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ORIGINAL ARTICLE

Solubilities and metal extraction behaviors for calix[4]arene acetic-acid derivatives in various organic solvents

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Abstract

Calixarene derivatives exhibit excellent extractability and selectivity for metal ions based on their chelating and size-discriminating effects; however, their poor solubility in aliphatic hydrocarbons, which are used as solvents in industrial processes, hinders their practical use. In this study, the relationship between solubility of calix[4]arene acetic-acid derivatives in various organic solvents and Hansen solubility parameters of the solvents was investigated. The center coordinates of the Hansen solubility sphere of the *p*-*tert*-octylcalix[4]arene acetic-acid derivative (^{t}Oct[4]CH_2COOH), as determined from its solubility in 50 different solvents, are $\delta_D = 17.24$, $\delta_P = 4.73$, $\delta_H = 4.45$, which indicate that this extractant is less polar than *p*-*tert*-butylcalix[4]arene acetic-acid derivative. The solubilities of ^{t}Oct[4]CH_2COOH in diethylene glycol dibutyl ether (DBC) and 2-nonanone (2-NON) were 92.6 mM and 91.1 mM, respectively. DBC and 2-NON are relatively preferable as solvents from the viewpoint of physical properties (low viscosity, relatively low water solubility, and high flash point). Extractability of Pb(II) using ^{t}Oct[4]CH_2COOH dissolved in various solvents was compared. Extraction in DBC proceeded at much higher pH than that in other solvents. Extraction of various metals in 2-NON proceeded at higher pH than that in chloroform. The order of metal selectivity of ^{t}Oct[4]CH_2COOH in 2-NON was similar to that in chloroform. The extraction reaction for Pb(II) using ^{t}Oct[4]CH_2COOH was determined by slope analysis. These results suggest that 2-NON can be an alternative to chlorinated solvents for use of ^{t}Oct[4]CH_2COOH as a metal extractant.

Keywords Calixarene · Solvent extraction · Solvent · Hansen solubility parameters · 2-Nonanone

Introduction

Extractants for metal extraction must meet many requirements for industrial processes. They should form complexes with the targeted metal ion under restricted aqueous conditions, and the resulting metal complex should distribute quantitatively into the organic phase. If the complexation reaction is selective, the targeted metal is separated from other impurity metals. It is desirable that the complexation reaction is rapid. The extraction reaction must be reversible to quantitatively strip the extracted metal under simple conditions. Extractants are typically dissolved in a solvent (diluent) for use, to enable adjustment of viscosity and easy phase separation. The solubility of the extractant in the solvent should be high to ensure high extraction capacity. Additionally, solvents must also meet various industrial requirements [1, 2]: low water solubility to minimize leakage into the aqueous phase, low viscosity for easy operation, low toxicity, and low volatility and high flash point for safety. Commercially available extractant-solvent combinations are very limited in meeting most of these requirements.

High extractability and high selectivity of the extractant are key for good separation processes, so numerous extractants for metal ions have been developed. Calixarene, a class of macrocyclic compounds, has been used as a platform to develop extractants for metal ions. Various functional groups can be attached to the upper and lower rims of calixarenes for ion exchange and coordination with metals. The resulting calixarene derivatives not only exhibit chelating effects based on their multifunctionality, but also acquire size-discriminating effects based on their

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macrocyclic structures [3, 4]. However, most calixarene derivatives are poorly soluble in the aliphatic hydrocarbons used in many solvent-extraction processes [5–7], so extraction of metals using calixarene derivatives has been performed in chlorinated solvents, such as dichloromethane and chloroform. Low solubility in solvents for separation processes is a hindrance to practical application of calixarene derivatives.

Calix[4]arene acetic-acid derivatives show high extractability for various metal cations based on proton-exchange reactions by several carboxyl groups. In 1995, *p*-*tert*-octylcalix[4]arene carboxylic-acid derivative (^{t}Oct[4]CH$_2$COOH, Fig. 1) was developed as an extractant for rare-earth metal ions [8]. Rare earth extraction using ^{t}Oct[4]CH$_2$COOH is enhanced in both kinetics and extractability by the co-extraction of Na(I) [8–11]. Extraction of divalent metals, such as Pb(II) and Cu(II), using ^{t}Oct[4]CH$_2$COOH has also been investigated and the extraction reactions have been confirmed [12–14]. Additionally, *p*-*tert*-butylcalix[4]arene carboxylic-acid derivative can selectively extract In(III) and Ga(III) from Zn(II) [15]. Solubility of ^{t}Oct[4]CH$_2$COOH in toluene is 19.1 mM [16]. Metal extraction using calixarene acetic-acid derivatives has been investigated in chloroform and toluene. Discovering novel good solvents for ^{t}Oct[4]CH$_2$COOH with low toxicity and safety, based on high flash point, might enable development of a new metal-refining process.

