan.
† To whom correspondence should be addressed.



Copyright © 1998 by Marcel Dekker, Inc. www.dekker.com

## INTRODUCTION

Calixarene is a cyclic host compound which possesses high extraction ability to various metal ions such as alkaline, alkaline earth, and base metal ions (1–5). Ordinary industrial extractants have been designed on the basis of a chelation effect for a target metal ion by choosing a proper functional group. On the other hand, calixarene is another type of extractant which can recognize the size of metal ions by the cavity of cyclic structures like crown ethers (6, 7). The cavity size of calixarenes is easily controlled by changing the number of phenol units which are connected at the 2- and the 6-positions of the benzene ring. Therefore, the recognition ability of calixarene for metal ions can make it useful as a specific receptor. In particular, calixarene shows a high affinity to alkaline metal ions: calix[4]arene and calix[6]arene have a high affinity for sodium and potassium ions, respectively.

Recently, calixarene has attracted much attention to a novel host compound for lanthanides and actinides (8, 9). Mutual separation among adjacent rare earth metal ions is a most difficult problem in the separation of metal ions due to their similar chemical and physical properties. In 1993, Ludwig et al. (8) first reported that a calixarene carboxylic butyl derivative shows a high extraction ability for rare earth metal ions. Later, Ohto et al. (10) designed calixarene octyl derivatives to improve the solubility of an organic solvent. More recently, the extraction behavior of rare earth metals, uranium, and thorium with calix[4]arene has been found to be strongly influenced by the addition of sodium ions (11, 12). Izatt et al. (1) first demonstrated that a calixarene compound is a useful carrier for metal ions in bulk liquid membranes. To date, some calixarene derivatives have shown good performance as mobile carriers in bulk and as a supported liquid membrane (1, 13–15). However, except for two research group (16, 17), there have been few studies of LSM extraction involving the calixarene derivative as a mobile carrier.

In a previous paper (17) we reported that the calixarene carboxylic octyl derivative is an efficient mobile carrier for rare earth metal ions with liquid surfactant membranes. In this study the effect of four different alkaline metal ions on the permeation behavior of rare earth metals by liquid.surfactant membranes containing a different ring size of calixarene as a mobile carrier was investigated. We discuss the unique extraction behavior of rare earth metals by the addition of alkaline metal ions.

## EXPERIMENTAL

### Materials

Figure 1 shows the structures and abbreviations of the calixarenes used in the present study along with the monomer analog. The extractants *p-tert-*

