

## 용매 추출계에서의 우라늄(VI)-유기인산에스테르 착물의 형성에 관한 연구

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## Complex Formation of Uranium(VI) with Organic Phosphate Ligands in the Solvent Extraction System

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**요 약.** 우라늄의 수용액 및 산성용액으로부터 추출제 DEPA 및 DPPA로 우라늄을 추출할 때의 메카니즘을 밝히기 위하여 추출 중에 형성되는 우라늄 착물을 분리, 유리한 후 적외선 스펙트럼, 핵자기공명 스펙트럼, 화학분석 및 분자량 측정결과 등을 이용하여 규명하였다.

우라늄은 추출과정에서 유기인산 에스테르인 추출제 DEPA 및 DPPA의 산성 수소와 이온 교환에 의하여 킬레이트형의 우라늄 착물을 형성하며 DEPA의 경우 분자량이 약  $2.1 \times 10^4$ 인 고분자물질임을 알았다. 또한 이러한 유리된 우라늄의 착물은 추출중에 형성되는 착물과 동일함을 밝혔으며 추출제 DEPA의 경우 우라늄의 추출 분배계수는 수용액의 경우 제일 크고 산성 수용액인 경우  $H_3PO_4 < H_2SO_4 < HClO_4$ 의 순으로 증가함을 알았다.

**ABSTRACT.** In order to elucidate the mechanism associated with the solvent extraction of uranium(VI) using DEPA and DPPA as extractant the uranium(VI) complexes formed during the solvent extraction were isolated and characterized by means of IR, NMR, chemical analysis and molecular weight determination.

It has been found that uranium(VI) replaces the acidic hydrogen ions of the extractants DEPA and DPPA to form chelated polynuclear complexes, the molecular weight of U(VI)-DEPA complex being  $2.1 \times 10^4$ . The isolated U(VI)-DEPA complex has been found to be the same chemical species as is formed during the solvent extraction process. In case of DEPA the distribution coefficient of uranium is the largest for the pure aqueous uranium solution and is increasing for the acidic solutions in the order of  $H_3PO_4 < H_2SO_4 < HClO_4$ .

### INTRODUCTION

In line with the rapid increase in interest of

utilization of the solvent extraction process for the recovery of uranium, a number of experimental studies on the extraction of uranium by organic extractants from aqueous acidic

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solutions have been carried out extensively. Especially alkylphosphoric acids have attracted scientific interest in extracting uranium, and subsequent investigations<sup>1-10</sup> for the use of alkyl phosphoric acids have been progressed.

Baes, *et al*<sup>10</sup>, suggested the extraction mechanism by combining the results of the isopiestic experiments, the viscosity measurements, and the dependence of the uranium(VI) extraction coefficient both on the concentration of di-(2-ethylhexyl)phosphoric acid and on the acidity of aqueous medium. According to them, at low uranium concentration the extraction into the organic phase is associated with the reaction  $UO_2^{2+}(aq) + 2(HX)_2(org) \rightleftharpoons UO_2X_4H_2(org) + 2H^+(aq)$  in which X represents the anion  $(RO)_2PO_2^-$  while in the vicinity of saturation of uranium in the organic phase the formation of chain polymers of the type  $HX_2UO_2X_2UO_2 \cdots X_2UO_2X_2H$  occurs. Peppard & Ferraro<sup>11</sup> prepared the yellow waxy solid complex of uranium(VI) with di-(2-ethylhexyl)-phosphoric acid by simple evaporation of the organic phase loaded with uranium, and determined the ratio of ligand/uranium to be 1.99. Recalling that dialkylphosphoric acids have generally been assumed to extract uranium(VI) by means of the ion-exchange reaction<sup>12,13</sup> other concrete evidences not yet considered by previous authors are necessary for elucidating the extraction mechanism.

In the present investigation di-(2-ethylhexyl)-phosphoric acid and diphenyl phosphoric acid (hereinafter referred to as DEPA and DPPA, respectively) were used to extract uranium(VI) from the aqueous and acidic solutions such as phosphoric, sulfuric and perchloric acids. The uranium(VI) complexes formed with the diester ligands have been isolated from the extraction systems and characterized by means of chemical analysis, molecular weight determination, and

IR spectroscopy. In addition NMR studies were carried out for the system of U(VI)-DEPA complex.

