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Solvent Extraction and Molecular Modeling of Uranyl and Thorium Ions with Organophosphorus Extractants

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The extraction behavior of bis(4-ethylcyclohexyl) hydrogen phosphate (D4ECHPA), bis(4-cyclohexyl-cyclohexyl) hydrogen phosphate (D4DCHPA) and bis(2-ethylhexyl) hydrogen phosphate (D2EHPA) have been investigated with regard to uranyl UO_2^{2+}) and thorium ions (Th^{4+}) from acidic aqueous nitrate media. From the concentration dependencies of the reactant species, i.e., hydrogen ion and extractant, on the distribution ratio of the metal ions, it was found that UO_2^{2+} was extracted with two molecules of the dimeric extractants (H_2R_2) in toluene as $UO_2(HR_2)_2$, and that Th^{4+} was extracted with three molecules of H_2R_2 along with one nitrate molecule as $Th(HR_2)_3(NO_3)$. The extraction equilibrium constants of UO_2^{2+} and Th^{4+} become greater in the order D4DCHPA > D4ECHPA > D2EHPA. The selectivity for Th^{4+} over UO_2^{2+} by D4DCHPA is ca. double that for D4ECHPA and D2EHPA. The structural effects of the extractant on the extractability of UO_2^{2+} and Th^{4+} are discussed in terms of the molecular modeling of uranyl and thorium complexes using molecular mechanics calculations.

Keywords: Solvent Extraction, Uranyl, Thorium, Organophosphorus extractant

1. Introduction

Extractants for the commercial-scale separation of actinides should satisfy at least the following three requirements: (1) high loading capacity without any trouble at high loading, (2) ease of stripping, (3) high selectivity among adjacent actinides, plus (4) resistance to radiation. Most of commercial separations and refining of actinides has been carried out by solvent extraction with organophosphorus extractants, such as tributyl phosphate (TBP) and bis(2-ethylhexyl) hydrogen phosphate (D2EHPA), and many fundamental studies on the extraction of actinides have been conducted [1-3]. Although these extractants provide adequate separation factors, the extracted actinide complexes are apt to polymerize giving rise to a gel that is insoluble in organic diluents, which greatly limits the effective use of the extractants. One approach to the design of extractant molecules without gel formation at high loading may be to introduce bulky substituents, which may impede the polymerization of the metal complexes. Ishida *et al.* [4,5] and Yoshizuka *et al.* [6] have reported on the structural effect of phosphoric esters having bulky alkyl groups on the equilibrium extraction of lanthanides. They synthesized ten different bisalkyl hydrogen phosphates containing alicyclic and/or aliphatic alkyl groups, and measured the extraction of lanthanides. It was found that the position of the bulky substituents in the bisalkyl hydrogen phosphates is closely related to the extractability and selectivity of the lanthanides.

In the present study, the extraction behavior of the uranyl ion (UO_2^{2+}) and the thorium ion (Th^{4+}) from acidic nitrate media was investigated with bis(4-ethylcyclohexyl) hydrogen phosphate (abbreviated as D4ECHPA, and expressed as HR for monomeric species, and H_2R_2 for dimeric species), bis(4-cyclohexylcyclohexyl) hydrogen phosphate (D4DCHPA), and bis(2-ethylhexyl) hydrogen phosphate (D2EHPA), as shown in Fig.1. The structural effect of these extractants on the extractability of UO_2^{2+} and Th^{4+} are discussed from the viewpoint of molecular modeling with novel molecular mechanics calculations.