Downloaded At: 11:19 25 January 2011

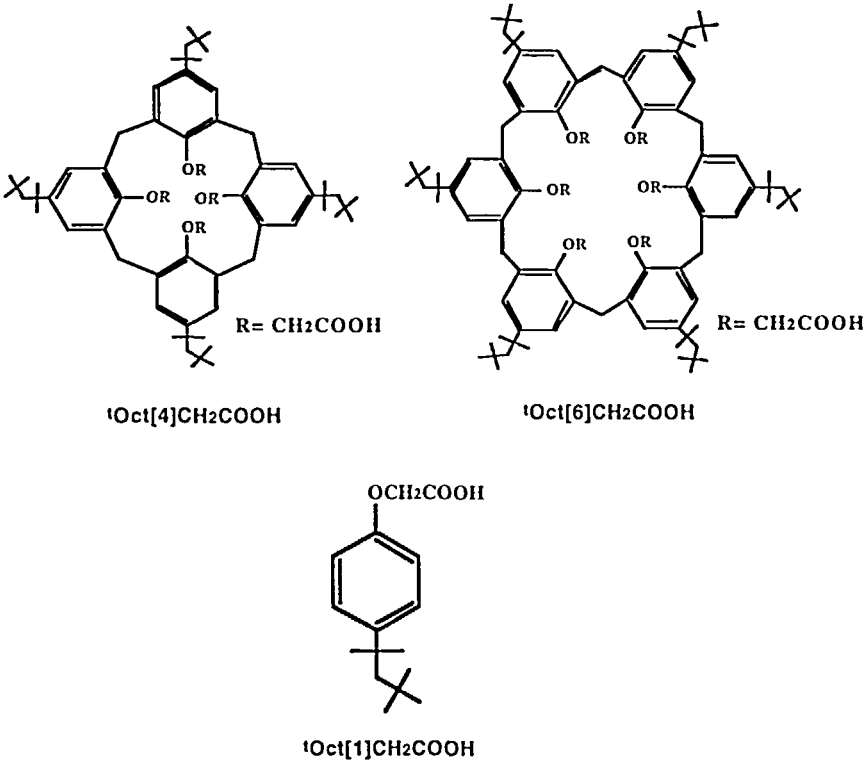


FIG. 1 Molecular structures and abbreviations of extractant.

Downloaded At: 11:19 25 January 2011

octylphenoxyacetic acid [*p*-(1,1,3,3,-tetramethylbutyl)phenoxyacetic acid] (abbreviated as $^t$Oct[1]$CH_2COOH$), the tetracarboxylate derivative of *p-tert*-octylcalix[4]arene [25,26,27,28-tetrakis(carboxymethoxy)-5,11,17,23-tetrakis(1,1,3,3,-tetramethylbutyl)calix[4]arene] (abbreviated as $^t$Oct[4]$CH_2$-COOH), the hexacarboxylate derivative of *p-tert*-octylcalix[6]arene [37,38,39,40,41,42-hexakis(carboxymethoxy)-5,11,17,23,29,35-hexakis (1,1,3,3,-tetramethylbutyl)calix[6]arene] (abbreviated as $^t$Oct[6]$CH_2COOH$), and the surfactant dioleyl-l-glutamate ribitol (abbreviated as $2C_{18}\Delta^9$GE) were synthesized according to the procedures given in previous papers (10, 18). The cyclic compound $^t$Oct [4]$CH_2COOH$ has four structural isomers. In this study the cone compound in which the four carboxyl groups are immobilized at the lower rim of the calixarene was isolated and used as a mobile carrier. However, the structural conformation of $^t$Oct[6]$CH_2COOH$ could not be immobilized due to the fact that the benzene rings in the hexamer tend to rotate

freely. The final products were purified by recrystallization and then identified by means of FT-IR, $^1$H-NMR, and elemental analyses. Analytical grade toluene was employed as an organic solvent in liquid–liquid extraction and liquid membrane operations. The other reagents were of reagent grade and were used as received.

### Extraction Equilibrium of Rare Earth Metals

Initially, two aqueous solutions were separately prepared by dissolving three different rare earth metal chlorides ($HoCl_3 \cdot H_2O$, $ErCl_3 \cdot H_2O$, $YCl_3 \cdot H_2O$) and an alkali chloride into either 100 mol/m$^3$ nitric acid or glycine solution. The pH of the aqueous solutions was adjusted by mixing the above two aqueous solutions. An organic solution was prepared by dissolving the extractant into the diluent toluene. The experimental procedure for the extraction equilibrium was the same as that described in a previous paper (19).

Downloaded At: 11:19 25 January 2011

### Extraction of Rare Earth Metals by LSMs

Dilute sulfuric acid solution containing copper ions as a break-up tracer was used as the internal aqueous solution. We confirmed that copper ions do not permeate across the membrane under the present experimental conditions. Therefore the presence of copper ions in the external phase could be limited to break-up of the W/O emulsion. The organic solution which made up the liquid membrane phase was prepared by dissolving the carrier and the surfactant in toluene. Three rare earth metals, Ho, Er, and Y, were included in the external feed aqueous solution. The pH of the aqueous solution was adjusted as described above. Alkali ions were also added to the feed aqueous solution. The experimental apparatus used for metal extraction by LSMs was a stirred glass cell equipped with four baffles. The inner diameter and the depth of the cell were 9.2 and 9.5 cm, respectively. Samples of the external phase were removed periodically during the course of a run. The experimental procedure was the same as that described in a previous paper (19). The concentrations of rare earth metals in the external feed aqueous solution were determined by an ICP-Atomic Emission Spectrometer (Shimadzu ICPS-5000). The detailed experimental conditions are listed in Table 1.

