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Extraction separation of trivalent minor actinides from lanthanides with hydrophobic derivatives of TPEN

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Abstract

We are developing a new MA/Ln separation process with TPEN (*N,N,N′,N′*-tetrakis(2-pyridylmethyl)ethylenediamine) and its derivatives for P&T technology of HLW from spent nuclear fuel reprocessing plants. TPEN is a hexadentate ligand that has six soft-donor sites as a kind of podand type molecule and can encapsulate a metal ion. TPEN has good selectivity of Am(III) from Ln(III) and has potential to establish partitioning of MA. However, there is a serious problem for the practical application. This is to the dissolution of a slight amount of TPEN (about 10^{-4} mol/L) to water. High enrichment of Am(III) will be restricted by the dissolution of TPEN to water. In this study, the hydrophobicity of TPEN is improved by introducing alkyl groups and the effect of the introduction of alkyl groups on the separation of Am(III) and Eu(III) is examined. We tried to synthesize four hydrophobic derivatives of TPEN, and three derivatives were synthesized successfully. The derivatives were examined both the extractability and selectivity of Am(III) and Eu(III). One of them, tpdben, showed good selectivity and the maximum separation factor, $SF_{Am/Eu}$, was 34 at pH 5.06. A hydrophobic derivative of TPEN that has potential of application to the MA/Ln separation process was synthesized successfully.

Keywords: Minor actinide; Long-lived nuclides; Partitioning; MA/Ln separation; TPEN; N-donor

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1. Introduction

Reduction of radioactive toxicity of HLW is very important to decrease the risk of the environmental impact of nuclear wastes disposed to deep underground. If several long-lived radioactive nuclides containing actinides are removed from HLW before the final disposal, these nuclides can be converted to short-lived ones by transmutation technology using high-energy neutron by fast reactors or accelerators. The environmental load of HLW will be reduced largely by the introduction of transmutation technology. However, lanthanides, whose total amount corresponds to up to 30 times that of actinides in HLW (Ando and Takano, 1999), adversely affects on the efficiency of the transmutation of actinides, because these elements absorb a large proportion of neutron. Therefore, the separation of actinides from lanthanides is one of the essential subjects to establish the transmutation technology.

It is well known that separating trivalent actinides (An(III)) and lanthanides (Ln(III)) is one of the most challenging issues, because of their similarity of chemical properties. One rational approach for the separation of An(III) is to use a soft-donor extractant based on its preferable coordination to softer An(III). Nitrogen-based soft-donor extractants have been attracted attention as a means of establishing a new sustainable separation process which has the feature of organic solvent waste free based on the combustibility of the extractant (Musikas, 1987). As a result, considerable efforts have been devoted to the development of new nitrogen-donor extractants for separating An(III) from Ln(III) (Karmazin et al., 2002). Jensen et al. reported that *N,N,N′,N′*-tetrakis(2-methylpyridyl)ethylenediamine (TPEN) demonstrates 100-fold preference for Am(III) over Ln(III) from the difference between stability constants with these metal ions in the aqueous phase (Jensen

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et al., 2000). TPEN is a hexadentate ligand which has six soft-donor sites as a kind of podand type molecule and can encapsulate a metal ion. We have reported that Am(III) was selectively extracted from the aqueous phase containing Ln(III) by TPEN in nitrobenzene and synergistic system with D2EHPA or decanoic acid in 1-octanol (Watanabe et al., 2002, 2004; Matsumura and Takeshita, submitted for publication). TPEN has good selectivity of Am(III) from Ln(III) and has potential to establish partitioning of minor actinides, however, there are several properties that should be improved for the application to the nuclear fuel cycle. The hydrophobicity of TPEN is one of such properties and the extractability of these trivalent metals further increases with decreasing the water solubility. Recently, we succeed to synthesize a hydrophobic derivative of TPEN which has availability of separation of An(III) from Ln(III).

Improvement of hydrophobicity of water-soluble nitrogen-donor ligand was reported (Cordier et al., 1998). Hydrophobicity of 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPTZ) was improved by introducing hydrophobic groups, and tertiarybutyl groups, which were connected to pyridyl groups in TPTZ molecule. The hydrophobic derivative of TPTZ, tritertiarybutyl-tri-pyridyltriazine (T^tBPTZ), showed about $\mathrm{SF}_{\mathrm{Am/Eu}} = 10$, whose value was same as TPTZ. As the analogue of the molecules, expected structures of hydrophobic derivatives of TPEN, which shows high selectivity of Am(III) from Ln(III), were shown in Fig. 1. Type (a) has hydrophobic alkyl groups connected with the molecular framework (N-C-C-N structure) in TPEN molecule, and type (b) has the alkyl groups connected with pyridyl groups in the molecule. Both the approaches will be effective for improvement of hydrophobicity, because the hydrophobic groups are connected to the position that the formation of metal complex is not affected by them. Previously, we reported that the nitrogen donors on the pyridyl groups contribute to the selectivity of Am(III) rather than nitrogen donors on the framework of the molecule (Matsumura and Takeshita, 2006). Therefore, the connection of hydrophobic groups to the framework of the molecule is valid for maintaining high selectivity of Am(III). Based on this idea, we synthesized three derivatives of type (a), in which two *n*-butyl groups or cyclohexyl group were connected to the framework of TPEN molecule, and examined both the extractability and selectivity of Am(III) and Eu(III).

