Selective separation of Am(III) from lanthanides(III) by solvent extraction with hydrophobic field of "superweak" anion

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The weakly coordinating hydrophobic anion TFPB$^-$, whose surface is covered with a hydrophobic field, gives rise to a selective separation of Am(III) from lanthanides(III) in their solvent extraction even with a hard-donor extractant that shows no selectivity for Am(III) in traditional solvent extraction.

The separation of trivalent 5f elements (actinides: An), such as americium (Am^{3+}), from 4f elements (lanthanides: Ln) is one of the most important subjects for the back end of the nuclear fuel cycle. This is, however, very difficult due to their similarity in chemical and physical properties. In recent years, it has been reported that some extractants (organic ligands) containing soft functional groups, such as bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301)[1] and 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine (BTP),[2] exhibit considerably good selectivities for Am^{3+} over trivalent lanthanides (Ln^{3+} ions). Such soft-donor extractants seem to recognize a slight softness difference between Am^{3+} and Ln^{3+} ions. However, these extractants suffer from chemical instability, for example, fragile functional groups by oxidation or complicated structure not so stable against hydrolysis. Therefore, the development of a new soft-donor extractant which is not only efficient but also stable is believed to be necessary for the 4f/5f separation technique. Meanwhile, hard-donor extractants containing hard functional groups, such as carbamoylmethylene phosphine oxides (CMPO),[3] are stable compounds, although they show no selectivity for Am^{3+} over Ln^{3+} ions in traditional solvent extraction. In the present study, we introduce a selective separation of Am^{3+} from Ln^{3+} ions by the effect of an inert counterion having a "hydrophobic field" on its surface, which occurs even with such a hard-donor extractant. This is a new idea for 4f/5f separation and does not rely on the development of a new soft-donor compound. Tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (TFPB$^-$), whose structure is shown in Fig. 1, is non-coordinating (or very weakly coordinating) to metal ions, and is thus called a "superweak" anion.[4–6] For instance, TFPB$^-$ paired with a centrosymmetric rhodium(I) dication is, practically, not bonded to the metal atoms; the closest contact of F atom in CF_3 groups in TFPB$^-$ is outside the sum of van der Waals radii for Rd and F.[6] In addition, TFPB$^-$ is highly hydrophobic with eight CF_3 groups arrayed to cover the anion surface. Therefore, TFPB$^-$ is promising as a counterion, which enhances the extraction of metal ions into an organic solvent owing to its hydrophobicity, without interfering in the complexation between the metal ions and an extractant owing to the lack of coordinating property. We recently reported that TFPB$^-$ greatly enhanced the extractability of an extractant for Ln^{3+} ions, as expected.[7] Moreover, TFPB$^-$ greatly improved also the separation among Ln^{3+} ions,[7] which was more than our expectations and interesting from the viewpoint of recognition chemistry. In the present study, we apply TFPB$^-$ to the selective separation of Am^{3+} from Ln^{3+} ions. Also, in order to clarify the origin of the counterion effect, the hydration of species extracted with TFPB$^-$ is examined.

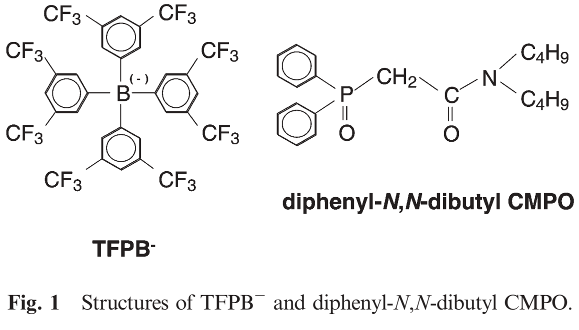

Fig. 1 Structures of TFPB$^-$ and diphenyl-*N*,*N*-dibutyl CMPO.

The experiments were carried out at 298 K. An aqueous solution of 0.1 M HNO_3 containing γ-active nuclides 2×10^{-9} M Am^{3+} and 3×10^{-9} M Eu^{3+} or containing 7×10^{-6} M nonradioactive Ln^{3+} ions and the same volume of a benzene solution containing a CMPO (see Fig. 1) and H^+TFPB^- were placed in a stoppered glass tube. The two phases were vigorously shaken for 20 min, and then, centrifuged. The γ-active nuclides in the both phases were determined by high-purity germanium spectrometry system (EG&G Ortec). The concentrations of 14 lanthanides (all lanthanides except promethium) in the aqueous phase were measured by inductively coupled plasma (ICP) mass spectrometry (VG PQΩ Fisons). The concentrations of these lanthanides in the organic phase were also determined after back-extracting them into an aqueous oxalic acid solution. The concentration of water extracted into benzene was measured by Karl-Fischer titration.

