## Article

# Solvent Extraction of Rare Earth and Precious Metals with Quaternary Ammonium Type of Calix[4]arene

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### Abstract

p-t-Calix[4]arene with quaternary ammonium groups at upper rim has been prepared to investigate solvent extraction behavior of trivalent rare earth metals in nitrate media and precious metals in chloride media. Rare earth metals are extracted as nitrate anion complex under a neutral condition of high nitrate concentration. Although calix[4]arene derivative has poor extraction ability compared with the corresponding monomeric analog and the commercial quaternary ammonium extractant due to not all but partial coordination of four quartenary ammonium groups and mismatching of nitrate anion complex to coordination site. Calix[4]arene derivative shows enhanced extractability to palladium and platinum due to the effect of its cyclic and rigid structure. They are extracted as chloroanion complex at high concentration of hydrochloric acid.

Key words: solvent Extraction, calix[4]arene, quaternary ammonium type of anion exchanger

# **1** Introduction

Calixarenes are cyclic oligomers and the third host compounds with discriminating properties for specific metal ions and organic compounds. A number of studies have been conducted on such properties of calixarenes and a number of studies of the specific behavior have been reviewed.[1,2] The authors have focused on the use of calixarene compounds as solvent extraction reagents for metal separation. In our previous works, cation exchange types of calixarene compounds have been prepared by introducing adequate cation exchangeable and neutral groups to phenolic oxygens, and the specific extraction behavior has been reported.[3] The only a few papers for anion exchange types of lipophilic calixarene as the extractants, however, has been reported.[4]

Trivalent rare earth metals are one of the metal groups that are quite difficult to be mutually separated due to similar size and chemical properties. In the previous works, phosphonic acid types of calix[4]arene compounds were prepared as the extractants for heavy rare earths, since phosphorus acid type of the extractants are preferable to extract smaller and heavier rare earth metals.[2(f, h)] On the contrary, quaternary ammonium nitrate type of the extractants are obviously anion exchangers.

In the present work, we have prepared O-nonylcalix[4]arene quaternary ammonium together with the corresponding monomeric one to investigate extraction behavior of trivalent rare earths and precious metals as anionic species.

## 2 Experimental

# 2.1 Reagents

In the present work, *O*-nonyl compounds have been prepared in a similar mannar to the corresponding *O*-octyl ones. Chemical structures and abbreviations of the extractants are shown in Fig.1. The synthetic scheme of calix[4]arene ex-



### Fig.1 Chemical structures and abbreviations of the present extractants.



Fig.2 Synthetic scheme of quaternary ammonium type of O-nonylcalix[4]arene.

tractant employed in the present work as a typical example is shown in Fig.2. That is, it has been prepared *via* cyclization, debutylation, *O*-nonylation, chloromethylation, introduction of ammonium group, and anion exchange (chloride to nitrate) from *p*-t-butylphenol. (The scheme showed from *O*-nonylation.) 3,5,5-Trimethylhexyl bromide as a reactant to introduce nonyl group to calix[4]arene and 2,6-dimethylphenol was prepared *via* tosylation and bromination from 3,5,5-trimethylhexanol. The preparation of tri-n-octylmethylammonium nitrate (TOMAN) from the commercial tri-n-octylmethylammonium chloride was described in the previous paper.[6]

# 5,11,17,23-Tetrakis(triethylammoniomethyl)-25,26,27,28-tetrakis(3,5,5-trimethylhexyl)calix[4]arene tetrachloride (TEQAC[4]Non)

To 25,26,27,28-tetrakis(3,5,5-trimethylhexyl)calix[4]arene (3.00 g, 3.24 mmol) were added paraformaldehyde (1.56 g, 51.9 mmol), 1,4-dioxane (400 cm<sup>3</sup>), concentrated hydrochloric acid (60 cm<sup>3</sup>, 38wt%, 720 mmol), glacial acetic acid (20 cm<sup>3</sup>, 32 mmol), and phosphoric acid (32 cm<sup>3</sup>, 85wt%, 470 mmol). The mixture was stirred and heated at 90°C for 48 h. After removal of the solvents *in vacuo*, chloroform was added to the solution to wash with distilled water until pH of the aqueous layer was around 4. The solvent was removed in vacuo. TLC (chloroform : hexane = 1 : 4)  $R_f$ =0.82.

