ELSEVIER

Journal of Nuclear Materials 247 (1997) 203–207

journal of nuclear materials

Temperature effect on technetium(VII) extraction by CMPO and TBP

Mitsuo Takeuchi [a,*], Satoru Tanaka [b], Michio Yamawaki [c]

[a] Low Level Radioactive Department, Japan Nuclear Fuel Ltd., Chiyoda-ku, Tokyo 100, Japan
[b] Department of Quantum Engineering and Systems Science, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan
[c] Nuclear Engineering Research Laboratory, The University of Tokyo, Tokai-mura, Ibaraki-ken 319-11, Japan

Abstract

Temperature effect on the extraction of technetium(VII) was investigated under the conditions of the absence and presence of uranium(VI) from nitric acid solution by *n*-octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (CMPO), tributyl phosphate (TBP) and a mixture of CMPO and TBP. The distribution coefficients of technetium by CMPO, TBP, and CMPO + TBP in the absence of uranium decreased with the increase of temperature. In the presence of uranium, the distribution coefficients of technetium were found to be quite larger than those in the technetium alone extraction system. Their thermodynamic parameters were obtained using the temperature effects on the distribution coefficients of technetium under various conditions. The information obtained from the thermodynamic parameters was discussed taking the extraction mechanism of technetium into account. © 1997 Elsevier Science B.V.

1. Introduction

Separation of technetium from radioactive waste is expected to be one of the measures mitigating the recent waste problem, since technetium-99 is a long-lived fission product and stays in nuclear waste for a long time. In this connection, extraction of technetium from nitric acid solution by TBP has been studied by many researchers [1–10]. A bidentate extractant, CMPO, was developed at Argonne National Laboratory to extract effectively transuranium elements. In recent times, the solvent extraction chemistry of technetium with CMPO has been studied under a variety of conditions by the present authors [11–15]. There is, however, little information about the temperature effect on the technetium extraction by the mixture of CMPO and TBP [16]. The thermodynamic data also would be indispensable for comprehending the whole extraction system.

In the present study, the temperature effect on the extraction of technetium in the absence and presence of uranium was investigated using CMPO, TBP and a mixture of CMPO and TBP.

2. Experimental

2.1. Reagents

CMPO (M and T Chemical and Atochem North America) with a purity higher than 97% was used without further purification. TBP (Wako Pure Chemical Industries), *n*-dodecane (Tokyo Chemical Industries) and decalin (Wako Pure Chemical Industries) were of reagent grade and used as received. Technetium(VII)-99 (Amersham) as NH_4TcO_4 in 0.21 mol/l NH_4OH solution was diluted with deionized water and HNO_3 to the desired concentrations as technetium, 4×10^{-5} mol/l in the absence of uranium and 1×10^{-4} mol/l in the presence of uranium. Uranium(VI) (Allied Chemical and Dye, USA) as $UO_2(NO_3)26H_2O$ was dissolved in HNO_3 and finally prepared to 1×10^{-4}, 1×10^{-3} and 5×10^{-3} mol/l as uranium in sample solutions.

2.2. Distribution measurements

Prior to the extraction of technetium and uranium, organic solutions including CMPO and TBP were washed three times with 0.5 mol/l Na_2CO_3 solution and pre-equilibrated with a desired concentration of HNO_3. One milliliter of aqueous HNO_3 solution containing technetium and uranium was mixed with an equal volume of the

---

[*] Corresponding author. Present address: Nuclear Power Department, Shikoku Electric Power Co. Inc., 2-5, Marunouchi, Takamatsu 760-91, Japan. Tel.: +81-878 21 5061; fax: +81-878 25 2052; e-mail: takeuchi09058@yonden.co.jp.

PII S0022-3115(97)00046-9

organic solution of CMPO and TBP for 20 min by a wrist action shaker (Yayoi, YS-8D) at 15 to 45°C. The phases were separated quickly by centrifugation with 2500 rpm for 5 min.

Technetium in both the phases was measured using a liquid scintillation spectrometer (Aloka, LSC-900 and Packard, 2550 TR/AB). The influence of uranium on scintillation counting was very small but the corrections were made on measurements, if necessary.