The authors recently investigated the potential of aromatic ethers as solvents for calixarene acetic-acid derivatives [16, 17]. Aromatic monoethers have structural similarity to calixarenes due to their aromatic ring and polar ethereal oxygen. The solubility of *p*-*tert*-octylcalix[6]arene carboxylic-acid derivative (^{t}Oct[6]CH$_2$COOH) in 1-butoxybenzene (BB) was 24.9 mM, which is much higher than that in hexane [18]. Amino acid esters and proteins were extracted using ^{t}Oct[6]CH$_2$COOH in BB. The solubility of ^{t}Oct[4]CH$_2$COOH in BB is 28.0 mM, which is higher than that in toluene and many aliphatic hydrocarbons [16]. Divalent metal ions, such as Cu(II), were extracted using ^{t}Oct[4]CH$_2$COOH in BB. As discussed, the discovery of novel solvents would enhance utility of extraction processes using calixarene derivatives.

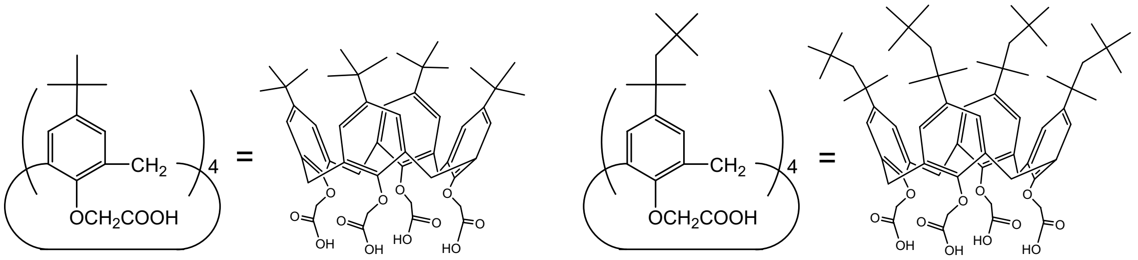
In this study, the solubilities of ^{t}Oct[4]CH$_2$COOH and *p*-*tert*-butylcalix[4]arene carboxylic-acid derivative (^{t}Bu[4]CH$_2$COOH, Fig. 1) in various solvents were investigated to find good solvents for solvent-extraction processes using these macrocyclic compounds. The relationship between the Hansen solubility parameters (HSPs) of the solvents and solubility of ^{t}Oct[4]CH$_2$COOH was investigated. Three-dimensional HSPs have evolved from the Hildebrand solubility parameter and have been developed as a tool to find solvents in a similar way to the basic rule of "like dissolves like" [19–21]. Therefore, HSPs can be utilized to understand the requirements of solvents that can dissolve ^{t}Oct[4]CH$_2$COOH. Extraction tests for various metal ions using ^{t}Oct[4]CH$_2$COOH in suitable identified solvents were performed.

Methods

Reagents

^{t}Bu[4]CH$_2$COOH and ^{t}Oct[4]CH$_2$COOH were synthesized according to procedures previously described [8]. The calix[4]arene derivatives have a cone conformation and the structure was confirmed by proton nuclear magnetic resonance spectroscopy (^{1}H-NMR).

Analytical-grade organic solvents were purchased as follows and used without further purification for the solvent-extraction tests: acetic acid, acetone, acetophenone, anisole, benzyl alcohol, chloroform, cyclohexane, dibenzyl ether, diethylene glycol, dipropylene glycol, dodecane, ethanol, ethyl acetate, hexane, isopropyl ether, methyl ethyl ketone, methyl isobutyl ketone, octanoic acid, 1-octanol, 1-propanol, 2-propanol, propionic acid, tetrahydrofuran, toluene, 2,2,4-trimethylpentane, *p*-xylene, diethylene glycol dibutyl ether (dibutyl carbitol, DBC), 1-nonanol, diphenyl ether



^{t}Bu[4]CH$_2$COOH
(cone conformation)

^{t}Oct[4]CH$_2$COOH
(cone conformation)

Fig. 1 Structures of ^{t}Bu[4]CH$_2$COOH and ^{t}Oct[4]CH$_2$COOH

(Wako Pure Chemical Ind. Ltd., Japan), γ-butyrolactone, cycloheptanone, diacetone alcohol, 2-methyl cyclohexanone, methyl isoamyl ketone, isopropyl benzene (cumene), 1,2-dimethoxybenzene, 1,1,3,3-tetramethoxypropane, hexanoic acid, 1,8-cineole, nonylbenzene, 2-nonanone (2-NON), 1-phenyl-1-butanone, *p*-methylacetophenone, 3,4-dimethoxyphenylacetone, valerophenone, 2-methyl valeric acid (Tokyo Kasei Co., Ltd., Japan), diethyl ketone (Merck, Germany), dipropyl ketone (Sigma-Aldrich Japan K.K., Japan), and cyclopentyl methyl ether (Zeon Co., Japan). Distilled water was also used.

Analytical-grade manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), lead(II), iron(III), gallium(III), indium(III), and lanthanum(III) chlorides (Wako Pure Chemical Industry, Ltd., Japan) were used to prepare test solutions of metal ions. All other reagents were reagent grade and were used as received.

