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Flotation of Uranium from Seawater with Phosphate Esters of C-Undecylcalix[4]resorcinarene

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Table-type chelating surfactants ([4]Ar*m*X-R$_{12}$, *m*X means the number of phosphates (P), carboxylic acid (Ac), and hydroxamic acid (Hx), respectively) have been derived from the calix[4]resorcinarene bearing tetradodecyl side chains ([4]Ar-R$_{12}$), and applied to a collector of uranium flotation. The surface tension of the aqueous solution was 35 mN m^{-1} for [4]Ar5.6P-R$_6$ (R$_n$ means the alkyl chain length), 52 mN m^{-1} for [4]Ar5.9P-R$_{12}$, 42 mN m^{-1} for [4]Ar8.0Ac-R$_{12}$, and 48 mN m^{-1} for [4]Ar5.1Hx-R$_{12}$. They formed UO$_2$ complexes and floated the UO$_2^{2+}$ from an aqueous solution by air-bubbling. Furthermore, [4]Ar5.9P-R$_{12}$ and [4]Ar6.3P-R$_{12}$ had competence to float the uranium from seawater. A trace amount of uranium in 450 cm^3 of seawater was floated at 68—94% using 1—10 mg of [4]Ar5.9P-R$_{12}$ or [4]Ar6.3P-R$_{12}$. On the other hand, [4]Ar5.1Hx-R$_{12}$ and [4]Ar8.0Ac-R$_{12}$ brought about lower floatabilities. [4]Ar*m*P-R$_{12}$ could be recycled several times by dissolving the scum (uranium complex) in 5 mol dm^{-3} H$_2$SO$_4$.

Inclusion compounds having a cage, such as cyclodextrin,$^{1)}$ crown ether,$^{2)}$ and calix[6]arene derivatives,$^{3)}$ have been investigated in recent years. The character of attractive inclusion has been further functionalized for high selectivity by introducing some specific groups; the functionalized inclusion compound derived from calix[6]arene had been applied as an extractant for uranium recovery from seawater.$^{3)}$ On the other hand, amphiphilic inclusion compounds have also been examined as specific reagents. The cyclotetramer of resorcinol (calix[4]resorcinarene, [4]Ar) has an inclusion ability for some organic molecules.$^{4,5)}$ The calix[4]-resorcinarene bearing four alkyl side chains (C-alkylcalix[4]-resorcinarene, [4]Ar-R$_n$), obtained in high yield, had showed excellent emulsification of water-in-oil, and floated Cs$^+$ in water selectively at pH 12—13.$^{6)}$ Four-chained [4]Ar-R$_n$ is easily soluble in some organic solvents, but is insoluble in water of neutral pH. The large solubility in the organic solvent is favorable for preparing its derivatives. Organophosphorus compounds, such as tri-*n*-butyl phosphate, are known as an extractant of uranium;$^{7)}$ chelating surfactants bearing amide oxime and aminohydroxamic groups had been applied as the collectors of the uranium flotation.$^{8)}$ However, effective collectors for seawater are limited in number. In this study, hydrophilic phosphate groups were introduced to [4]-Ar-R$_n$, and the resulting amphiphilic calix[4]resorcinarenes ([4]Ar*m*P-R$_n$) were investigated concerning their abilities as collectors of uranium flotation, compared with the hydroxamic acid derivative ([4]Ar5.1Hx-R$_{12}$) and with the carboxylic acid derivative ([4]Ar8.0Ac-R$_{12}$). No chelating inclusion compounds bearing four alkyl side chains, i.e., table-type chelating surfactants, have yet been reported, as far as the present authors are aware.

Experimental

Syntheses of [4]Ar*m*P-R$_{12}$. [4]Ar-R$_{12}$ was prepared by the condensation of resorcinol with the dodecanal in the same manner as that reported in a previous paper.$^{6,9)}$ The phosphate derivatives, [4]Ar*m*P-R$_{12}$, were obtained by substituting the hydroxyl proton in [4]Ar-R$_{12}$ with phosphoryl chloride, followed by hydrolysis.$^{10)}$

