Fundamental Studies on the Extraction of Uranium from Phosphoric Acid with various Organophosphorus Compounds

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Abstract

The particular emphasis has been placed upon the items as followed; 1) The selection of diluents to obtain higher distribution ratios, 2) The effect of their concentration of reagents, 3) The effect of extracting temperature, 4) The condition of reducing uranium (VI) to (IV). As a reducing agent, iron powder is most effective. The extraction ratio of uranium (IV) was remarkably decreased with the addition of TOPO in organic phases and on the other hand the addition of it outstandingly enhanced the extraction ratio of uranium (VI). It seems that reagents such as TOPO or D2EHPA play a role of a diluent or a solvent and the employment of such polar solvents is unsuitable for the extraction of uraninm. Further, the both extraction reaction would proceed exothermically. The composition of the complex of uranium (VI) extracted was $UO_2(D2EHPA)_2TOPO$. The distribution ratio of uranium (IV), 140 was obtained when the mixture of 3 g of OPPA, 0.5 g of biphenyl, and 0.5 g of naphthalene was used as the organic phase, and the distribution ratio of uranium (VI), 12 was obtained when the mixture of 1 g of TOPO, 3.4 g of D2EHPA and 1.6 g of paraffin (mp 48°C) was used.

Introduction

The researches for the fuels which may take the place of fossil fuels have been carried out since 1973 which is the years of oil crisis in the world. The recovery of uranium contained in sea water (about 3 μg/l)[1-3] or wet process

phosphoric acid (about 0.1 g/l)[4-5] has been investigated in several countries, and uranium in phosphoric acid has been recovered in some countries in idustrial scale. With regard to the extraction and recovery of uranium from wet process phosphoric acid, there are several reports on the extractants of di-2-ethylhexylphosphoric acid (D2EHPA) and trioctylphosphine oxide (TOPO), diluted with kerosene or decane, however, the number of the reports with respect to the extraction of uranium (IV)[6-8] is fewer than the reports with regard to uranium (VI). In this report, the effects of the ratio of TOPO and D2EHPA and extracting temperature, and the composition of the complex of uranium (VI) extracted are described. The researches will be continued in more detail on the basis of the data described in this paper.

Experimental

Reagents. Standard uranium (VI) solution was prepared by dissolving 0.422 g of uranyl nitrate in demineralized water and diluting to 100 ml. D2EHPA, OPPA and mono-D2EHPA purchased from Daihachi Kagaku were used without further purification. TOPO purchased by Hokko Kagaku was used. DPA was prepared in our laboratory and the main components were determined by neutrarization titration with the 0.5 M potassium hydroxide solution. Main components in the wet process phosphoric acid used were analyzed and the results are shown in Table 1. These values agreed considerably with the values of the components in many wet process phosphoric acids manufactured industrially. Other chemicals such as solvents, reagents or acids are of analytical grade.

Table 1. Analytical results for a wet process phosphoric acid.

Constituent	Concentration, g/l	
PO_4^{3-}	5.65 mol/l	5.0-6.0 mol/l*
U	0.11	0.14-0.17*
Fe (total)	5.5	7.0-10.0*
SO_4^{2-}	20.7	19.0-31*
F^-	26.4	21.0-30.0*
H_3O^+	12.3 mol/l	

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Synthesis of DPA. Put 35.5 g of P_2O_5 and 186.3 g of dodecylalcohol into 100 ml of kerosene in a 500 ml separable flask and stir the mixture for 30 min. Then add half its original volume of hydrochloric acid in it and reflex for 2 h at 120°C.

Remove volatile materials such as kerosene and hydrochloric acid by evaporating and wash the residue with hot water to remove phosphoric acid remained. The results of the analysis of DPA and OPPA, marketed in Daihachi Kagaku are shown in Table 2.

Table 2. Composition of 1 g of octylphenylphosphoric acid (OPPA) or dodecylphosphoric acid (DPA).

	OPPA	DPA
Mono-	1.47×10^{-3} mole (wt. % 42.0)	2.23×10^{-3} mole (wt. % 50.8)
Di-	1.14×10^{-3} mole (wt. % 54.0)	1.04×10^{-3} mole (wt. % 34.0)
Acid value (KOH mg/g)	234.5	251.7
P (wt. %)	8.1	10.4