Relationships between solubility of calix[4]arene derivatives and Hansen solubility parameters of solvents

HSPs have been developed as a tool for the prediction of solubility of organic compounds [19]. HSPs consist of three intermolecular bonding forces: nonpolar (dispersion) interactions (δ_D), polar (dipole–dipole and dipole–induced dipole) interactions (δ_P), and hydrogen-bonding interactions (δ_H) [22]. The three HSPs of a solvent can be expressed by a coordinate in a three-dimensional space called the Hansen space. On the basis of the “like dissolves like” principle, the HSP coordinates of an organic compound and its good solvents are located in the same region of Hansen space. Therefore, the set of coordinates of HSPs for good solvents are located in close proximity to each other, which is called the Hansen sphere. To specify the requirements for good solvents to dissolve the calix[4]arene derivatives, construction of the Hansen spheres was attempted: solubility of 10 mM ^{t}Bu[4]CH_2COOH or ^{t}Oct[4]CH_2COOH in fifty solvents at room temperature (25 °C) was visually checked. Good solvents and poor solvents were classified using the solubility threshold of 10 mM. Classification of the solvents was shown in Hansen space using HSPiP (Hansen Solubility Parameters in Practice) software ver. 5.19. HSP values for each solvent were obtained from the software database. A Hansen sphere was created so that good solvents were placed within the sphere and poor solvents were outside.

The distance for the HSPs between two materials (*Ra*) is given by Eq. (1):

$$\mathrm{Ra} = \sqrt{4\left(\delta_{D2} - \delta_{D1}\right)^2 + \left(\delta_{P2} - \delta_{P1}\right)^2 + \left(\delta_{H2} - \delta_{H1}\right)^2} \quad (1)$$

where δ_{D1}, δ_{P1}, and δ_{H1} represent the HSP values of a solvent, while δ_{D2}, δ_{P2}, and δ_{H2} represent those of the other compound. The radius of the Hansen sphere is called the interaction radius (R_0). The relative energy distance (RED), which is the ratio of *Ra* to R_0 (Eq. (2)), was calculated as an index to estimate the similarity of HSPs between the calixarene derivatives and solvents:

$$\mathrm{RED} = R_a/R_0 \quad (2)$$

The saturated solubility of ^{t}Oct[4]CH_2COOH in some solvents was quantified as follows: excess ^{t}Oct[4]CH_2COOH was added to each organic solvent so that the solute remained undissolved. After filtration of the undissolved solute using Kiriyama No. 5C filter paper (Kiriyama Glass Works Co., Japan), the filtrate (5.00 mL) was dried *in vacuo* to recover dissolved ^{t}Oct[4]CH_2COOH. The dry mass of the dissolved solute was weighed using an electronic balance (Sartorius CP225D, Germany) to determine the solubility. The logarithm of the partitioning coefficient between 1-octanol and water (log*P*) was used as an index for the hydrophilic/hydrophobic balance for organic compounds. The log*P* values of some solvents were obtained using MarvinSketch 6.2.1 software (ChemAxon Ltd., Hungary) and the KLOP method [23].

Solvent-extraction tests for metal ions

Aqueous solutions of Mn(II), Co(II), Ni(II), Cu(II), Pb(II), Ga(III), In(III), Fe(III), or La(III) were prepared at a concentration of 0.10 mM. The pH of the aqueous solution was adjusted using 100 mM HEPES (4-(2-hydroxyethyl)-1-piperazine ethanesulfonic acid) buffer and a small quantity of HCl or LiOH. An organic solution was prepared by dissolving 10 mM ^{t}Oct[4]CH_2COOH in organic solvents (chloroform, toluene, 2-NON, DBC, acetophenone). The organic solution (1.0 mL) and aqueous solution (5.0 mL) were mixed in a screw-capped glass vial; the volume ratio between the organic phase and aqueous phase was 1:5 (O/A = 0.2). The mixture was shaken (120 rpm) in a thermostatted water bath at 30 °C [16, 17]. After 24 h, when the extraction had attained equilibrium, each phase was separated. The equilibrium pH was measured using a pH meter (DKK-TOA Co. HM-30G, Tokyo, Japan), which was calibrated against buffers of pH 4, 7 and 10. The initial and equilibrium concentrations of metal ions in the aqueous phases were determined using an atomic adsorption spectrophotometer (Shimadzu AA-7000, Japan) or inductively coupled plasma mass spectrometer (Agilent 7850 ICP-MS, Agilent Technologies Japan, Ltd., Japan). The extraction percentage and distribution ratio (*D*) of the metal were calculated according to Eqs. (3) and (4), respectively:

$$Extraction\,[\%] = \frac{[\mathrm{M}]_{aq,init} - [\mathrm{M}]_{aq,eq}}{[\mathrm{M}]_{aq,init}} \times 100 \quad (3)$$

$$D = \frac{[\mathrm{M}]_{org,eq}}{[\mathrm{M}]_{aq,eq}} = \frac{5 \times \left([\mathrm{M}]_{aq,init} - [\mathrm{M}]_{aq,eq}\right)}{[\mathrm{M}]_{aq,eq}} \tag{4}$$

where $[\mathrm{M}]_{aq,init}$ represents the initial concentration of metal ion in the aqueous phase, and $[\mathrm{M}]_{aq,eq}$ and $[\mathrm{M}]_{org,eq}$ are the total concentrations of metal ions in the aqueous and organic phases, respectively, at equilibrium. The concentration of metal ion is concentrated by a factor of 5 in the organic phase (O/A = 0.2), so the decrease of metal concentration in the aqueous solution is multiplied by a factor of 5 in Eq. (4).