## RESULTS AND DISCUSSION

### Extraction Equilibrium

Figure 2 shows the effect of alkali ions on the extraction behavior of yttrium ions with $^t$Oct[4]$CH_2$COOH. In the presence of sodium ions, the extraction abilities of rare earth metal ions were significantly enhanced. On the other hand, the extraction behavior of rare earth metal ions in the presence of

TABLE 1
Experimental Conditions for Rare Earth Metals Extraction by LSMs

| | |
|---|---|
| Internal aqueous phase | $V_i$ = 25 mL |
| | $C_H$ = 100 mol/m$^3$ |
| | Break-up tracer: $Cu^{2+}$ (10 mol/m$^3$) |
| Organic phase | $V_{org}$ = 25 mL |
| | Solvent: toluene |
| | Carrier: $^t$Oct[4]COOH (2 mol/m$^3$) |
| | $^t$Oct[6]COOH (2 mol/m$^3$) |
| | $^t$Oct[1]COOH (8 mol/m$^3$) |
| | Surfactant: $2C_{18}\Delta^9$GE (30 mol/m$^3$) |
| Internal aqueous phase | $V_e$ = 250 mL |
| | pH 3.2–5.3 |
| | Rare earth metals: $Ho^{3+}$ (0.1 mol/m$^3$) |
| | $Er^{3+}$ (0.1 mol/m$^3$) |
| | $Y^{3+}$ (0.1 mol/m$^3$) |
| | Alkali metals: $Li^+$, $Na^+$, $K^+$, $Cs^+$ (0–50 mol/m$^3$) |
| Stirring speed | 300 rpm |
| Temperature | 303 K |

Downloaded At: 11:19 25 January 2011

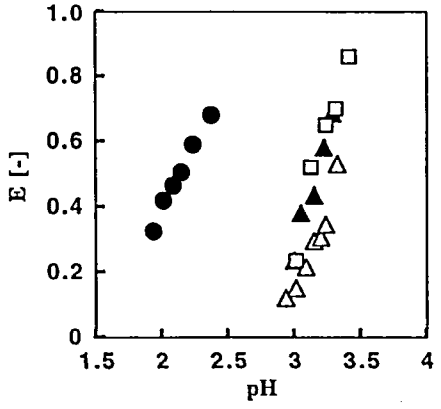


FIG. 2 Effect of alkali ions on the extraction of yttrium ($Ho^{3+}$, $Er^{3+}$, $Y^{3+}$, 0.1 mol/m$^3$; alkali metal, 100 mol/m$^3$; $^t$Oct[4]COOH, 5 mol/m$^3$): alkali ions free (□), LiCl (△), NaCl (●), KCl (▲).

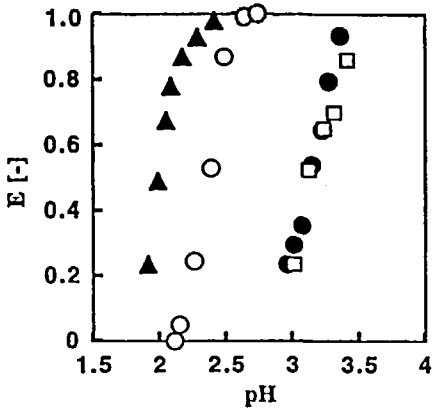


FIG. 3 Effect of sodium concentration on the extraction of yttrium ($Ho^{3+}$, $Er^{3+}$, $Y^{3+}$, 0.1 mol/m$^3$; $^t$Oct[4]COOH 5 mol/m$^3$): alkali ions free (□), [NaCl] = 0.1 mol/m$^3$ (●), [NaCl] = 5 mol/m$^3$ (○), [NaCl] = 50 mol/m$^3$ (▲).