Extraction procedures of uranium (IV) and (VI).   Put 25 ml of phosphoric acid containing uranium (IV) into a 100 ml Erlenmyer flask and further put appropriate amounts of OPPA and diluent of which sum is adjusted to 4 g precisely. Heat the flask on a water bath at about 70°C until OPPA and diluent melt completely. Stand for 1 h in a water bath kept at 50°C. Shake vigorously for a few minutes and remove the flask from the bath. Collect the aqueous phase with a pipette at the same temperature and determine uranium in it spectrophotometrically with 5-Br-PADAP (2-(5-bromo-2pyridylazo)-5-diethylaminophenol)[9] method. The extraction of uranium (VI) was carried out in a similar manner. But TOPO was added in the organic phase. That is, put 25 ml of phosphoric acid containing uranium (VI), into a 100 ml flask and further and TOPO, D2EHPA and diluent. The amount of TOPO was kept at 1 g and that of diluent was kept at 1 g and D2EHPA, ranging from 1 to 7 ml was added in it. Further the experiments were carried out by changing the amount of TOPO from 1 g to 2 or 3 g, but other condition was kept constant. The distribution ratios were calculated from the difference between the initial and remaining concentrarions of uranium in phosphoric acid.

Determination of uranium in phosphoric acid.   Put 1 ml of phosphoric acid, containing less than 100 μg of uranium (IV) or (VI) into a 100 ml separatory funnel. Add 1.5 ml of nitric acid, 1 ml of 5 % ascorbic acid and 1 ml of the 2 % sodium fluoride solution and dilute the mixed solution to 10 ml with water. Extract uranium (VI) with 5 ml of the 0.1 M TOPO in benzene solution. Remove the aqueous phase from the separatory funnel and wash the organic phase with 10 ml of the 2 M

nitric acid. Transfer 2 ml of the organic phase into a 10 ml measur-ing flask and add 0.5 ml of the 10% triethanolamine solution and 1 ml of 0.05% CyDTA (trans-1, 2-cyclohexanediamine-N, N, N', N'-tetraacetic acid) solution and dilute the mixed solution to 10 ml with ethanol. After standing 30 min, measure the absorbance of the solution at 575 nm.

Results and Discussion

The reduction of uranium (VI) to (IV).   The phosphoricacid immediately after being manufactured contain uranium (IV) and (VI) in the ratio of about 1 : 1. But there is a little uranium (IV) in the phosphoric acid used, as uranium (IV) was oxidized to uranium (VI) by standing for a long time. So tests were carried out on reducing uranium (VI) with iron powder, sodium hyposulfite, and sodium hydrogen sulfite to investigate the extraction of uranium (IV). After treating 25 ml of the phosphoric acid with 1 g of hyposulfite or 0.15 g of iron powder, the acid was filtrated through No 5A and uranium (IV) in it was extracted with the mixture of 3.5 g of OPPA and 2 g of the mixtures of biphenyl and naphthalene (1 : 1). By treating with iron powder, more than 90% of uranium was extracted from the acid, while only 30% of it was extracted by treating with hyposulfite or sulfite. So the reduction with iron powder was examined in detail. Uranium in 25 ml of the acid was reduced by shaking with various amounts of iron powder, ranging from 0.05 to 0.2 g at 60°C and it was extracted with 4.5 g of the mixture of 2 g OPPA, 1 g biphenyl and 1 g naphthalene at 50°C. The extraction percentage was calculated from the difference between the initial and remaining concentration of it in the acid. It was revealed that 95% of uranium was extracted from the acid when more than 0.15 g of iron powder was added into 25 ml of the acid. The effect of shaking time on the extraction was examined similarly by using 25 ml of the acid 0.15 g of iron powder. It was found that shaking for 30 min is sufficient for the maximum recovery of uranium even if the concentration of the phosphoric acid was changed between 2 and 6 M.

Effect of extracting temperature.   The effect of extracting temperature was examined by extracting uranium (IV) in 25 ml of the acid with 3.5 g OPPA, 1 g biphenyl and 1 g naphthalene at various temepratures. After extraction, the aqueous phase was collected at the same temperature at once. Uranium in it was determined and the percentage of uranium extracted was calculated from the difference between the initial and remaining concentrations of uranium in the acid.

