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Synergistic Effects in the Extraction of Uranium(VI) by Di-4-octylphenyl Phosphoric Acid

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Abstract

The extraction of uranium(VI) from sulfuric acid solutions by di-4-octylphenyl phosphoric acid (DOPPA) is enhanced by the addition of neutral organophosphorus compounds due to synergistic action. The effect of tri-*n*-butyl phosphate (TBP), dibutylbutyl phosphonate (DBBP), and tri-*n*-octyl phosphine oxide (TOPO) was studied. The synergistic effect increased in this order. In the case of TBP and DBBP the extraction coefficient for U(VI) decreased with increasing concentration of synergistic agent after reaching a maximum. With TOPO, on the other hand, there was an increase even after this limit. This was because of the extraction of uranium by TOPO itself. The effect of uranium loading in the organic phase on the synergistic behavior was studied and the results were compared with those obtained with di-2-ethylhexyl phosphoric acid (DEHPA) in the presence of the same synergistic agents. The results with these two extractants indicate that with TOPO the synergism is mainly due to the formation of substitution products of the type $UO_2A_2B_2$ and with TBP addition products of the type $UO_2(HA_2)_2B$.

INTRODUCTION

Extraction of uranium(VI) from mineral acid solutions by di-4-octylphenyl phosphoric acid (DOPPA) was discussed in an earlier paper (*1*). As in the case of dialkyl phosphoric acids (*2*, *3*), enhanced synergistic extraction is observed with DOPPA in the presence of neutral organophosphorous compounds. This aspect is reported here along with a discussion of the possible mechanism.

EXPERIMENTAL

Extraction tests were made by equilibrating equal volumes of aqueous uranyl sulfate solutions and organic phases of predetermined composition for 15 min at ambient temperature, allowing the two layers to separate and analyzing the aqueous layer for residual uranium by spectrophotometric (*4*) or by fluorimetric (*5*) methods. In each case the extraction coefficient

$$E_u = \frac{\text{total uranium concentration in the organic phase}}{\text{total uranium concentration in the aqueous phase}}$$

was calculated.

The three neutral organophosphorous compounds tri-*n*-butyl phosphate (TBP), dibutylbutyl phosphonate (DBBP), and tri-*n*-octyl phosphine oxide (TOPO) were used as synergistic agents and heptane as diluent for the organic phase.

RESULTS AND DISCUSSION

Effect of TBP, DBBP, and TOPO Concentration

The extraction of U(VI) from 4 N H_2SO_4 with 0.025 to 0.10 F DOPPA in the presence of varying concentrations of the synergistic agents was carried out. In each case ΔE_u, the increase in the extraction coefficient caused by the addition of the synergistic agent over what is obtained in its absence, is calculated. The results presented in Figs. 1 and 2 show that ΔE_u shows a maximum. In the case of TBP and DBBP, beyond this concentration there is only a gradual decrease of ΔE_u. However, in the case of TOPO the trend is reversed after a certain concentration.

In the case of extraction of a ternary complex represented by a general reaction

$$M_{(a)} + cA_{(o)} + dB_{(o)} \rightleftarrows (MA_cB_d)_o \qquad (1)$$

Where (a) and (o) represent the aqueous and organic phases, respectively. It was shown by Baes (*6*) that