To 5,11,17,23-tetrakis(chloromethyl)-25,26,27,28-tetrakis(3,5,5-trimethylhexyl)calix[4]arene (1.20 g, 1.07 mmol) was added triethylamine (13.0 g, 129 mmol), acetone (100 cm<sup>3</sup>) and THF (25 cm<sup>3</sup>). The mixture was stirred and heated at 55°C for a week. The solvent was removed *in vacuo* and the residue was reprecipitated from ethyl acetate. 49% from 25,26,27,28-tetrakis(3,5,5-trimethylhexyl)calix[4]arene. White powder; TLC (chloroform : heptane = 4 : 1 and chloroform : methanol = 3 : 1)  $R_f$ =0.00 and 0.00; <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>, TMS, 25°C)  $\delta$  0.92 (36H, s, C(<u>CH<sub>3</sub>)<sub>3</sub></u>), 1.04 (12H, d, CH(<u>CH<sub>3</sub></u>)CH<sub>2</sub>), 1.21 (8H, m, <u>CH<sub>2</sub></u>C(CH<sub>3</sub>)<sub>3</sub>), 1.55 (4H, s(br), <u>CH</u>(CH<sub>3</sub>)CH<sub>2</sub>), 1.80 (36H, s(br), N(CH<sub>2</sub><u>CH<sub>3</sub></u>)<sub>3</sub>), 1.96 (8H, s(br), OCH<sub>2</sub><u>CH<sub>2</sub></u>), 3.37 (24+4H, m, N(<u>CH<sub>2</sub></u>CH<sub>3</sub>)<sub>3</sub>+ArCH<sub>2</sub>Ar(*exo*)), 3.93 (8H, m, O<u>CH<sub>2</sub></u>), 4.37 (4H, d, ArCH<sub>2</sub>Ar(*endo*)), 4.88 (8H, s, ArCH<sub>2</sub>N), 7.78 (8H, s, ArH); Found: H,10.47; C,72.47, N,3.73%, Calcd for C<sub>92</sub>H<sub>160</sub>Cl<sub>4</sub>N<sub>4</sub>O<sub>4</sub>: H,10.55; C,72.31, N,3.67%.

# 5,11,17,23-Tetrakis(triethylammoniomethyl)-25,26,27,28-tetrakis(3,5,5-trimethylhexyl)calix[4]arene tetranitrate (TEQAN[4]Non)

5,11,17,23-Tetrakis(triethylammoniomethyl)-25,26,27,28-tetrakis(3,5,5-trimethylhexyl)calix[4]arene tetrachloride was dissolved in toluene to wash with 2 M (M = mol dm<sup>-3</sup>) hydrochloric acid twice, distilled water five times, and 2 M ammonium nitrate. The organic solution was dried over anhydrous sodium sulfate. After filtration, the solution was diluted with toluene to 5 mM.

### 4-Triethylammoniomethyl-2,6-dimethyl-1-(3,5,5-trimethylhexyl)benzene chloride (TEQAC[1]Non)

For the monomeric extractant, the similar procedures have been carried out from 2,6-dimethylphenol.

To 5-chloromethyl-1,3-dimethyl-2-(3,5,5-trimethylhexoxy)benzene (5.00 g, 17.7 mmol) were added triethylamine (8.79 g, 23.0 mmol) and THF (50 cm<sup>3</sup>). The mixture was stirred and heated at 80°C for 97 h. To the mixture was added triethylamine (5.02 g, 49.7 mmol). The mixture was stirred at 80°C for 3 days. The solvent was removed *in vacuo* and the residue was purified by column chromatography (chloroform : methanol = 3 : 1). After evaporation, the residue was dried by vacuum pump. 46% from the chloromethyl compound. brown viscous liquid; TLC (chloroform : methanol = 3 : 1)  $R_{\rm f}$ =0.06, <sup>1</sup>H-NMR (300MHz, CDCl<sub>3</sub>, TMS, 25°C)  $\delta$  0.92 (9H, s, C(CH<sub>3</sub>)<sub>3</sub>), 0.98 (3H, d, CH(CH<sub>3</sub>)CH<sub>2</sub>), 1.21 (2H, m, CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 1.46 (9H, t, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 1.63 (1H, m, CH(CH<sub>3</sub>)CH<sub>2</sub>), 1.81 (2H, m, OCH<sub>2</sub>CH<sub>2</sub>), 2.27 (6H, s, Ar(CH<sub>3</sub>)<sub>2</sub>), 3.46 (6H, t, N(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 3.78 (2H, t, OCH<sub>2</sub>), 4.55 (2H, s, ArCH<sub>2</sub>N), 7.10 (2H, s, ArH).