The results are shown in Fig. 1. The extraction percentage increases from 74 to 82% when temperature is reduced from 80 to 50°C. When the wet process phosphoric acid is fed to the solvent extraction process without cooling, the temperature of the acid would be about 60°C. The uranium extraction at high temperature such as 60°C, is economically advantageous, because the cost of cooling is generally expensive. It was found that the extraction percentage from the wet process phosphoric acid is lower than that from the 6 M phosphoric acid solution, prepared with the reagent of analytical grade, in spite of a little difference between the concentrations of phosphate ion of them. It is well known that the presence of iron (III)[10] interfere the extraction of uranium (IV). Probably much amounts of iron (III) containing in the acid must interfere the extraction of uranium.
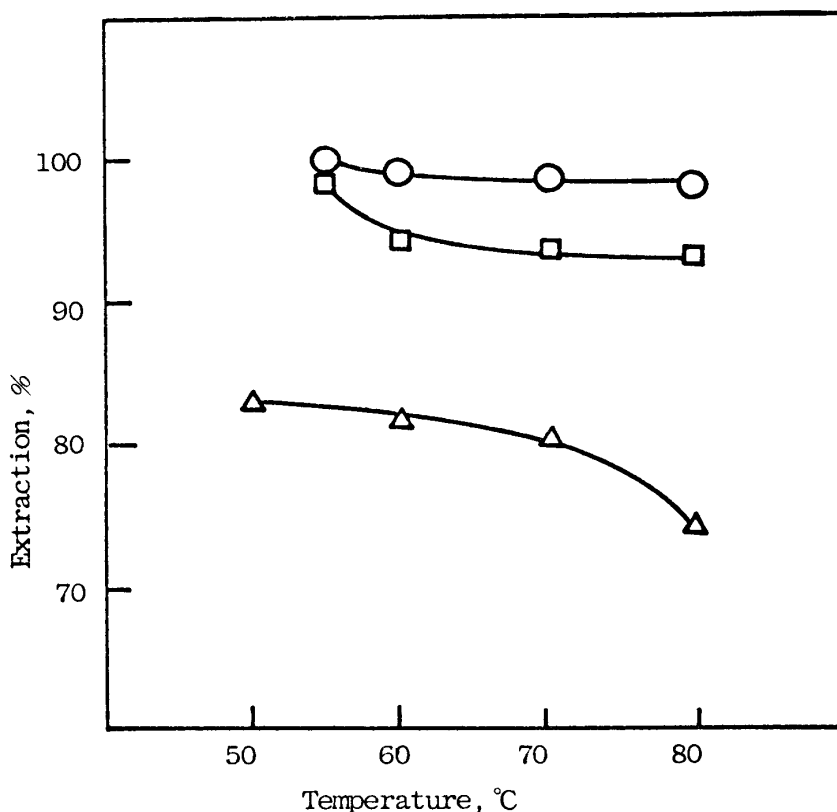

Fig. 1 Effect of temperature on the extraction of uranium (IV).
OPPA : 3.5 g, Diphenyl-naphthalene (1 : 1) : 2 g,
Uranium : 5.48×10^{-3} mol dm^{-3}
-O- 2 mol dm^{-3} H$_3$PO$_4$, -□- 6 mol dm^{-3} H$_3$PO$_4$
-△- crude H$_3$PO$_4$

Effect of diluent. The diluent significantly affects extraction performance and phase separation characteristics. In many of the tests, n-decane was used, however equivalent extraction results were obtained with cheaper aliphatic diluents. Although ordinary kerosene is probably a suitable diluent for process application, the

use of the aliphatic diluent which has a refined high boiling point and a high flash point, such as Amsco, is advantageous and recommended. There is a little knowledge about the distridution ratio when aromatics solvent was used as diluent. The test used aromatic solvents as diluents was carried out. A part of the results tested are shown in Fig. 2. Biphenyl, naphthalene and the mixture of the two
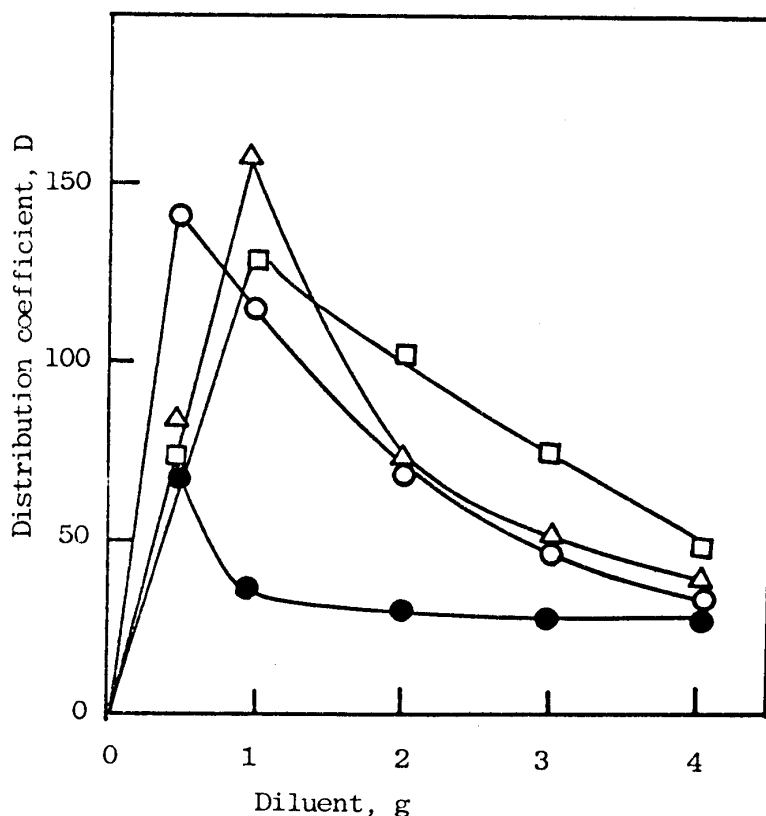