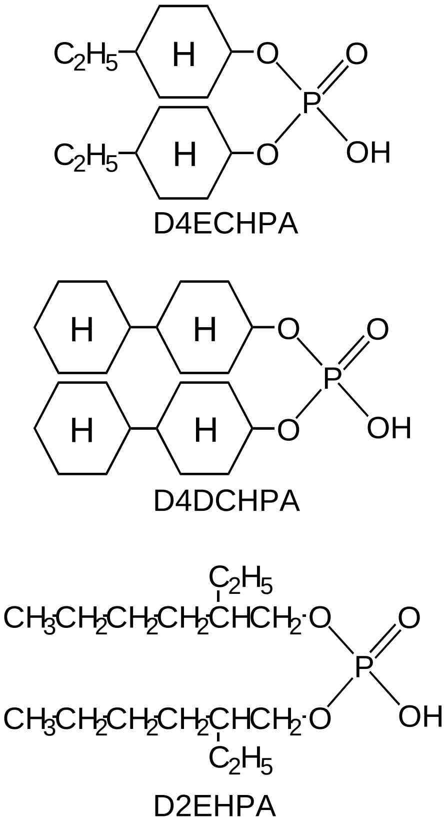

Fig.1. Chemical structures of D4ECHPA, D4DCHPA, D2EHPA

2. Experimental

2.1 Extraction Equilibria

The measurement of the extraction equilibria of UO_2^{2+} and Th^{4+} was carried out batchwise by the conventional method [6]. The two phases (10mL each) were shaken for 2 h to attain equilibrium in a water bath incubator maintained at 303 K. The concentrations of metal ions were measured using an ICP-AES spectrophotometer (Shimadzu ICP-5000). The amount of metal extracted was calculated from the difference in the concentration in the aqueous phase before and after equilibration. The experimental conditions were as follows: initial concentration of metal ion = 0.1 mM, initial concentration of the extractant = 5 - 20 mM, initial concentration of hydrogen ion = 0.1 - 1.0 M HNO_3 and organic solvent = toluene.

2.2 Molecular mechanics calculations

The molecular mechanics calculations were performed with the strain energy minimization program MOMEC97 [7] and the corresponding force field [8]. Within the molecular mechanics frame work, the structure of a molecule is modified in order to minimize its total strain energy (U_{total}) consisting of bond length deformation (E_b), valence angle deformation (E_θ), torsion angle deformation (E_ϕ) and nonbonded interaction (E_{nb}), as expressed by Eq.(1). Though other terms may be included to account for out-of-plane deformation, electrostatic interactions and hydrogen bonding, we have not attempted to model these effects.

$$U_{\text{total}} = \sum (E_{\text{b}} + E_{\theta} + E_{\varphi} + E_{\text{nb}}) \tag{1}$$

The functional forms and the parameters for the organic backbone of the ligands are described elsewhere [8]. A harmonic M-L stretching potential is used for the metal-donor interaction. The angular geometry around the metal center is modeled by interligand nonbonded interactions, while torsional potentials, as well as nonbonded interactions involving the metal center are neglected [8-9]. No symmetry restrictions were imposed on the local coordination sphere. This approach has also been taken by others in earlier force field calculations of transition metal complexes [10,11], and some lanthanide complexes [12,13].

Input coordinates of uranyl and thorium complexes were obtained from X-ray crystal structure data from the Cambridge Crystal Structure Data Centre (CCSD). The X-ray structural data of 32 uranyl complexes and 12 thorium complexes having phosphorus moieties are available for constructing the force field parameter sets. Table 1 lists some examples of the uranyl and thorium complexes available from the CCSD. The strain-free bond length and force constant for each type of bond were adjusted until an optimal agreement between calculated and observed structures was obtained throughout the entire range of available structures. For each metal–O atom (M-O) bond, the discrepancies between the calculated and observed bond lengths were also examined in all complexes that contained that bond type and parameters were adjusted in such a way as to minimize those discrepancies. The final differences between observed and computed bond distances are ≤0.02Å, those for valence angles are ≤3°. The structures of the metal-free ligand molecules were also computed with PM3 using MOPAC2000 [18] (convergence criteria for GNORM = 0.01 and SCFRT = 0.00001).

Table 1. Typical uranyl and thorium complexes cited in CCSD

Metal complex	Compound Name	Abbreviation	Reference
Uranyl	Uranyl nitrate trimethylphosphate	BIZXUD	14
Uranyl	Uranyl nitrate triethyl phosphate	UNOEPO	15
Thorium	Tetrakis(diphenyl-thiophosphinato)-thorium dichloromethane solvate	DIYBUI	16
Thorium	Bis(dimethylsulfoxide)-tris(bis(diphenyl-phosphino)aminato)-thorium nitrate	KOHXAG	17

3. Results and Discussion

3.1 Extraction equilibria of UO_2^{2+}

Figure 2 shows the effect of the pH on the distribution ratios of UO_2^{2+} (*D*) for D4ECHPA, D4DCHPA and D2EHPA, respectively. The plots are straight lines with a slope of 2 for all extractants. This indicates that the extraction of UO_2^{2+} with these extractants has an inverse second order dependency on the hydrogen ion activity based on the cation-exchange extraction reaction.