## EXPERIMENTAL

**Chemicals.** Fisher's reagent grade uranyl nitrate ( $UO_2(NO_3)_2 \cdot 6H_2O$ ) was used as uranyl ion source without further purification. DEPA used as extractant was reagent grade of Eastman Kodak Co. DPPA was prepared according to Brigl & Müller<sup>14</sup> and identified by melting point, chemical analysis, and IR spectroscopy. All other reagents were also reagent grade unless specified.

**Solvent Extraction and Preparation of U(VI)-DEPA Complex.** Uranium in 100 ml of 0.02 M aq. uranyl nitrate solution was extracted into organic phase by scrubbing for 10 min at 25 °C with 100 ml of 0.02 M DEPA-*n*-hexane solution. If further loading with uranium was necessary the partially loaded organic phase was repeatedly contacted with fresh portions of the aqueous uranium solution. In order to isolate the uranium complexes thus extracted the organic phase was separated and then allowed to evaporate. The yellow waxy solid resultant from evaporation was purified using solvent pair of dichloromethane and methanol. The purified solid complex was obtained when methanol was added to the concentrated dichloromethane solution of the crude product. The exactly same procedure of solvent extraction and purification was applied to the systems of DEPA in hexane and each of the acidic aqueous solutions of 0.02 M U(VI)-0.1 M  $H_3PO_4$ , 0.02 M U(VI)-0.1 M  $H_2SO_4$ , and 0.02 M U(VI)-0.1 M  $HClO_4$ . All complexes were dried over phosphorus pentoxide in vacuo.

**Preparation of U(VI)-DPPA Complex.** Solid U(VI)-DPPA complex was precipitated when 100 ml solution of 0.02 M DPPA in diethylether was contacted with 100 ml of 0.02 M aq. U(VI) solution. U(VI)-DPPA com

plex is insoluble in most of common solvents except for *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO). The precipitated solid was washed with methanol and dried over phosphorus pentoxide in vacuo. The same extraction procedure was applied to the acidic aq. U(VI) solutions containing each of 0.1 *M* H<sub>3</sub>PO<sub>4</sub>, 0.1 *M* H<sub>2</sub>SO<sub>4</sub> and 0.1 *M* HClO<sub>4</sub>.

**Chemical Analysis and Spectroscopic Measurements.** Uranium(VI)-organic phosphate complexes were analyzed and identified as follows. Uranium was determined by means of X-ray fluorescence using the Norelco Universal Vacuum Spectrograph and *n*-hexane and DMF were used as solvents for the preparation of sample solutions of U(VI)-DEPA and U(VI)-DPPA complexes, respectively. Carbon and hydrogen were analyzed with Coleman Carbon-Hydrogen Analyzer. The results of elemental analyses for U(VI)-DEPA and U(VI)-DPPA are given in Table 1. The IR spectra of the complexes were recorded on the Beckman IR-12 Spectrophotometer. The IR spectra of U(VI)-DEPA complexes were determined as film on KBr plate and those of U(VI)-DPPB complexes as KBr wafer. All the NMR spectra were measured using Varian HA-100 D Spectrometer.

**Molecular Weight Determination.** The molecular weight of U(VI)-DEPA complex was determined with Hitachi Perkin-Elmer 115 Molecular Weight Apparatus. Working temperature of main oven was 40 °C and carbon tetrachloride was used as solvent. No proper solvent was found for the molecular weight determination of U(VI)-DPPA complex.

## RESULTS AND DISCUSSION

The attempts of solvent extraction of uranium(VI) by trialkyl or triaryl-phosphate ligands were not successful whereas the mono and disubstituted phosphates have shown good extra-

ction efficiency. Such a result strongly indicates that uranyl ion forms ionic salts with the partially substituted phosphate ligands and as such uranium is extracted by the ion exchange mechanism as was suggested by Baes, *et al.*<sup>10</sup> The infrared spectra of the isolated products from the extraction are also consistent with the above result.

