Journal of Radioanalytical and Nuclear Chemistry, Vol. 239, No. 2 (1999) 377–380

Solvent extraction of technetium(VII) by cyclic amides

S. Suzuki,[1]* K. Tamura,[1] S. Tachimori,[1] Y. Usui[2]

[1] *Japan Atomic Energy Research Institute, Tokai-mura, Ibaraki, Japan*
[2] *Ibaraki University, Mito, Ibaraki, Japan*

(Received April 8, 1998)

The extraction behavior of heptavalent technetium with cyclic amides in *n*-dodecane from nitric acid solution was studied. The amides investigated are N-(2-ethyl)hexylbutyrolactam(EHBLA), N-(2-ethyl)hexylvalerolactam(EHVLA), N-(2-ethyl)hexyl-caprolactam (EHCLA), N-octylcaprolactam(OCLA), a mixture of 3-octyl-N-(2-ethyl)hexylvalerolactam and 4-octyl-N-(2-ethyl)hexylvalerolactam (3,4,OEHVLA), 2-octyl-N-(2-ethyl)hexylcaprolactam(2OEHCLA), a mixture of 3-octyl-N-(2-ethyl)hexylcaprolactam and 5-octyl-N-(2-ethyl)hexylcaprolactam(3,5,OEHCLA) and that of 3-octyl-N-octylcaprolactam and 5-octyl-N-octylcaprolactam(3,5,OOCLA). From the results of the distribution ratio of Tc(VII) as a function of acid concentration, cyclic amides concentration and $HTcO_4$ concentration, the effects of both the ring size of cyclic amide and structure of the substituents attached to different positions of the cyclic ring on the extraction behavior of Tc(VII) were discussed. A clear steric hindrance was observed. For applications, 3,4,OEHVLA is proposed as the best extractant for Tc from acidic solution.

Introduction

N,N-dialkyl carboxylic amides[1–6] have been studied extensively as possible alternative extractants to tributylphosphate (TBP) for the separation of actinide elements. As cyclic amides are also useful for the extraction of actinides, the extraction behavior of hexavalent actinides by N-alkyl-caprolactam has been reported so far.[7–9]

Separation of technetium is still a key issue in radioactive waste management because of its high fission yield and long half-life. Furthermore, in the present nuclear fuel reprocessing Tc coextracted with uranium, plutonium and zirconium in the first extraction stage of the PUREX process may interfere catalytically with the reductive stripping of Pu, which is necessary for the separation of plutonium from uranium. The extraction of Tc by alkyl monoamides has been reported,[10] but no information about Tc extraction with cyclic amides has been published.

In this study, solvent extraction of Tc(VII) by substituted cyclic amides, (1)~(6) (Scheme 1), was studied under various conditions.

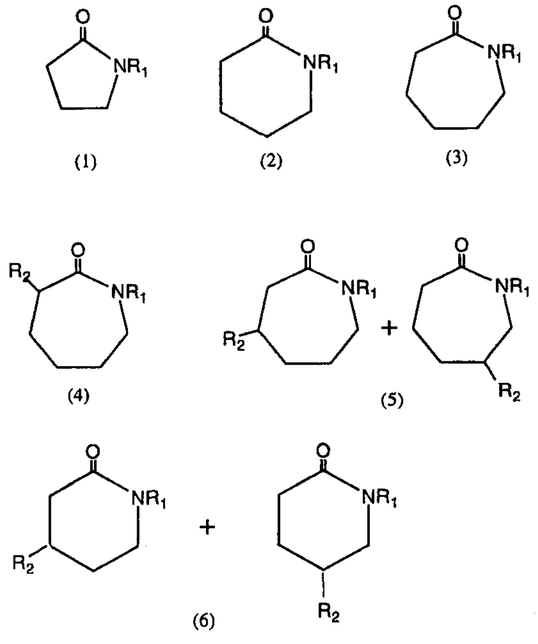
The relationship between the distribution ratio of Tc(VII): D_{Tc} and ring structure was investigated by using (1), (2) and (3). Cyclic amides (4) and (5) have been synthesized in order to increase the lipophilicity of (3). Compound (5) is a mixture of 3OEHCLA and 5OEHCLA (3,5,OEHCLA) and that of 3OOCLA and 5OOCLA (3,5,OOCLA).

