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A study on pyrrolidone derivatives as selective precipitant for uranyl ion in HNO₃

Yasuhisa Ikeda^{a,*}, Emiko Wada^a, Masayuki Harada^a, Takahiro Chikazawa^b, Toshiaki Kikuchi^b, Hideaki Mineo^c, Yasuji Morita^c, Masanobu Nogami^d, Kazunori Suzuki^d

^a Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8550, Japan

^b Mitsubishi Materials Co., 1-3-25 Koishikawa, Bunkyo-ku, Tokyo 112-0002, Japan

^c Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan

^d Institute of Research and Innovation, 1201 Takada, Kashiwa, Chiba 277-0861, Japan

Abstract

We have found out that *N*-cyclohexyl-2-pyrrolidone (NCP) can selectively precipitate UO_2^{2+} ions in HNO₃ solutions. In order to investigate factors of such a specific property of NCP, we have examined reactions of NCP with UO_2^{2+} ions in HCl, HClO₄, or H₂SO₄, and the precipitation abilities of pyrrolidone derivatives other than NCP for UO_2^{2+} in HNO₃ solutions. As a result, it was found that UO_2^{2+} ions in HCl, HClO₄, or H₂SO₄ are not precipitated by NCP, that *N*-methyl-2-pyrrolidone (NMP) and *N*-ethyl-2-pyrrolidone (NEP) with lower hydrophobicity than NCP do not precipitate UO_2^{2+} , and that hydrophobic *N*-dodecyl-2-pyrrolidone can precipitate UO_2^{2+} . Furthermore, we have investigated the crystal structures of $UO_2(NO_3)_2(L)_2$ (L = NMP, NEP) complexes to compare with that of $UO_2(NO_3)_2(L)_2$ (L = NMP, NEP). From these results, it is proposed that the specific property of NCP is ascribed to its relatively high hydrophobicity owing to cyclohexyl group, to its strong coordination ability to UO_2^{2+} for forming the symmetrical complex accompanied by two bidentate NO_3^{-} , and to the surface of $UO_2(NO_3)_2(NCP)_2$ which is surrounded by the hydrophobic cyclohexyl groups of coordinated NCP.

Keywords: Uranyl complexes; Pyrrolidone; Precipitation; Crystal structure; Hydrophobicity

1. Introduction

In most of commercial reprocessing plants, spent nuclear fuels have been treated by Purex method [1], in which U and Pu are extracted from HNO₃ solutions of spent nuclear fuels by using the extractant (30% tributyl phosphate/*n*-dodecane), and separated from most of fission products and other transuranium elements. Hence, facilities of extraction processes and amounts of extractant become relatively large. This results in complexity of processes and an increase in amounts of radioactive wastes. If a large portion of UO_2^{2+} can be selectively separated from HNO₃ solutions of spent nuclear fuels using simple method, subsequent extraction processes are expected to become extremely simple or useless.

On the basis of such a viewpoint, we have investigated simple reprocessing processes based on precipitation methods [2–4]. Recently, we found out that *N*-cyclohexyl-2-pyrrolidone (NCP) can selectively precipitate UO_2^{2+} as $UO_2(NO_3)_2(NCP)_2$ in 1–7 M (M = mol/dm³) HNO₃ solutions containing UO_2^{2+} and other metal ions [5], and proposed a simple reprocessing process which used the specific property of NCP [6].

On the other hand, from aspects of coordination chemistries of UO_2^{2+} , it is interesting to examine factors inducing selective precipitation ability of NCP for UO_2^{2+} in HNO₃ solutions. In our previous study [5], we found out that NO₃⁻ and cyclohexyl group of NCP play important roles in the selective precipitation, because CF₃CO₂⁻ and CH₃SO₃⁻ ions do not give precipitates under analogous conditions, and *N*-methyl-2-pyrrolidone (NMP) does not precipitate UO_2^{2+} in HNO₃ solutions. Furthermore, in more recent study [7], we clarified that the structure of $UO_2(NO_3)_2(NCP)_2$ is similar to those of $UO_2(NO_3)_2(L)_2$

^{*} Corresponding author. Tel.: +81-3-5734-3061;

fax: +81-3-5734-2959.

E-mail address: yikeda@nr.titech.ac.jp (Y. Ikeda).

(L = unidentate oxygen donor ligands) [8–12], i.e., the equatorial site of UO_2^{2+} is occupied by two trans NO_3^- and L ligands. However, the factors inducing unique precipitation ability of NCP are still ambiguous.