Fig. 2   Relation between distribution ratio and amount of diluents.
    -O- OPPA 3 g, Diphenyl-naphthalene (1 : 1)
    -△- OPPA 3.5 g, Diphenyl-naphthalene (1 : 1)
    -□- OPPA 4 g, Diphenyl-naphthalene (1 : 1)
    -●- OPPA 3.5 g, Kerosene

solvents mentioned about were used as diuents, and the uranium extraction ratios with the reagent-diluent combinations were compared with the result used kerosene as a diluent. It was carried out that uranium in 25 ml of the acid was extracted with the organic phases which was changing the various ratios of OPPA to diluents. Outstandingly high distribution ratios were obtained with aromatic diluents. Other extractants and other diluents were tested in similar manners. The values of the maximum extraction ratio of uranium obtained are listed in Table 3. It is observed that mono-OPPA is more effective than di-OPPA, but the extractability with mono-OPPA was not affected by containing above 50% diOPPA in weight. The uranium extraction ratio with the organic phase of OPPA, biphenyl and naphthalene is out-

standing, but its phase separation from the acid was very slow because the both phases are very viscous.

Table 3. Distribution ratio of uranium (IV)

Extractant	Diluent	Distribution ratio, D	Extractant	Diluent	Distribution ratio, D
OPPA (m, d-)	diphenyl-naphthalene (1 : 1)	130*	DPA	diphenyl-naphthalene (1 : 1)	8
	Xylene	45		Xylene	17
	toluene	48		toluene	11
	isopropylbenzene	51		isopropylbenzene	15
	m-diisopropylbenzene	92		m-diisopropylbenzene	15
	p-diisopropylbenzene	110		p-diisopropylbenzene	18
	sec-butylbenzene	64		sec-butylbenzene	24
	kerosene	35		kerosene	13
	paraffin (liquid)	2.2		paraffin (liquid)	12
	paraffin (solid)	1.2		paraffin (solid)	3
d-OPPA	diphenyl-naphthalene (1 : 1)	50	D2EHPA	diphenyl-naphthalene (1 : 1)	—
	xylene	22		xylene	5
	toluene	15		toluene	2
	isopropylbenzene	20		isopropylbenzene	—
	m-diisopropylbenzene	16		m-diisopropylbenzene	6
	p-diisopropylbenzene	31		p-diisopropylbenzene	8
	sec-butylbenzene	26		sec-butylbenzene	—
	kerosene	8		kerosene	—
	paraffin (liquid)	1		paraffin (liquid)	1.2
	paraffin (solid)	—		-paraffin (solid)	—

Effect of TOPO. It is desirable that uranium (IV) and (VI) can be extracted with a organic phase at the same time. It is known that the addition of TOPO into organic phases enhances the extraction of uranium (VI). So we obtained the uranium (IV) extraction ratio when TOPO was added to a organic phase which consisted of 2 g OPPA and 1.5 g biphenyl and 1.5 g naphthalene. The experiments were carried out by extracting uranium (IV) in 25 ml of the acid with mixtures which consist of the various ratios of TOPO and OPPA kept at 2 g. The results are shown in Fig. 3. It became clear that addition of more than 1 g of TOPO brought about the sharp depressing of the distribution ratios. The extraction of uranium (IV) and (VI) at the same time, seems to be difficult. Species of the complex extracted would be $U(diOPPA)_4$ or $U(mono\text{-}OPPA)_2$.