Uranium in the aqueous phase was measured using ICP-MS (Fisons, PQ Omega). Since the reproducibility of measurements in the aqueous solutions stripped by Na_2CO_3 could not be obtained, the concentration of uranium in the organic phase was obtained from the initial and final concentrations in the aqueous phase.

The distribution coefficient (D) was defined as follows:

$$D = \frac{\text{metal concentration in the organic phase}}{\text{metal concentration in the aqueous phase}}.$$

3. Results and discussion

3.1. Data analysis

The extraction equilibria of technetium and uranium from nitric acid by a mixture of CMPO and TBP have been reported by the present authors [11,13–15]. These equilibria are expressed as follows.

(1) Tc-CMPO-TBP system:

$$\mathrm{H^+(aq) + TcO_4^-(aq) + 2CMPO(org)} \rightleftharpoons \mathrm{HTcO_4 \cdot 2CMPO(org)}\ (K_1), \tag{1}$$

$$\mathrm{H^+(aq) + TcO_4^-(aq) + 3TBP(org)} \rightleftharpoons \mathrm{HTcO_4 3TBP(org)}\ (K_2), \tag{2}$$

$$\mathrm{H^+(aq) + TcO_4^-(aq) + CMPO(org) + 2TBP(org)} \rightleftharpoons \mathrm{HTcO_4 \cdot CMPO \cdot 2TBP(org)}\ (K_3). \tag{3}$$

(2) Tc-U-CMPO-TBP system:

$$\mathrm{UO_2(NO_3)_2 \cdot \mathit{n}CMPO(org) + TcO_4^-(aq)} \rightleftharpoons \mathrm{UO_2NO_3TcO_4 \cdot \mathit{n}CMPO(org) + NO_3^-(aq)}\ (K_4), \tag{4}$$

where $n = 2$ and/or 3,

(3) U-CMPO-TBP system:

$$\mathrm{UO_2^{2+}(aq) + 2NO_3^-(aq) + 2CMPO(org)} \rightleftharpoons \mathrm{UO_2(NO_3)_2 \cdot 2CMPO(org)}\ (K_5). \tag{5}$$

The terms K_1, K_2, K_3, K_4 and K_5 are the equilibrium constants. In the case of the coextraction of technetium with uranium, where the initial concentration of technetium is 1×10^{-4} mol/l and that of uranium ranged from 1×10^{-4} to 5×10^{-3} mol/l, the contribution of TBP to the technetium and uranium extractions in the present system was found to be negligibly small [13].

The equilibrium constants of these extractions are expressed by

$$K_1 = \frac{D_{\mathrm{Tc}}^1[1 + [\mathrm{H^+}]_{\mathrm{aq}}/K_0]}{[\mathrm{H^+}]_{\mathrm{aq}}[\mathrm{CMPO}]_{\mathrm{org}}^2}, \tag{6}$$

$$K_2 = \frac{D_{\mathrm{Tc}}^2[1 + [\mathrm{H^+}]_{\mathrm{aq}}/K_0]}{[\mathrm{H^+}]_{\mathrm{aq}}[\mathrm{TBP}]_{\mathrm{org}}^3}, \tag{7}$$

$$K_3 = \frac{D_{\mathrm{Tc}}^3[1 + [\mathrm{H^+}]_{\mathrm{aq}}/K_0]}{[\mathrm{H^+}]_{\mathrm{aq}}[\mathrm{CMPO}]_{\mathrm{org}}[\mathrm{TBP}]_{\mathrm{org}}^2}, \tag{8}$$

$$K_4 = \frac{[\mathrm{UO_2NO_3TcO_4 \cdot 2CMPO}]_{\mathrm{org}}[\mathrm{NO_3^-}]_{\mathrm{aq}}}{[\mathrm{UO_2(NO_3)_2 \cdot 2CMPO}]_{\mathrm{org}}[\mathrm{TcO_4^-}]_{\mathrm{aq}}}, \tag{9}$$

$$K_5 = \frac{D_{\mathrm{U}}[1 + K_{\mathrm{U}}^0[\mathrm{NO_3^-}]_{\mathrm{aq}}^2}{[\mathrm{NO_3^-}]_{\mathrm{aq}}^2[\mathrm{CMPO}]_{\mathrm{org}}^2}, \tag{10}$$