Figure 3 shows the effect of the concentration of the dimeric species of the extractant in the organic

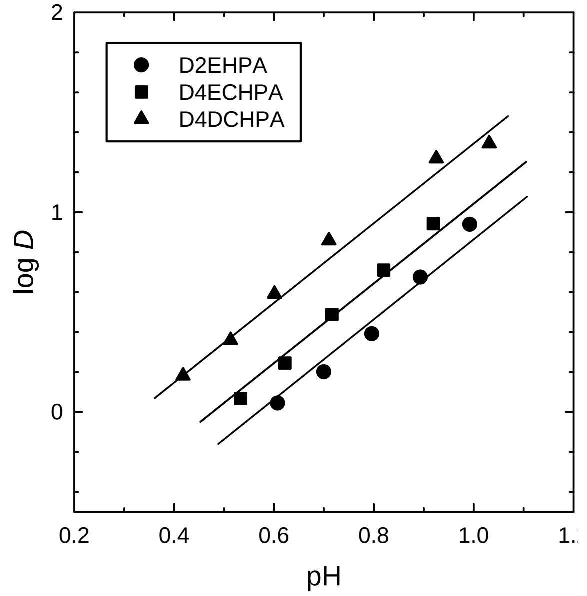

Fig.2. The effect of the pH on the distribution ratio of UO_2^{2+}

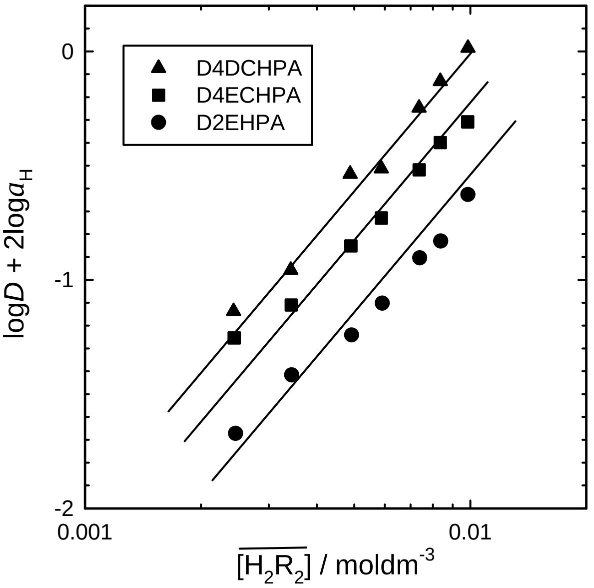

Fig.3. The effect of $\overline{[H_2R_2]}$ on the distribution ratio of UO_2^{2+}

phase ($\overline{[H_2R_2]}$) on the distribution ratio of UO_2^{2+} (D). The concentrations of $\overline{[H_2R_2]}$ were calculated by using the dimeric constants of the extractants in toluene [6] and the analytical concentration of the extractant (C_{HR}). The plots are straight lines with a slope of 2 for all extractants. This suggests that the extraction reaction of UO_2^{2+} shows a second order dependency on $\overline{[H_2R_2]}$.

From the results described above, UO_2^{2+} is extracted with these extractants according to the following extraction reaction:

$$UO_2^{2+} + 2\overline{H_2R_2} \overset{K_{ex,UO_2}}{\rightleftharpoons} \overline{UO_2(HR_2)_2} + 2H^+ \tag{2}$$

The extraction equilibrium constant (K_{ex,UO_2}) is expressed by:

$$K_{ex,UO_2} = \frac{[\overline{UO_2(HR_2)_2}][H^+]^2}{[UO_2^{2+}][\overline{H_2R_2}]^2} \tag{3}$$

Equation (3) can be rearranged as:

$$\log D + 2\log a_H = 2\log[\overline{H_2R_2}] + \log K_{ex,UO_2} \tag{4}$$

Equation (4) is satisfactory for all of the experimental results shown in Figs. 2 and 3. From all of the experimental results, the extraction equilibrium constants of UO_2^{2+} with D4ECHPA, D4DCHPA and D2EHPA (K_{ex,UO_2}) were obtained as listed in Table 2.