The IR spectra of free ligands DEPA and DPPA and their corresponding uranium salts are shown in Fig. 1 and 2. The spectrum of the U(VI)-DEPA complex in Fig. 1 is identical

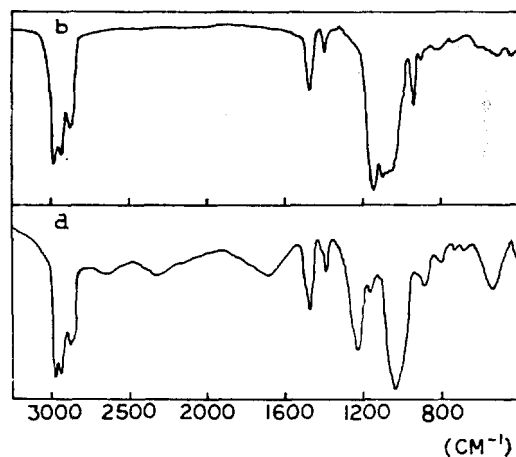


Fig. 1. Infra-red absorption spectra of (a) DEPA and (b) U(VI)-DEPA complex.

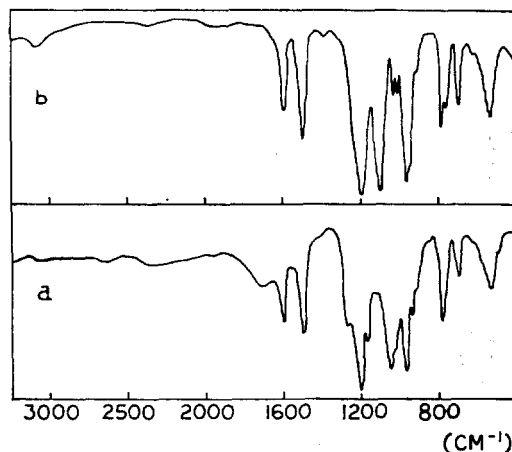


Fig. 2. Infra-red absorption spectra of (a) DPPA and (b) U(VI)-DPPA complex.

with the previously reported by Peppard and Ferraro<sup>11</sup> and has shown exactly the same absorption pattern independantly of acidity and the kind of acids involved in the aqueous uranium solutions. The acidic O-H stretching frequencies at  $2650\text{ cm}^{-1}$  and the P-O-H bending mode at  $1690\text{ cm}^{-1}$  in the free ligand DEPA (Fig. 1a) all disappears when it is coordinated to uranium(VI) as is seen in Fig. 1b, which means the acidic hydrogen was replaced probably by uranyl cation. It is also worthwhile to point out that the P=O stretching frequency undergoes red shift from  $1230\text{ cm}^{-1}$  to  $1145\text{ cm}^{-1}$  by complexation, which suggests that the P=O oxygen is coordinated to uranium resulting in a chelated structure as is shown in Fig. 3.

In case of DPPA the acidic O-H stretching bands are only weakly observed but the strong P-O-H bending mode at  $1710\text{ cm}^{-1}$  clearly disappears in its uranium complex as is shown in Fig. 2. Also the P=O stretching band at  $1275\text{ cm}^{-1}$  of free DPPA is evidently shifted to lower

frequency in its complex although its shifted position is not clearly located because of its adjacent strong band at  $1200\text{ cm}^{-1}$ . Consequently the molecular structure of the U(VI)-DPPA complex seems to be similar to that of the U(VI)-DEPA complex.

Along with the above-mentioned infrared data the results of chemical analyses of the isolated DEPA- and DPPA-U(VI) complexes lead to formulation of two possible molecular structures illustrated in Fig. 3. One is monomeric (structure I) and the other is a polynuclear uranium(VI) complex (structure II). The ligand to uranium ratio in the polymeric chain structure,  $(\text{UO}_2)_n\text{L}_{2n+2}\text{H}_2$ , approaches to the same value  $1/2$  as in the monomeric structure if  $n$  is large. Therefore it is difficult yet to determine which is the real molecular structure without further information. Since no proper solvent was found for U(VI)-DPPA complex only the U(VI)-DEPA complex was subjected to molecular weight determination. The measured molecular weight of the U(VI)-DEPA complex was found to be approximately  $2.1 \times 10^4$  resulting in the  $n$ -value of 22, which is in good agreement with