After adding 100 cm^3 of benzene–pyridine (20 : 1) containing 1.8 mmol [4]Ar-R$_{12}$ dropwise to prescribed amounts of phosphoryl chloride, the reaction mixture was refluxed for 4 h. A precipitate of pyridinium chloride was filtered off, and the residue in the filtrate was added to 100 cm^3 of water after evaporating the benzene. The resulting precipitate ([4]Ar*m*P-R$_{12}$) was recrystallized with water–methanol (1 : 1). The number (*m*) of phosphates in [4]Ar-R$_{12}$ increased along with the amounts of phosphoryl chloride: *m* was 1.0 mol upon adding an equimolar amount of phosphoryl chloride to the OH unit in [4]Ar-R$_{12}$, 1.9 mol by two-fold addition, 3.9 mol by 4-fold, 4.9 mol by 6-fold, 5.9 mol by 30-fold, and 6.3 mol by 39-fold. Thus, the contents were maximum at about 6 mol, even if excess of phosphoryl chloride was added. The esters produced at below 4-fold molar of phosphoryl chloride should have been diphenyl phosphates, and those at above 4 must have been a mixture of mono- and diphenyl phosphates. The ratio of both phosphates was determined from data obtained in an analysis of P$^{11)}$ and the titration curves of their solutions; e.g., the product, [4]Ar5.4P-R$_4$, upon the addition of 30-fold phosphoryl chloride means 2.6 (= 8—5.4) mol of diphenyl phosphates and 2.8 (= 5.4—2.6) mol of monophenyl phosphates. [4]Ar5.9P-R$_{12}$ express 2.1 (= 8—5.9) mol of diphenyl phosphates and 3.8 (= 5.9—2.1) mol of monophenyl phosphates. [4]Ar*m*P-R$_n$ IR (KBr) ν_{OH} 3500—3000, ν_{CH} 2900, 2800, $\nu_{\mathrm{PO(OH)_2}}$ 1300—900 cm^{-1}. ^{1}H NMR (CDCl$_3$, TMS) $\delta = 0.8$—0.9 (12H, –CH$_3$), 1.2—2.2 (80H, –CH$_2$–), 4.6 (4H, –CH<), 6.7 (4H, Ar-H), 7.2 (4H, Ar-H). [4]Ar5.4P-R$_4$ Yield 49%. Found: C, 44.16; H, 5.07; P, 15.9%. Calcd for C$_{40}$H$_{52.2}$O$_{23.6}$P$_{5.4}$·2H$_2$O: C, 44.57; H, 5.05; P, 15.52%. [4]Ar5.6P-R_6 Yield 23%. Found: C, 47.83; H, 5.83; P, 14.0%. Calcd for $C_{48}H_{68.8}O_{24.4}P_{5.6}\cdot 2H_2O$: C, 47.66; H, 5.91; P, 14.34%. [4]Ar6.3P-R_8 Yield 67%. Found: C, 48.13; H, 6.56; P, 13.64%. Calcd for $C_{56}H_{86.9}O_{27.2}P_{6.3}\cdot 2H_2O$: C, 48.37; H, 6.47; P, 14.03%. [4]Ar1.0P-R_{12} Yield 13%. Found: C, 74.82; H, 10.45; P, 2.31%. Calcd for $C_{72}H_{104.0}O_{10.0}P_{1.0}$: C, 74.51; H, 9.03; P, 2.67%. [4]Ar1.9P-R_{12} Yield 19%. Found: C, 71.73; H, 9.32; P, 4.31%. Calcd for $C_{72}H_{104.9}O_{11.8}P_{1.9}$: C, 70.99; H, 8.68; P, 4.83%. [4]Ar3.9P-R_{12} Yield 29%. Found: C, 64.13; H, 8.38; P, 7.80%. Calcd for $C_{72}H_{106.9}O_{15.8}P_{3.9}$: C, 64.24; H, 8.00; P, 8.97%. [4]Ar4.9P-R_{12} Yield 22%. Found: C, 58.74; H, 8.15; P, 10.14%. Calcd for $C_{72}H_{114.7}O_{21.6}P_{4.9}\cdot 2H_2O$: C, 58.52; H, 8.02; P, 10.27%. [4]Ar5.9P-R_{12} Yield 78%. Found: C, 55.56; H, 7.76; P, 11.14%. Calcd for $C_{72}H_{117.7}O_{25.6}P_{5.9}\cdot 2H_2O$: C, 54.88; H, 7.71; P, 11.60%. [4]Ar6.3P-R_{12} Yield 48%. Found: P, 12.0%. Calcd for $C_{72}H_{118.9}O_{27.2}P_{6.3}\cdot 2H_2O$: P, 12.08%. Monomeric P-R_{12} was prepared by the action of phosphoryl chloride on 4-dodecylresorcinol.

Carboxylic Acid Derivative. The derivative, [4]Ar8.0Ac-R_{12}, was prepared by a reaction with two molar amounts of bromoacetic acid to the OH unit in [4]Ar-R_{12}. A small amount of sodium methoxide was added to dry methanol containing [4]Ar-R_{12} and bromoacetic acid; the mixture was stirred at 65 °C for 24 h under a nitrogen atmosphere. The precipitate of NaBr in the hot reaction mixture was filtered off and the filtrate was concentrated to one-third of its original volume under reduced pressure. The resulting product ([4]Ar8.0Ac-R_{12}) by adding a 35% HCl was recrystallized with chloroform–hexane. Yield 71%. Mp 105—109 °C. IR (KBr) ν_{CH} 2900—2800, ν_{CO} 1730 cm^{-1}. ^1H NMR ($CDCl_3$) $\delta = 0.8$ (12H, $-CH_3$), 1.2, 1.8 (80H, $-CH_2-$), 3.4—3.8 (4H, $-CH<$), 3.8—4.6 (16H, $-OCH_2CO-$), 6.4, 7.2 (8H, Ar-H). Found: C, 66.82; H, 8.29%. Calcd for $C_{88}H_{128}O_{24}\cdot H_2O$: C, 66.56; H, 8.25%.