Fig. 2 shows the distribution ratios ($D_M = [M^{3+}]_{o,t}/[M^{3+}]_{a,t}$) of Am^{3+} and Ln^{3+} ions between 0.1 M HNO_3 solution and benzene containing 0.05 M CMPO, comparing the results obtained in the presence of 1×10^{-3} M TFPB$^-$ with those obtained in its absence. The subscripts "a" and "o" denote an aqueous phase and an organic phase, respectively. The subscript "t" denotes a total: $[\ ]_{a,t}$ and $[\ ]_{o,t}$ mean total concentration of a species in the aqueous phase and that in the organic phase in molarity. The distribution ratio of Am^{3+} increases from 5.6×10^{-4} to 84 and that of Eu^{3+}, which is located at the same position as Am in the lanthanide series, increases from 6.9×10^{-4} to 2.8. This means not only greatly enhanced extractability but also much improved selectivity in the presence of TFPB$^-$; the separation factor, which is the distribution ratio of Am^{3+} divided by that of Eu^{3+}, increases from 0.81 to 30. The hydration of species extracted with TFPB$^-$ is also

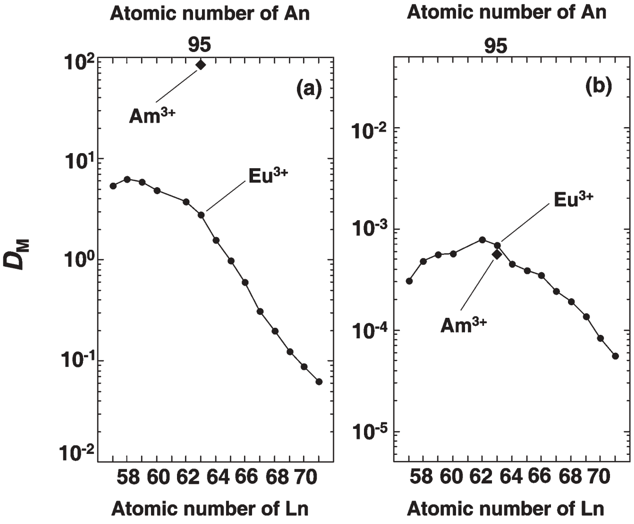

Fig. 2 Distribution ratios ($D_M = [M^{3+}]_{o,t}/[M^{3+}]_{a,t}$) of Am^{3+} and 14 Ln^{3+} ions between 0.1 M HNO_3 and benzene containing 0.05 M CMPO plotted against atomic number (a) in the presence of 1×10^{-3} M H^+TFPB^- and (b) in its absence.

checked by measuring co-extracted water into the organic phase. Fig. 3(a) shows the concentration of water in the organic phase as a function of $[H^+TFPB^-]_{o,t}$ examined prior to the metal extraction experiments. As is seen from this figure, the more $TFPB^-$ added to the system, the less water is found in the organic phase. Fig. 3(b) shows the concentration of water in the organic phase as a function of total concentration of Eu^{3+} extracted into the organic phase at $[H^+TFPB^-]_{o,t} = 0.03$ M that corresponds to the right-hand side end of the data in Fig. 3(a). Also, Fig. 3(b) compares the results of two different counterions, $TFPB^-$ and NO_3^-. As is seen from this figure, in the case of NO_3^-, $[H_2O]_{o,t}$ is greatly increased by an increase in $[Eu^{3+}]_{o,t}$, that reflects the hydration of the metal. On the other hand, in the case of $TFPB^-$, $[H_2O]_{o,t}$ is, inversely, decreased by the $[Eu^{3+}]_{o,t}$ increase. These data were analysed by taking account of the following experimental results obtained in a separate study.[8] In the absence of Eu^{3+}, H^+TFPB^- is in the form of $H(CMPO)^+TFPB^-$ in benzene containing a sufficient amount of the CMPO. The CMPO free from H^+TFPB^- is in the form of the CMPO molecule or a mono-hydrate $CMPO(H_2O)$ in the organic phase equilibrated with 0.001 M HNO_3. When Eu^{3+} is extracted from 0.001 M HNO_3 into the organic phase containing the CMPO and H^+TFPB^-, the extracted Eu^{3+} is in the form of $Eu(CMPO)_4{}^{3+}(TFPB^-)_3$. From these, mass balances of CMPO, H^+TFPB^-, and H_2O in the organic phase can be written as:

$$[CMPO]_{o,t} = [CMPO]_o + [CMPO(H_2O)]_o + [H(CMPO)^+TFPB^-(H_2O)_{n'}]_o + 4\,[Eu^{3+}]_{o,t} \quad (1)$$

$$[H^+TFPB^-]_{o,t} = [H(CMPO)^+TFPB^-(H_2O)_{n'}]_o + 3\,[Eu^{3+}]_{o,t} \quad (2)$$

$$[H_2O]_{o,t} = [H_2O]_o + [CMPO(H_2O)]_o + n'\,[H(CMPO)^+TFPB^-(H_2O)_{n'}]_o + n\,[Eu^{3+}]_{o,t} \quad (3)$$