Compound (6) is also a mixture of 3OEHVLA and 4OEHVLA (3,4,OEHVLA) which was designed to improve the lipophilicity of (2), and has been compared with (5) to see the effect of ring size. Thus, the present study clarified the effects of amide structure, i.e., ring size, the branched alkyl group: R_1 attached to nitrogen atom and the position of substituted octyl group: R_2 on the extraction of Tc(VII) by cyclic amides.

Experimental

Reagents

Cyclic amides, i.e., N-(2-ethyl)hexylbutyrolactam (EHBLA), N-(2-ethyl)hexylvalerolactam (EHVLA), N-(2-ethyl)hexylcaprolactam (EHCLA), N-octylcaprolactam (OCLA), a mixture of 3-octyl-N-(2-ethyl)hexyl-



Scheme 1

---

[*] E-mail: suzuki@mummy.tokai.jaeri.go.jp

0236–5731/99/USD 17.00

Elsevier Science B. V., Amsterdam
Akadémiai Kiadó, Budapest

valerolactam and 4-octyl-N-(2-ethyl)hexylvalerolactam (3,4,OEHVLA), 2-octyl-N-(2-ethyl)hexylcaprolactam (2OEHCLA), a mixture of 3-octyl-N-(2-ethyl)hexylcaprolactam and 5-octyl-N-(2-ethyl)-hexylcaprolactam (3,5,OEHCLA) and that of 3-octyl-N-octylcaprolactam and 5-octyl-N-octylcapro-lactam (3,5,OOCLA) were synthesized in our laboratory by the method similar to the one reported by MARVEL et al.[11] The cyclic amides prepared were characterized by gas-chromatography, IR-spectra and NMR. N-dodecane (Wako Pure Chemical Industries, Ltd.) as a diluent was of reagent grade and used as received. All other reagents were of GR grade. Technetium-99 was used as a tracer.

Distribution experiment

Equal volumes of an aqueous solution with the predetermined amount of acid and Tc(VII), and an organic solution of n-dodecane of containing cyclic amides (0.008~1.0M) pre-equilibrated by the required concentration of HNO_3 (0.01M~7.0M) were shaken for 10 minutes in a thermostated box kept at 25±0.1 °C. The initial Tc concentration changed from $1.15\cdot10^{-5}$ to $1.5\cdot10^{-1}$M. After the equilibration, both phases were separated by centrifugation and aliquots of each phase were submitted to the measurement of Tc(VII) activity. The D_{Tc} between the aqueous nitric acid and the organic solution was determined. The Tc(VII) activity was measured by using a liquid scintillation counter (Packard, 2700TR/AB).