where K_0 is the dissociation constant of $HTcO_4$, K_U^0 is the overall stability constant of $UO_2(NO_3)_2$ in the aqueous phase, and D_{Tc}^1, D_{Tc}^2, D_{Tc}^3 and D_U denote distribution coefficients for their equilibria (Eqs. (1)–(3) and (5), respectively). Under the condition in which $[H^+]_{aq}$, $[NO_3^-]_{aq}$, $[CMPO]_{org}$ and $[TBP]_{org}$ are considered constant, the equilibrium constants for Eqs. (6)–(8) and (10) can be written only as a function of the distribution coefficients. The K_4 is calculated in a similar way as described in our previous study [14]. From the general relationship $\Delta G^0 = -RT \ln K = \Delta H^0 - T\Delta S^0$, these thermodynamic parameters are obtained by using semilogarithmic plots of $\ln D_{Tc}$, $\ln D_U$ and $\ln K_4$ vs. $1/T$, respectively. Unfortunately, the D_{Tc}^3 cannot be obtained directly. Therefore, the D_{Tc}^3 is defined in terms of the experimental distribution coefficient (D_{ex}) obtained in the mixed CMPO-TBP system as follows:

$$\begin{aligned} D_{\mathrm{ex}} &= ([\mathrm{HTcO_4 \cdot 2CMPO}]_{\mathrm{org}} + [\mathrm{HTcO_4 \cdot 3TBP}]_{\mathrm{org}} \\ &\quad + [\mathrm{HTcO_4 \cdot CMPO \cdot 2TBP}]_{\mathrm{org}}) \\ &\quad /([\mathrm{TcO_4^-}]_{\mathrm{aq}} + [\mathrm{HTcO_4}]_{\mathrm{aq}}) \\ &= D_{\mathrm{Tc}}^1 + D_{\mathrm{Tc}}^2 + D_{\mathrm{Tc}}^3, \end{aligned} \tag{11}$$

hence,

$$D_{\mathrm{Tc}}^3 = D_{\mathrm{ex}} - D_{\mathrm{Tc}}^1 - D_{\mathrm{Tc}}^2. \tag{12}$$

In order to avoid the significant effect of the nitric acid extraction by the extractants, the data at the nitric acid concentrations less than 0.1 mol/l were used in the calculation of the thermodynamic parameters [16–18].

3.2. Extraction of technetium in the absence of uranium

Table 1 shows distribution coefficients of technetium at various temperatures in the absence of uranium. Typical

Table 1
Distribution coefficients of Tc at various temperatures in the absence of U

HNO_3 (mol/l)	15°C	25°C	35°C	45°C
0.2 mol/l CMPO in decalin (D^1_{Tc})				
0.1	2.13	1.04	0.441	0.241
0.5	3.22	1.67	0.898	0.560
1	1.55	0.800	0.538	0.294
1.4 mol/l TBP in decalin (D^2_{Tc})				
0.1	1.34	0.531	0.249	0.122
0.5	2.70	1.48	0.689	0.368
1	1.90	1.06	0.623	0.334
0.2 mol/l CMPO + 1.4 mol/l TBP in decalin (D_{ex})				
0.1	7.13	3.10	1.58	0.882
0.5	11.0	6.50	3.32	1.88
1	6.22	4.05	2.29	1.31
0.2 mol/l CMPO + 1.4 mol/l TBP in dodecane (D_{ex})				
0.1	9.65	4.49	2.00	1.16
0.5	14.9	8.69	4.06	2.22
1	8.20	5.03	2.96	1.51

Table 2
Thermodynamic parameters on the Tc extraction in the absence of U

HNO_3 (mol/l)	ΔG^0_{298} (kJ/mol)	ΔH^0_{298} (kJ/mol)	ΔS^0_{298} (J/mol K)
0.2 mol/l CMPO in decalin (D^2_{Tc})			
0.1	−14.4	−56.3	−140
1.4 mol/l TBP in decalin (D^2_{Tc})			
0.1	−2.24	−60.6	−196
0.2 mol/l CMPO + 1.4 mol/l TBP in decalin (D^3_{Tc})			
0.1	−9.71	−49.0	−132
0.2 mol/l CMPO + 1.4 mol/l TBP in decalin (D_{ex})			
0.1	–	−53.0 [a]	–
0.2 mol/l CMPO + 1.4 mol/l TBP in dodecane (D_{ex})			
0.1	–	−54.6 [a]	–

