Journal of Alloys and Compounds 408–412 (2006) 1052–1055

www.elsevier.com/locate/jallcom

Effect of counter-anions on the adsorption of trivalent actinides and lanthanides on tertiary pyridine resin in alcoholic chloride and nitrate solutions

Atsushi Ikeda[a,*], Keisuke Itoh[b], Tatsuya Suzuki[a], Masao Aida[a], Yasuhiko Fujii[a], Toshiaki Mitsugashira[c], Mitsuo Hara[c], Masaki Ozawa[a,d]

[a] *Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, Ookayama 2-12-1, Meguro-ku, Tokyo 152-8550, Japan*
[b] *Graduate School of Material Science and Engineering, Shibaura Institute of Technology, Shibaura 3-9-14, Minato-ku, Tokyo 108-8548, Japan*
[c] *Institute for Materials Research, Tohoku University, Narita-machi 2145-2, Oarai-machi, Higashiibaraki-gun, Ibaraki 311-1313, Japan*
[d] *Japan Nuclear Cycle Development Institute, Narita-machi 4002, Oarai-machi, Higashiibaraki-gun, Ibaraki 311-1393, Japan*

Abstract

Chromatography experiments using a tertiary pyridine resin have been carried out in methanolic nitric acid solution for the separation of trivalent actinides (An) and lanthanides (Ln). The elution behavior of trivalent An (Am and Cm) is similar to that of middle Ln series in the nitric acid system, while the trivalent An are separated from Ln in methanolic hydrochloric acid solution. The calculated distribution coefficients (K_d) indicate that the adsorbability of trivalent An and Ln depends on their ionic radii in the nitric acid system. The different separation behavior observed between nitric acid and hydrochloric acid systems is discussed from the viewpoint of solvation structures.

Keywords: Actinides; Lanthanides; Pyridine; Alcohol; Nitrate ion; Chloride ion

---

1. Introduction

The actinide elements (An) over $_{93}$Np, which are commonly called transuranium (TRU) elements, are generally produced in nuclear reactors with a variety of fission products (FPs). Due to their high radioactivity and long half-lives, most of the TRU elements are considered as high-level radioactive wastes (HLW) and their treatment is one of the vital problems in nuclear industry. The partitioning and transmutation is one of the powerful strategies for reducing HLW [1]. In this strategy, the separation (partitioning) of TRU elements from FPs is required before transmuting them into other stable or lower-level nuclides.

The majority of FPs can be easily removed from TRU elements by using general chemical separation techniques, such as precipitation or solvent extraction. However, the separation from lanthanides (Ln) is not so simple. The FPs contain a considerable amount of Ln. It is well known that the chemical properties of Ln are similar to those of An and this similarity poses a difficulty for the separation of these elements. Especially, the separation of Ln from the An over $_{95}$Am, that form trivalent cations (M^{3+}) in solution, is quite difficult due to their same oxidation states and similar ionic radii [2]. Although a large number of studies have concentrated on the separation of trivalent An from Ln and many separation techniques have been developed [3–6], a novel separation technique is still expected for the practical use.

Recently, we have developed a chromatographic separation technique using a tertiary pyridine resin for the partitioning of trivalent An from Ln and confirmed that the trivalent An of Am and Cm are separated from Ln in alcoholic hydrochloric acid solutions [7–9]. However, there are little data on the separation behavior of trivalent An and Ln by using the pyridine resin in nitric acid system. The present nuclear fuel reprocessing, PUREX, is operated in nitric acid solution and, therefore, the real HLW are generally produced as nitric acid solution. In order to improve our separation technique

---

[*] Corresponding author. Tel.: +81 3 5734 2958; fax: +81 3 5734 2958.
E-mail address: aikeda@nr.titech.ac.jp (A. Ikeda).

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2004.11.096

for practical use, the separation behavior of An and Ln in nitric acid solution should be confirmed.

In this paper, chromatographic separation of trivalent An (Am and Cm) and Ln are performed by using the tertiary pyridine resin in alcoholic nitric acid solutions. The results are compared with those previously obtained in the chloride media and the effect of counter-anions on the separation behavior is discussed in terms of their different solvation structures.