Results and discussion

Effect of ring size on D_{Tc}

The extractant dependency of D_{Tc} for EHBLA, EHVLA and EHCLA is shown in Fig. 1. D_{Tc} increased with an increase in extractant concentration from 0.008 to 1.0M at aqueous concentration of 0.1M HNO_3. At a concentration less than 0.2M, the slopes of curves for EHBLA, EHVLA and EHCLA were 1.9, 1.9 and 2.2, respectively, which indicates that about two amide molecules are involved in the Tc extraction. On the other hand, at concentrations higher than 0.2M, the slopes for EHBLA, EHVLA and EHCLA were between 3.3 and 5.5, which indicates that approx. 3 to 6 amide molecules are involved in the Tc extraction. CONDAMINES[11] suggested that the slopes for Tc by branched monoamides: DEHBA and N,N-di-(2-ethylhexyl)-3.3-dimethylbutylamide (DEHDMBA) are 2.2 and 2.7. Complexes of Tc-monoamides were $(HTcO_4)(AMIDE)_{2-3}$ for DEHBA and $(HTcO_4)(HNO_3(AMIDE))_{2-3}$ for DEHDMBA. Our study[12] showed that the slope for Tc by monoamide: DHOA was 2.3, thus the suggested complex of Tc-monoamide was $(HTcO_4)(AMIDE)_{2-3}$. The present results with cyclic amides, however, revealed the highest solvation of more than 5, particularly for the smallest ring EHBLA at a high extractant concentration. Figures 2 and 3 show a comparison of ring size effect on the D_{Tc} profile as a function of HNO_3 by 1M amides and 0.1M amides in dodecane, respectively. D_{Tc} by EHBLA, EHVLA and EHCLA of a respective concentration of 1M amide in dodecane increased with an increase in acid concentration and a third phase appeared at 0.1M HNO_3 for EHBLA, 0.3M HNO_3 for EHVLA, 0.5M HNO_3 for EHCLA and 1M HNO_3 for OCLA. This difference of solubility of the amides must be due to the distinction of physical property of cyclic amides relating to the number of carbon atoms, thus the extent of the third phase formation is EHBLA > EHVLA > EHCLA. Interestingly the order of D_{Tc} is also EHBLA > EHVLA > EHCLA. Figure 3 shows the nitric acid dependency of the D_{Tc} with a low (0.1M) concentration of amides, where the effect of HNO_3 extraction by monoamide clearly appeared. Consequently the values of D_{Tc} have a maximum in aqueous solutions of 2.0M HNO_3 for EHBLA, 1.0M HNO_3 for EHVLA, and 1.0M HNO_3 for EHCLA. Thereby at a high acidity, D_{Tc} decreased due to competition with HNO_3. In Fig. 4 the effect of ring size of cyclic part on D_{Tc} for bulky extractant with octyl group attached is seen. The slopes of linear curves for 3,4,OEHVLA and 3,5,OEHCLA were 1.7 and 1.8, which indicates that one to two amide molecules are involved in the Tc extraction. In comparison to EHVLA and EHCLA (Fig.1), the bulky molecules like 3,4,OEHVLA and 3,5,OEHCLA could not form highly solvated complexes at high amide concentration region. D_{Tc} by 2OEHCLA and 3,5,OEHCLA at a respective concentration of 1M in dodecane is lower than that of EHCLA (Fig. 2). Yet the third phase has not appeared at all aqueous conditions performed, which seems to be due to increasing lipophilicity of the amides as a result of the introduction of octyl group: R_2 into the ring part.

Effect of branching of alkyl group: R_1

The branching effect of alkyl group: R_1 on the extraction of Tc(VII) can be seen also in Fig. 2 (1M amide) and Fig. 3 (0.1M amide). At a high amide concentration, D_{Tc} with a branched R_1, EHCLA, showed constantly lower values of D_{Tc} at the whole HNO_3 concentration. This might be due to a large steric hindrance by the branched alkyl. However, at 0.1M amide D_{Tc} with EHCLA has a maximum at 1.0M HNO_3 and showed higher values than those by OCLA around it. This reversal in the order seems to be related to the extraction mechanism, which is under study.