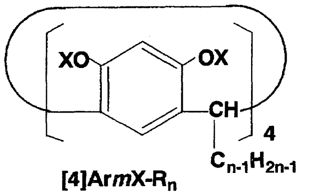
Hydroxamic Acid Derivative. The derivative, [4]Ar5.1Hx-R_{12}, was derived from [4]Ar8.0Ac-R_{12}. [4]Ar8.0Ac-R_{12} was treated with a 100-fold molar amount of thionyl chloride; the resulting acid chloride of [4]Ar8.0Ac-R_{12} was reacted with 10-fold molar of hydroxylamine in tetrahydrofuran.[12] After evaporation of the tetrahydrofuran, the remaining solution was adjusted to pH 4; the precipitate ([4]Ar5.1Hx-R_{12}) was first filtered and then washed with an excess of cold water. The number of the hydroxamic acid ligands in [4]Ar5.1Hx-R_{12} (5.1 mol of hydroxamic acid) was determined by elementary analyses. IR(KBr) ν_{OH} 3500—3000, ν_{CH} 2900—2800, ν_{CO}, δ_{NH} 1700—1610 cm^{-1}. Yield 56%. Found: C, 59.96; H, 7.74; N, 4.09%; C/N = 14.73%/%. Calcd for $C_{88}H_{132.1}O_{24.0}N_{5.1}\cdot 2NaCl$: C, 60.02; H, 7.62; N, 4.07%; C/N = 14.74%/%. The structures of these derivatives and the abbreviations are shown in Fig. 1.

Apparatus and Procedures. The apparatus and procedures of ion flotation were the same as those previously reported.[6] A uranium solution was prepared by dissolving $UO_2(NO_3)_2$ in an aqueous solution, while seawater was taken at the seacoast of Kawachi, Hotaku-gun, Kumamoto, in February, 1992. Extraction was carried out by a general method. The flotation procedures were as follows: [4]Ar*m*P-R_{12} was added to 450 cm^3 of a UO_2^{2+} solution or seawater in a flotation vessel; air was then introduced through a sintered-glass disk (No.4) at the bottom of the vessel at a rate of 30—40 cm^3 min^{-1} for 20 min. The amounts of uranium in the solution and seawater were determined from the absorbance of the uranium–arsenazo III complex (660 nm).[13]

The extractabilities and floatabilities for the uranium ions were calculated using the following equation:

$$F(\%) = \frac{a_0 - a_1}{a_0} \times 100,$$

where a_0 and a_1 denote the initial and final concentrations of the uranium in the solution or seawater, respectively.



Abbreviation	n	Substituent X (*m* unit mol)
[4]Ar-R_{12}	12	-H 8.0
[4]Ar5.4P-R_4	4	>POOH 2.6 + $-PO(OH)_2$ 2.8
[4]Ar5.6P-R_6	6	>POOH 2.4 + $-PO(OH)_2$ 3.2
[4]Ar6.3P-R_8	8	>POOH 1.7 + $-PO(OH)_2$ 4.6
[4]Ar1.0P-R_{12}	12	>POOH 1.0 + -H 6.0
[4]Ar1.9P-R_{12}	12	>POOH 1.9 + -H 4.2
[4]Ar3.9P-R_{12}	12	>POOH 3.9 + -H 0.2
[4]Ar4.9P-R_{12}	12	>POOH 3.1 + $-PO(OH)_2$ 1.8
[4]Ar5.9P-R_{12}	12	>POOH 2.1 + $-PO(OH)_2$ 3.8
[4]Ar6.3P-R_{12}	12	>POOH 1.7 + $-PO(OH)_2$ 4.6
[4]Ar8.0Ac-R_{12}	12	$-CH_2COOH$ 8.0
[4]Ar5.1Hx-R_{12}	12	$-CH_2CONHOH$ 5.1 + $-CH_2COOH$ 2.9

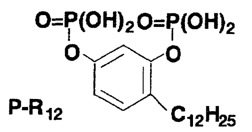


Fig. 1. The structures and the abbreviations.

Results and Discussion

Surface Activities. Surface tensions were measured using a Wilhelmy surface-tension balance. A solution of [4]Ar*m*P-R_n was surface active in the acidic-to-alkali region because of the introduction of hydrophilic phosphates, while that of the resorcinol-type [4]Ar-R_{12} was surface active only at a pH above 10.[6] The surface tension of [4]Ar6.3P-R_8 was 32 $mN\,m^{-1}$ at pH 1.0 (cmc: 4.7×10^{-5} $mol\,dm^{-3}$) and 38 $mN\,m^{-1}$ at pH 8.0 (1×10^{-3} $mol\,dm^{-3}$); that of [4]Ar5.6P-R_6 was 35 $mN\,m^{-1}$ at pH 8.0 (4×10^{-3} $mol\,dm^{-3}$). The area of the cross section of a molecule calculated from the Gibbs equation[14] was 123 $Å^2$ for [4]Ar6.3P-R_8 at pH 1.0.