In order to investigate the origins of specific property of NCP in more detail, we have examined whether NCP shows such a property in acid solutions other than HNO₃ and whether the pyrrolidone derivatives other than NCP can precipitate UO_2^{2+} in HNO₃ solutions. Moreover, we have analyzed the crystal structures of $UO_2(NO_3)_2(NMP)_2$ (1) and $UO_2(NO_3)_2(NEP)_2$ (2) (NEP = *N*-ethyl-2-pyrrolidone) complexes to compare with that of $UO_2(NO_3)_2(NCP)_2$ (3).

2. Experimental

2.1. Materials and methods

As pyrrolidone derivatives, NCP (Aldrich, 99%), NMP (Kanto Kagaku, 99%), NEP (Aldrich, 98%), NOP (*N*-octyl-2-pyrrolidone, Aldrich, 98%), and NDP (*N*-dodecyl-2-pyrrolidone, Aldrich, 99%) were used without further purification. All other chemicals used in the present study are reagent grade and were used without further purification. ¹H and ¹³C NMR spectra were measured using a JEOL JNM LA 300 WB FT-NMR spectrometer. Dichloromethane-d₂ (CD₂Cl₂) and tetramethylsilane were used as solvent and a reference for chemical shifts, respectively. IR spectra (KBr pellet) were recorded on a Shimadzu FT-IR-8400S spectrophotometer. Elemental analyses were carried out by using CE INSTRUMENTS Flash EA1112.

2.2. Syntheses of $UO_2(NO_3)_2(NMP)_2$ and $UO_2(NO_3)_2(NEP)_2$ complexes

UO₂(NO₃)₂·6H₂O (2.517 g, 5.014 mmol) was dissolved in ethanol (30 ml) and then NMP (1.971 g, 19.88 mmol) was added. The solution was stirred for 1.5 h. Yellow precipitates were separated, washed with hexane, and dried. This product was recrystallized from warm ethanol solution containing a small amount of NMP. The resulting yellow crystals were filtered off and dried in vacuo for one night. Anal. Calcd. for UO₂(NO₃)₂(NMP)₂: C, 20.8; H, 3.28; N, 9.71. Found: C, 20.3; H, 3.06; N, 9.71. IR (KBr): 1631 v(C=O) and 932 cm⁻¹ ν (O=U=O). ¹H NMR (CD₂Cl₂): δ = 2.24 (4H, m), 2.86 (4H, t), 3.35 (6H, s, -CH₃), and 3.82 (4H, t). ¹³C NMR (CD₂Cl₂): $\delta = 17.8$ (s), 31.3 (s), 31.6 (s), 51.5 (s), and 182.0 (s). In a similar manner, the crystals of $UO_2(NO_3)_2(NEP)_2$ were also prepared. Anal. Calcd. for UO₂(NO₃)₂(NEP)₂: C, 23.0; H, 3.75; N, 9.18. Found: C, 23.2, H, 3.57; N, 9.03. IR (KBr): 1626 ν (C=O) and 926 cm⁻¹ ν (O=U=O). ¹H NMR (CD₂Cl₂): $\delta = 1.38$ (6H, t, -CH₃), 2.24 (4H, m), 2.86 (4H, t), 3.83 (4H, m, -CH₂-), and 3.89 (4H, m). ¹³C NMR (CD₂Cl₂):

Table 1

 $Crystallographic data for UO_2(NO_3)_2(NMP)_2 (1), UO_2(NO_3)_2(NEP)_2 (2), and UO_2(NO_3)_2(NCP)_2 (3) complexes (1) and (1$

	Compound		
	1	2	3
Empirical formula	$C_{10}H_{18}N_4O_{10}U$	$C_{12}H_{22}N_4O_{10}U$	$C_{20}H_{34}N_4O_{10}U$
Formula weight	592.30	620.36	728.54
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\overline{1}$
a (Å)	7.602 (2)	7.321 (1)	8.627 (1)
b (Å)	6.813 (2)	7.299 (1)	8.748 (1)
<i>c</i> (Å)	16.642 (6)	18.252 (3)	9.707 (1)
α (°)			113.61 (1)
β (°)	90.72 (3)	96.45 (1)	93.73 (1)
γ (°)			108.74 (1)
V (Å ³)	861.8 (5)	969.2 (3)	619.6 (1)
Ζ	2	2	1
Temperature (K)	93 ± 1	93 ± 1	113 ± 1
$D_{\text{calc}} (\text{g cm}^{-3})$	2.282	2.126	1.952
<i>F</i> (000)	556	588	354
Radiation (λ (Å))	Μο Κα (0.71075)	Μο Κα (0.71075)	Μο Κα (0.71075)
$\mu \text{ (cm}^{-1})$	94.78	84.33	66.11
Crystal size (mm)	$0.15 \times 0.08 \times 0.05$	$0.15 \times 0.10 \times 0.05$	$0.40\times0.50\times0.30$
Crystal color/shape	Yellow/block	Yellow/block	Yellow/block
2θ range max (°)	60.1	60.1	55.0
Observed data $[I > -10.00 \sigma(I)]$	2506	2840	2822
R1 ^a	0.021	0.019	0.014
wR2 ^b	0.071	0.045	0.038