The reaction for the extraction of Pb(II) using ^{t}Oct[4]CH_2COOH was investigated by slope analysis at a volume ratio between the organic and aqueous phases of 1:5 (O/A = 0.2). The effect of equilibrium pH on the distribution ratio (*D*) of Pb(II) was investigated using 10 mM ^{t}Oct[4]CH_2COOH. The effects of ^{t}Oct[4]CH_2COOH concentration on *D* were investigated at pH 1.43 ± 0.01 in chloroform and at pH 2.74 ± 0.01 in 2-NON.

To confirm the reversibility of the extraction reaction in 2-NON, back extraction of Pb(II) extracted using ^{t}Oct[4]CH_2COOH was examined as follows: after forward extraction of 0.1 mM Pb(II) using ^{t}Oct[4]CH_2COOH in 2-NON (45.0 mL/9.0 mL) in a similar manner to that described above, the organic phase containing Pb(II) (1.0 mL) was contacted with 4.0 mL fresh aqueous solution containing nitric acid. After shaking the mixture at 30 °C for 24 h, the phases were separated and the concentration of Pb(II) in the aqueous phase was analyzed. The percentage of back extraction was determined from mass balance.

Results and discussion

Relationships between solubility of ^{t}Oct[4]CH_2COOH and Hansen solubility parameters of solvents

Calix[4]arene carboxylic-acid derivatives have been developed as ion-exchangeable calixarene derivatives [24–26]. Solubilities of ^{t}Bu[4]CH_2COOH in chloroform and toluene were reported to be 50.1 mM and 9.3 mM, respectively, while that in aliphatic hydrocarbons is quite small [18]. Therefore, extraction of metals using ^{t}Bu[4]CH_2COOH has generally been performed in chlorinated solvents [24]. ^{t}Oct[4]CH_2COOH was developed to increase the solubility of this molecule type in hydrocarbons [8]. The solubility of ^{t}Oct[4]CH_2COOH in chloroform (63.0 mM) and toluene (19.3 mM) is higher than that of ^{t}Bu[4]CH_2COOH [18]. In this study, the solubilities of ^{t}Bu[4]CH_2COOH and ^{t}Oct[4]CH_2COOH in fifty different solvents were examined. From the results, the solvents were qualitatively classified as good or poor, with a threshold of 10 mM (Tables S1 and S2). ^{t}Oct[4]CH_2COOH was dissolved in 13 solvents; five ethers, six ketones, toluene, and chloroform. ^{t}Bu[4]CH_2COOH was dissolved in 13 different solvents, including ethyl acetate, benzyl alcohol, and acetone; however, the set of good solvents did not completely match that for ^{t}Oct[4]CH_2COOH. Both calixarene derivatives were dissolved by acetophenone, chloroform, 2-methylcyclohexanone, methyl isoamyl ketone, tetrahydrofuran, cyclopentyl methyl ether, and *p*-methylacetophenone. Partial mismatch of good solvents for both calixarene derivatives suggests that they have different physical properties.

Using the results of solubility tests, HSPs of the fifty solvents were plotted in three-dimensional space to create a Hansen sphere [22, 27] (Fig. 2). For ^{t}Bu[4]CH_2COOH, the Hansen sphere was obtained with center coordinates at $\delta_D = 17.33$, $\delta_P = 6.98$, $\delta_H = 7.67$, and a radius of 4.5. Of the 13 good solvents for ^{t}Bu[4]CH_2COOH, HSPs of eight solvents were located within the sphere (RED < 1), while five solvents (acetone, acetophenone, benzyl alcohol, methyl

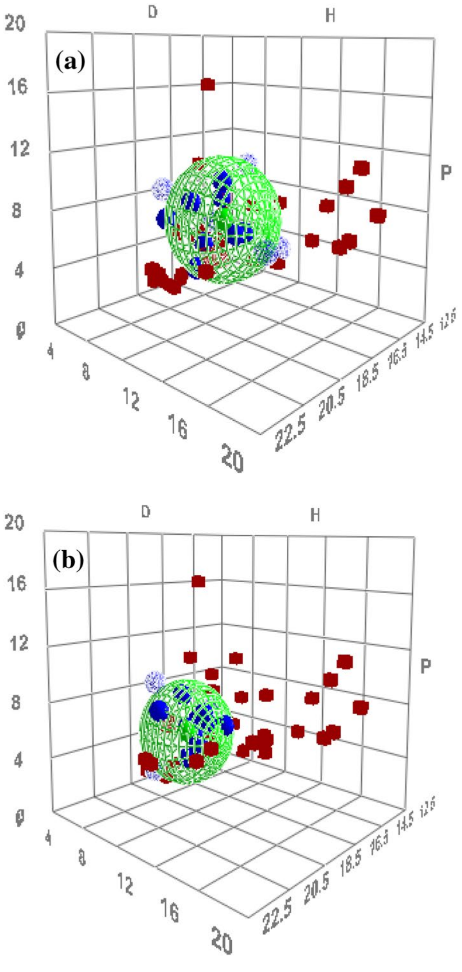


Fig. 2 3D HSP diagrams of ^{t}Bu[4]CH_2COOH (**a**) and ^{t}Oct[4]CH_2COOH (**b**) as well as those of 50 solvents with a solubility limit of 10 mM (sphere). Blue keys correspond to good solvents and red keys to poor solvents

isoamyl ketone, and 1-octanol) fell incorrectly outside the sphere (RED > 1). Additionally, HSPs of three poor solvents (3,4-dimethoxyphenylacetone, anisole, and dipropyl ketone) were incorrectly located within the sphere. For the Hansen sphere of ^{t}Oct[4]CH$_2$COOH, the center coordinates were $\delta_D = 17.24$, $\delta_P = 4.73$, $\delta_H = 4.45$, and the radius was 4.0.