$$\left(\frac{\delta \log \Delta E_u}{\delta \log [B]}\right)_{[A]} = d$$

and

$$\left(\frac{\delta \log \Delta E_u}{\delta \log [A]}\right)_{[B]} = c$$

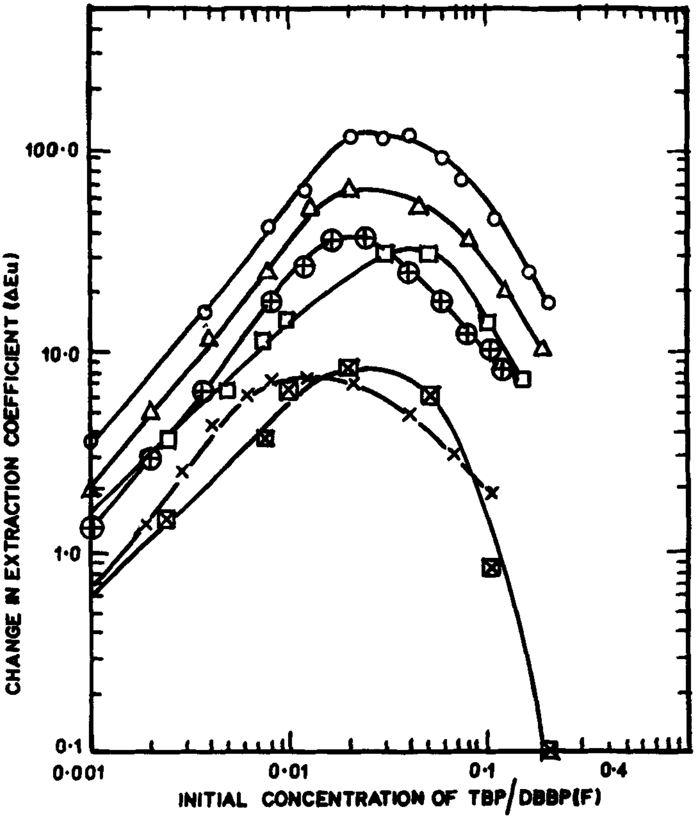

Fig. 1. Effect of TBP/DBBP on the extraction of uranium with DOPPA. In all cases, organic 25 ml and aqueous 25 ml of 0.0035 M uranium in 4 N H_2SO_4. (□) 0.1 F and (⊠) 0.05 F DOPPA with TBP as synergistic agent. (○) 0.1 F, (△) 0.075 F, (⊕) 0.05 F, and (×) 0.025 F DOPPA with DBBP as the synergistic agent.

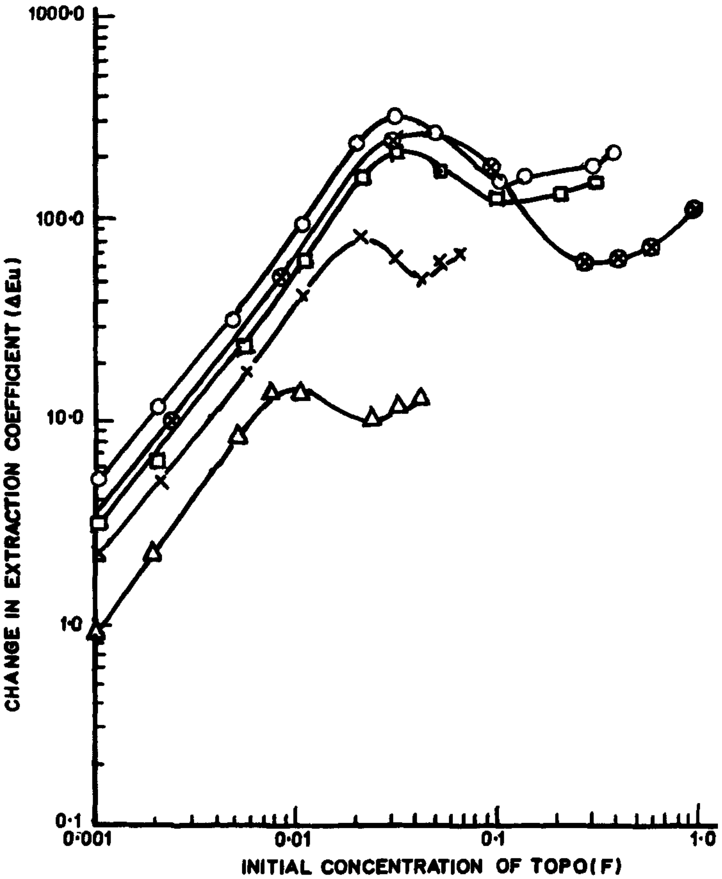

FIG. 2. Effect of TOPO on the extraction of uranium with DOPPA and DEHPA. Organic: 25 ml 0.1 *F* DOPPA (○), 0.1 *F* DEHPA (⊗), 0.075 *F* DOPPA (□), 0.05 *F* DOPPA (×) and 0.025 *F* DOPPA (△) with varying concentrations of TOPO. Aqueous: 25 ml 0.0035 *M* uranium in 4 *N* H_2SO_4 for DOPPA and 0.0035 *M* uranium in 3 *N* H_2SO_4 for DEHPA.

On this basis log ΔE_u vs log [B] (where B = synergistic agent) plots should show a slope of $+d$ before ΔE_u reaches a maximum. The results presented in Figs. 1 and 2 show a slope of +1 for this part of the curves. The general decrease in ΔE_u with further increases in the concentration of synergistic agent has been explained (*3*) on the basis of interaction between the acidic extractant and the neutral molecule. Blake and co-workers (*7*) reported that for U(VI) extraction with DEHPA and neutral organophosphorous compounds, the synergistic effect increases in the order phosphate < phosphonate < phosphinate < phosphine oxide. The results with DOPPA are in line with this.