^a $R1 = \sum ||Fo| - |Fc|| / \sum |Fo|.$

^b wR2 = { $\sum [w(Fo^2 - Fc^2)^2] / \sum w(Fo^2)^2$ }^{1/2}.

 $\delta = 12.5$ (s), 17.9 (s), 32.0 (s), 39.4 (s), 48.7 (s), and 181.6 (s).

2.3. X-ray crystal structure determination of $UO_2(NO_3)_2(NMP)_2$ and $UO_2(NO_3)_2(NEP)_2$ complexes

Yellow block crystals of UO₂(NO₃)₂(NMP)₂ (1) and $UO_2(NO_3)_2(NEP)_2$ (2) were mounted in loops. Intensity measurements were carried out at 93 K on a Rigaku RAXIS RAPID diffractometer with Mo Ka radiation $(\lambda = 0.71075 \text{ Å})$. Crystal data and data collection parameters are listed in Table 1. The structures were solved by using heavy-atom Patterson method [13] and expanded using DIRDIF-99 program [14]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinements on F^2 were based on 2506 and 2840 reflections and 124 and 135 variable parameters for $UO_2(NO_3)_2(NMP)_2$ and $UO_2(NO_3)_2(NEP)_2$ crystals, respectively, and converged with unweighted and weighted agreement factors (R1 = 0.021 and 0.019, wR2 = 0.071and 0.045) for $UO_2(NO_3)_2(NMP)_2$ and $UO_2(NO_3)_2(NEP)_2$ crystals, respectively. All calculations were carried out by using Crystal Structure 3.10 crystallographic software package [15,16]. Furthermore, the crystal structure of $UO_2(NO_3)_2(NCP)_2$ (3) was determined again with higher precision than the previous measurement [7].

3. Results and discussion

3.1. Role of NO_3^- ions in the precipitation of UO_2^{2+} by NCP

In our previous paper [5], we proposed that NO₃⁻ ions play an important role in the precipitation of UO₂²⁺ by NCP. In order to confirm the validity of our proposal, actions of NCP on UO₂²⁺ were examined by adding 0.2 ml of NCP to 2.9 M HCl, HClO₄, or H₂SO₄ (4 ml) solution containing 0.1 M UO₂²⁺. As expected, precipitation phenomena were not observed in these solutions. Furthermore, the UO₂(NO₃)₂(NCP)₂ complex was found to be soluble in dilute HNO₃ solutions. This is considered to be due to phenomenon that the equilibrium reaction, $UO_2^{2+} + 2NO_3^- + 2NCP = UO_2(NO_3)_2(NCP)_2$, is shifted to left in the dilute HNO₃ solution. From these results, it is concluded that the existence of a large excess of NO₃⁻ is essential for the precipitation of UO₂²⁺ by NCP.

In addition, the trans coordination of two bidentate NO_3^- to UO_2^{2+} seems to be an important factor, because this coordination accompanied by two NCP molecules contributes to the formation of non-charged and symmetrical uranyl complex with coordination number of 6 in the equatorial plane [7]. On the other hand, anions such as Cl⁻, ClO₄⁻, and SO₄²⁻ should not coordinate to UO_2^{2+} more strongly than NO_3^- . Even if the former anions react with UO_2^{2+} to form the non-charged uranyl complexes with NCP, their



Fig. 1. ORTEP drawing of the molecular structure of $UO_2(NO_3)_2(NMP)_2$ showing atomic numbering. The thermal ellipsoids are drawn at 50% probability level.



-Fig. 2. ORTEP drawing of the molecular structure of $UO_2(NO_3)_2(NEP)_2$ showing atomic numbering. The thermal ellipsoids are drawn at 50% probability level.