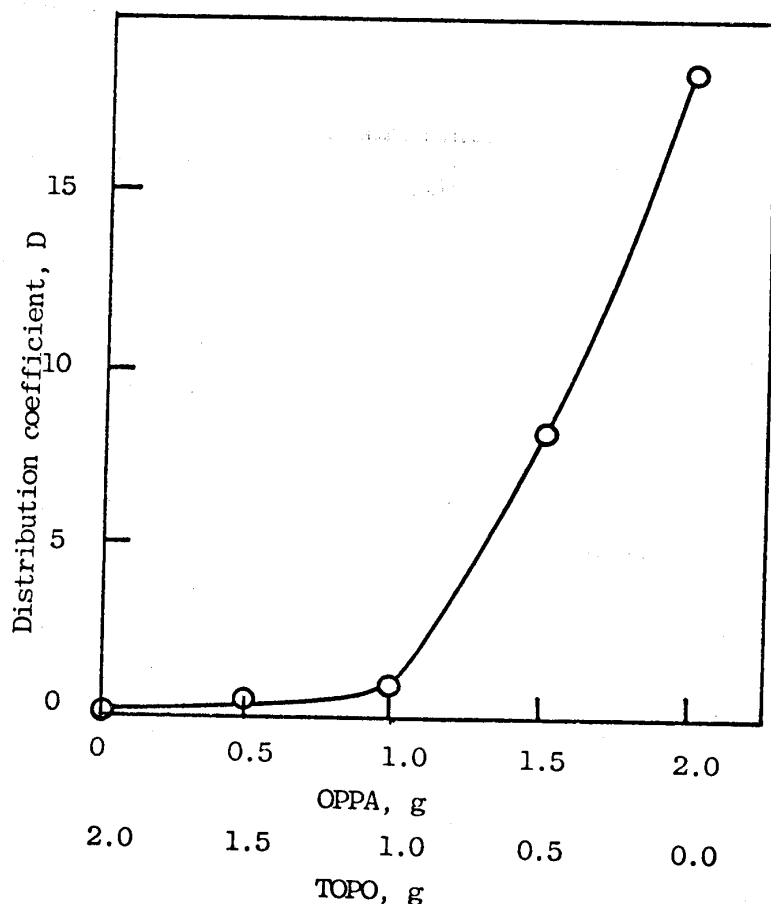Fig. 3   Effect of amount of OPPA and that of TOPO on the extraction.
Diphenyl-naphthalene $(1:1)$: 3g,   Uranium : 5×10^{-4} mol dm^{-3}

Extraction of uranium (VI)

Effect of diluent.   The TOPO plays a role as a solvent at the same time for the extraction of uranium (VI). So kerosene or decane are used as a diluent, but there are only a few reports of molten-solvent systems. A series of preliminary investigations were carried out with molten-solvents. In some extractions which used TOPO or D2EHPA, we could not obtain more than 3 of the distribution ratio. When a mixture of TOPO, D2EHPA and diluent is used, the distribution ratio increases with increasing the concentration of the both reagents and reaches a maximum. These phenomena are often found when the species of the complexes to be extracted change. But it is well known that the employment of a polar solvent such as chloroform, methyl isobutyl ketone brings about low distribution ratios. As TOPO and D2EHPA play a role of diluent, uranium might be poorly extracted by such a polar organic phase. The presence of the neutral ligand TOPO brings about an important enhancement for the extraction of uranium (VI). It was investigated how the distribution ratio changed with adding TOPO and D2EHPA in detail. The

amount of diluent such as biphenyl, kerosene and paraffin was kept constant. The results are shown in Fig. 4. The distribution ratios have each maximum values,
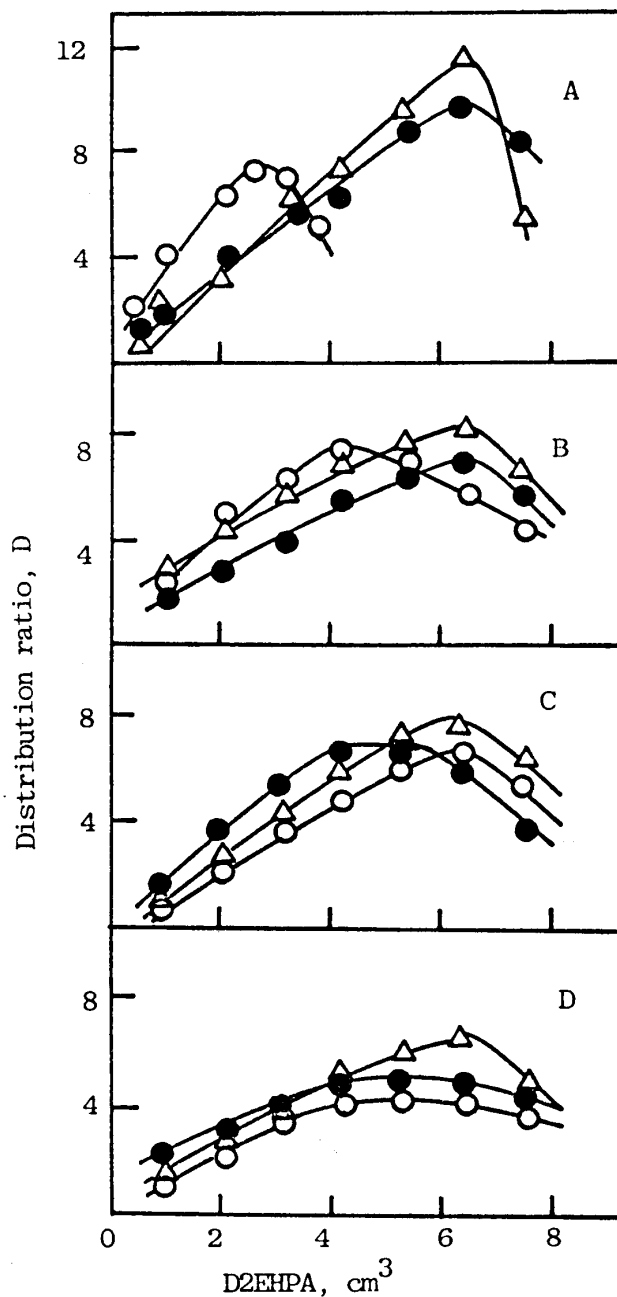