A [4]Ar*m*P-R_n bearing short side chains (n=6, 8) had foaming properties. Foaming with a lapse of 1 min after shaking 10 cm^3 of a solution containing 1×10^{-4} $mol\,dm^{-3}$ of [4]Ar5.6P-R_6 or [4]Ar6.3R_8 was high above pH 7, as shown in Fig. 2. The inflection points of the curves at pH 2 and pH 7 should mean acid dissociation based on monophenyl phosphate (pK_a=1.46, 6.50).[15] However, butyl-chained [4]Ar5.4P-R_4 was too hydrophilic to foam stably. On the other hand, [4]Ar6.3P-R_{12} bearing tetradodecyl chains was too hydrophobic, and had no foaming property (γ_{cmc}: 52 $mN\,m^{-1}$ at 1×10^{-3} $mol\,dm^{-3}$). The collector should be recovered perfectly from the water or seawater. Therefore, the long-chained [4]Ar*m*P-R_{12} was considered to be favorable if it was floated as scum by air-bubbling.

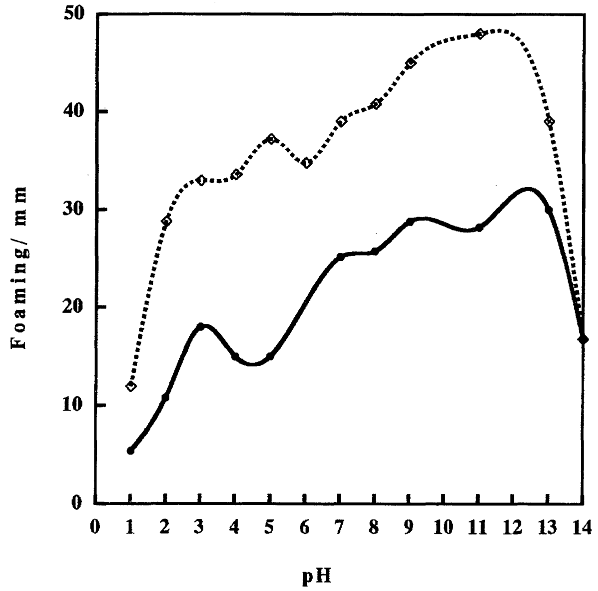


Fig. 2. Foaming abilities of [4]ArmP-R$_n$. Foaming ability: Foam height in glass cylinder, with lapse of 1 min after shaking 10 cm^3 of 1×10^{-4} mol dm^{-3} [4]ArmP-R$_n$ soln. ◇: [4]Ar5.6P-R$_6$, ●: [4]Ar6.3P-R$_8$.

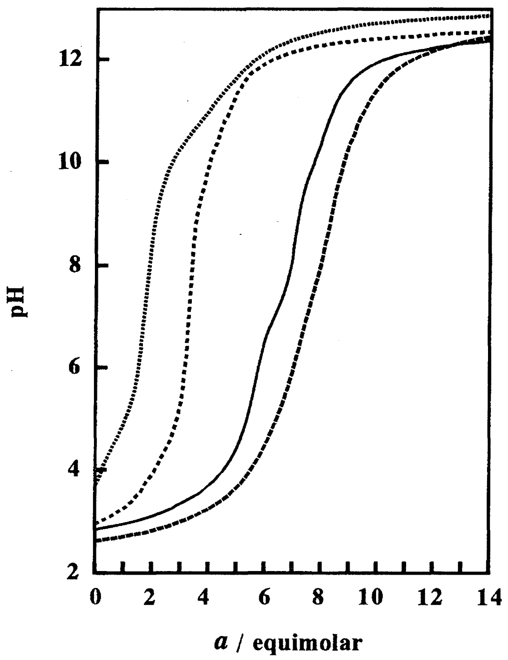


Fig. 3. Titration curves of [4]ArmP-R$_{12}$. [4]ArmP-R$_{12}$, UO_2^{2+}: 2.5×10^{-5} mol in 25 cm^3 of THF–H_2O (2 : 3), titrant: 0.05 mol dm^{-3} NaOH. ····: [4]Ar1.9P-R$_{12}$, - - -: [4]Ar3.9P-R$_{12}$, —: [4]Ar5.9P-R$_{12}$, - - -: [4]Ar5.9P-R$_{12}$+UO_2^{2+} (1 : 1).

The carboxylic acid and the hydroxamic acid derivatives also showed lowering abilities of surface tension at pH 8.0, the values of which were γ_{cmc} 42 mN m^{-1} for 6×10^{-4} mol dm^{-3} [4]Ar8.0Ac-R$_{12}$ (cmc: 1.6×10^{-4} mol dm^{-3}) and 48 mN m^{-1} for 6×10^{-4} mol dm^{-3} [4]Ar5.1Hx-R$_{12}$ (above 6×10^{-4} mol dm^{-3}).

Complex Formation. The formation of a UO_2 complex was examined by pH titration, extraction, and a continuous variation method.

The titration curves of [4]ArmP-R$_{12}$, recorded on a Kyoto Electronics AT-310J, are shown in Fig. 3. The number of phosphates did not increase by more than 6.3 (=about 6) unit mol in spite of a reaction with excess $POCl_3$ (as mentioned in the Experimental section). The neighboring hydroxyl groups on a diagonal line would be easier to be esterified, since the two pairs in the four hydroxyl groups are arranged so as to be conformationally easy to approach each other. Therefore, 2 mol of diphenyl phosphates should be formed predominantly, and the remaining 4 OH units (=8—2×2) would become mono- and diphenyl phosphates according to the amounts of $POCl_3$.