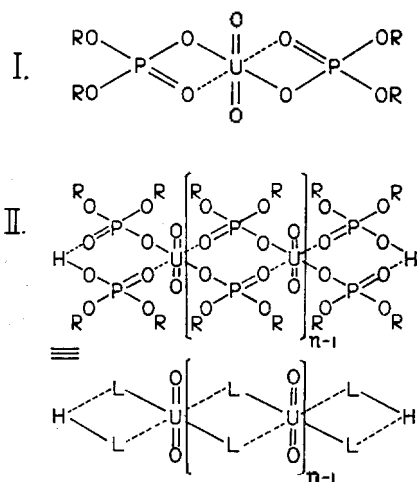


Fig. 3. Proposed molecular structures for U(VI) complexes with DEPA and DPPA: I, monomeric complex and II, polymeric chain complex. The term R represents phenyl or 2-ethylhexyl group and L denotes  $(\text{RO})_2\text{POO}$  anion.

Table 1. Results of chemical analysis of U(VI) Complexes with DEPA and DPPA.

		Calc. (%) <sup>a</sup>		Obs. (%)
		Structure I	Structure II <sup>b</sup>	
U(VI)-DEPA	U	26.1	25.3	26.0
	C	42.1	42.7	43.0
	H	7.50	7.61	7.54
U(VI)-DPPA	U	31.0	30.2	30.5
	C	37.5	38.0	37.8
	H	2.60	2.65	3.29

<sup>a</sup> The model structures which were used for calculations are given in Fig. 3.

<sup>b</sup> For U(VI)-DEPA complex the value of  $n=22$  obtained from its molecular weight measured was used and for U(VI)-DPPA complex calculation was carried out based on the arbitrary value of  $n=25$ .

the observed value as is seen in Table 1. After all it may be concluded that the ligand DEPA forms a polynuclear uranium complex during the solvent extraction process at least in the reasonably concentrated range of the organic phase. If the U(VI)-DPPA complex is assumed to be also polymeric as is envisioned from its IR spectrum the  $n$ -value seems to be fairly large ( $>20$ ).

Now in order to elucidate the nature of the solvent extraction mechanism of U(VI)-phosphate systems the results of NMR studies may be examined. The NMR spectra of DEPA and its uranium(VI) complex in carbon tetrachloride are reproduced in Fig. 4. The bands  $\beta$  and  $\gamma$  in the figure are due to the protons of the alkyl group other than the  $\alpha$ -protons (P-

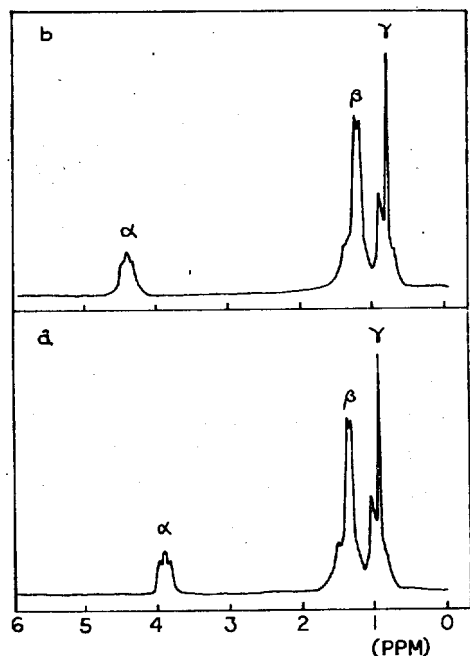
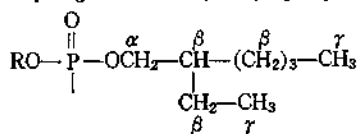


Fig. 4. NMR spectra of (a) DEPA and (b) U(VI)-DEPA complex in carbon tetrachloride.  $\alpha$ ,  $\beta$  and  $\gamma$  denote the hydrogens in 2-ethylhexyl group as follows:



$\text{OCH}_2$ ), which resonate at 3.89 ppm in the free ligand.<sup>15</sup> As is expected, the chemical shift of the  $\alpha$ -protons undergoes downfield shift to 4.42 ppm when the ligand is coordinated to uranium whereas the resonances by  $\beta$  and  $\gamma$ -protons remain nearly unchanged. However, more important is that the NMR study presents evidences for the isolated solid complex being the same species as exists in the organic phase during solvent extraction. The NMR spectra of organic phases after extraction from aqueous uranium solutions have been compared with those of free DEPA and isolated U(VI)-DEPA complex in *n*-hexane solvent which was used as diluent of the organic phase for the solvent extraction system.