Fig. 4 Relation between distribution ratio and amount of D2EHPA.

A : Paraffin 1.6 g, -○- TOPO 1 g, -●- TOPO 2 g, -△- TOPO 2.5 g
B : Diphenyl 1 g, -○- TOPO 1 g, -△- TOPO 2 g. -●- TOPO 3 g
C : Naphthalene 1 g, -●- TOPO 1 g, -△- TOPO 2 g, -○- TOPO 3 g
D : Kerosene 1 cm³, -●- TOPO 2 g, -△- TOPO 3 g, -○- TOPO 4 g

when the concentration of D2EHPA changes in several fixed concentrations of TOPO and diluents. The synergistic effect is noteworthy as shown in Fig. 4. The highest value in the distribution ratios among them were obtained when paraffin was used
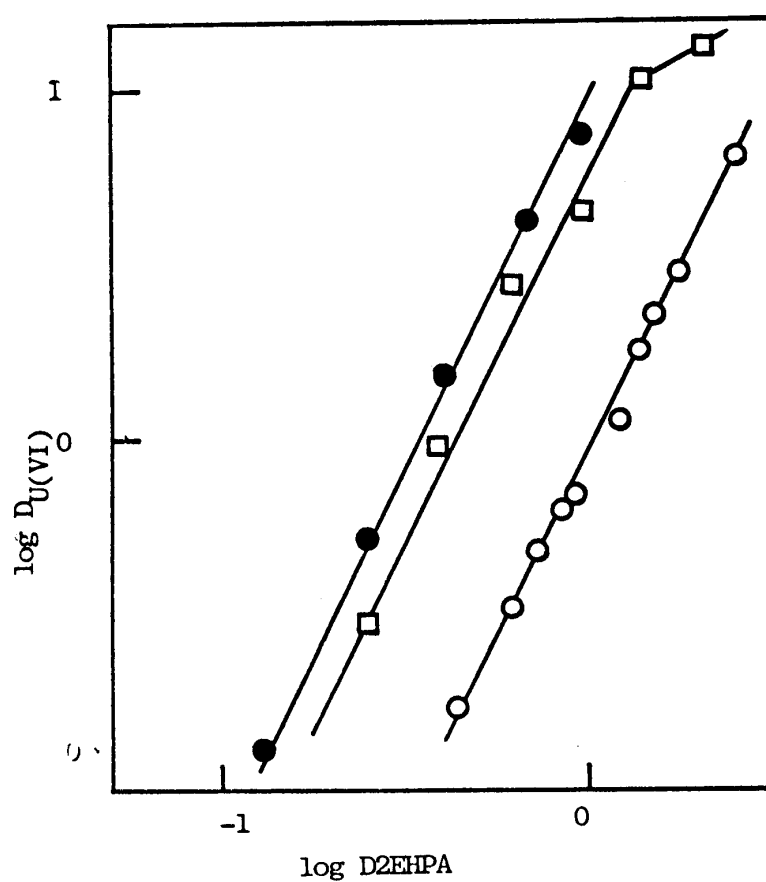
Fig. 5 Uranium (VI) extraction from 4 M H_3PO_4 solution with. D2EHPA and TOPO in diphenyl-naphalene at 60°C.
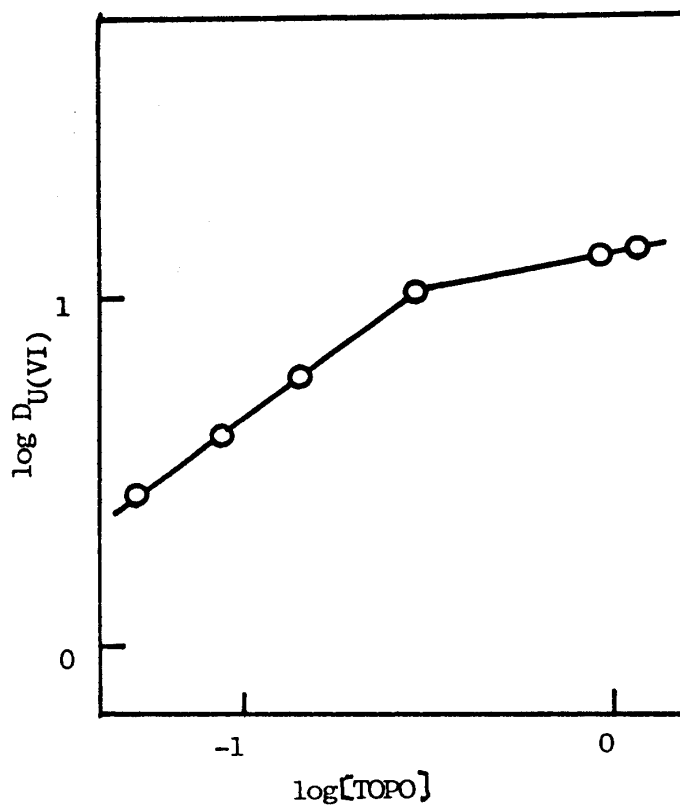-○- D2EHPA, -□- D2EHPA-0.19 M TOPO, -●- D2EHPA0-55 M TOPO