Downloaded At: 11:19 25 January 2011

lithium ions or potassium ions was similar to that without alkali ions. To explain the unusual extraction behavior in the sodium-incorporated system, the effect of the concentration of sodium ions on the extraction behavior of rare earth metal ions was investigated (Fig. 3). The enhancement effect increased with an increase in the concentration of sodium ions in the aqueous phase. We also found that the pH dependence of extraction was affected by the addition of sodium ions. This phenomenon was attributed to the change in the organic composition of extracted complexes in the sodium and sodium-free system. In this study sodium ions were coextracted with the target metals into the membrane.

The ionic diameter of sodium ions is well-known to fit the cavity size of calix[4]arene; therefore, a sodium ion is preferentially extracted by calix[4]arene derivatives (2). In this case it is suggested that rare earth metal ions are coextracted with sodium ions by $^t$Oct[4]$CH_2$COOH. Ohto et al. (20) proposed a coextraction model of sodium and copper(II) ions with $^t$Oct[4]$CH_2$COOH as follows: In the coextraction mechanism, a sodium ion is first extracted by one of the carbonyl groups and phenoxy oxygens, and in the next step a copper ion is extracted and coordinated by the rest of the carboxyl groups. In the present study a similar mechanism is considered to apply to rare earth metal extraction.

The formation of the complex between a sodium ion and $^t$Oct[4]$CH_2$COOH is proposed in Fig. 4. Coordination of a sodium ion into the cavity of $^t$Oct[4]$CH_2$COOH facilitates the acidic dissociation of the carboxyl groups,

which makes a proton release for the extraction of rare earth metal ions easier. In addition, the uptake of a sodium ion in the cavity increases the structural rigidity and provides preorganization in the structure of $^t$Oct[4]$CH_2$COOH. These factors work more effectively toward accepting the rare earth metal ions, which have a relatively small ionic radius, than the sodium ion, in spite of the electric repulsion between the sodium and rare earth metal ions. It is deduced that the Na-calix[4]arene complex exhibits superior extractability and thus coextracts the trivalent rare earth metal ions.

We observed that when lithium ions or potassium ions coexist, the extraction behavior of rare earth metal ions is little changed compared with the

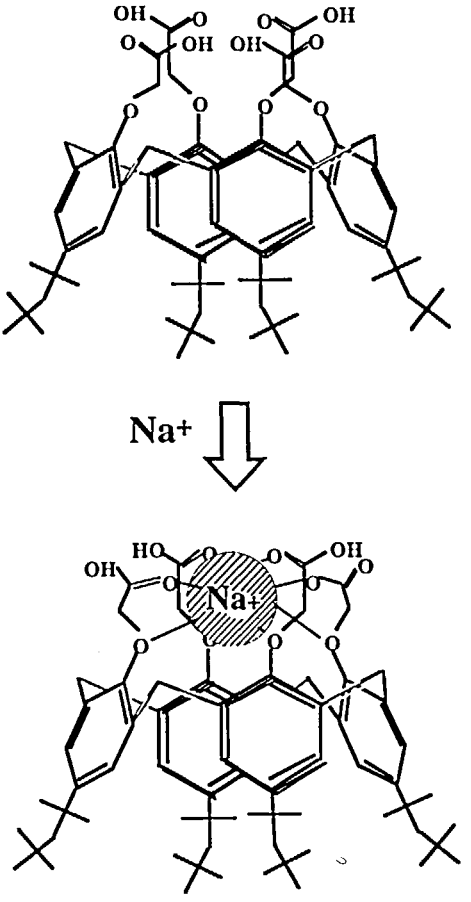


FIG. 4 Formation of the complex between a sodium ion and $^t$Oct[4]COOH.