Fig. 3. ORTEP drawing of the molecular structure of $UO_2(NO_3)_2(NCP)_2$ showing atomic numbering. The thermal ellipsoids are drawn at 50% probability level.

structures should not be symmetrical. These may be also reasons why UO_2^{2+} ions are precipitated by NCP in only HNO₃ system. However, some amide complexes of uranyl nitrate, which are not precipitated in aqueous solutions and synthesized using non-aqueous solvent, are known to have similar structure to that of $UO_2(NO_3)_2(NCP)_2$ [17–19]. Hence, it is considered that the formation of non-charged and symmetrical uranyl complex is not necessarily the conditions for the selective precipitation of UO_2^{2+} in HNO₃ by NCP.

3.2. Precipitation abilities of pyrrolidone derivatives for UO_2^{2+} in HNO₃ solutions

As one of factors for the specific property of NCP, the hydrophobicity of NCP should be proposed, because NMP being lower hydrophobic compound than NCP does not precipitate UO_2^{2+} in HNO₃ solutions [5]. Hence, we investigated the precipitation abilities of pyrrolidone derivatives (NEP, NOP, and NDP) with different hydrophobicity. We used the octanol-water partition constants $(\log P)$ [20,21] as the measure of hydrophobicity of pyrrolidone derivatives. The calculated values of log P for NMP, NEP, NCP, NOP, and NDP are -0.11 (experimental value: -0.38), 0.38 (-0.04), 2.16, 3.33, and 5.30 (4.20), respectively. The former three compounds are miscible with water, while NOP and NDP are not. As expected from $\log P$ values, NEP was found to have no precipitation ability for UO_2^{2+} in HNO₃. Furthermore, it was found that NOP and NDP can extract and precipitate UO_2^{2+} in HNO₃ solutions, respectively. As an example of other pyrrolidone derivatives, Doyle et al. have reported that N,N'-ethylenebis(2-pyrrolidone) (NEBP) reacts with uranyl nitrate in non-aqueous solvents to form solid product, i.e., helical chain polymer $[UO_2(NO_3)_2(NEBP)]_n$ [22]. The log P value of NEBP is estimated to be -0.55, which is comparable with those of NMP and NEP. These results suggest that the pyrrolidone derivatives with low hydrophobicity cannot precipitate UO_2^{2+} in aqueous solutions, and indicate that the unique precipitation ability of NCP is due to its miscibility with water and relatively high hydrophobicity.

3.3. Comparison of precipitation abilities of pyrrolidone derivatives for UO_2^{2+} based on their coordination abilities and structural aspects of complexes

As mentioned above, only NCP of three pyrrolidone derivatives (NMP, NEP, and NCP), which are miscible with water, was found to be able to precipitate UO_2^{2+} in HNO₃ solutions. Hence, in order to examine the differences in precipitation abilities of pyrrolidone derivatives from the viewpoint of their coordination abilities and structural aspect of their uranyl complexes, IR measurements and crystal structural analyses of $UO_2(NO_3)_2(L)_2$ (L = NMP, NEP) were carried out, and their results were compared with that of $UO_2(NO_3)_2(NCP)_2$.

From IR measurements, the shifts to lower frequencies in the C=O stretching modes of coordinated NMP, NEP, and NCP were found to be 56, 60, 76 cm⁻¹, respectively, and are comparable with the shifts observed in uranyl nitrate complexes with unidentate amides [17–19]. These results suggest that UO₂(NO₃)₂(L)₂ (L = NMP, NEP, NCP) are typical amide complexes of uranyl nitrate, and that NCP of three pyrrolidone derivatives coordinates most strongly to uranium atom via C=O oxygen. Furthermore, the uranyl asymmetric stretching bands [ν (O=U=O)] of UO₂(NO₃)₂(L)₂ (L = NMP, NEP, NCP) are observed at 932, 926, and 927 cm⁻¹, respectively. This is consistent with the general tendency that the larger is the ligand donation, the lower is the asymmetric stretching frequency of O=U=O bond [23,24].