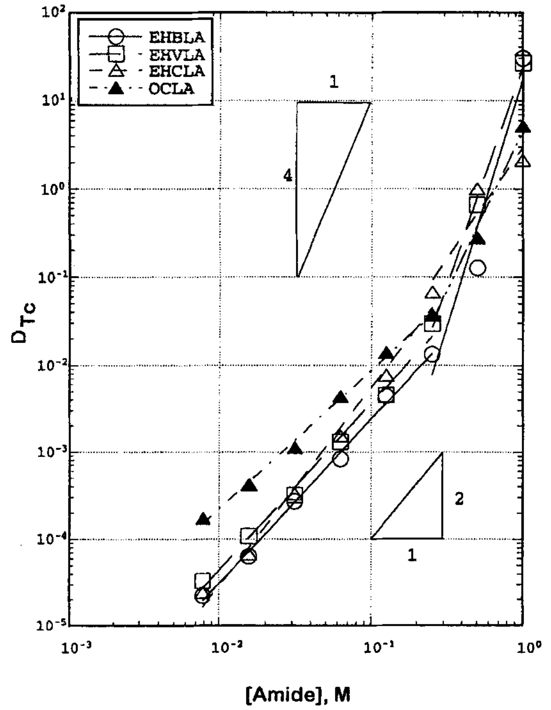


Fig. 1. Ring size effect on the D_{Tc} profile as a function of amide concentration (initial $HTcO_4$ concentration; $1.15 \cdot 10^{-3}$M, HNO_3: 0.1M)

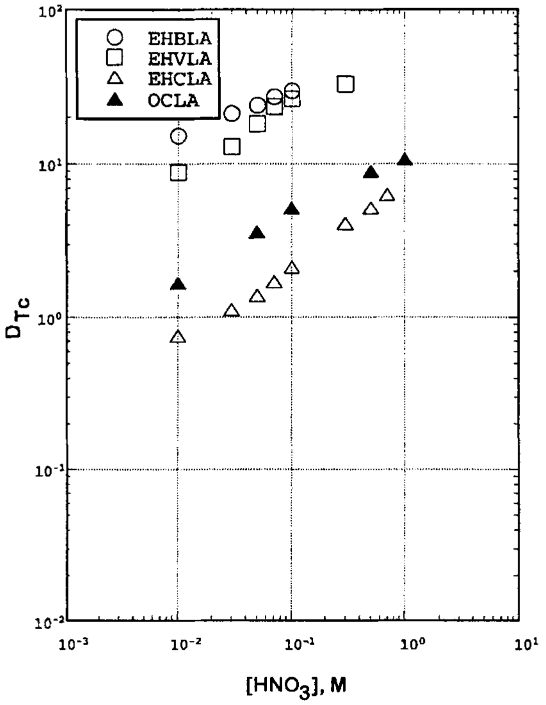


Fig. 2. Nitric acid dependency of D_{Tc} by 1.0M amides in dodecane (initial $HTcO_4$ concentration; $1.15 \cdot 10^{-3}$M)

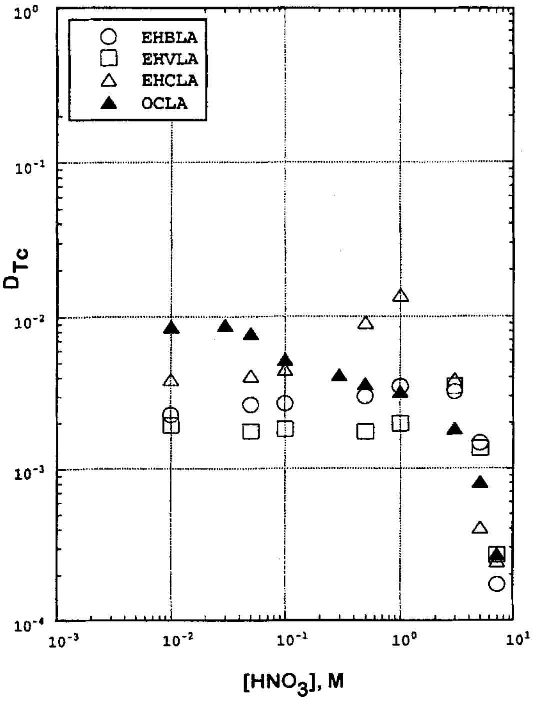


Fig. 3. Nitric acid dependency of D_{Tc} by 0.1M amides in dodecane (initial $HTcO_4$ concentration; $1.15 \cdot 10^{-3}$M)