2. Experimental

2.1. Materials

^{241}Am and ^{242}Cm were used as trivalent An samples in the present work. A mixed sample of ^{241}Am and ^{242}Cm was produced by irradiating $^{241}AmO_2$ in the Japan Materials Testing Reactor (JMTR). The radioactive Ln samples of ^{141}Ce, ^{147}Nd and ^{160}Tb were generated by the irradiation of their stable isotopes using an electron linear accelerator at the Laboratory of Nuclear Science, Tohoku University. In the experiments using non-radioactive Ln, a mixed sample of yttrium and several Ln was prepared from their nitrates or oxides. All chemicals used in this study, except radioactive materials, were reagent grade and supplied by Wako Pure Chemical Ind., Ltd., Japan and Kanto Kagaku, Japan.

The resin employed in this study was a tertiary pyridine resin embedded in silica beads. The chemical structure of tertiary pyridine resin is given in Fig. 1. The resin was synthesized in our laboratory and detailed properties of the resin have been described in the previous papers [7,10,11].

2.2. Chromatography experiments

In the experiments using An and radioactive Ln, the pyridine resin was packed in a plastic column with Ø1 cm × 10 cm. The column was preliminarily conditioned with the same eluent used in each chromatography experiment. Feed solutions were prepared by dissolving a mixture of the trivalent An and radioactive Ln samples into a desired concentration of methanolic nitrate solution. A 0.5 cm^3 portion of the feed solutions, containing approximately 0.5 mg of An for the total amount, was introduced from the top of the resin column and eluted with an eluent. The eluent was identical with that used for the preparation of feed solutions. Effluent from the bottom of the column was collected in fractions and the An and Ln in the fractions were detected by α- or γ-ray spectroscopy as described previously [9]. The experiments were performed at ambient temperature (about 293 K) with a constant flow rate of 100 cm^3/h. On the other hand, a longer resin column of Ø1 cm × 50 cm was employed for non-radioactive experiments using stable Ln. The column was surrounded by a water jacket and kept at a constant temperature of 293 K. Feed solutions were the mixtures of yttrium and 8 or 14 lanthanides (La–Lu, except Pm) dissolved in a desired concentration of methanolic nitrate solutions. The concentration of each element was 0.01 mol/dm^3. A 5.0 cm^3 of the feed solutions was injected into the column at a constant flow rate of 50 cm^3/h and, then, the Ln in the effluent were detected by ICP-AES (OPTIMA-3000, PerkinElmer Inc.).

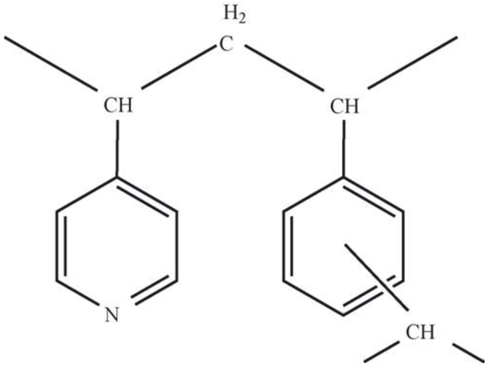

Fig. 1. Chemical structure of tertiary pyridine resin.

3. Results and discussion

Fig. 2 shows the elution chromatogram of the trivalent An and Ln using the mixture of 70 vol.% of concentrated nitric acid solution (13.5 mol HNO_3/dm^3) and 40 vol.% of methanol. The trivalent An of Am and Cm were eluted between Tb and Nd. This elution order is quite different from that in hydrochloric acid system, as shown in Fig. 3. As an increase of the methanol content in the mixed solution, the retention volume of each element became larger and their elution curves were separated individually, although the elution order was unchanged.

The elution order of trivalent An and Ln observed in Fig. 2 follows the reverse order of ionic radii. In order to clarify this relationship quantitatively, the distribution coefficients

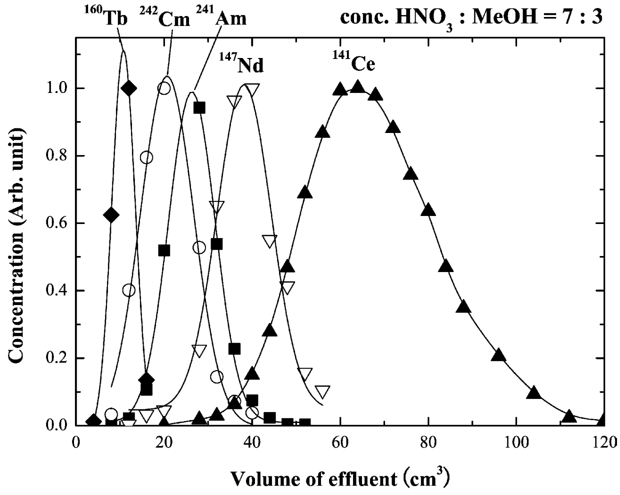

Fig. 2. Elution chromatogram of trivalent An and Ln in methanolic nitric acid solution at ambient temperature (solvent: 70 vol.% conc. HNO_3/30 vol.% MeOH).