Downloaded At: 11:19 25 January 2011

alkali-free system. The ionic diameters of lithium and potassium ions do not fit well into the cavity of $^t$Oct[4]$CH_2$COOH, hence calix[4]arene has a low affinity toward these ions and cannot coextract them along with rare earth metal ions. In the lithium/potassium incorporated systems, rare earth metal ions were extracted by the "free" calix[4]arene. The extraction mechanisms are similar to that without alkali ions. Futhermore, we found that the preferential extraction of excess alkali ions Li and K prevents extraction of the rare earth metal ions.

Therefore, the unusual extraction behavior occurs only in the presence of sodium ions whose diameter fits the cavity size of the tetracalixarene derivative.

## Extraction Behavior of Rare Earth Metals by LSMs

In the previous study (17) we reported the extraction behavior of rare earth metals by LSMs using calixarene derivatives in an alkali-free system. However, we have found that the calix[4]arene carboxylate derivative offers better prospects as a good carrier for the permeation of rare earth metals by LSMs. In the present study the effect of alkali ions on the extraction of rare earth metals by LSMs containing a different ring size of calixarenes as mobile carriers was investigated. Effective conditions for the extraction were also examined. The concentration of the surfactant was adjusted to 30 mol/m$^3$, and the emulsions obtained were very stable under the present experimental conditions. The degree of emulsion break-up was less than 3% within 10 minutes of mixing.

Downloaded At: 11:19 25 January 2011

Figure 5 shows the effect of alkali ions on the extraction of yttrium by LSMs using $^t$Oct[4]$CH_2$COOH. In the absence of alkali ions, the extraction rates of rare earth metals were comparatively slower at pH 4.5, and the degree of yttrium extracted from the feed solution was about 25% at 1200 seconds. By contrast, in the presence of 50 mol/m$^3$ sodium ions, the extraction rate of rare earth metal ions became very fast, and even yttrium ions whose extraction rate is the slowest among the three rare earth metal ions was completely extracted in 300 seconds. Under the present experimental conditions, sodium ions are preferentially extracted with $^t$Oct[4]$CH_2$COOH, leading to preorganization calix[4]arene conformation. The preorganized carrier has a greater potential for extracting rare earth metal ions than does sodium-free calix[4]arene. Hence the extraction rate of rare earth metals with calix[4]arene was considerably enhanced in the presence of sodium ions.

It was surprising to observe that the extraction rate of rare earth metals increased slightly in a lithium/potassium-incorporated system compared to the alkali-free system because, based on the extraction equilibria results, the extraction profiles were similar. The reason why the addition of lithium and

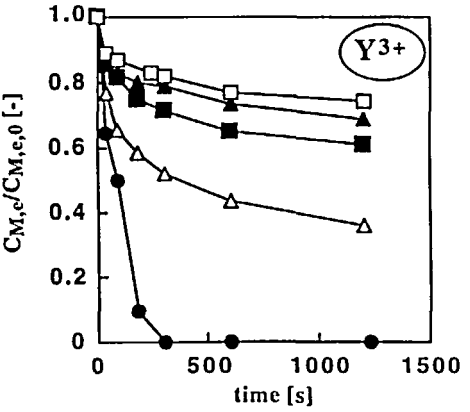


FIG. 5 Effect of alkali ions on the extraction of yttrium by LSMs containing $^t$Oct[4]COOH at pH 4.5: alkali ion free (□), $[LiCl]_{ex}$ = 50 mol/m$^3$ (△), $[NaCl]_{ex}$ = 50 mol/m$^3$ (●), $[KCl]_{ex}$ = 50 mol/m$^3$ (■), $[CsCl]_{ex}$ = 50 mol/m$^3$ (▲).