[a] Calculated from the plots of ln D_{ex} vs. $1/T$.

semilogarithmic plots of distribution coefficients are shown in Fig. 1. These curves should be linear with a slope of $-\Delta H^0_{298}/R$. The values of ΔG^0_{298} and ΔS^0_{298} at 25°C are also calculated using the equilibrium constants and ΔH^0_{298} values obtained from the slopes. The thermodynamic parameters are summarized in Table 2.

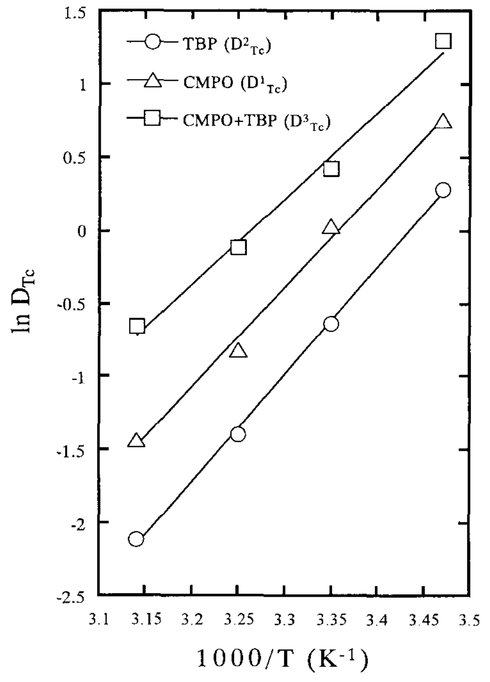

Fig. 1. Plots of ln D_{Tc} vs. $1/T$ for the technetium extraction in the absence of uranium. [CMPO] = 0.2 mol/l; [TBP] = 1.4 mol/l; [CMPO + TBP] = 0.2 mol/l CMPO + 1.4 mol/l TBP in decalin; $[HNO_3]$ = 0.1 mol/l.

The distribution coefficient of technetium due to either CMPO, TBP or CMPO + TBP in the absence of uranium decreases with increasing temperature. This shows that these extraction reactions are exothermic. In case of the absence of the appropriate activity coefficient data for various species involved in particular equilibrium, the relevant thermodynamic parameters cannot be calculated with high exactness. Nonetheless, approximate values of these parameters can be obtained from the equilibrium constants. The thermodynamic parameters, ΔH^0_{298} and ΔS^0_{298}, for TBP obtained in the present study are actually in good agreement with those in the literature [19].

The values of ΔG^0_{298} for the CMPO system were negatively larger than those for the TBP system. This indicates that CMPO can extract technetium more effectively than TBP does. In addition, the values of the ΔH^0_{298} for the CMPO system were similar to those for the TBP system, whereas the values of ΔS^0_{298} for the CMPO system were larger than those for the TBP system. Therefore, it was concluded that the difference in the ΔG^0_{298} values for the CMPO and TBP systems is mainly ascribed to the entropy change.

The negatively large entropy terms for CMPO and TBP are consistent with large amounts of ordering that must occur for four molecules in the CMPO system and for five molecules in the TBP system on the left-hand side of Eqs. (2) and (3), respectively. If CMPO behaves as a bidentate ligand, the value of ΔS^0_{298} for CMPO is expected to be somewhat negatively greater than that for monodentate TBP due to the chelate effect. The experimental results, however, show that the values of ΔS^0_{298} for CMPO are negatively smaller than those for TBP. This suggests that

Table 3
Distribution coefficients of Tc at various temperatures in the presence of U