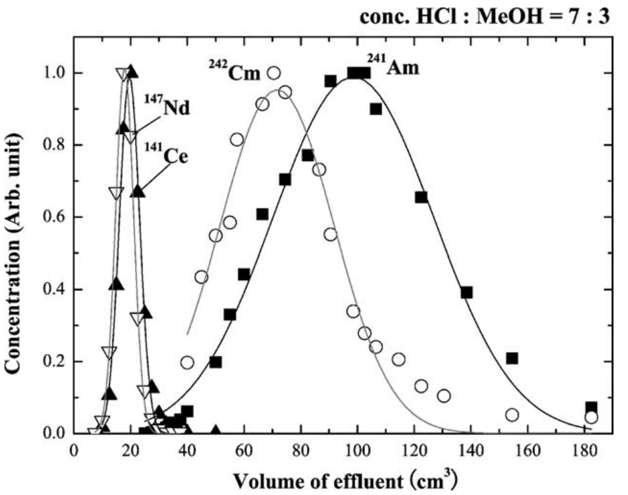

Fig. 3. Elution chromatogram of trivalent An and Ln in methanolic hydrochloric acid solution at ambient temperature [8] (solvent: 70 vol.% conc. HCl/30 vol.% MeOH).

(K_d) were calculated as described previously [9] from the elution curves and the results were plotted in Fig. 4 against their ionic radii. The distribution coefficients of Ln were calculated from a non-radioactive chromatography experiment using stable Ln. As shown in Fig. 4, the distribution coefficients of trivalent An and Ln decrease with a decrease of effective ionic radii (r_{eff}). The trivalent An of Am and Cm show the middle values between Nd and Sm, suggesting that the separation of these An from the middle-Ln series would be difficult to achieve in this system. It should be noted that the separation factors ($\alpha_B^A = K_{dA}/K_{dB}$) between lighter Ln (La–Pr) and heavier Ln (Gd–Lu) are more than 10. This means that the present nitric acid system can be useful for the separation of lighter Ln from heavier Ln.

Fig. 5 shows the variation of distribution coefficients of trivalent An and Ln in a methanolic hydrochloric acid solution

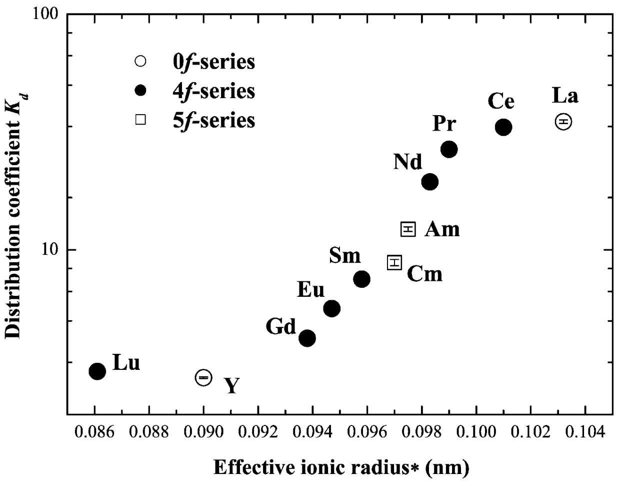

Fig. 4. Distribution coefficients of trivalent An and Ln on tertiary pyridine resin in methanolic nitric acid medium (solvent: 70 vol.% conc. HNO_3/30 vol.% MeOH, *: the values from Ref. [2]).

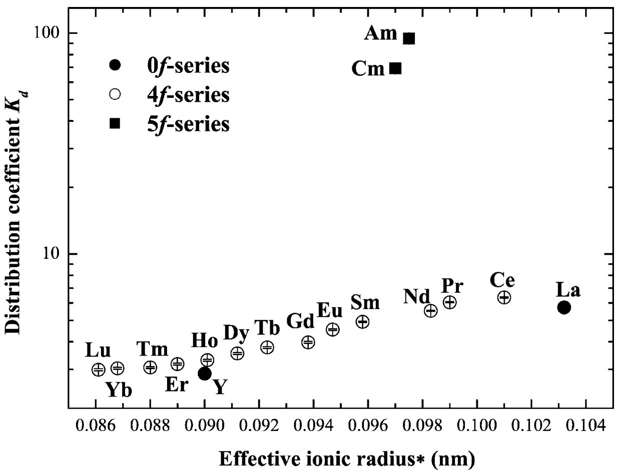

Fig. 5. Distribution coefficients of trivalent An and Ln on tertiary pyridine resin in methanolic hydrochloric acid medium [8] (solvent: 70 vol.% conc. HCl/30 vol.% MeOH, *: the values from Ref. [2]).