The titration curves were different depending on the number of phosphates. Dodecyl-chained [4]Ar1.9P-R$_{12}$ showed one equivalent point (a=1.9) at a pH below 9, and a curve having a gentle slope at pH above 10. The former should correspond to the dissociation of 1.9 mol diphenyl phosphates (monobasic acid), and the latter to neutralization of the hydroxyl groups. [4]Ar3.9P-R$_{12}$ having 3.9 mol of phosphates (below 4) showed one equivalent point (a=3.8) based on the diphenyl phosphates. On the other hand, [4]Ar5.9P-R$_{12}$ showed nearly the same curve as that of butyl-chained [4]Ar5.4P-R$_4$, and the curve was similar to that of monoalkyl phosphate (dibasic acid). Although the first equivalent point (a=5.6) was clear, the second one was complicated. The curve rose steeply at a=7.2, became gentle, then steep for $7.2<a\leq9.3$. The acid-dissociation constant (pK_a) of D-glucose 1-phosphate (monoester) has been reported to be 1.46 and 6.50;[15] pK_a of diester is considered to be about 1.5. It was presumed from both equivalent points (a=5.6 and 9.3) that the phosphates in [4]Ar5.9P-R$_{12}$ are a mixture of diphenyl and monophenyl phosphates. The first equivalent point (a=5.6) should correspond to the first acid dissociation of both phosphates; the difference of both equivalent points (9.3−5.6=3.7 mol) would be based on the second acid dissociation of monophenyl phosphate and the difference between the first equivalent point and the former difference (5.6−3.7=1.9 mol) would be based on the acid dissociation of diphenyl phosphate, respectively. The dissociation of about 2 protons (9.3−7.2=2.1 mol) in the high-pH region has been estimated for a pair of protons stably binding to the [4]Ar5.9P-R$_{12}$. The binding force would be formed by hydrogen bonding between both phosphates[16] and by inclusion. A similar stability of the hydrogen bonding in calix[6]arene had been reported by Sinkai et al.[3] The ratio of both phosphates was finally determined by elementary analysis (see Fig. 1).

The titration curve of [4]Ar5.9P-R$_{12}$ in the presence of UO_2^{2+} showed an obliquely straight rise, which means the release of the protons from the phosphate ligands based on the formation of the UO_2 complex. The curve at a=6 (acidic region) must indicate the UO_2 complex of coordination number six, and that until a=10 (alkali region) would mean the release of the protons from both phosphates, based on the complex formation (structure: 9.7=2.1+3.8×2; titration: 9.3=1.9+3.7×2) or on hydrolyzation of the UO_2 complex.

Extraction suggests complex formation. UO_2^{2+} in an aqueous solution could be extracted into a $CHCl_3$ layer by using [4]Ar6.3P-R_{12}, [4]Ar5.1Hx-R_{12}, and [4]Ar8.0Ac-R_{12} (Fig. 4). The extractabilities were 100% at neutral pH by using 2.5—10 mg of [4]Ar6.3P-R_{12}. However, the short-chained [4]Ar5.4P-R_4 and [4]Ar5.6P-R_6 could not extract, because of the less participation to $CHCl_3$. Furthermore, the composition of the UO_2 complex was examined by a continuous-variation method, as shown in Fig. 5. The absorbance curves indicate that the UO_2^{2+}/[4]Ar6.3P-R_{12} ratio of the complex is 1 : 2 at pH 2.0 and 1 : 1 at pH 8.0. Since the pK_{a1} of [4]Ar5.9P-R_{12} is considered to be about 1.5,[15] [4]Ar6.3P-R_{12}, having a similar structure, should bind twice at pH 2 (half dissociation) as much as that at pH 8 (complete dissociation) to the UO_2^{2+}, and the complex would be extracted in a neutral form as sodium salt. The surrounding phosphates in the calix[4]arene cavity would form a stable UO_2 complex cooperatively, which is the inclusion effect.

Flotation for UO_2^{2+} Solution. The hydrophilic–lipophilic balance (HLB) suitable for ion flotation is known to be in the range of 4—14.[8] The HLB value calculated according to the Oda equation[17] was 12 for [4]-Ar6.3P-R_{12}, 11 for [4]Ar5.1Hx-R_{12}, and 8 for [4]Ar8.0Ac-R_{12}. Therefore, these derivatives, being able to form UO_2 complexes, would float uranium from an aqueous solution. Flotation for a 10 ppm UO_2^{2+} solution is shown in Fig. 6. The floatabilities of UO_2^{2+} were nearly 100% at neutral pH by using 2.5—10 mg of [4]Ar6.3P-R_{12}. Since the UO_2^{2+} may float as the hydroxide,[18] the composition was examined. The analytical data (C=46.96%, H=6.24%) of the scum, based on using [4]Ar6.3P-R_{12}, agreed with the calculated values for the composition of a 1 : 1 complex; the extracted complex (C=47.14%, H=6.43%) also had the same composition. Therefore, the UO_2^{2+} should be recovered as a 1 : 1 complex of [4]Ar6.3P-R_{12}. [4]Ar5.1Hx-R_{12}; [4]Ar8.0Ac-R_{12} also brought about high floatabilities, but less than that of [4]Ar6.3P-R_{12}.

