New Water-soluble Organic Ligands for Actinide Cations Complexation

Yuji Sasaki,*[1] Hideya Suzuki,[1] Yumi Sugo,[1] Takaumi Kimura,[1] and Gregory R. Choppin[2]
[1]*Japan Atomic Energy Research Institute, Tokai, Naka-gun, Ibaraki 319-1195*
[2]*Florida State University, Tallahassee, FL 32306-4390, U.S.A.*

(Received October 31, 2005; CL-051364; E-mail: sasaki.yuji@jaea.go.jp)

Novel water-soluble organic ligands, *N*,*N*,*N*′,*N*′-tetramethyldiglycolamide (TMDGA), *N*,*N*,*N*,*N*′-tetraethyldiglycolamide (TEDGA), *N*,*N*,*N*′,*N*′-tetrapropyldiglycolamide (TPDGA), and *N*,*N*-dipropyldiglycolamic acid (DPDGAc), were synthesized and examined for complexation with An(III) and An(IV). These reagents are readily soluble in water and form more stable complexes with Pu(IV) and Am(III) than does EDTA of hexadentate ligand. TEDGA and TPDGA can back-extract effectively An into the aqueous phase.

New alkylamide extractants have been synthesized for study of their use in separations of actinides (An). Diglycolamide (DGA) compounds (general formula: $O(CH_2CON(R_1R_2)_2)_2$), neutral tridentate ligands, have strong extraction ability for An(III) and An(IV).[1–3] *N*,*N*,*N*′,*N*′-tetraoctyldiglycolamide, TODGA, has a high solubility in aliphatic solvent, making it a promising extractant for the recovery of An from spent nuclear fuel. Necessary in such use of TODGA is to find the strong reagent for the reverse extraction of An. The technique for the back-extraction of all An with a condition is available to establish the simple process.

The aim of this work is to find strong reagents for the reverse extraction of An. Water-soluble DGA derivatives, e.g., *N*,*N*,*N*′,*N*′-tetramethyl-3-diglycolamide (TMDGA), *N*,*N*,*N*′,*N*′-tetraethyl-3-diglycolamide (TEDGA), and *N*,*N*,*N*′,*N*′-tetrapropyl-3-diglycolamide (TPDGA) can be prepared by the organic synthesis. These new DGA compounds were studied for stripping trivalent and tetravalent An cations, and are compared with other available masking agents.

Both commercially available and newly synthesized ligands were investigated in this study for the reverse stripping of An into an aqueous phase. The structures of the reagents studied are diglycolic acid (DGAc, general formulae: $O(CH_2COOH)_2$), 3,6-dioxaoctanedioic acid (DODA, $(CH_2OCH_2\text{-}COOH)_2$), ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (EDTA, $(CH_2N\text{-}(CH_2COOH)_2)_2$), *N*,*N*-dipropyldiglycolamic acid (DPDGAc, $COOHCH_2OCH_2CON(C_3H_7)_2$), TMDGA, TEDGA, and TPDGA. DGAc, DODA, and EDTA can be purchased and used without purification; however, the reagents, DPDGAc, TMDGA, TEDGA, and TPDGA, were synthesized for this study. The synthetic methods of TMDGA, TEDGA, and TPDGA were the same as that reported for TODGA.[4,5] DPDGAc can be synthesized by mixing diglycolic anhydride with dipropylamine in ethylacetate.[4] After purification by repeated passage through silica gel columns, the reagents obtained were used for Pu(IV) and Am(III) extraction.

The solubilities in water at 25 °C were determined as: DGAc, 2.4 mol/dm^3 (=M); DODA, 2.7; EDTA, 0.13; DPDGAc, 0.2; TMDGA, 1.0; TEDGA, 4; and TPDGA, 0.28. The affinity for An was measured by solvent extraction. The distribution ratios (*D*, defined as the ratio of $[M]_o$ in an organic phase of 0.2 M TODGA/*n*-dodecane vs. $[M]_a$ in an aqueous phase of 0.24 M HNO_3 containing ligand) of actinide ions, ^{241}Am(III) and ^{238}Pu(IV), were measured. The *D* values for Am(III) and Pu(IV) by extraction into 0.2 M TODGA/*n*-dodecane from 0.24 M HNO_3 in the absence of the ligands were determined to be 0.53 and 1.0, respectively.

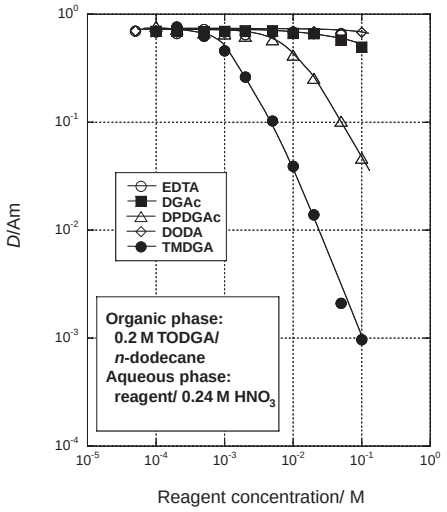

Figure 1. Relationship between ligand concentration and *D*(Am).