4-Triethylammoniomethyl-2,6-dimethyl-1-(3,5,5-trimethylhexyl)benzene nitrate (TEQAN[1]Non)

4-Triethylammoniomethyl-2,6-dimethyl-1-(3,5,5-trimethylhexyl)benzene chloride was also dissolved in toluene to wash with 2 M ( $M = mol dm^{-3}$ ) hydrochloric acid twice, distilled water five times, and 2 M ammonium nitrate. The organic solution was dried over anhydrous sodium sulfate. After filtration, the solution was diluted with toluene to 20 mM.

### 2.2 Distribution study of trivalent rare earth metals

Organic phase was directly used as toluene solution described above. Aqueous phase was prepared by dissolving three rare earth chlorides to 10 M ammonium nitrate. Equal volumes (0.5 cm<sup>3</sup>) of both phases were mixed and gently shaken at 303K for more than 3 h. After phase separation, the aqueous solution was diluted 21 times with 0.1 M hydrochloric acid. The metal concentrations in the aqueous solutions before and after equilibrium were measured by ICP-AES (Shimadzu ICPS-8100). The extracted metal ion concentrations were calculated from the mass balance.

### 2.3 Distribution study of precious metals

Organic phase was prepared by diluting TEQAC[4]Non or TEQAC[1]Non in chloroform to 5 mM. For aqueous phase, each chloride salt of rhodium, palladium, gold, platinum was dissolved in appropriate concentrations of hydrochloric acid. Equal volumes (2.0 cm<sup>3</sup>) of both phases were mixed and gently shaken at 303K for more than 24 h. After phase separation, the aqueous solution was diluted 5 times with hydrochloric acid solution. The metal concentrations in the aqueous solutions before and after equilibrium were measured by ICP-AES (Shimadzu ICPS-8100). The extracted metal ion concentrations were calculated from the mass balance.

## **3** Results and Discussion

#### 3.1 Distribution study of trivalent rare earth metals

In the previous work,[6] lanthanum extraction with TOMAN under various experimental conditions was investigated.[6] From the result, it was found that lanthanum was extracted hardly into chloroform, effectively into toluene, and was hardly from nitric acid solution, effectively from ammonium nitrate solution. For the diluent

used, relatively polar diluent such as chloroform is not preferable to extract rare earths with quaternary ammonium type of the extractants due to suppression of the complexation. At such high acidic media, dissociation of nitrate acid is not sufficient and actual activity of nitrate anion must be low. Furthermore, although the lanthanum extractability is dependent on the concentration of ammonium nitrate, the relation between logarithm of distribution ratio, log D and logarithm of the concentration of nitrate anion,  $log([NO^{3-}] / mol dm^{-3})$  is not linear. It means that the extraction is significantly affected by salting-out effect of ammonium nitrate. For these two reasons, the extractability is just poor under such an acidic condition.

Relation between %Extraction and sequence of trivalent rare earth metals with 4 kinds of quaternary ammonium extractant is shown in Fig.3. The x axis represents the reciprocal number of ionic radii of trivalent rare earths. The sequence of the plots from left to right corresponds with that from light to heavy rare earths, i.e. La, Pr, Nd, Sm, Eu, Gd, Ho, Y, and Er. The plots for all extractants are similar and show light rare earths selectivity, compared with those for phosphorus acid types of the extractants with heavy rare earths selectivity.[7] Calix[4]arene quaternary ammonium compounds have less extraction ability than the



Fig.3 Relation between % Extraction and sequence of trivalent rare earth metals.