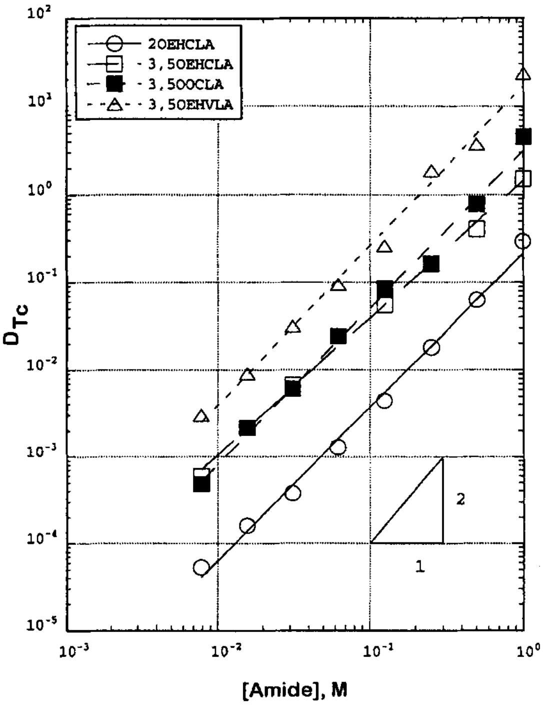


Fig. 4. Ring size effect on the D_{Tc} profile as a function of amide concentration (initial $HTcO_4$ concentration; $1.15 \cdot 10^{-3}$M, HNO_3: 0.1M)

Effect of the introduction of octyl group: R_2

As shown in Figs 5 and 6, the effect of the introduction of octyl group: R_2 in the carbon ring is clear. 2OEHCLA having an octyl group attached at the nearest carbon atom to the C=O group showed a drastic decrease of the D_{Tc} value due to a larger steric hindrance compared to that in 3,5,OEHCLA. Figure 4 shows the extractant dependency of D_{Tc} by 2OEHCLA and 3,5,OEHCLA. Slopes of the curves for 2OEHCLA and 3,5,OEHCLA are 1.8 and 1.7, respectively. It can be concluded that approx. 1 to 2 amide molecules are involved in the Tc extraction irrespective of steric hindrance around an oxygen donor atom.

Conclusions

The solvent extraction of heptavalent technetium from nitric acid solution by cyclic amides were investigated. The following conclusions were obtained.

(1) The extraction behavior of technetium by cyclic amides depends on the ring size of the cyclic amides.

(2) It is considered that the complexes with Tc are $(HTcO_4)(AMIDE)_{1-2}$ and $(HTcO_4)(AMIDE)_{3-6}$.

(3) The effects of branching, particularly of its position in the R_1 alkyl group, on the extraction of Tc(VII) were clearly observed.

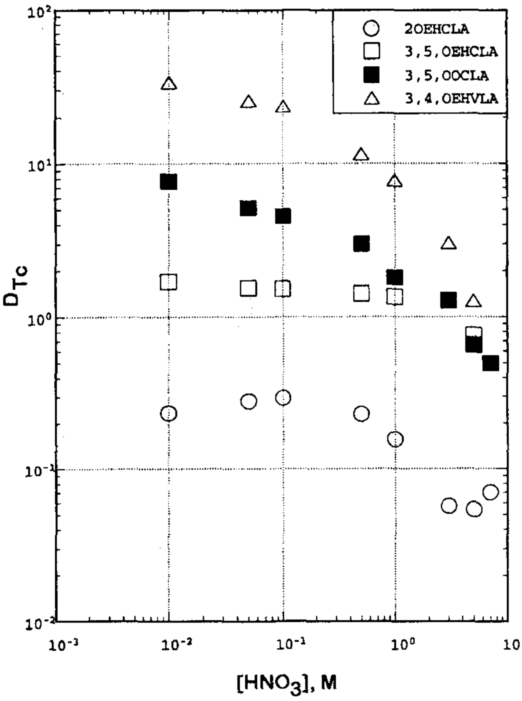


Fig. 5. Nitric acid dependency of D_{Tc} by 1.0M amides in dodecane (initial $HTcO_4$ concentration; $1.15 \cdot 10^{-3}$M)