The *D*(Am) and *D*(Pu) values are plotted against the concentration of the ligand in Figures 1 and 2. Figure 1 indicates that 1) *D*(Am) values decreased with increase in the concentrations of TMDGA and DPDGAc, 2) TMDGA is more effective for An-complexation than DPDGAc, and 3) the other reagents have little effect on Am(III) extraction. TMDGA and DPDGAc may bind in a tridentate mode due to three oxygen atoms of one ether and two amides or of one ether, an amide and a carboxylic acid.[3] EDTA, a strong multidentate ligand, is weaker than TMDGA and DPDGAc, used in the present study, for the reverse extraction of Am(III). DGAc, DODA, and EDTA in the form of deprotonated anions show strong complexation under high pH. *D*(Pu) decreases upon addition of the five reagents. Figure 2 suggests these ligands have strong complexation with Pu(IV) in the aqueous phase. The order of their complexing ability, determined by the *D* values, is: DPDGAc > EDTA ≈ TMDGA > DGAc > DODA. In general, the extractability of An has the following order: An(IV) > An(VI) > An(III) > An(V).[6] An(IV) has a relatively high affinity with the donor. Pu(IV) can be back-extracted by the multidentate ligands mentioned above, due to complexation with the electron donors in the ionized carboxylate, ether oxygen and/or amide groups. In addition, the stripping effects on U(VI) for these reagents were also investigated. The

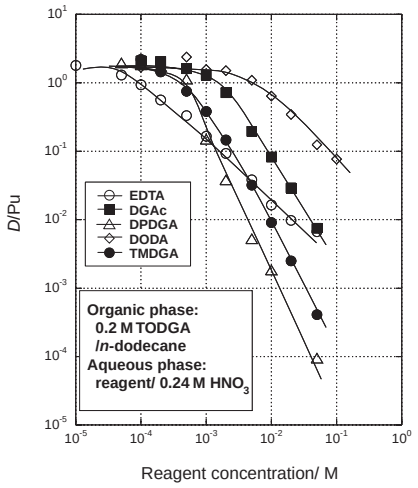

Figure 2. Relationship between ligand concentration and *D*(Pu).

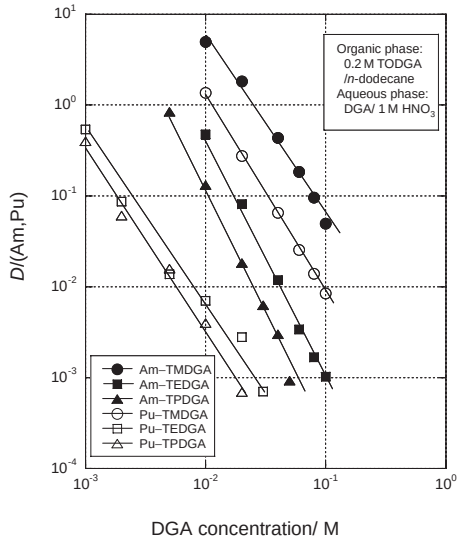

Figure 3. Relationship between DGA concentration and *D*(Am, Pu).

results show that the *D*(U) is constant at the different ligand concentration. From these results, the back-extraction of U(VI) is not readily performed for the above experimental condition.

Using the aqueous-phase containing TMDGA, TEDGA, and TPDGA, solvent extraction of Am(III) and Pu(IV) was performed with results shown in Figure 3. The values of both *D*(Am) and *D*(Pu) in the absence of ligand were determined to be about 100 and 70, respectively.[1] The *D*(Pu) value is lower than *D*(Am) under the same condition as shown in Figure 3, which suggests that Pu(IV) is more complexed by DGA than Am(III). The slope values (Am–TMDGA, -2.0 ± 0.1; Am–TEDGA, -2.72 ± 0.05; Am–TPDGA, -2.85 ± 0.11; Pu–TMDGA, -2.2 ± 0.02; Pu–TEDGA, -1.79 ± 0.14; Pu–TPDGA, -2.02 ± 0.12) in Figure 3 suggest that the molar ratio of these metal-complexes (M:DGA) in the aqueous phase are 1:2 and 1:3. Am(III) and Pu(IV) with TODGA form 1:3 and 1:4

Table 1. Recovery of DGA into polar organic solvents from water

	Recovery (%)		
	TMDGA	TEDGA	TPDGA
Amyl alcohol	7.2	72	100
1-Hexanol	0	69	100
1-Octanol	0	52	98
0.2 M TODGA /*n*-dodecane	2	1.3	32

metal:TODGA complexes in *n*-dodecane.[7,8] Three or four molecules of DGA can also be coordinated to An in the inner and the outer coordination sites. TMDGA shows relatively high *D* values compared to those of TEDGA and TPDGA, which suggests lower stability of the latter metal-complexes. The strongest complexation is exhibited by TPDGA; however, it is accompanied by a relatively high solubility into the extracting solvent. Indeed, about 32% of TPDGA was extracted by 0.2 M TODGA/*n*-dodecane, as shown in Table 1. TEDGA is the best complexing agent among the reagents examined in this work.

The extraction of water-soluble DGA compounds into polar organic solvent from an aqueous phase was studied for recovery after use in extraction. Three primary alcohols, amyl alcohol, 1-hexanol, and 1-octanol, were employed as the extracting solvents. The reason for selecting these alcohols is that the concentrations of the ligand in the aqueous phase can be determined by UV spectrometry, as they have no significant absorption interference at the wavelengths at which DGA compounds have absorption. The recovery ratio (%) for the ligand concentration in the organic phase after extraction ($[L]_{org}$) against that in the aqueous phase before extraction ($[L]_{ini}$) is summarized in Table 1. The recovery increases with the number of carbon atoms in DGA compounds and decreases with carbon atoms in alcohol. Because of the relatively high lipophilicity, TPDGA is extracted efficiently by the polar solvent. A simple test of extraction of Am(III) and Pu(IV) in 0.1 M TEDGA–0.24 M HNO_3 using these alcohols was performed in order to measure the separation properties of An and water-soluble DGA. The *D*(Am) and *D*(Pu) values are lower than 0.05 under these conditions, and TEDGA can be separated from An using amyl alcohol and 1-hexanol.

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