[8]. As compared with the nitric acid system, the trivalent An show far larger distribution coefficients than Ln. As a result, the group separation of trivalent An from Ln can be easily achieved, as shown in Fig. 3. Moreover, La and Y, which have no f-electron in their orbits, deviate from the relational curve of other 4f-Ln series. This deviation was not observed in the nitric acid system. We considered the cause of these differences between hydrochloric acid and nitric acid systems as their different solvation characters.

In the present separation system using a pyridine resin with nitric acid (or hydrochloric acid) solution, the following four factors are mainly involved in the adsorption–desorption process of cations. That is, (1) coordination of pyridine groups to the cations, (2) hydration of the cations, (3) solvation of the cations with nitrate or chloride ions, and (4) protonation of pyridine groups. Pyridine groups generally coordinate to metal cations by using N-atoms and they are categorized as soft-donor type ligands [14]. It has been reported that pyridine-type N-donor ligands can selectively extract trivalent An from Ln [12,13], suggesting that the pyridine groups have a larger affinity for An than for Ln(III) [15]. On the other hand, trivalent An and Ln cations are tightly hydrated with 8–9 water molecules in aqueous solution [16–19]. Hence, the coordination of pyridine groups is considered a competitive reaction with the hydration of the cations. The hydration enthalpies ($-\Delta H_h$) for An and Ln series gradually increase with an increase of atomic numbers [20] and the water-exchange rates of Ln aquo-complexes decreases with the increase of atomic numbers [21,22], implying that the hydration of Ln (An) becomes firmer with the increase of atomic numbers. Strong hydration prevents the coordination of pyridine groups and, therefore, the interaction between pyridine groups and Ln cations should be weaken for heavier Ln cations compared with the lighter ones. This hypothesis is in agreement with the observed decreasing tendency on the distribution coefficients of Ln with the increase of atomic

Table 1
Stability constants of Eu(III) and Am(III) with nitrate and chloride ions

Anions	Eu(III)	Am(III)	Ref.
NO_3^-	2.0	1.8	[21]
	1.4	1.4	[22]
	1.80	1.93	[23]
Cl^-	0.9	0.9	[21]
	0.8	0.9	[22]
	0.64	0.72	[23]

numbers both for nitric acid and for hydrochloric acid systems.

In addition to the hydration, the solvation by anionic species must be considered in the present system. Metal cations are solvated with nitrate ions (NO_3^-) in nitric acid solution and with chloride ions (Cl^-) in hydrochloric acid solution. The stability constants for Eu and Am with nitrate and chloride ions reported in some references [23–25] are listed in Table 1. These stability constants indicate that the nitrate complexes are more stable than the chloride complexes, although the stability of Eu complexes is similar to that of Am ones in the same medium. Furthermore, several studies [26–28] have suggested that the coordination style of nitrate ions (NO_3^-) to Ln (An) cations is different from that of chloride ions (Cl^-): nitrate ions form inner-sphere complexes with the cations, while chloride ions hardly coordinate to the inner-sphere and they form outer-sphere complexes. In higher nitric acid concentration (∼6 mol HNO_3/dm^3), two nitrate ions coordinate to the cations with bidentate mode [27,28] and these coordinating nitrate ions are not easily substituted for other non-coordinating (i.e. bulky) nitrate ions or water molecules [27,29], preventing the coordination of pyridine groups to the cations. This inhibition by nitrate ions may weaken the selectivity of pyridine groups for An over Ln, with the result that no enhanced adsorption of An was observed in nitric acid solutions. On the other hand, there is no considerable obstacle to the complexation with pyridine groups in chloride solutions except hydration. Consequently, the pyridine groups can selectively extract An from Ln in chloride solutions. However, further study is required for the detailed discussion about the adsorption–desorption mechanism in the present system.