Fig. 6 Uranium (VJ) extraction from 4 M H_3PO_4 solution with 1.19 M D2EHPA and various concentration of TOPO in diphenyl-naphthalene at 60°C.

as a diluent. As naphthalene sublimes easily, the composition of the organic phase
changes during extracting. The organic phase which consist of TOPO, D2EHPA
and biphenyl are hard to melt at lower temperature than 60°C. When the mixture
of biphenyl and naphthalene is used as the diluent, the maximum distribution ratio
is 12, while the maximum is 6 in the case of using kerosene. But it requires
longer time to separate the extraction phase consisted of biphenyl and naphthalene,
and further the organic phase adheres to the wall of an extracting vessel.

Composition of complex extracted.   Uranium complex in extraction phase was
investigated by keeping constantly the total volume of the extraction phases and
the concentration of TOPO. The distribution ratios of uranium (VI) from approxi-
mately 4 M phosphoric acid solution by D2EHPA in biphenylnaphthalene (3 : 1)
ranging from 0.1 to 2 M at 60°C are plotted in Fig. 5. In each case, there is a
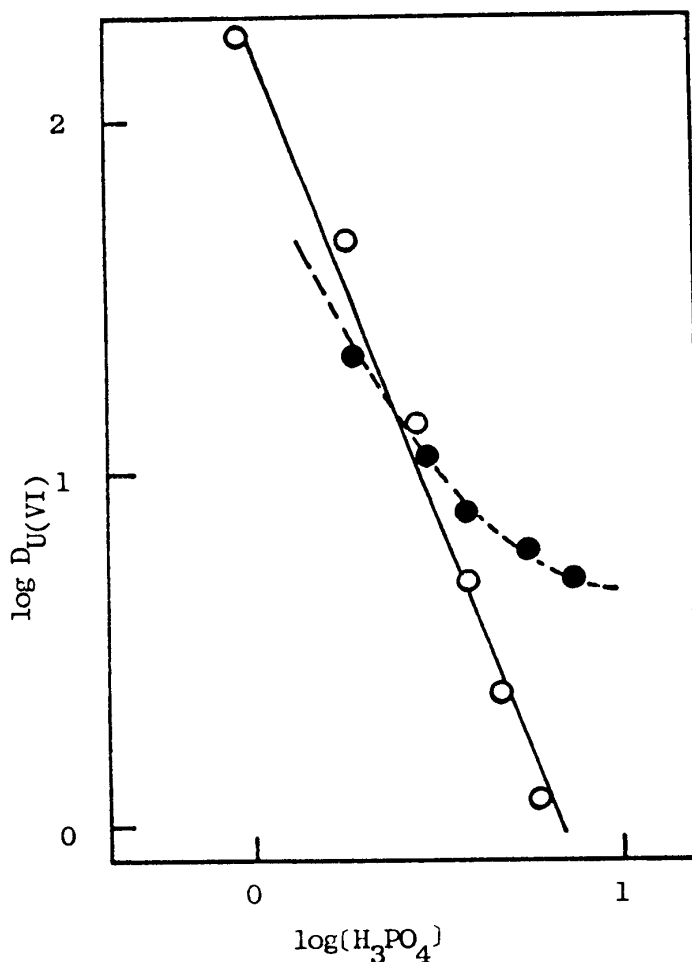linear dependence of log D on log [D2EHPA]. We can obtain the coordination number

Fig. 7 Uranium (VI) extraction vs H_3PO_4 concentration.
      -○- 1 M D2EHPA and 0.2 M TOPO, -●- 1.86 M D2EHPA
      and 0.53 M TOPO, Extracting temperature at 60°C.

of D2EHPA of 2 in the presence or the absence of TOPO. It seems, juging from the slope, that one molecules of TOPO coordinates to one molecule of uranium (VI) when D2EHPA is present.