ORTEP views of $UO_2(NO_3)_2(NMP)_2$ and $UO_2(NO_3)_2$ (NEP)₂ complexes are shown in Figs. 1 and 2. These complexes are found to have the same symmetrical structures as that of $UO_2(NO_3)_2(NCP)_2$ (see Fig. 3). Selected bond distances and angles for three uranyl complexes are listed in Table 2. As seen from this table, significant differences are observed in the U1–O2–C1 moiety, i.e., the U1–O2 bond distance and the bend of U1–O2–C1 in $UO_2(NO_3)_2(NCP)_2$ are the smallest in three complexes. This is similar to results observed in $UO_2(NO_3)_2(L_{P=O})_2$ ($L_{P=O}$: triphenylphosphine oxide, hexaethylphosphoric triamide, and diphenyl-*N*-ethylphosphine amide) complexes, where the U–O(P) distances shorten with an increase in linearity of U–O–P angle [12,25,26]. Furthermore, the

Table 2

Selected bond distances (Å) and angles (°) of $UO_2(NO_3)_2(NMP)_2$ (1), $UO_2(NO_3)_2(NEP)_2$ (2), and $UO_2(NO_3)_2(NCP)_2$ (3) complexes

	Compound			
	1	2	3	
U1-O1	1.769 (4)	1.763 (3)	1.771 (2)	
U1-O2	2.368 (4)	2.371 (3)	2.348 (2)	
U1-O3	2.510 (3)	2.519 (3)	2.525 (2)	
U1-O4	2.546 (4)	2.535 (2)	2.536 (2)	
O2C1	1.255 (6)	1.251 (4)	1.253 (3)	
O3-N2	1.283 (6)	1.279 (4)	1.273 (3)	
O4-N2	1.273 (6)	1.274 (4)	1.274 (3)	
O5-N2	1.211 (6)	1.216 (4)	1.218 (3)	
O1-U1-O2	90.2 (2)	91.4 (1)	91.8 (1)	
O1-U1-O3	89.9 (2)	88.1 (1)	88.6 (1)	
01-U1-O4	89.2 (2)	92.5 (1)	93.8 (1)	
O2-U1-O3	65.7 (1)	65.8 (1)	65.1 (1)	
O2-U1-O4	116.0 (1)	115.9 (1)	114.8 (1)	
O3-U1-O4	50.3 (1)	50.4 (1)	50.2 (1)	
U1O2C1	136.1 (3)	140.5 (2)	147.7 (2)	
U1-O3-N2	98.3 (3)	97.6 (2)	97.8 (1)	
U1-O4-N2	96.8 (3)	97.0 (2)	97.3 (1)	
O2C1C2	127.9 (5)	126.9 (3)	124.3 (2)	
O2-C1-N1	123.3 (5)	122.7 (3)	125.1 (2)	
O3-N2-O4	114.5 (4)	115.0 (3)	114.8 (2)	
O3-N2-O5	121.7 (5)	122.3 (3)	122.8 (2)	
O4-N2-O5	123.8 (5)	122.8 (3)	122.4 (2)	

distance of U1–O1 in UO₂(NO₃)₂(NCP)₂ is longer than those in UO₂(NO₃)₂(L)₂ (L = NMP, NEP). These results are consistent with the matters expected from IR measurements, and suggest that one of the origins for the specific property of NCP is the relatively strong coordination ability of NCP to UO₂²⁺.

In addition, as seen from Fig. 3, the surface of $UO_2(NO_3)_2(NCP)_2$ complex is surrounded by the cyclohexyl groups of two NCP ligands. This structural characteristic contributes to over-all hydrophobicity of $UO_2(NO_3)_2(NCP)_2$ itself and results in the selective precipitation of UO_2^{2+} in HNO₃ solutions.

4. Summary

The results of present study are summarized as follows.

- Existence of a large excess of NO_3^- ions is essential for the precipitation of UO_2^{2+} by NCP, because UO_2^{2+} ions in HCl, HClO₄, and H₂SO₄ are not precipitated by NCP, and the resulting precipitates are soluble in dilute HNO₃ solutions.
- The pyrrolidone derivatives with lower hydrophobicity than NCP, such as NMP and NEP, do not precipitate UO₂²⁺ ions in HNO₃ solutions, while NDP being more highly hydrophobic than NCP can precipitate. This indicates that the specific property of NCP is attributed to its relatively high hydrophobicity owing to cyclohexyl group.
- NCP seems to coordinate to UO₂²⁺ more strongly through the C=O oxygen than other pyrrolidone derivatives, such as NMP and NEP, because the bond distance between uranium and C=O oxygen in UO₂(NO₃)₂(NCP)₂ is shorter than those of UO₂(NO₃)₂(L)₂ (L = NMP, NEP).
- The UO₂(NO₃)₂(NCP)₂ complex has symmetrical structure and its surface is surrounded by the hydrophobic cyclohexyl groups of two NCP ligands.
- Factors mentioned above contribute to the unique property that NCP can precipitate selectively UO_2^{2+} in HNO₃ solution.

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