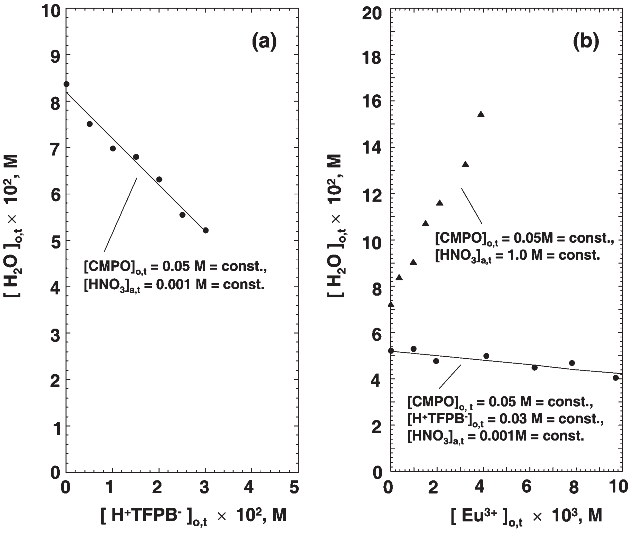

Fig. 3 Decrease in $[H_2O]_{o,t}$ with the extraction of $TFPB^-$ species. (a) $[H_2O]_{o,t}$ as a function of $[H^+TFPB^-]_{o,t}$, (b) $[H_2O]_{o,t}$ as functions of $[Eu^{3+}]_{o,t}$, comparing two counterions, $TFPB^-$ and NO_3^-. The solid lines are values calculated by introducing $n' = 0$ into eqn. (4) and $n = 0$ into eqn. (5), respectively.

where n and n' are observed hydration numbers of $Eu(CMPO)_4{}^{3+}(TFPB^-)_3$ and $H(CMPO)^+TFPB^-$, respectively. $[H_2O]_o$ is the concentration of blank water dissolved in pure benzene. In the absence of Eu^{3+}, the relationship among $[CMPO]_{o,t}$, $[H^+TFPB^-]_{o,t}$, and $[H_2O]_{o,t}$ can be written as:

$$K_{hf}\,a_w([H_2O]_{o,t} - [H_2O]_o) = (1 + K_{hf}\,a_w)[CMPO]_{o,t} - (1 + K_{hf}\,a_w - n'\,K_{hf}\,a_w)[H^+TFPB^-]_{o,t} \quad (4)$$

where a_w and K_{hf} are the activity of water and the equilibrium constant for the CMPO mono-hydrate formation $(=[CMPO(H_2O)]_o/([CMPO]_o\ a_w))$, respectively. The data in Fig. 3(a) were analysed by using eqn. (4): a_w, K_{hf}, and $[H_2O]_o$ were introduced as already known values.[8] As the result, it was found that $n' = 0$ with the 3σ error $\pm$ 0.1. Meanwhile, in the presence of Eu^{3+}, the following relationship can be written on the basis of the mass balance equations introducing $n' = 0$ into eqn. (3).

$$K_{hf}\,a_w([H_2O]_{o,t} - [H_2O]_o) = (1 + K_{hf}\,a_w)([CMPO]_{o,t} - [H^+TFPB^-]_{o,t}) - (1 + K_{hf}\,a_w - n\,K_{hf}\,a_w)[Eu^{3+}]_{o,t} \quad (5)$$

By analysing the data in Fig. 3(b) using eqn. (5), it was found that $n = 0$ with the 3σ error $\pm$ 0.1. Thus, the cationic complexes of $Eu(CMPO)_4{}^{3+}$ and $H(CMPO)^+$ paired with $TFPB^-$ are almost completely dehydrated; while, the "superweak" anion, itself, does not participate in the coordination.[4–6] The "hydrophobic field" of $TFPB^-$ occurring on its *water-fearing* surface ought to affect the dehydration of the cationic complexes, although the mechanism is not yet clear. Without hydrating water molecules, the coordination should be much more efficiently performed. This may also induce the selectivity improvement, however, further studies are necessary for a complete understanding.

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