Downloaded At: 11:19 25 January 2011

potassium enhanced the permeation rate of rare earth metals in LSMs is not clear. In the cesium-incorporated system, the extraction rate of rare earth metal ions showed comparatively little change. The ionic diameter of a cesium ion is larger than the cavity size of calix[4]arene, therefore it is difficult to form a complex with $^t$Oct[4]$CH_2$COOH, which would in turn accelerate the extraction of rare earth metal ions. When the concentration of cesium ions was increased up to 100 mol/m$^3$, they inhibited the permeation of rare earth metal ions, and the extraction rates were significantly lowered.

Figure 6 shows the effect of alkali ions on the extraction behavior of yttrium by LSMs using a monomer analog $^t$Oct[1]$CH_2$COOH. Here the concentration of the monomer analog was kept at 8 mol/m$^3$ to adjust the number of functional carboxyl groups in the $^t$Oct[4]$CH_2$COOH carrier. In this case the extraction rates of rare earth metals in the presence of every alkali ions were similar to the rates without alkali ions. This result indicates that the cyclic structure of calixarenes is a key factor for obtaining the acceleration effect of alkali ions, and their functional groups are themselves not important.

The cavity size of calix[6]arene is a little larger than that of calix[4]arene, and several reports have shown that calix[6]arene derivatives display a higher affinity for cesium ion compared to smaller alkali ions. Therefore, when cesium ions were added to LSM systems containing $^t$Oct[6]$CH_2$COOH as a carrier, the acceleration effect on the extraction rate of rare earth metal ions was expected to compare well with that of the sodium–$^t$Oct[4]$CH_2$COOH complex. Figure 7 exhibits the effect of alkali ions on the extraction of yttrium

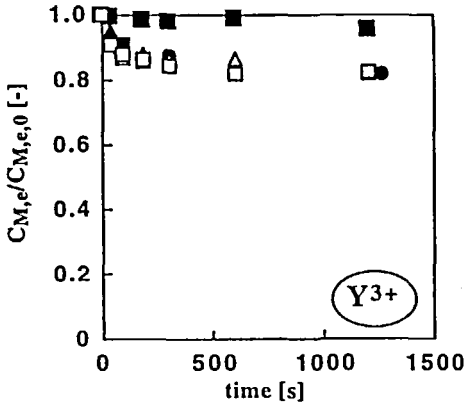


FIG. 6 Effect of alkali ions on the extraction of yttrium by LSMs containing 'Oct[1]COOH at pH 5.3: alkali ion free (□), $[LiCl]_{ex}$ = 50 mol/m$^3$ (△), $[NaCl]_{ex}$ = 50 mol/m$^3$ (●), $[KCl]_{ex}$ = 50 mol/m$^3$ (■), $[CsCl]_{ex}$ = 50 mol/m$^3$ (▲).

Downloaded At: 11:19 25 January 2011

by LSMs containing 'Oct[6]$CH_2$COOH. Contrary to expectation, the extraction rate of rare earth metal ions in the presence of cesium ions is similar to that without alkali ions as well as to those of other alkali ions. We suggest the following explanation for the poor acceleration effect of cesium ions: 1) Because of its larger cavity size, 'Oct[6]$CH_2$COOH has a higher flexibility

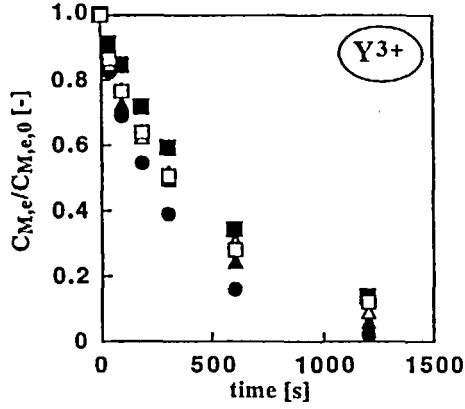


FIG. 7 Effect of alkali ions on the extraction of yttrium by LSMs containing 'Oct[6]COOH at pH 4.5: alkali ion free (□), $[LiCl]_{ex}$ = 50 mol/m$^3$ (△), $[NaCl]_{ex}$ = 50 mol/m$^3$ (●), $[KCl]_{ex}$ = 50 mol/m$^3$ (■), $[CsCl]_{ex}$ = 50 mol/m$^3$ (▲).