HNO_3 (mol/l)	$[U]_{initial}$ (mol/l)	17°C	25°C	35°C	45°C
0.2 mol/l CMPO in decalin					
0.01	1×10^{-4}	3.84	2.71	1.46	0.952
	1×10^{-3}	37.0	20.2	17.2	8.79
	5×10^{-3}	175	85.7	67.9	40.4
0.04	1×10^{-4}	2.31	1.28	0.726	0.494
	1×10^{-3}	12.7	7.37	5.74	3.61
	5×10^{-3}	59.0	31.9	23.5	13.4
0.2 mol/l CMPO + 1.4 mol/l TBP in decalin					
0.01	1×10^{-4}	4.43	3.01	1.99	1.26
	1×10^{-3}	39.1	18.6	16.5	8.61
	5×10^{-3}	156	77.1	51.3	37.5
0.04	1×10^{-4}	4.78	2.61	1.68	1.01
	1×10^{-3}	16.0	9.66	7.56	4.94
	5×10^{-3}	57.6	36.9	28.9	14.9
0.2 mol/l CMPO + 1.4 mol/l TBP in dodecane					
0.01	1×10^{-4}	6.35	3.82	2.03	1.52
	1×10^{-3}	43.5	22.4	19.0	10.5
	5×10^{-3}	143	80.3	72.8	57.3
0.04	1×10^{-4}	5.12	3.23	1.71	1.14
	1×10^{-3}	19.6	13.3	10.5	5.42
	5×10^{-3}	72.2	45.4	34.8	21.3

CMPO behaves as thought it were a monodentate extractant like TBP in the present extraction systems. This idea is supported by the results in our previous study using spectroscopic analysis [12].

The values of ΔH^0_{298} for the mixed CMPO-TBP complex are closer to the results for CMPO than those for TBP. This supports the supposition that technetium is mainly extracted by CMPO in preference to TBP [11,12]. Comparison of the values obtained in decalin with those in *n*-dodecane revealed no significant difference. This means that the distinction between decalin and *n*-dodecane has no influence on the present extraction mechanism.

3.3. Coextraction of technetium with uranium

The distribution coefficients of technetium in the presence of uranium are shown in Table 3. The coextraction mechanism of technetium with uranium by CMPO is distinct from the extraction mechanism of technetium alone as mentioned above. It is considered that technetium is coextracted via an interface anion exchange reaction between $UO_2(NO_3)_2 \cdot n$CMPO ($n = 2$ and/or 3) in the organic phase and TcO_4^- in the aqueous phase. Therefore, TcO_4^- bonds to the uranium atom instead of NO_3^-. On the other hand, in the absence of uranium, TcO_4^- bonds to the phosphoryl group (P=O) of CMPO through hydrogen bonding. The discrepancy in the bonding nature for these two extraction systems of technetium may be reflected upon their thermodynamic parameters. Table 4 shows the thermodynamic parameters obtained from the plots of ln K_4 vs. $1/T$ for the CMPO system under the conditions of $[U]_{initial} = 5 \times 10^{-3}$ mol/l and of $[Tc]_{initial} = 1 \times 10^{-4}$ mol/l, where the coextraction of technetium with uranium mainly occurs [13]. In addition, for the uranium alone system, its thermodynamic parameters are summarized in Table 5. In the case of calculation for the uranium alone system, UO_2^{2+} is supposed to be the dominant species in the low nitric acid concentrations, that is, $1 \gg K_U[NO_3^-]^2_{aq}$ in Eq. (10).

Table 4
Thermodynamic parameters on the Tc extraction in the presence of 5×10^{-3} mol/l as U

HNO_3 (mol/l)	ΔG^0_{298} (kJ/mol)	ΔH^0_{298} (kJ/mol)	ΔS^0_{298} (J/mol K)
0.2 mol/l CMPO in decalin			
0.01	−14.7	−29.3	−49.0
0.04	−14.2	−37.3	−77.5

Table 5
Thermodynamic parameters on the U extraction in the absence of Tc. $[U]_{initial} = 1\times10^{-4}$ mol/l

HNO_3 (mol/l)	ΔG^0_{298} (kJ/mol)	ΔH^0_{298} (kJ/mol)	ΔS^0_{298} (J/mol K)
0.2 mol/l CMPO in decalin			
0.01	−34.0	−30.4	12.0
0.04	−32.5	−36.3	−12.8

The thermodynamic parameters for technetium and uranium reflected obviously their different extraction systems. The values of ΔH^0_{298} and ΔS^0_{298} for the coextraction of technetium are negatively smaller than those in the extraction of technetium alone. On the other hand, the values of ΔH^0_{298} for the extraction of uranium alone are similar to those for the coextraction of technetium, though the values of ΔS^0_{298} for uranium are larger.