[Rare eaerth(III)] : 0.1 mM each, three rare earths coexists in a sample (La, Pr, Nd), (Sm, Eu, Gd), (Ho, Er, Y), 10 M ammonium nitrate, TEQAN[4]Non (5 mM), TEQAN[4]Oct (5 mM), TEQAN[1]Oct (20 mM), TOMAN (20 mM) in toluene.

corresponding monomeric analogue, TEQAN[1]Oct, and the commercial quaternary ammonium extractant, TOMAN, due to not all but partial coordination among four quaternary ammonium groups and size-mismatching of nitrate anion complex to coordination site at upper rim of calix[4]arene. Various contradictions, such as use of low polar diluent for effective extraction and poor solubility of extractants into such diluents, requirement of extremely high salt concentration for salting-out effect and high dilution with acid solution for safe measurement by ICP-AES, make the extraction conditions limited. Separation factors for the extractants are listed in Table 1. Separation factor is defined by ratio of distribution ratio of prior metal ion to posterior one.

The separation efficiency for calix[4]arene type of the extractants are comparable to or relatively higher than that for commercial extractant, although more precise measurement of metals is necessary.

Table 1 Separation factors for the extractants.				
-	Separation factor $\beta$			
	TEQAN[4]Non	TEQAN[4]Oct	TEQAN[1]Oct	TOMAN
La / Pr	0.664	1.46	1.98	1.59
Pr / Nd	1.76	2.33	2.22	2.02
Nd / Sm	-	2.06	3.22	1.34

#### 3.2 Distribution study of precious metals

Rare earth metal ions are generally cations and the extraction of them as anions was observed under abnormal condition of extremely high concentration of ammonium nitrate. Quaternary ammonium extractants would be excellent anion exchangers for metal anions such as precious metals. Effects of hydrochloric acid concentration on the extractability of gold (III), platinum (IV), palladium (II), and rhodium (III) with TEQAC[4]Non, TEQAC[1]Non, and TOMAC are shown in Figs.4. Gold was quantitatively extracted over the whole concentration region of hydrochloric acid (0.1 to 3 M) with all extractants. Platinum(IV) was also quantitatively extracted over the whole concentration region of hydrochloric acid (0.1 to 3 M) with TEQAC[4]Non, while it was extracted to the extent with monomeric TEQAC[1]Non and the commercial extractants. Palladium (II) were extracted to the extent with all extractants and their extractabilities decrease with increasing the hydrochloric acid concentration due to high stability constants with chloride anion. Rhodium (III) was hardly extracted over the whole concentration region of hydrochloric acid with all extractants. Except for rhodium, precious metals were extracted as chloroanion from the acidic media. For platinum, chloro complex of platinum is extracted as  $PtCl_6^{2}$  anion by coordinating with quaternary ammonium groups. During the extraction, counter chloride ions to quaternary ammonium groups would be exchanged with chloride ions of PtCl<sub>6</sub><sup>2-</sup> anion. For releasing chloride ion, the extractability of platinum decreases with increasing hydrochloric acid concentration.

The extraction from ammonium chloride media was slightly less than that from hydrochloric acid media, whereas those from nitric acid and ammonium nitrate media were significantly lower than that from hydrochloric acid media except for gold. It is the reason why precious metals become anions by complexing with chloride ions and not with nitrate ion. Different from rare earths extraction that nitrate ions act as counter anions, salting out is not dominant but just anion exchange is dominant extraction mechanism for precious metals extraction.



Fig.4 Effects of hydrochloric acid concentaration on the extractability of gold (III), platinum (IV), palladium (II), and rhodium (III) with TEQAC[4]Non, TEQAC[1]Non, and TOMAC. [metal ion] : 0.1 M, TEQAC[4]Non (5 mM), TEQAC[1]Non (20 mM), TOMAC (20 mM) in chloroform.

The extraction of rare earths with TEQAN[4]Non was not effective due to only partial coordination of four quaternary ammonium groups and mismatching of nitrate anion complex to coordination site. On the contrary, compared with the monomeric extractant, TEQAC[1]Non, calix[4]arene derivative, TEQAC[4]Non shows higher extraction ability to platinum (IV) and palladium (II). It means that TEQAC[4]Non behaves as an anion exchanger . Furthermore, it would be attributed that cyclic structure of calix[4]arene at upper rim fits to the size of chloro anion complex of platinum (IV) and palladium (II) or all ammonium groups participate in coordination, or

both.

