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A COMPARATIVE STUDY OF THE COMPLEXATION OF URANIUM(VI) WITH OXYDIACETIC ACID AND ITS AMIDE DERIVATIVES

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1 INTRODUCTION

There has been significant interest in recent years in the studies of alkyl-substituted amides as extractants for actinide separation because the products of radiolytic and hydrolytic degradation of amides are less detrimental to separation processes than those of organophosphorus compounds traditionally used in actinide separations. Stripping of actinides from the amide-containing organic solvents is relatively easy. In addition, the amide ligands are completely incinerable so that the amount of secondary wastes generated in nuclear waste treatment could be significantly reduced.

One group of alkyl-substituted oxa-diamides have been shown to be promising in the separation of actinides from nuclear wastes.¹⁻³ For example, tetraoctyl-3-oxa-glutaramide¹ and tetraisobutyl-oxa-glutaramide³ form actinide complexes that can be effectively extracted from nitric acid solutions. To understand the thermodynamic principles governing the complexation of actinides with oxa-diamides, we have studied the complexation of U(VI) with dimethyl-3-oxa-glutaramic acid (DMOGA) and tetramethyl-3-oxa-glutaramide (TMOGA) in aqueous solutions, in comparison with oxydiacetic acid (ODA) (Figure 1). Previous studies have indicated that the complexation of U(VI) with ODA is strong and entropy-driven.⁴⁻⁶ Comparing the results for DMOGA and TMOGA with those for ODA could provide insight into the energetics of amide complexation with U(VI) and the relationship between the thermodynamic properties and the ligand structure.

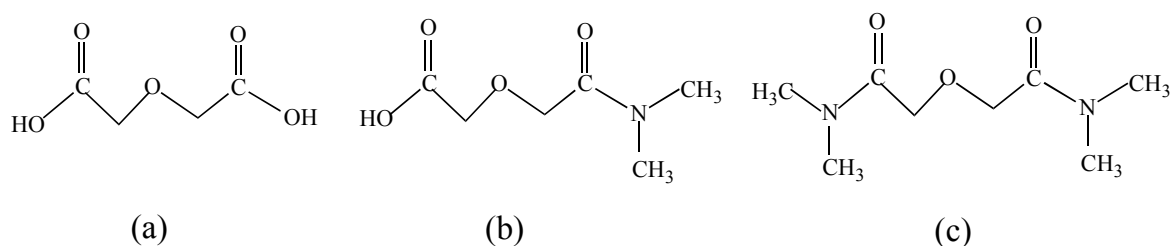


Figure 1 (a) Oxydiacetic acid (ODA); (b) dimethyl-3-oxa-glutaramic acid (DMOGA); (c) tetramethyl-3-oxa-glutaramide (TMOGA).

2 METHOD AND RESULTS

2.1 Stability Constants of the U(VI) Complexes with DMOGA and TMOGA

All thermodynamic measurements were conducted at $I = 1.0 \text{ mol}\cdot\text{dm}^{-3}$ (NaClO_4) and $t = 25$ °C. Potentiometry was used to determine the protonation constant of DMOGA and the stability constants of the U(VI) complexes with DMOGA. Details of potentiometry are provided elsewhere.⁶ Prior to each complexation titration, the electrode was calibrated with a standard acid/base titration in order to calculate the hydrogen ion concentrations from the electrode potential in the subsequent titration. Spectrophotometry was used to determine the stability constants of the U(VI) complexes with DMOGA and TMOGA. Sets of absorption spectra of U(VI) in solutions of different concentrations of DMOGA or TMOGA were collected on a Cary-5G spectrophotometer.

The program Hyperquad⁷ was used to calculate the stability constants from potentiometry and spectrophotometry. The results are summarized in Table 1.