Flotation of Uranium from Seawater. Many salts are highly dissolved in seawater, though the concentration of uranium is only 3 ppb. [4]Ar*m*P-R_{12} is expected to float uranium from seawater, since it is surface active, and formed the stable UO_2 complex. Table 1 shows the recovery of uranium from seawater. Determinations of the uranium concentration

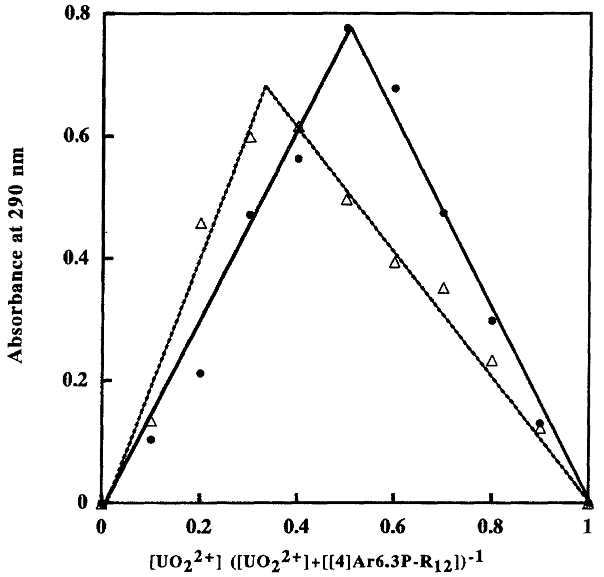


Fig. 5. Composition of uranium complexes by continuous variation method. [UO_2^{2+}]+[[4]Ar6.3P-R_{12}]=5×10^{-4} mol dm^{-3}, absorbance after 10 h, 1 cm of cell length, pH 13. △: pH 2.0, ●: pH 8.0.

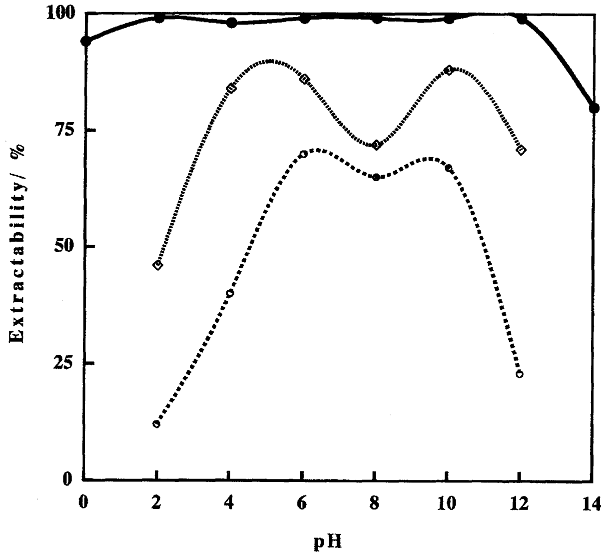


Fig. 4. Extraction for UO_2^{2+} solution. UO_2^{2+} soln: 450 cm^3 of 10 ppb uranium, [4]Ar6.3P-R_{12}, [4]Ar8.0Ac-R_{12}, [4]-Ar5.1Hx-R_{12}: 10 mg in 20 cm^3 of $CHCl_3$, time: 15 min. ●: [4]Ar6.3P-R_{12}, ◇: [4]Ar5.1Hx-R_{12}, ○: [4]Ar8.0Ac-R_{12}.

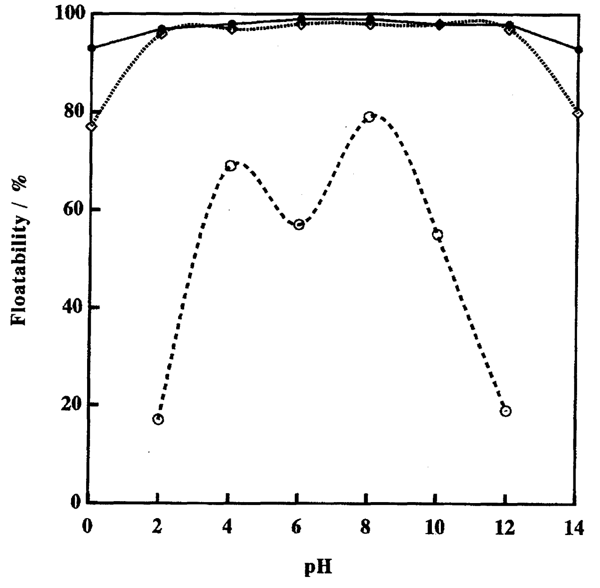


Fig. 6. Flotation for UO_2^{2+} solution. Soln: 450 cm^3 of 10 ppb uranium, collector: 10 mg, time: 15 min. ●: [4]-Ar6.3P-R_{12}, ○: [4]Ar8.0Ac-R_{12}, ◇: [4]Ar5.1Hx-R_{12}.