For the central coordinates of the Hansen sphere of ^{t}Oct[4]CH$_2$COOH, the δ_D and δ_P values are much smaller than those of ^{t}Bu[4]CH$_2$COOH. This result is attributed to the non-polar *tert*-octyl groups of ^{t}Oct[4]CH$_2$COOH at the upper rim. The coordinates of the Hansen spheres confirmed that ^{t}Oct[4]CH$_2$COOH is more soluble than ^{t}Bu[4]CH$_2$COOH in many hydrocarbons. For ^{t}Oct[4]CH$_2$COOH, 45 solvents (90%) were appropriately classified as good and poor solvents by the Hansen spheres. HSPs of two solvents among the exceptions were also located very close to the interface of the Hansen sphere; methyl isobutyl ketone, RED = 1.037, toluene, RED = 1.095. The result suggests that HSPs can be used for tentative solubility prediction of the combination between calixarene derivatives and various solvents. However, there were also many solvents that gave incorrect correspondences in the Hansen spheres for ^{t}Bu[4]CH$_2$COOH and were inconsistent with predictions based on the Hansen sphere. HSPs probably do not reflect stereochemical factors of the macrocyclic calixarene. Despite partial discrepancies, HSPs seem to be effective to predict the solubility of calix[4]arene acetic-acid derivatives in organic solvents.

To assess their industrial utility, the physical properties of some good solvents for ^{t}Oct[4]CH$_2$COOH are compared in Table 1. It should be noted that the solubilities of ^{t}Oct[4]CH$_2$COOH in DBC (92.6 mM) and 2-NON (91.1 mM) are higher than those in chloroform and BB, which was developed as a potential solvent in our recent study [17]. From the viewpoint of continuous solvent-extraction operation and reduction of aqueous-phase contamination, water solubility of the solvents should be low. DBC, 2-NON, and acetophenone are less soluble in water than chloroform. In particular, the solubility of 2-NON is very small and comparable with that of toluene. For safe operation, the flash point of the solvent should be high. The flash points of DBC, 2-NON, and acetophenone are above 70 °C, so they are classified in the No. 3 petroleum group in Japan and can be safely used. The density of acetophenone is close to that of water, so acetophenone is disadvantageous to handle in extraction operations.

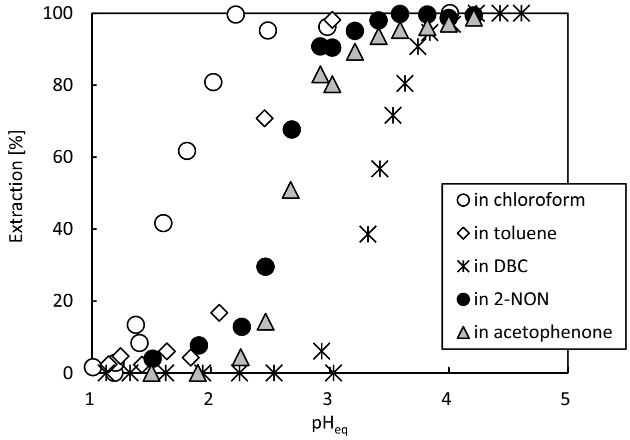


Fig. 3 Extraction profiles of Pb(II) using ^{t}Oct[4]CH$_2$COOH in various organic solvents

These results suggest that DBC and 2-NON can replace chloroform as a solvent for ^{t}Oct[4]CH$_2$COOH. Extraction behavior of various metal ions using ^{t}Oct[4]CH$_2$COOH in these solvents (Fig. S1) is compared in the next section.

Extraction of metal ions using ^{t}Oct[4]CH$_2$COOH in various solvents

Figure 3 shows extraction profiles of Pb(II) using ^{t}Oct[4]CH$_2$COOH in various solvents. Extraction of cationic

Table 1 Properties of organic solvents

Solvent	Molar mass (g mol^{-1})	Density (g/dm^3)	Viscosity (mPa·s)	Boiling point (°C)	Flash point (°C)	logP ^{a} (–)	Solubility in water (g/L)	Solubility of ^{t}Oct[4]CH$_2$COOH in each organic solvent (mM)
DBC	218.3	0.88	2.40	256	118	3.11	3.0	92.6
2-Nonanone	142.2	0.82	1.3	195	76	3.13	0.5	91.1
Acetophenone	120.2	1.03	1.8	202	82	1.63	5.5	13.3
Chloroform	119.4	1.48	0.53	61	Nonflammable	1.97	8.0	63.0
Toluene	92.1	0.867	0.59	111	4	2.73	0.47	18.4
BB^b	150.2	0.956	1.79	204	–	3.14	3.9×10^{-3}	28.0

–, not measured

^{a}estimated by using *MarvinSketch 6.2.1* software (ChemAxon Ltd., Budapest, Hungary) and the KLOP method

^{b}Properties of butoxybenzene was cited from Ref. [17]