The NMR spectrum of an organic phase partially loaded with uranium has shown exactly the same resonance pattern except that the chemical shift of  $\alpha$ -protons appears in the intermediate field between those of the free DEPA and the pure U(VI)-DEPA complex. The more organic phase was loaded with uranium, the closer its chemical shift of  $\alpha$ -protons to that of pure U(VI)-DEPA complex. Surprisingly the resonance peaks by  $\alpha$ -protons of free and complexed ligands were not resolved in the spectra of partially loaded organic phases, which means that fast exchange between the free and complexed ligands occurs in our experimental conditions. In order to confirm further the NMR spectra of *n*-hexane solutions simulated by dissolving different ratio of free DEPA to the pure isolated U(VI)-DEPA complex have been examined and the same phenomenon was observed. Therefore, it may be concluded that the isolated solid uranium complex is the same chemical species as exists in the organic phase during the solvent extraction and furthermore the relative value of the chemical shift of  $\alpha$ -protons of the phosphate ligand may be used

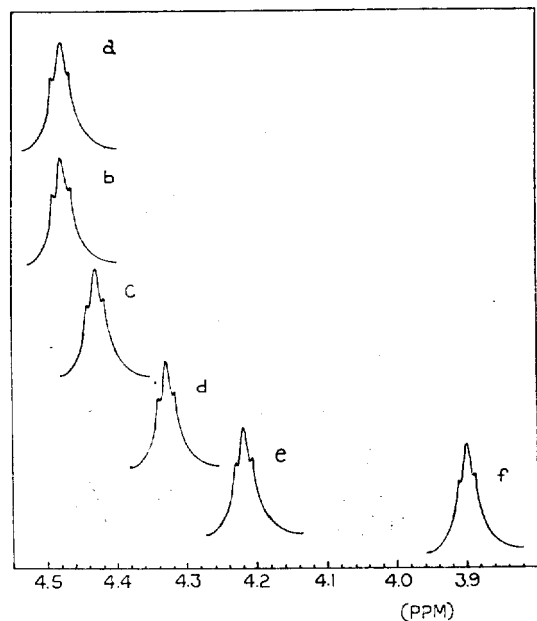


Fig. 5. The chemical shifts of  $\alpha$  protons ( $=\text{P}-\text{OCH}_2$ -protons) in *n*-hexane : (a) isolated U(VI)-DEPA complex; concentrated organic solutions contacted with (b) aq. U(VI) solution, (c) aq. U(VI)-HClO<sub>4</sub> solution, (d) aq. U(VI)-H<sub>2</sub>SO<sub>4</sub> solution, and (e) aq. U(VI)-H<sub>3</sub>PO<sub>4</sub> solution; (f) DEPA.

as a measure for the degree how much the organic phases are loaded with uranium.

Finally, it seems worthwhile to comment on the influence of acidic properties of aqueous uranium solutions to be extracted upon the extracting power of the phosphate ligands. Thus the aqueous uranium solutions (0.02 M U(VI)) containing the same molar concentration (0.1 M) each of phosphoric, sulfuric or perchloric acid were extracted once by contacting under the same conditions with the organic phase containing the same amount of DEPA, and then the NMR spectra of the organic phases loaded with uranium were examined. The resonance peaks of  $\alpha$ -protons ( $\text{P}-\text{OCH}_2$ -) of the ligand are reproduced in Fig. 5 and here it is envisioned that pure aqueous solution of uranium is most easily extracted while its phosphoric acid solu-

tion is least extractable. In other words, the distribution coefficient of uranium between the aqueous and organic phases containing DEPA in this single step extraction changes depending on the kind of acids involved in the uranium solutions in the increasing order of  $\text{H}_3\text{PO}_4 < \text{H}_2\text{SO}_4 < \text{HClO}_4 < \text{H}_2\text{O}$ , which is the reverse order of their general complexing power with metals in aqueous solutions.

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