than $^t$Oct[4]$CH_2$COOH. Therefore, $^t$Oct[6]$CH_2$COOH has several conformation isomers because ring rotation is not suppressed, while $^t$Oct[4]$CH_2$COOH is a cone-type compound whose four functional groups are immobilized at one side of the calixarene. It appears that these structural difference in the carriers affect the difference in their extraction behavior in the presence of alkali ions. 2) The extraction of rare earth metal ions with $^t$Oct[4]$CH_2$COOH is performed by forming 1:2 (metal:ligand) complexes, while in the case of $^t$Oct[6]$CH_2$COOH the metal ions are extracted by forming 1:1 (metal:ligand) complexes (17). Thus the difference in the extraction reaction mechanism may affect the acceleration effect in the presence of sodium ions. Based on the results, we conclude that coexisting sodium ions enhance the extraction rate of rare earth metals by LSMs, and furthermore, the effect is predominant when $^t$Oct[4]$CH_2$COOH is used as a mobile carrier in LSMs.

Figure 8 shows the difference in the permeation rates among the three different rare earth ions at pH 3.2 with and without sodium ions. No single rare earth metal ion was extracted in the absence of sodium ions at the low pH condition, while all the rare earth metal ions were smoothly extracted into W/O emulsions in the presence of 50mol/m$^3$ sodium ions. The separation factor between yttrium and holmium or erbium was significantly enhanced. We confirmed that the extracted metal complexes in the liquid membrane phase were completely transferred to the internal recovery phase by breaking the W/O emulsion and measuring the concentration of rare earth metals. This result shows that the sodium–calix[4]arene complex works as a good carrier, applicable for the separation of rare earth metals in the lower pH region.

Downloaded At: 11:19 25 January 2011

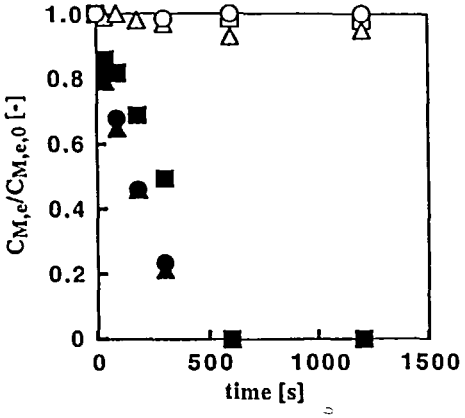


FIG. 8 Extraction profiles of $Ho^{3+}$, $Er^{3+}$, $Y^{3+}$ by LSMs containing $^t$Oct[4]COOH at pH 3.2. Open symbols: alkali ion free $Ho^{3+}$ (○), $Er^{3+}$ (△), $Y^{3+}$ (□). Filled symbols: $[NaCl]_{ex}$ = 50 mol/m$^3$ $Ho^{3+}$ (●), $Er^{3+}$ (▲), $Y^{3+}$ (■).

## CONCLUSION

The effect of alkali ions on the extraction equilibrium of rare earth metal ions by means of different ring sizes of the novel carrier calixarenes has been quantified. In the presence of sodium ions the extractability of rare earth ions at equilibrium considerably increased compared with that of an alkali ion-free system. The presence of the other alkali ions showed little effect on the extraction behavior. The desirable pre complexation of extractant $^t$Oct[4]$CH_2$-COOH with sodium ions was most effective for accepting rare earth metal ions. Among the four alkali ions (Li, Na, K, Cs) investigated, sodium ions showed a significant accelerative effect on the extraction behavior of rare earth metal ions by LSMs containing the calixarene derivative $^t$Oct[4]$CH_2$-COOH as a mobile carrier. An acceleration effect was not obtained for the permeation of rare earth metals when other carriers were used. This study introduces an efficient extraction system for rare earth metals using tetracarboxylated calixarene preorganized by sodium ions.