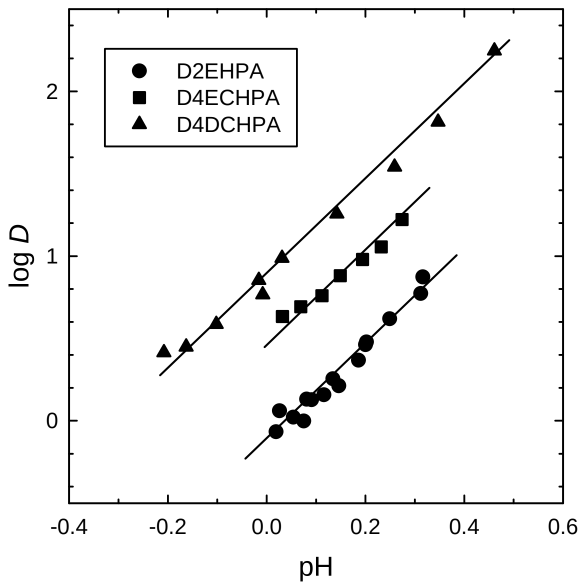

Fig.4. The effect of the pH on the distribution ratio of Th^{4+} (*D*)

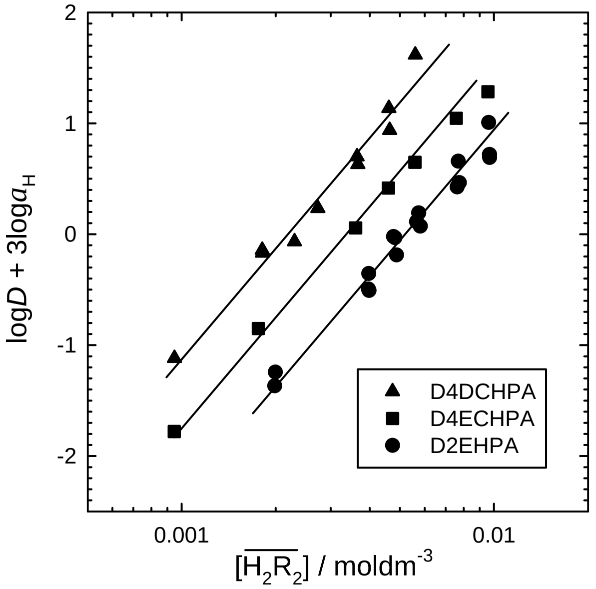

Fig.5. The effect of $[\overline{H_2R_2}]$ on the distribution ratio of Th^{4+} (*D*)

3.2 Extraction equilibria of Th^{4+}

Figure 4 shows the effect of the pH on the distribution ratios of Th^{4+} (*D*) for D4ECHPA, D4DCHPA and D2EHPA, respectively. The plots are straight lines with a slope of 3 for all extractants. This suggests that the extraction of Th^{4+} with these extractants has an inverse third order dependency on the hydrogen ion activity.

Figure 5 shows the effects of the concentration of the dimeric species of the extractant in the organic phase ($[\overline{H_2R_2}]$) on the distribution ratio of Th^{4+} (*D*). The plots are straight lines with a slope of 3 for all extractants. This suggests that the extraction reaction of Th^{4+} shows a third order dependency on $[\overline{H_2R_2}]$.