Effect of TEQAC[4]Non concentration on distribution ratio of platinum from hydrochloric acid media (3 M hydrochloric acid) is shown in Fig.5. The plots lie on a straight line with the slope of 1. It means that anionic platinum complex was extracted with a single molecule of TEQAC[4]Non. At 3 M hydrochloric acid, platinum ion exists as  $PtCl_6^{2-}$  anion. The extraction equation is considered as follows;

 $PtCl_6^{2-} + RN_4^{4+} \bullet 4Cl^{-} \neq PtCl_6^{2-} \bullet RN_4^{4+} \bullet 2Cl^{-} + 2Cl^{-}$ 

Where  $RN_4^{4+}$ •4Cl<sup>-</sup> represents TEQAC[4]Non. As described above, for releasing chloride ion, the extractability of platinum decreases with increasing hydrochloric acid concentration.



Fig.5 Effect of extractant concentration on distribution ratio of platinum from hydrochloric acid media (3 M HCl).

### References

- 1) C.D. Gutsche, Calixarenes revisited, Royal Society of Chemistry, Cambridge, 1996.
- 2) Z. Asfari, V. Boehmer, J.M. Harrowfield, and J. Vicens, *Calixarenes 2001*, Kluwer Academic Publishers, Netherlands, 2001.
- e.g.(a)K. Ohto, M. Yano, K. Inoue, T. Yamamoto, M. Goto, F. Nakashio, S. Shinkai, and T. Nagasaki, Anal. Sci., 11, 893-902 (1995), (b) K. Ohto, K. Maruishi, T. Shinohara, and K. Inoue, Solv. Extr. Res. Dev., Jpn., 3, 231-237 (1996), (c) K. Ohto, K. Shiratsuchi, K. Inoue, M. Goto, F. Nakashio, S. Shinkai, and T. Nagasaki, Solvent Extr. Ion Exch., 14, 459-478 (1996), (d) K. Ohto, E. Murakami, T. Shinohara, K. Shiratsuchi, K. Inoue, and M. Iwasaki, Anal. Chim. Acta, 341, 275-283 (1997), (e) K. Ohto, H. Yamaga, E. Murakami, and K. Inoue, Talanta, 44, 1123-1130 (1997), (f) K. Ohto, H. Ota, and K. Inoue, Solv. Extr. Res. Dev., Jpn., 4, 167-182 (1997), (g) K. Ohto, H. Higuchi, and K. Inoue, Solv. Extr. Res. Dev., Jpn., 8, 37-46 (2001), (h) K. Ohto, T. Matsufuji, A. Tada, T. Oshima, and K. Inoue, Solvent Extraction for Sustainable Development, Proc. Int. Conf. Solv. Extr. 2005, 846-851 (2005).
- 4) for example (a) K. Ohto, A.Taira, H. Higuchi, and K. Inoue, *Rikougakubu Shuho* (Saga Univ.), 33, 21-24 (2004).
  (b) J. K. Cherif, M. Mahouachi, R. Abidi, and J. Vicens, *J. Incl. Phenom. Macrocy. Chem.*, 55, 51-57 (2006).
- 5) e.g. (a) J. S. Preston and A. C. Du Preez, *Process Metall.1992*, 7A (Solvent Extr.1990, Pt.A), 883-894 (1992),
  (b) A. K. Pyartman, A. A. Kopyrin, E. A. Puzikov, and K. B. Bogatov, *Russ. J. Inorg. Chem.*, 41, 663-666 (1996), (c) I. Komasawa, K. Hisada, and M. Kiyamura, *J. Chem. Eng. Jpn.*, 23, 308-315 (1990).
- 6) K. Ohto, R. Sugiyama, H. Ishii, and K. Inoue, Rikougakubu Shuho (Saga Univ.), 34, 15-19 (2005).
- 7) for example (a)T. B. Pierce and P. F. Peck, *Analyst*, 88, 217-221 (1963). (b) Z. Kolarik and H.Pankova, *J. Inorg. Nucl. Chem.*, 28, 2325-2333 (1966).