Table 2 The $pH_{1/2}$ values of for the extraction of Pd(II) using ^{t}Oct[4]CH_2COOH in various solvents

Solvent	Chloroform	Toluene	2-Nonanone	Acetophenone	DBC
$pH_{1/2}$	1.66	2	2.55	2.77	3.38

species is based on proton-exchange reactions, so extraction increased with increasing pH. In chloroform, Pb(II) was extracted at very low pH, as reported for toluene [12]. Extraction in toluene was adjacent to that in chloroform. Extraction profiles of the ketone compounds, 2-NON and acetophenone, were similar. Extraction of Pb(II) in DBC, which is a triether compound, increased under the highest pH condition. Table 2 summarizes the $pH_{1/2}$ values shown in Fig. 3. The $pH_{1/2}$ values (pH at which 50% extraction is measured) of ketones are approximately 1 pH unit higher than those in chloroform. These results indicate that extractability in ketones and DBC is lower than that in chloroform. This result is in contrast to the similar extraction profiles of divalent metals, such as Cu(II), in BB and chloroform that were reported in a recent study [17].

The effect of solvents on metal extraction based on proton-exchange reactions is complicated: solvent polarity affects the coordination bonding between the extractant and metal ions, as well as dehydration of the complex. Therefore, it is not easy to specify the reason why the extraction profiles in the solvents are different. Participation of phenoxy oxygens and carbonyl oxygens of ^{t}Oct[4]CH_2COOH in complexation with Pb(II) was suggested in previous studies [12, 28–30]. Etheral oxygens of the triether compound DBC may inhibit complexation between Pb(II) and ^{t}Oct[4]CH_2COOH, resulting in low extraction in DBC. 2-NON is likely a potential solvent for ^{t}Oct[4]CH_2COOH, taking into account its physical properties. The extraction behaviors for metal ions in chloroform and 2-NON are compared in the following sections.

Extraction selectivity for metal ions

Owing to its macrocyclic structure, ^{t}Oct[4]CH_2COOH exhibits high extractability for various metal cations by the inclusion effect. Extraction of metals using ^{t}Oct[4]CH_2COOH in chloroform and 2-NON as a function of equilibrium pH is compared in Fig. 4. As reported in previous studies, a variety of metal ions were extracted using ^{t}Oct[4]CH_2COOH as the pH increased. Pd(II) is selectively extracted from divalent metals [12, 17, 28]. Inclusion by the macrocyclic structure of ^{t}Oct[4]CH_2COOH seems to contribute to the extraction of Pb(II). In both chloroform and 2-NON, trivalent metal ions were also extracted using ^{t}Oct[4]CH_2COOH with increasing pH.

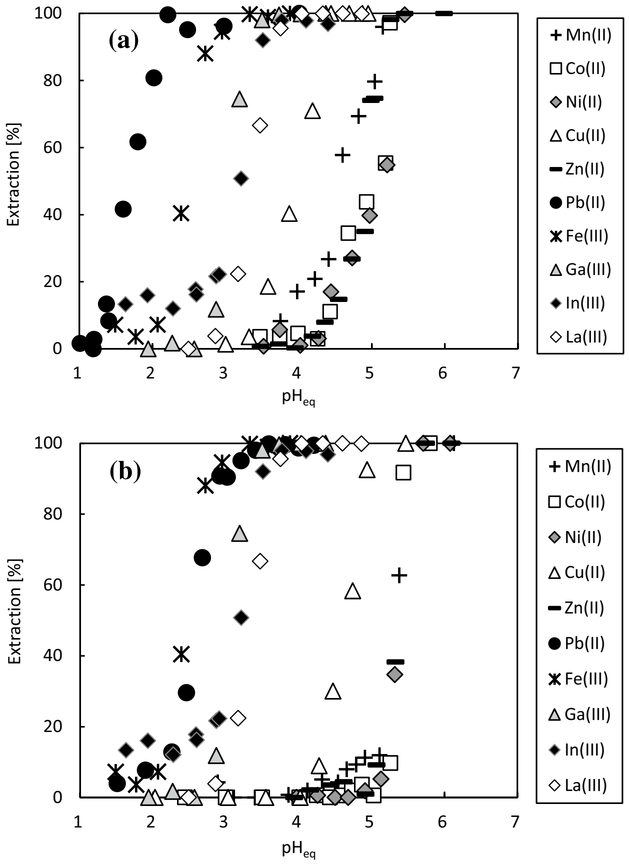


Fig. 4 Extraction profiles of metal ions using ^{t}Oct[4]CH_2COOH in chloroform (**a**) and in 2-NON (**b**)

The $pH_{1/2}$ values were determined to compare extractabilities in chloroform and 2-NON (Table 3). The order of extraction for divalent metal ions in chloroform and 2-NON was consistent: Pb(II) > Cu(II) > Mn(II) > Co(II), Ni(II), Zn(II). The order for trivalent metal ions was also similar: Fe(III) > In(III) > Ga(III) > La(III). Differences of the differences ($\Delta pH_{1/2}$) between the values in 2-NON and chloroform were also determined to compare extractability in the solvents. For divalent metal ions, the $\Delta pH_{1/2}$ values fell within a narrow range from 0.65 (Zn(II)) to 0.89 (Mn(II)). This result means that the effect of the solvent on extraction of divalent metal ions does not significantly vary. In contrast, the $\Delta pH_{1/2}$ values for trivalent metal ions differed. In particular, the pH range of La(III) extraction in 2-NON was much higher than that in chloroform. The reason for the different $\Delta pH_{1/2}$ values is not clear. The reactions and coordination numbers for extraction of the trivalent metal ions would be different, which would influence extraction behavior in each solvent. These results suggest that extraction using ^{t}Oct[4]CH_2COOH in 2-NON can be applied to separation processes for metal ions such as the aluminum group, rare-earth metals, and base metals.