Table 1 *Thermodynamic parameters of U(VI) complexation with DMOGA and TMOGA*

Ligand	Reaction	$\log \beta$	ΔH , $\text{kJ}\cdot\text{mol}^{-1}$	ΔS , $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
DMOGA	$\text{H}^+ + \text{L}^- = \text{HL}(\text{aq})$	3.49 ± 0.03	0.83 ± 0.01	70 ± 1
	$\text{UO}_2^{2+} + \text{L}^- = \text{UO}_2\text{L}^+$	$3.84 \pm 0.02^{\text{a}}$	15.0 ± 0.1	124 ± 1
	$\text{UO}_2^{2+} + 2\text{L}^- = \text{UO}_2\text{L}_2(\text{aq})$	$5.88 \pm 0.02^{\text{a}}$	21.6 ± 0.2	185 ± 1
TMOGA	$\text{UO}_2^{2+} + \text{L}^- = \text{UO}_2\text{L}^+$	1.71 ± 0.03	5.72 ± 0.09	52 ± 1
	$\text{UO}_2^{2+} + 2\text{L}^- = \text{UO}_2\text{L}_2^{2+}$	2.94 ± 0.01	19.0 ± 0.2	120 ± 1
ODA ^b	$\text{UO}_2^{2+} + \text{L}^{2-} = \text{UO}_2\text{L}(\text{aq})$	5.01 ± 0.04	16.4 ± 0.2	152 ± 1
	$\text{UO}_2^{2+} + 2\text{L}^{2-} = \text{UO}_2\text{L}_2^{2-}$	7.64 ± 0.07	23.8 ± 0.1	227 ± 2

^a The average value from potentiometry and spectrophotometry.

^b Data for ODA are from the literature.⁶

2.2 Enthalpy of Complexation

The enthalpy of complexation of U(VI) with DMOGA and TMOGA was determined by calorimetry with an isothermal microcalorimeter (Model ITC 4200, Calorimetry Sciences Corp.). Detailed descriptions of the microcalorimeter and its calibration are provided elsewhere.⁸ The enthalpy of complexation was calculated from the reaction heat by the computer program Letagrop.⁹ The results are summarized in Table 1.

3 CONCLUSION

From ODA to DMOGA and TMOGA, the enthalpy of complexation (ΔH) becomes less endothermic and more favourable to the complexation while the entropy of complexation (ΔS) becomes smaller and less favourable to the complexation (Figure 2). Such trends imply that the amide group is less hydrated than the carboxylate group. When forming complexes with U(VI), less energy is required to dehydrate the amide group and fewer water molecules are released from the hydration sphere of the amide group than the carboxylate group. As a result, the enthalpy and the entropy of complexation both decrease

in the order: ODA > DMOGA > TMOGA, making opposite contributions to the stability of the complexes. The overall effect is that replacement of the carboxylate group(s) with the amide group(s) decreases the stability of complexes with U(VI), which seems to make the amide ligands less attractive for actinide separations. However, they are still promising because of the properties previously discussed. Large alkyl groups can be easily attached to the amides, making them highly soluble in organic solvents. Besides, using amides of higher denticity can enlarge the entropy effect, resulting in stronger complexes.

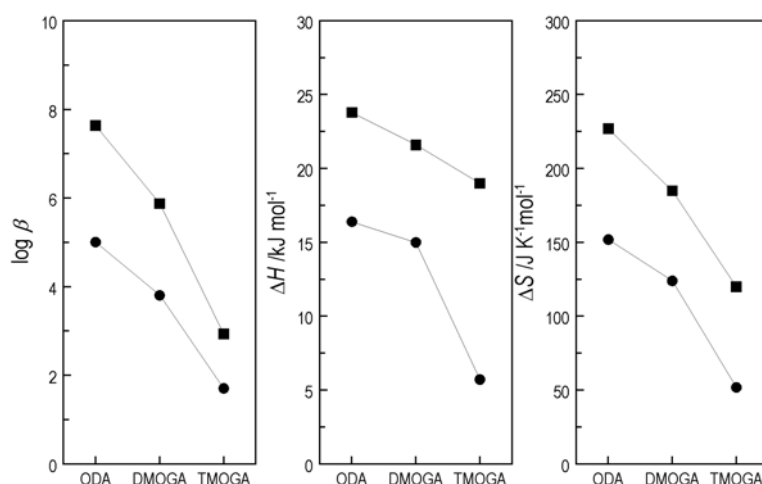


Figure 2 Comparison of thermodynamic parameters of U(VI) complexation with ODA and its amide derivatives. (●) ML; (■) ML₂ complexes.

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