Downloaded At: 11:19 25 January 2011

## REFERENCES


1. R. M. Izatt, J. D. Lamb, R. T. Hawkins, P. R. Brown, S. R. Izatt, and J. J. Christensen, *J. Am. Chem. Soc., 105*, 1782 (1983).
2. S.-K. Chang and I. Cho, *J. Chem. Soc., Perkin Trans., 1*, 211 (1986).
3. T. Nagasaki and S. Shinkai, *Bull. Chem. Soc. Jpn., 65*, 471 (1992).
4. R. Ludwig and S. Tachimori, *Solv. Extr. Res. Dev., Jpn., 3*, 244 (1996).
5. P. D. Beer, M. G. B. Drew, M. Kan, P. B. Leeson, M. I. Ogden, and G. Williams, *Inorg. Chem., 35*, 2202 (1996).
6. C. D. Gutsche, *Acc. Chem. Res., 16*, 161 (1983).
7. G. Montavon, G. Duplatre, Z. Asfari, and J. Vicens, *New J. Chem., 20*, 1061 (1996).
8. R. Ludwig, K. Inoue, and T. Yamamoto, *Solv. Extr. Ion Exch., 11*, 311 (1993).
9. F. Arnaud-Neu, V. Böhmer, J.-F. Dozol, C. Grüttner, R. A. Jakobi, D. Kraft, O. Mauprivez, H. Rouquette, M.-J. Schwing-Weill, N. Simon, and W. Vogt, *J. Chem. Soc., Perkin Trans. 2, 2*, 113 (1995).
10. K. Ohto, M. Yano, K. Inoue, T. Yamamoto, M. Goto, F. Nakashio, S. Shinkai, and T. Nagasaki, *Anal. Sci., 11*, 893 (1995).
11. K. Ohto, M. Yano, K. Inoue, T. Nagasaki, M. Goto, F. Nakashio, and S. Shinkai, *Polyhedron, 16*, 1655 (1997).
12. G. Montavon, G. Duplatre, Z. Asfari, and J. Vicens, *Solv. Extr. Ion Exch., 15*, 169 (1997).
13. C. D. Gutsche and K. C. Nam, *J. Am. Chem. Soc., 110*, 6153 (1988).
14. J. Soedarsono, M. Burgard, Z. Asfari, and J. Vicens, *Solv. Extr. Ion Exch., 13*, 755 (1995).
15. F. Arnaud-Neu, S. Fanni, L. Guerra, W. McGregor, K. Ziat, M.-J. Schwing-Weill, G. Barrett, M. A. McKervey, D. Marrs, and E. M. Seward, *J. Chem. Soc., Perkin Trans. 2, 2*, 113 (1995).
16. Y. Koide, H. Sato, H. Shosenji, and K. Yamada, *Bull. Chem. Sci. Jpn., 69*, 315 (1996).
17. T. Kakoi, T. Nishiyori, T. Oshima, F. Kubota, M. Goto, S. Shinkai, and F. Nakashio, *J. Membr. Sci., 136*, 261(1997).
18. M. Goto, M. Matsumoto, K. Kondo, and F. Nakashio, *J. Chem. Eng. Jpn., 20*, 157 (1987).

19. M. Goto, T. Kakoi, N. Yoshii, K. Kondo, and F. Nakashio, *Ind. Eng. Chem. Res.*, *32*, 1681 (1993).
20. K. Ohto, K. Shiratsuchi, K. Inoue, M. Goto, F. Nakashio, S. Shinkai, and T. Nagasaki, *Solv. Extr. Ion Exch.*, *14*, 459 (1996).

*Received by editor October 30, 1997*
*Revision received January 1998*

Downloaded At: 11:19 25 January 2011