Table 3 The $pH_{1/2}$ values of for the extraction of metal ions using ^{t}Oct[4]CH_2COOH in chloroform and in 2-NON and the difference of the $pH_{1/2}$ values ($\Delta pH_{1/2}$)

	Solvent	Mn(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)	Pb(II)	Fe(III)	Ga(III)	In(III)	La(III)
$pH_{1/2}$	Chloroform	4.00	4.27	4.44	3.61	4.54	1.78	2.21	2.95	2.75	3.12
	2-NON	4.89	5.10	5.23	4.39	5.19	2.54	2.57	3.43	3.27	4.09
$\Delta pH_{1/2}$		0.89	0.83	0.79	0.78	0.65	0.76	0.36	0.48	0.52	0.97

Extraction reaction of Pb(II) using ^{t}Oct[4]CH_2COOH

The extraction of Pb(II) using ^{t}Oct[4]CH_2COOH in chloroform and 2-NON was investigated by slope analysis. The relationship between the logarithm of the distribution ratio of Pb(II) and equilibrium pH was investigated (Fig. S2). The slope of the line obtained by plotting the relationship was 2, suggesting that two hydrogen ions are released from each ^{t}Oct[4]CH_2COOH molecule for the extraction. The relationship between the logarithm of the distribution ratio of Pb(II) and logarithm of the equilibrium concentration of ^{t}Oct[4]CH_2COOH in 2-NON was also studied (Fig. S3). The distribution ratio increased with increasing concentration of ^{t}Oct[4]CH_2COOH. The slope of the line obtained by plotting the relationship was roughly one, which suggests that a 1:1 complex formed for the extraction of Pb(II).

From the results, Eq. (5) can be proposed for the extraction of Pb(II) using ^{t}Oct[4]CH_2COOH in 2-NON:

$$Pb^{2+} + \overline{H4R} = \overline{Pb^{2+}H_2R^{2-}} + 2H^{+} \tag{5}$$

where overlining denotes species in the organic phase and H_4R denotes ^{t}Oct[4]CH_2COOH. A 1:1 complex between ^{t}Oct[4]CH_2COOH and Pb(II) was formed and the charge was neutralized by the release of two protons.

Based on Eq. (5), the extraction equilibrium constant for Pb(II) ($K_{Pb(II)}$) is given by Eq. (6):

$$K_{Pb(II)} = \frac{\left[\overline{Pb^{2+}H_2R^{2-}}\right][H^{+}]^2}{[Pb^{2+}]\left[\overline{H_4R}\right]} \tag{6}$$

The distribution ratio of Pb(II) between the organic and aqueous phases can be defined by Eq. (7):

$$D = \frac{[Pb(II)]_{org,eq}}{[Pb(II)]_{aq,eq}} = \frac{\left[\overline{Pb^{2+}H_2R^{-2}}\right]}{[Pb^{2+}]} \tag{7}$$

From Eqs. (6) and (7), Eq. (8) can be obtained in its logarithmic form:

$$\log D = 2pH + \log[\overline{H_4R}] + \log K_{Pb(II)} \tag{8}$$

From Eq. (8), the experimental log$D$ data used in Figs. S2 and S3 are plotted in Fig. 5. Plots of the dependencies of equilibrium pH (Fig. S2) and ^{t}Oct[4]CH_2COOH concentration (Fig. S3) fell almost on the same straight line, suggesting that Eq. (8) applies for the extraction of Pb(II) in chloroform and 2-NON. From the intercept of the theoretical straight line with the ordinate in Fig. 5, the extraction equilibrium constants $K_{Pb(II)}$ were determined as 0.102 [M] in chloroform and 1.91×10^{-3} [M].

In previous studies, one molecule of ^{t}Oct[4]CH_2COOH was confirmed to extract two Pb(II) ions [12], which is inconsistent with the results of Fig. 5 in this study. In this study, the slope analysis shown in Figs. S2 and S3 was performed under the condition of excess of ^{t}Oct[4]CH_2COOH over Pb(II). Extraction of Pb(II) should proceed stepwise according to Eqs. (5) and (9):

$$Pb^{2+} + \overline{Pb^{2+}H_2R^{2-}} = \overline{\left(Pb^{2+}\right)_2R^{4-}} + 2H^{+} \tag{9}$$