Unfortunately, since the present coextraction systems containing synergistic effect by the mixture of CMPO and TBP are very complicated [13], the thermodynamic parameters cannot be obtained. However, all the data reveal the exothermic tendency as shown in Table 3.

4. Conclusions

In the absence or presence of uranium, the temperature effect on the technetium extraction was studied using CMPO, TBP and the mixture of CMPO-TBP. The following conclusions were obtained.

(1) All the extractions of technetium were exothermic reactions.

(2) The extraction of uranium was also exothermic, but the values of ΔH^0_{298} were negatively smaller than those for the extraction of technetium alone.

(3) In the absence of uranium, the values of ΔH^0_{298} for the mixture of CMPO-TBP were closer to the results for CMPO than those for TBP. This was consistent with the idea that technetium was mainly extracted by CMPO.

(4) The extraction of technetium in the absence and presence of uranium was characterized by the negatively large enthalpy and entropy changes.

(5) The distinction between decalin and *n*-dodecane as solvents has no influence on the present extraction mechanism.

Acknowledgements

The authors wish to thank Power Reactor and Nuclear Fuel Development Corporation and Ishikawajima–Harima Heavy Industries Co., Ltd. for sample supply. They would also like to thank Dr S. Tachimori and Dr S. Usuda of Japan Atomic Energy Research Institute for useful discussions.

References

[1] F. Macasek, Radiochem. Radioanal. Lett. 22 (3) (1975) 175.
[2] K.H. Lieser, A. Kruger, R.N. Singh, Radiochim. Acta 28 (1981) 97.
[3] T.N. Jassim, J.O. Liljenzin, R. Lundqvist, G. Persson, Solvent Extr. Ion Exch. 2 (3) (1984) 405.
[4] D.J. Pruett, Oak Ridge National Laboratory Report ORNL/TM-8668, 1984.
[5] D.J. Pruett, Trans. Am. Nucl. Soc. 39 (1981) 144.
[6] K.H. Lieser, R.N. Singh, Radiochim. Acta 32 (1983) 203.
[7] T.N. Jassim, J.O. Liljenzin, G. Persson, Radiochim. Acta 33 (1983) 163.
[8] B. Kanellakopulos, P. Konig, Radiochim. Acta 33 (1983) 169.
[9] Z. Kolarik, P. Dressler, Solvent Extr. Ion Exch. 7 (4) (1989) 625.
[10] S. Tachimori, S. Suzuki, Proc. Symp. Solvent Extraction 1992, Japanese Association of Solvent Extraction, Tokyo (1992) p. 75.
[11] M. Takeuchi, S. Tanaka, M. Yamawaki, Radiochim. Acta 63 (1993) 97.
[12] M. Takeuchi, S. Tanaka, M. Yamawaki, Solvent Extr. Ion Exch. 12 (5) (1994) 987.
[13] M. Takeuchi, S. Tanaka, M. Yamawaki, S. Tachimori, Solvent Extr. Ion Exch. 13 (1) (1995) 43.
[14] M. Takeuchi, S. Tanaka, M. Yamawaki, S. Tachimori, J. Radioanal. Nucl. Chem. 191 (1) (1995) 189.
[15] M. Takeuchi, S. Tanaka, M. Yamawaki, S. Tachimori, J. Nucl. Sci. Technol. 32 (5) (1995) 450.
[16] G.F. Vandegrift, D.J. Chaiko, D.R. Fredrickson, P.-K. Tse, Argonne National Laboratory Report ANL-88-28, 1988.
[17] D.J. Chaiko, G.F. Vandegrift, Nucl. Technol. 82 (1988) 52.
[18] D.S. Wisnubroto, S. Nagasaki, Y. Enokida, A. Suzuki, Proc. Int. Solvent Extraction Conf. 1993, Vol. 3, York, UK, 1993, p.1813.
[19] D.J. Pruett, Sep. Sci. Technol. 16 (1981) 1157.