4. Conclusions

Chromatographic separation experiments of trivalent An and Ln have been performed by using a tertiary pyridine resin in methanolic nitric acid solution and the results have been compared with those obtained in methanolic hydrochloric acid solution. The distribution coefficients (K_d) of trivalent Am and Cm show the intermediate values between those of Nd and Sm in the nitric acid medium, indicating that the adsorbability of trivalent An and Ln simply depends on their ionic radii in the nitric acid system. On the other hand, the trivalent An show far larger K_d values than Ln in hydrochloric acid solutions and this enhanced adsorption of trivalent An enables a clear separation of trivalent An from Ln. The different separation behavior observed between nitric acid system and hydrochloric acid system may be due to the different solvation characters of nitrate and chloride ions.

Acknowledgement

The authors are grateful to Dr. Tsuyoshi Yaita, Japan Atomic Energy Research Institute, for offering valuable comments and discussion.

References

[1] S. Chwaszczewski, B. Słowiński, Appl. Energy 75 (2003) 87.
[2] R.D. Shannon, Acta Crystallogr. A 32 (1976) 751.
[3] J. Starý, Talanta 13 (1966) 421.
[4] J.N. Mathur, Solv. Extract. Ion Exch. 1 (1983) 349.
[5] H. Freiser, Solv. Extract. Ion Exch. 6 (1988) 1093.
[6] K.N. Nash, Solv. Extract. Ion Exch. 11 (1993) 729.
[7] T. Suzuki, M. Aida, Y. Ban, Y. Fujii, M. Hara, T. Mitsugashira, J. Radioanal. Nucl. Chem. 255 (2003) 581.
[8] A. Ikeda, T. Suzuki, M. Aida, K. Ohtake, Y. Fujii, K. Itoh, M. Hara, T. Mitsugashira, J. Alloys Compd. 374 (2004) 245.
[9] A. Ikeda, T. Suzuki, M. Aida, Y. Fujii, K. Itoh, T. Mitsugashira, M. Hara, M. Ozawa, J. Chromatogr. A 1041 (2004) 195.
[10] M. Nogami, M. Aida, Y. Fujii, A. Maekawa, S. Ohe, H. Kawai, M. Yoneda, Nucl. Technol. 115 (1996) 293.
[11] M. Nogami, Y. Fujii, T. Sugo, J. Radioanal. Nucl. Chem., Art. 203 (1996) 109.
[12] R. Wietzke, M. Mazzanti, J.-M. Latour, J. Pécaut, P.-Y. Cordier, C. Madic, Inorg. Chem. 37 (1998) 6690.
[13] M.P. Jensen, L.R. Morss, J.V. Beitz, D.D. Ensor, J. Alloys Compd. 303/304 (2000) 137.
[14] J.O. Edwards, J. Am. Chem. Soc. 76 (1954) 1540.
[15] G.R. Choppin, J. Alloys Compd. 223 (1995) 174.
[16] A. Habenschuss, F.H. Spedding, J. Chem. Phys. 70 (1979) 2797.
[17] A. Habenschuss, F.H. Spedding, J. Chem. Phys. 70 (1979) 3758.
[18] H. Kanno, J. Hiraishi, J. Phys. Chem. 86 (1982) 1488.
[19] S.D. Conradson, Appl. Spectrosc. 52 (1998) 252A.
[20] F. David, J. Less-Comm. Met. 121 (1986) 27.
[21] C. Cossy, L. Helm, A.E. Merbach, Inorg. Chem. 27 (1988) 1973.
[22] C. Cossy, L. Helm, A.E. Merbach, Inorg. Chem. 28 (1989) 2699.
[23] D.F. Peppard, G.W. Mason, I. Hucher, J. Inorg. Nucl. Chem. 24 (1962) 881.
[24] B.M.L. Bansal, S.K. Patil, H.D. Sharma, J. Inorg. Nucl. Chem. 26 (1964) 993.
[25] P.K. Khopkar, P. Narayanankutty, J. Inorg. Nucl. Chem. 33 (1971) 496.
[26] J. Reidler, H.B. Silber, J. Chem. Soc., Chem. Commun. 10 (1973) 354.
[27] T. Yaita, D. Ito, S. Tachimori, J. Phys. Chem. B 102 (1998) 3886.
[28] T. Yaita, H. Narita, S. Suzuki, S. Tachimori, H. Motohashi, H. Shiwaku, J. Radioanal. Nucl. Chem. 239 (1999) 371.
[29] I. Abrahamer, Y. Marcus, J. Inorg. Nucl. Chem. 30 (1968) 1563.