From the results described above, Th^{4+} is extracted with these extractants according to the following extraction reaction:

$$\mathrm{Th}^{4+} + 3\overline{\mathrm{H_2R_2}} + \mathrm{NO_3^-} \overset{K_{\mathrm{ex,Th}}}{\rightleftarrows} \overline{\mathrm{Th(HR_2)_3(NO_3)}} + 3\mathrm{H}^+ \qquad (5)$$

where one molecule of nitrate ion (NO_3^-) is extracted together with Th^{4+} and 3 molecules of H_2R_2, due to the neutralization of the thorium complex in the organic phase. The extraction equilibrium constant ($K_{\mathrm{ex,Th}}$) is expressed by:

$$K_{\mathrm{ex,Th}} = \frac{[\overline{\mathrm{Th(HR_2)_3(NO_3)}}][\mathrm{H}^+]^3}{[\mathrm{Th}^{4+}][\mathrm{NO_3^-}][\overline{\mathrm{H_2R_2}}]^3} \qquad (6)$$

Equation (6) can be rearranged as:

$$\log D + 3\log a_{\mathrm{H}} = 3\log[\overline{\mathrm{H_2R_2}}] + \log(K_{\mathrm{ex,Th}} \cdot [\mathrm{NO_3^-}]) \qquad (7)$$

Equation (7) is satisfactory for all of the experimental results shown in Figs. 4 and 5. Since $[\mathrm{NO_3^-}]$ is too high to be considered to be constant in the experimental conditions, the apparent extraction equilibrium constants of Th^{4+} with D4ECHPA, D4DCHPA and D2EHPA ($K'_{\mathrm{ex,Th}} = K_{\mathrm{ex,Th}}[\mathrm{NO_3^-}]$) were obtained as listed in Table 2, together with the selectivities of Th^{4+} over $\mathrm{UO_2}^{2+}$ ($K'_{\mathrm{ex,Th}} / K_{\mathrm{ex,UO_2}}$).

The extraction equilibrium constants of uranyl and thorium ions increases in the order D4DCHPA > D4ECHPA > D2EHPA. The $K'_{\mathrm{ex,Th}} / K_{\mathrm{ex,UO_2}}$ value for D4DCHPA is ca. double those for D4ECHPA and D2EHPA. It can be considered that the extractabilities and selectivities depend on the structures of the cyclohexyl groups adjacent to the PO(OH) group [6].

Table 2. Extraction equilibrium constants of $\mathrm{UO_2}^{2+}$ and Th^{4+}

Extractant	D4ECHPA	D4DCHPA	D2EHPA
$K_{\mathrm{ex,UO_2}}$ [-]	$5.71\mathrm{x}10^3$	$1.04\mathrm{x}10^4$	$2.29\mathrm{x}10^3$
$K'_{\mathrm{ex,Th}}$ [-]	$2.51\mathrm{x}10^7$	$7.94\mathrm{x}10^7$	$1.02\mathrm{x}10^7$
$K'_{\mathrm{ex,Th}} / K_{\mathrm{ex,UO_2}}$ [-]	$4.40\mathrm{x}10^3$	$7.63\mathrm{x}10^3$	$4.45\mathrm{x}10^3$

3.3 Molecular mechanics calculations of uranyl and thorium complexes

The parameters necessary to describe metal complexes can be conceptually divided into two types: metal-independent and metal-dependent. A common simplification is to assume that metal-independent parameters, derived for metal-free ligands, are transferable to coordinated ligands. This assumption of transferability seems quite reasonable in the light of the ionicity of M-L bonding [8,12,13].

Figure 6 shows the proposed structures of the uranyl complex with D4DCHPA according to the extraction mechanism given above. The optimized structures of the complexes *in vacuo* were calculated by the molecular mechanics method, MOMEC. It was elucidated that four O atoms in the extractants are horizontally coordinated with the U atom and two uranyl O atoms exist perpendicularly. In particular, the bulky cyclohexylcyclohexyl substituents of D4DCHPA surrounded the $\mathrm{UO_2}^{2+}$ ion very tightly.

Table 3 lists the steric energies (U_{total}) and molecular volumes (V_{mol}) of the uranyl and thorium complexes of these extractants calculated by MOMEC. The variations in the steric energies and molecular volumes of both complexes are approximately in agreement with the order of extractability of these extractants. This may be due to the bulkiness and lipophilicity of the 4-ethylcyclohexyl and 4-cyclohexylcyclohexyl substituents of the extractants, compared to the 2-ethylhexyl substituents of

D2EHPA.