Effect of concentration of phosphoric acid.   Phpsphoric acid is a weak acid and its first dissociation constant, $K_1=7.5\times10^{-3}$, is very important. The values of K_2 and K_3 are 2×10^{-8} and 5×10^{-13}, respectively. Therefore complex species formed in the phosphoric acid are UO_2^{2+}, $UO_2(H_2PO_4)^+$, $UO_2(H_2PO_4)_2$, $UO_2(H_2PO_4)_2H_3PO_4$, etc. having stability constants of 15.5, 21.8 and 10.2 respectively.[10] By using the distribution ratios in the absence of phosphoric acid, $D_0=[UO_2^{2+}]_{org}/[UO_2^{2+}]_{aq}$, D in the presence of phosphoric acid is shown in the following equation: $D=D_0/(1+\sum_n \beta K_n(H_2P_4^-)^n)$. We can estimate that the distribution ratios D decreases with increasing the H_3PO_4 concentration from the above equation. The results are shown in Fig. 7. The results fit in the expections. Further, when the H_3PO_4 concentration is high, it seems that the extraction phases, containing TOPO and
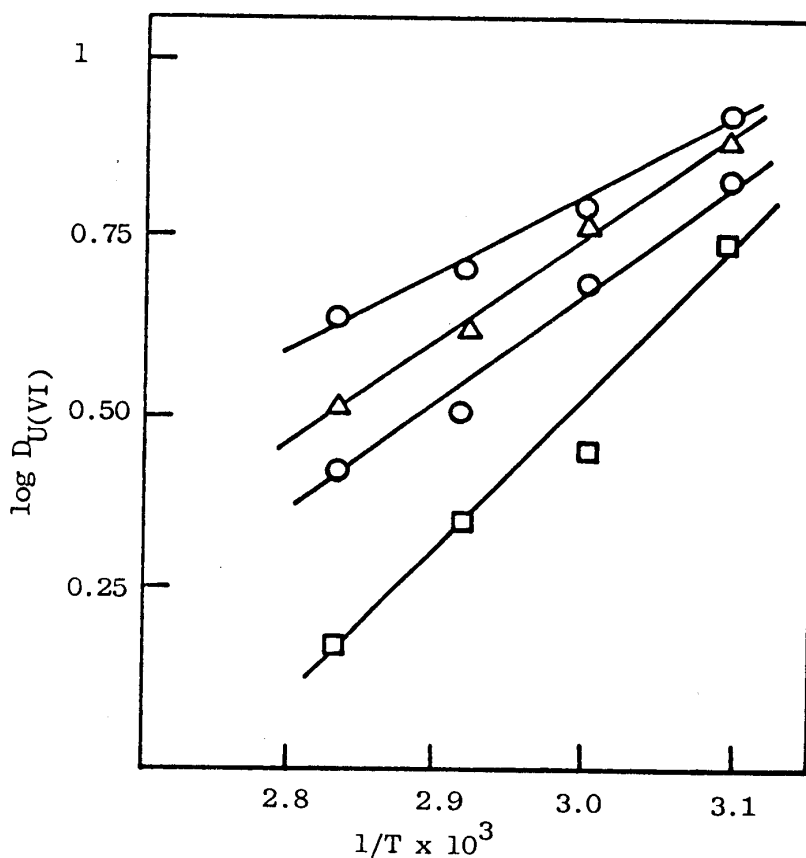

Fig. 8 log D vs 1/T from H_3PO_4 solution. Effecting of varying temperature.
-○- Crude H_3PO_4 (5.8 M), TOPO 2 g, D2EHPA 6 cm³, Diphenyl 1 g
-△- Pure H_3PO_4 (4.0 M, contained 112 ppm of uranium). D2EHPA 3 cm³,
     Mixed solvent (diphenyl-naphthalene : 3/1) 2 g
-●- Crude H_3PO_4 (5.8 M), TOPO 2 g, D2EHPA 6 cm³, Naphthalene 1 g
-□- Crude H_3PO_4 (5.8 M), TOPO 3 g, D2EHPA 6 cm³, Kerosene 1 cm³

D2EHPA in high content give the distribution ratios in high degree.

Effect of temperature.   The extraction of uranium with kerosene, biphenyl, naphthalene and biphenyl-naphthalene were examined as a function of temperature. Fig. 8 represents the variation of log D for uranium against the inverse of the absolute temperature for various initial extractant concentrations. It is found that the distribution ratio decreases with increasing temperature. It seems that the extraction reaction may be proceeded exothermically.

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