Table 1. Recoveries of Uranium from Seawater.

Collector	Extraction		Flotation	
	%	mg/g-col	%	mg/g-col
[4]Ar-R_{12}	0	0	0	0
[4]Ar6.3P-R_{12}	48	0.06	94	0.13
[4]Ar6.3P-R_{12}	—	—	$76^{a)}$	$0.27^{a)}$
[4]Ar6.3P-R_{12}	—	—	$75^{b)}$	$0.44^{b)}$
[4]Ar8.0Ac-R_{12}	0	0	50	0.07
[4]Ar5.1Hx-R_{12}	16	0.02	60	0.09

Seawater: 450 cm^3. Extraction: $CHCl_3$ 20 cm^3. Flotation: a) Seawater + 5 ppb U. b) Seawater + 10 ppb U. Collector: 10 mg.

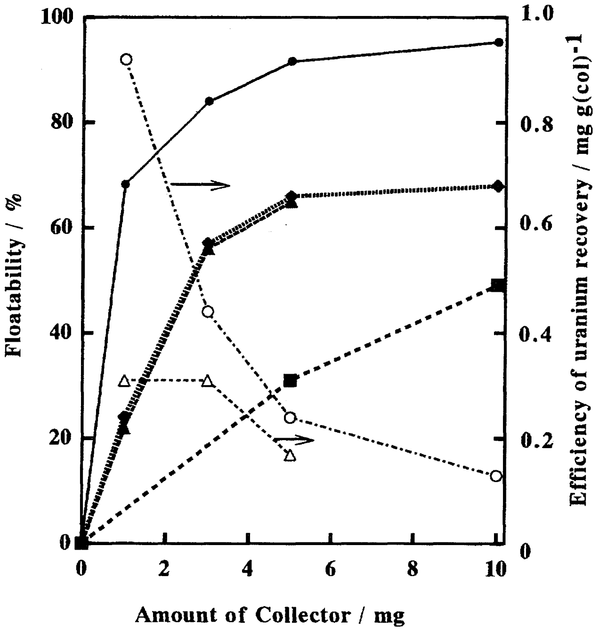


Fig. 7. Relation between amount of collector and uranium flotation. Seawater: 450 cm^3. ▲△: P-R_{12}, ●○: [4]Ar6.3P-R_{12}, ■: [4]Ar8.0Ac-R_{12}, ◆: [4]Ar5.1Hx-R_{12}.

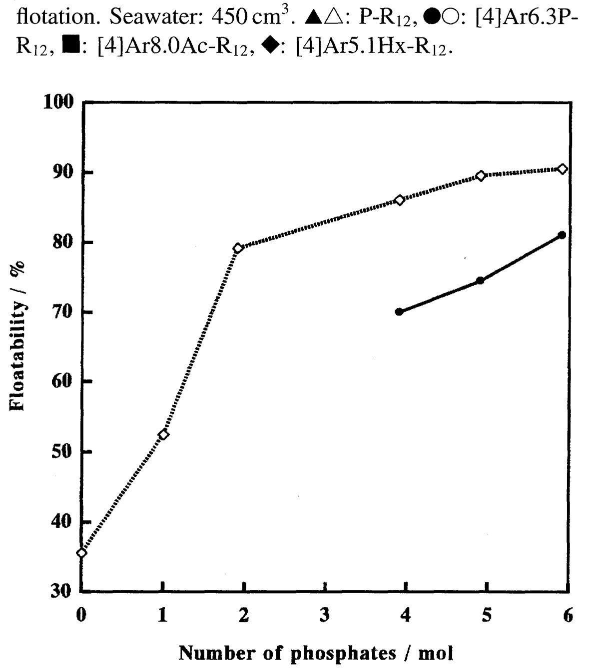


Fig. 8. Relation between number of phosphates in [4]ArmP-R_{12} and floatability of uranium. [4]ArmP-R_{12} (m=0, 1.0, 1.9, 3.9, 4.9, 5.9): 2 mg, 14 °C. ◇: 450 cm^3 of 10 ppb $U(UO_2{}^{2+})$ soln, ●: 450 cm^3 of seawater.

were carried out using the standard additive method.