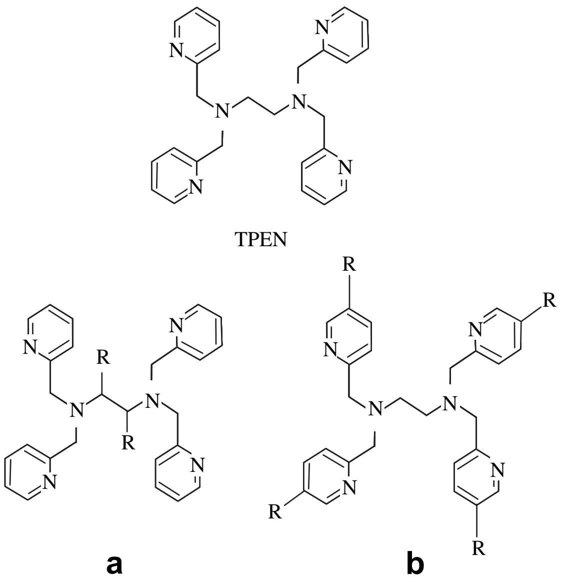

Fig. 1. Candidate molecular structure of hydrophobic derivatives of TPEN.

2. Experimental

2.1. Synthesis of the hydrophobic derivatives of TPEN

Reagents used in the synthesis were reagent grade. 1,2-Bis(*n*-butyl)-2-ethylenediamine and 1,2-Bis(tertiarybutyl)-2-ethylenediamine were purchased from AZUMA corporation, and *trans*-1,2-diaminocyclohexane, *cis*-1,2-diaminocyclohexane and 2-(chloromethyl)pyridine hydrochloride and other chemicals were purchased from Wako Pure Chemical Industries Ltd. and used without further purification. Fig. 2 shows the chemical structures of the hydrophobic derivatives of TPEN and their synthesis procedures. These procedures are similar to the synthesis of TPEN as reported previously (Chang et al., 1990; Morss and Rogers, 1997). 2-(Chloromethyl)pyridine hydrochloride (0.040 mol) was dissolved in 5.0 mL of water and the resulting solution was neutralized by adding 5.4 mol/L NaOH solution. 1,2-Bis(*n*-butyl)-2-ethylenediamine, 1,2-Bis(tertiarybutyl)-2-ethylenediamine, *trans*-1,2-diaminocyclohexane or *cis*-1,2-diaminocyclohexane (0.010 mol) was added dropwise in the solution. The pH value was kept in the range of 8.0 ± 0.1 by a pH-stat (COMTITE-900, Hiranuma Ltd.) using 1 mol/L NaOH solution. The reaction mixtures were stirred at room temperature for 1 week. Wax-like precipitates were observed in all mixtures. The object compounds were obtained by the extraction of impurities from these precipitates by diethyl ether and were purified highly by a silica gel column using a mixture of methanol and ethyl acetate as an eluent. After evaporation of appropriate fraction, three derivatives of TPEN, *N,N,N′,N′*-tetrakis(2-methylpyridyl)dibutylethylenediamine (tpdben), *N,N,N′,N′*-tetrakis(2-methylpyridyl)-*trans*-1,2-diaminocyclohexane (*t*-tpcn), and *N,N, N′,N′*-tetrakis(2-methylpyridyl)-*cis*-1,2-diaminocyclohexane (*c*-tpcn), were obtained and identified by mass spectroscopic analysis (ZQ2000, Waters Co. Ltd.) and elemental analysis. The yields of the derivatives were 20% for tpdben, 15% for *t*-tpcn, and 8% for *c*-tpcn. *N,N,N′,N′*-tetrakis(2-methylpyridyl)-ditertiarybutylethylenediamine (tpdtben), which would be synthesize from 1,2-bis(tertiarybutyl)-2-ethylenediamine and 2-(chloromethyl)pyridine hydrochloride, was not detected by the mass spectroscopy. The reason of impossibility of the tpdtben synthesis can be explained by steric hindrance between tertiarybutyl groups and pyridyl groups because the tertiarybutyl groups are voluminous. Tpdben was white powder, and *t*-tpcn and *c*-tpcn were yellow viscous liquid.