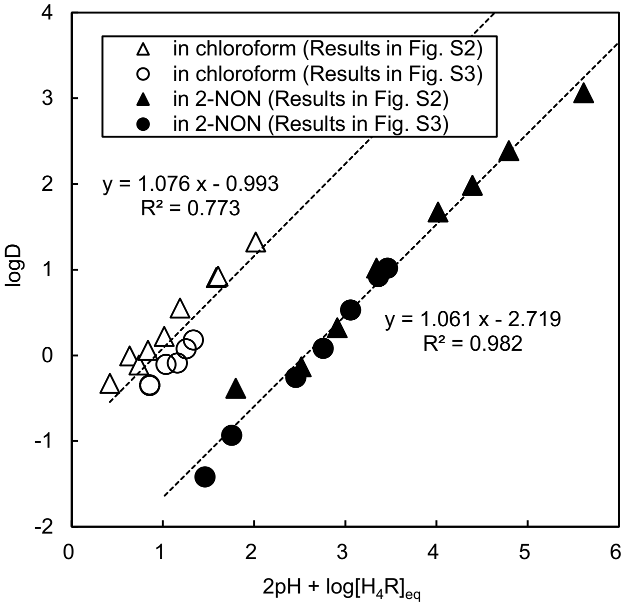


Fig. 5 Logarithmic distribution ratio of Pb(II) using ^{t}Oct[4]CH_2COOH as a function of pH and the concentration of ^{t}Oct[4]CH_2COOH in chloroform and 2-NON. The solid line is the theoretical line

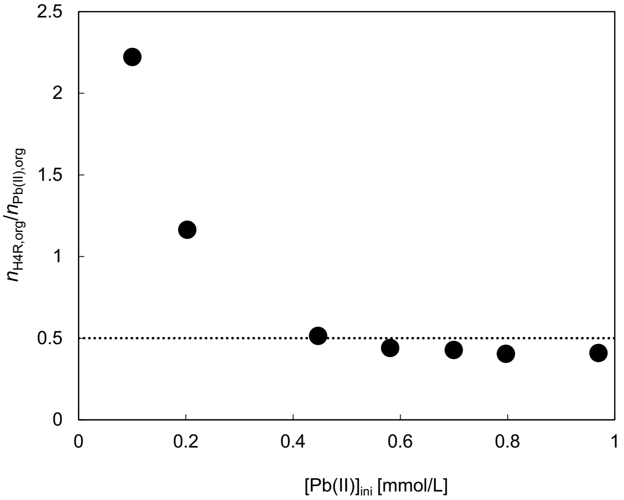


Fig. 6 Loading profile of Pb(II) to ^{t}Oct[4]CH$_2$COOH. pH 4.85 ± 0.09, O/A = 0.2, [Pb(II)]$_{\mathrm{init}}$ = 0.02–1.00 mmol/L, [^{t}Oct[4]CH$_2$COOH] = 1.0 mmol/L

Table 4 Back extraction of Pb(II) extracted using ^{t}Oct[4]CH$_2$COOH from 2-nonanoe

Concentration of nitric acid	Back-extraction (%)
0.1 mol/L	97.2
1.0 mol/L	95.4
3.0 mol/L	96.7
5.0 mol/L	96.5
8.0 mol/L	100

O/A=1.0, [Pb(II)]$_{\mathrm{init}}$=0.1 mmol/L, [^{t}Oct[4]CH$_2$COOH]=10 mmol/L

As performed in the previous study [12], a loading test was carried out under the condition of excess Pb(II) concentration (Fig. 6). The ratio of ^{t}Oct[4]CH$_2$COOH to Pb(II) in the organic phase decreased with increasing initial concentration of Pb(II) in the aqueous phase and asymptotically approached approximately 0.5. Therefore, the 1:2 complex can also be formed in 2-NON.

Back extraction of Pb(II) from 2-NON

Extraction of metal ions using ^{t}Oct[4]CH$_2$COOH is based on a proton-exchange reaction, so the extracted species should be stripped by contact with an acidic aqueous solution. The percentages of back-extraction of Pb(II) from the 2-NON solution using stripping solutions containing different concentrations of nitric acid are summarized in Table 4. Pb(II) was quantitatively recovered from the organic phase by contact with 0.1–8.0 mol/L nitric acid. From this result, metal-separation processes involving forward and back extraction in the 2-NON system can be envisaged.

Conclusions

The low solubility of calixarene derivatives in hydrocarbons has been an obstacle to their practical application in metal extraction. In this study, the solubilities of calix[4]arene acetic-acid derivatives in fifty organic solvents were compared to estimate the range of HSPs for good solvents. From the results, narrowing down of good solvents based on HSPs was partially achieved; however, there were also solvents for which predictions of solubility based on HSPs did not match the results. Owing to their macrocyclic structure, there may be limitations to predicting the solubility of calixarene derivatives based only on HSPs. The solubility of ^{t}Oct[4]CH$_2$COOH in DBC and 2-NON was high, at above 90 mM. Owing to their preferred properties, such as low viscosity, low water solubility, and high flash point, these solvents are satisfactory as industrial solvents. Extraction of Pb(II) using ^{t}Oct[4]CH$_2$COOH in DBC was very low compared with that in other solvents. DBC is a triether compound and has a podand-like structure. The lone pair of etheral oxygens might influence coordination to metal ions and hydration of metal complexes, resulting in reduced extractability. However, it is difficult to specify the effect of the solvent on extraction only from the results in this study. Metal extractability in 2-NON was lower than that in chloroform, but acceptable. In summary, these results suggest that 2-NON has high potential as a solvent for metal-extraction processes using ^{t}Oct[4]CH$_2$COOH.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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