[4]Ar6.3P-R_{12} and [4]Ar5.1Hx-R_{12} extracted uranium, the extractability of which was 33% when using 1 mg of [4]-Ar6.3P-R_{12} {efficiency: 0.43 mg g-(collector)$^{-1}$}, 67% for 5 mg (0.18 mg g^{-1}), 48% for 10 mg (0.06 mg g^{-1}), and 16% for 10 mg of [4]Ar5.1Hx-R_{12} (0.02 mg g^{-1}), respectively. [4]ArmP-R_{12} and [4]Ar5.1Hx-R_{12} should effect uranium recovery because of their affinity groups for uranium; also, the difference of both efficiencies would be attributed to the stability constant and the electrostatic force between the ligands and the uranium in seawater. However, [4]Ar-R_{12} and [4]-Ar8.0Ac-R_{12} did not extract the uranium. [4]Ar-R_{12} has no affinity groups for uranium, and the carboxyl groups in the [4]Ar8.0Ac-R_{12} would combine with an excess of alkaline-earth metal ions in seawater (0.04% Ca^{2+} and 0.13% Mg^{2+}, etc.). Flotation was more effective than extraction. The floatability of uranium was 75—81% when using 2 mg of [4]Ar4.9P-R_{12} or [4]Ar5.9P-R_{12}, and 94% when using 10 mg of [4]Ar6.3P-R_{12}. Flotation from seawater containing additive uranium (5—10 ppb) was for 75—76% recovery. On the other hand, 10 mg of [4]Ar5.1Hx-R_{12} and [4]Ar8.0Ac-R_{12} resulted in medium floatabilities, and [4]Ar-R_{12} had no affinity for seawater uranium. [4]ArmP-R_{12} and [4]Ar5.1Hx-R_{12} would complex with uranium, and the [4]Ar8.0Ac-R_{12} complexes of alkaline-earth metal ions may be floated with uranium, since macrocyclic hexacarboxylic acid has a large stability constant.[19)]

The floatabilities increased along with the number of collectors. However, the recovery per collector (efficiency) decreased, as shown in Fig. 7. The floatability was 68% when using 1 mg of [4]Ar6.3P-R_{12} {efficiency: 0.92 mg g-(collector)$^{-1}$}, 92% for 5 mg (0.25 mg g^{-1}), 94% for 10 mg (0.13 mg g^{-1}), 31% for 5 mg of [4]Ar8.0Ac-R_{12} (0.08 mg g^{-1}), and 65% for 5 mg of [4]Ar5.1Hx-R_{12} (0.17 mg g^{-1}). [4]ArmP-R_{12} is the cyclotetramer of P-R_{12}. P-R_{12}-bearing 2 mol of phosphates had high affinity for seawater uranium. However, the efficiency of P-R_{12} was lower than that of [4]ArmP-R_{12}, and that in molar was even lower (about one quarter).

The number of phosphates in [4]ArmP-R_{12} should affect uranium flotation. The flotation for a $UO_2{}^{2+}$ solution increased steeply to 2 mol of phosphates, and that from seawater increased slightly in 4—6 mol phosphates (Fig. 8). The metal complex of diethyl phosphate is known to be slightly unstable compared to that of monoalkyl phosphate.[20)] Since the phosphates in [4]ArmP-R_{12} is considered to be diphenyl phosphates in the range $m<4$, the floatabilities should increase steeply in m=1—2 and then increase slightly along with the number of the phosphates, in the order [4]Ar4.9P-R_{12}, [4]Ar5.9P-R_{12}, and [4]Ar6.3P-R_{12}. The phosphates in a cavity would include the uranium cooperatively, in addition to complex formation.

The amount of uranium was additionally determined by radioactivation analysis. A neutron-activation analysis for the scum was carried out at the Inter-University Laboratory for the Common Use of JAERI Facilities {Nippon-genshiryoku kenkyusho JRR-2, ^{238}U(n, γ)^{239}U, ^{239}U$\rightarrow$^{239}Np (104.69 keV) + β^-}. The uranium in scum, recovered from a 450 cm^3 of seawater using 10 mg of [4]Ar6.3P-R$_{12}$, was 0.6—0.7 μg (about 50% recovery). Therefore, [4]Ar6.3P-R$_{12}$ should form the uranium complex preferentially from seawater.

Recycle of Collector. The collector used in flotation should be recycled in an economical way and considering environmental aspects. The scum resulting from a 10 ppb uranium (UO_2^{2+}) solution using [4]Ar6.3P-R$_{12}$ was dispersed in an acidic solution. The dissociation of the scum was 55% in 1 mol dm^{-3} H_2SO_4 and 99% in 5 mol dm^{-3} H_2SO_4. Therefore, the resulting scum from the seawater was dissolved in 20 cm^3 of 5 mol dm^{-3} H_2SO_4. After being dissolved in 5 mol dm^{-3} H_2SO_4, the precipitate of the collector and concentrated uranium solution was obtained. The uranium in the solution became a trace amount of uranium hydroxide upon neutralizing it with NaOH; the precipitate of the collector, [4]Ar6.3P-R$_{12}$, was then used for the next flotation. The uranium in a different sample of seawater was floated at 92% using 5 mg of the regenerated [4]Ar6.3P-R$_{12}$; the collector could be recycled several times. Their floatabilities were nearly the same as the first one.

It was thus concluded that the amphiphilic calix[4]arenes bearing phosphates and tetradodecyl side chains form a stable uranium complex, and float seawater uranium effectively.

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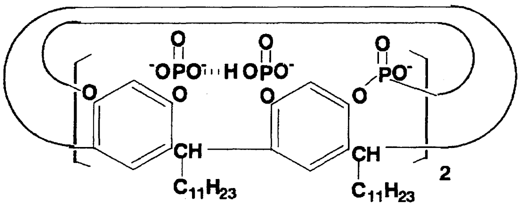

Chart 1.

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