

Separation of Americium(III) from Lanthanide by Encapsulating Hexadentate-ligand

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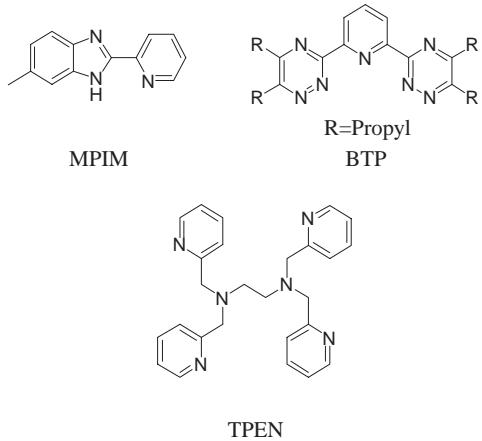
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Am(III) is encapsulated in an aqueous phase by a podand-type ligand, *N,N,N',N'*-tetrakis(2-methylpyridyl)ethylenediamine (TPEN), and is extracted selectively over trivalent lanthanide in an organic phase using nitrobenzene. The extraction of Am(III) using TPEN shows higher selectivity and chemical stability than other conventional ones using nitrogen-donor ligands.

Encapsulating metal ions with a podand-type ligand is an attractive field in supramolecular chemistry and has a high potentiality for the application of metal separation.¹ In particular, a podand type ligand is useful for formation of stable complex of f-block metal ion with high coordination number, because water molecules coordinating strongly around the metal ion are removed by the encapsulation with a podand-type ligand and the encapsulated metal ion is shielded from the attack of water molecules.² One strategy being pursued in this paper is to apply the podand-type ligand to the separation of trivalent actinide (An) from lanthanide (Ln).



Separating Am(III) from Ln(III) has been one of the most challenging issues because of their similarity of chemical properties. One promising approach for separating Am(III) from Ln(III) is to use soft-donor ligand based on its preferable coordination to softer Am(III). Some sulfur based soft-donor ligands are successfully used for separation of Am(III) from Ln(III) by solvent extraction method.³ Nitrogen-containing heterocycle based multidentate ligands have been more presently attracted by their combustibility.⁴ As a consequence of this criteria, considerable efforts have been devoted to the development of new ligands for separating Am(III) from Ln(III).⁵ The first successful nitrogen based soft donor ligand is 5-methyl-2-(2-pyridyl)benzimidazole (MPIM).⁶ However, this ligand requires thiocyanate ion as a co-ligand to achieve good selectivity of

Am(III) over Ln(III). The only type of the ligand which has good selectivity between Am(III) and Ln(III) without any co-ligand is 2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (BTP) and its analogues.⁷ A problem of this ligand is its chemical stability under its extraction conditions.

Here we report the second case on the selective extraction system of Am(III) from Ln(III) by nitrogen based soft-donor ligand. Key concept underlined by this work is that the proposed separation system is not necessary to add any weak counter anion as a co-extractant, by using an encapsulating ligand, *N,N,N',N'*-tetrakis(2-methylpyridyl)ethylenediamine (TPEN)⁸ in nitrobenzene. Jensen et al. predicted that TPEN has a good potential for separating Am(III) from Ln(III) by investigating stability constants of Am(III) and Ln(III) with TPEN.⁹

Figure 1¹⁰ shows that the plot of the distribution ratio of Am(III) and Eu(III) against TPEN concentration at pH 4.0. Am(III) was selectively extracted over Eu(III) by TPEN. The distribution ratios of each metal ion increased with increasing TPEN concentration and the slope showed about 1.0. This result indicates that one molecule of TPEN coordinates more strongly to Am(III) than Eu(III) and corresponds to the complexation mechanism Am(III) and Ln(III) complexes of TPEN.

From the crystal structure of lanthanide complex of TPEN, TPEN coordinated as a hexadentate ligand and three nitrates coordinated with bidentate mode.¹¹ Lanthanide ion was effec-

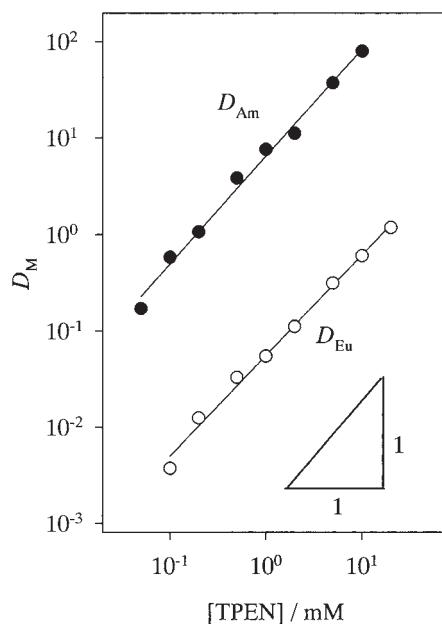


Figure 1. The dependence of TPEN concentration on the distribution ratio of Am(III) and Eu(III) at $\text{pH}_{\text{eq}} = 4.0$.

tively encapsulated by TPEN and well shielded from water molecule. Shielding water molecules is one of the important factors to produce a stable complex which is required for favorable extraction. Then the extraction equilibrium is represented as,



Table 1 shows that the comparison of the separation factor (SF) between Am(III) and Eu(III) for the selected ligands. The SF is defined by D_{Am}/D_{Eu} . MPIM was the first successful ligand which is constructed by nitrogen based soft-donor to separate Am(III) from Eu(III) and gave a good SF, 60. However, MPIM required thiocyanate anion and 4-methyl-2-pentanone as co-ligands to achieve this selectivity. BTP gave more feasible SF, 128 but the condition is more severe for the ligand. In this work, the separation factor is around 100 so that the efficient separation of Am(III) from Eu(III) can be achieved under more gentle condition than BTP's.

Table 1. The comparison of selected extractants for separating Am(III) from Eu(III) with separation factor (SF)

Ligand	Acidity	SF	Ref
MPIM ^a	pH 5.1	60	6
BTP ^b	0.5 M HNO ₃	128	7
TPEN	pH 4.0	100	

^aXylene was used for organic phase, 1.0 M of SCN⁻ ion in NH₄SCN added as a co-ligand and 4-methyl-2-pentanone was added as a modifier.

^bTetrapropylhydrogenc (TPH) was used for organic phase and butyraldehyde was added as a modifier.

In conclusion, we have newly found that the extraordinary selectivity of Am(III) over Eu(III) by TPEN and simple method to separating Am(III) from Ln(III). Moreover, we have found that the chemical stability of TPEN is feasible. The scope and application of separation of Am(III) by TPEN, therefore, are in progress.

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and properties of TPEN.

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- 10 A general procedure for liquid-liquid extraction: Eu(III) was used as a representative of lanthanide. Trace amount of ²⁴¹Am and ¹⁵²Eu, 240 kBq/L, was added to the 0.1 M of NH₄NO₃ aqueous solution adjusted at pH 4.0. The organic phase was pre-equilibrated with the corresponding conditions of the extraction. Same volume of the aqueous phase and organic phase was contacted for 15 min at 298 ± 1 K. The distribution ratio was estimated as, $D_M = [\text{metal concentration of organic phase}] / [\text{metal concentration of aqueous phase}]$. The concentration of organic phase and aqueous phase was measured the radioactivity of ²⁴¹Am (59.54 KeV) and ¹⁵²Eu (121.78 KeV) by a high-purity germanium spectrometer system.
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