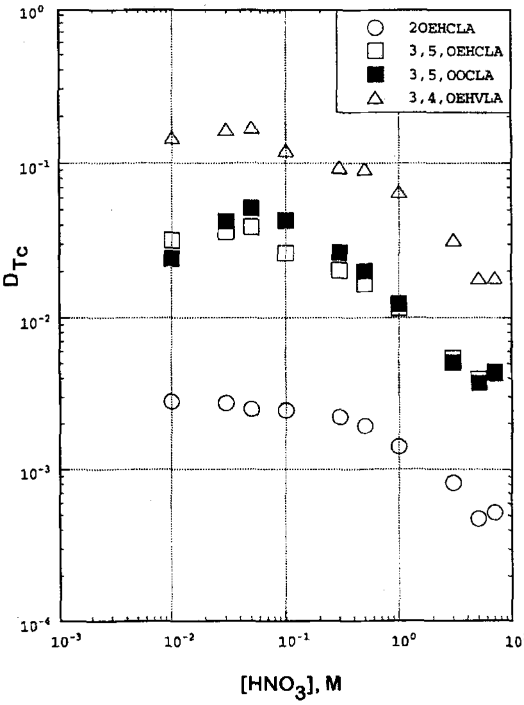


Fig. 6. Nitric acid dependency of D_{Tc} by 0.1M amides in dodecane (initial $HTcO_4$ concentration; $1.15 \cdot 10^{-3}$M)

(4) The introduction of an alkyl group R_2 to the ring part to increase the lipophilicity was effective to suppress the third phase formation, but the appending of R_2 to the position of carbon atom neighboring the functional C=O group depressed D_{Tc} by steric hindrance around an oxygen donor atom.

References

1. T. H. SIDDALL III, J. Phys. Chem., 64 (1960) 1863; DP-541, 1961.
2. G. M. GASPARINI, G. GROSSI, Sep. Sci. Technol., 15 (1980) 825.
3. G. M. GASPARINI, G. GROSSI, Solv. Ext. Ion Exch., 4 (1986) 1233.
4. C. MUSIKAS, Sep. Sci. Technol., 23 (1988) 1211.
5. C. MUSIKAS, N. CONDAMINE, C. CUILLERDIER, Anal. Sci., 7 (1991) 11.
6. N. CONDAMINE, C. MUSIKAS, Solv. Ext. Ion Exch., 10 (1992) 69.
7. C. SHEN, B. BAO, G. WANG, J. QIAN, J. Radioanal. Nucl. Chem., 162 (1992) 207.
8. B. BAO, C. SHEN, G. WANG, J. QIAN, Solvent Extraction in the Process Industries, Proceedings of ISEC'93, Vol. 3, D. H. LOGSDAIL and M. J. SLATER (Eds), El, 1993, p. 1821.
9. L. YANG, S. AKITA, H. TAKEUCHI, Value Adding Through Solvent Extraction, Proceedings of ISEC'96, Vol. 2, D. C. SHALLCROSS, R. PAIMIN and L. M. PRVCIC (Eds), The University of Melbourne, 1996, p. 1321.
10. N. CONDAMINE, C. MUSIKAS, H. D. DELMAU, CEA-CONF 11456, 1991.
11. C. S. MARVEL, W. W. MOYER, J. Org. Chem., 22 (1957) 1065.
12. S. SUZUKI, S. TACHIMORI, Proc. Intern. Conf. on Evaluation of Emerging Nuclear Fuel Cycle Systems (GLOBAL'95), 1995, p. 1216.