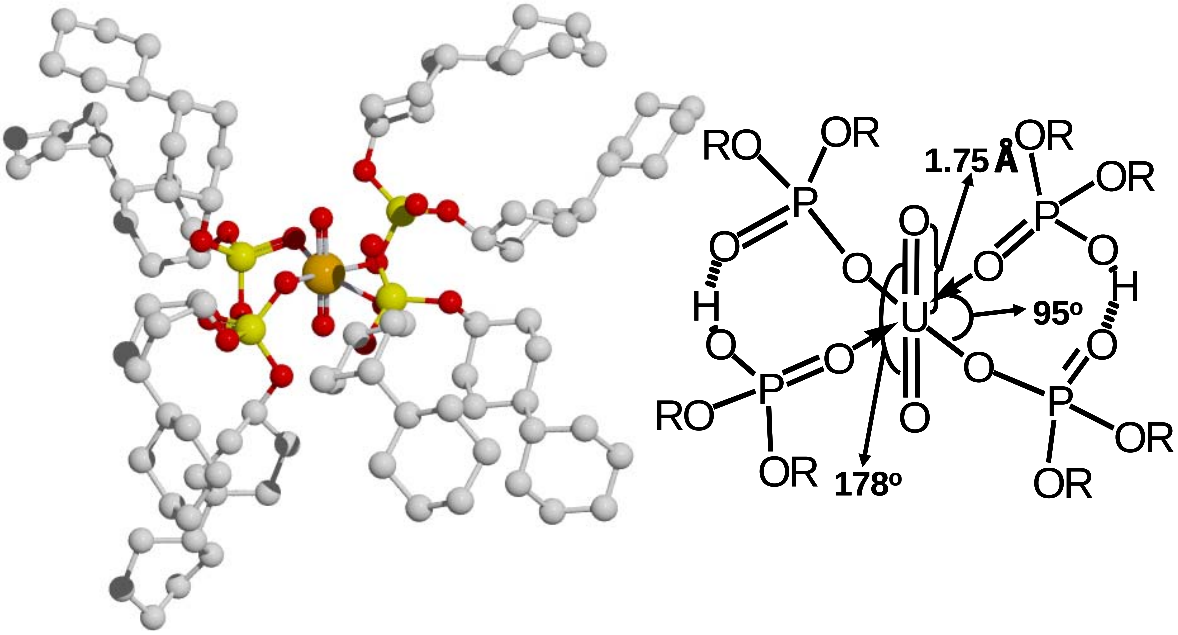

Fig.6. Optimal structure of the uranyl complex with D4DCHPA calculated by MOMEC (H atoms are omitted for clarity)

Table 3. Steric energies and molecular volumes of uranyl and thorium complexes with D4ECHPA, D4DCHPA and D2EHPA calculated by MOMEC

Extractant	D4ECHPA	D4DCHPA	D2EHPA
U_{total} of uranyl complex [kJ/mol]	1285.5	1520.8	1061.8
V_{mol} of uranyl complex [nm^3]	4.80	5.80	4.44
U_{total} of thorium complex [kJ/mol]	2285.6	2480.2	1758.4
V_{mol} of thorium complex [nm^3]	6.18	6.42	5.78

4. Conclusion

Studies on the extraction equilibria of UO_2^{2+} and Th^{4+} with D4ECHPA, D4DCHPA and D2EHPA were conducted from the nitrate media at 303 K. The extracted species of UO_2^{2+} and Th^{4+} are $UO_2(HR_2)_2$ and $Th(HR_2)_3(NO_3)$, and the extraction equilibrium constants for these extractants were obtained. The extraction equilibrium constants of both metal ions increase in the order D4DCHPA > D4ECHPA > D2EHPA and the selectivity of D4DCHPA for Th^{4+} over UO_2^{2+} is ca. double that of D4ECHPA and

D2EHPA. Furthermore, molecular modeling computations using molecular mechanics were carried out in order to elucidate the structural effect of the extractant on complex formation. The variations in the steric energies and molecular volumes of uranyl and thorium complexes with these extractants are approximately in agreement with the variations in the extractabilities of these extractants.

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