Effect of DOPPA Concentration

Variation of E_u with DOPPA concentration for a fixed TBP and DBBP concentration is shown in Fig. 3. Since, by themselves, TBP and DBBP extract uranium from sulfate medium to a negligible extent, $E_u \simeq \Delta E_u$, and the observed slope $\simeq +2$ indicates that in the extracted complex $UO_2^{2+}:(HA)_2 = 1:2$. Taking into account the earlier observation on the effect of TBP and DBBP, the extraction mechanism on the basis of Eq. (1), can be shown as

$$UO_2{}^{2+}{}_{(a)} + 2(HA)_{2(o)} + B_{(o)} \rightleftarrows UO_2(HA_2)_2B_{(o)} + 2H^+{}_{(a)} \qquad (2)$$

Effect of Sulfuric Acid Concentration

Since the DOPPA–TOPO system showed a high extraction of uranium, the effect of aqueous sulfuric acid concentration on the extraction coefficient was studied using 0.1 *F* DOPPA + 0.05 *F* TOPO. Log E_u decreased linearly with log [H] over the range 4 to 16 *N*. However, even at 10 *N* acid, E_u was 20, indicating that this synergistic combination can be employed for the extraction of uranium from fairly strong sulfuric acid solution. This also means that stripping of uranium from the organic phase by acid solutions is difficult.

Extraction in Presence of TOPO

When TOPO was used as a synergistic agent the ΔE_u vs TOPO concentration curve showed a maximum and a minimum. The rise in ΔE_u beyond a certain value of TOPO concentration (Fig. 2) is not readily understood. A similar behavior was noted when DEHPA was used as an extracting

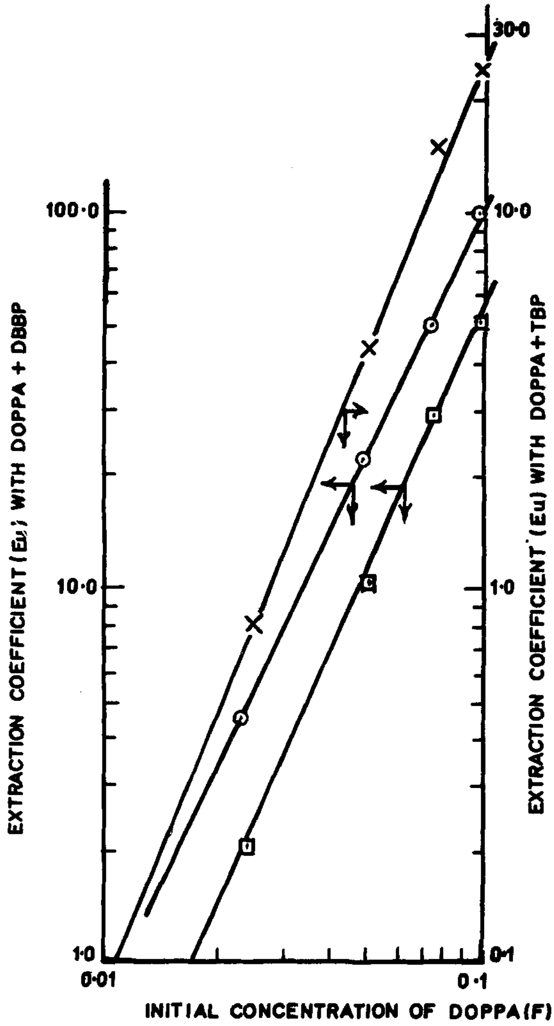

FIG. 3. Effect of DOPPA on the extraction of uranium with TBP or DEBP. Organic: 25 ml. 0.25 *F* TBP (×), 0.05 *F* DBBP (⊡), and 0.1 *F* DBBP (◉) with varying concentrations of DOPPA. Aqueous: 25 ml 0.0035 *M* uranium in 4 *N* H_2SO_4.

agent. However, Blake and co-workers (*7*), who studied the system DEHPA–TBPO (tributyl phosphine oxide) have not reported any such behavior. From other available literature data, no significant difference between TBPO and TOPO is expected. The omission may be due to the limited range of concentration of TBPO employed, 0.2 *F* as compared to 1.0 *F* (TOPO) in the present work. From the data of Blake, Brown, and Coleman (*8*) and those of White and Ross (*9*), there is sufficient evidence for extraction of U(VI) from H_2SO_4 solution by TOPO itself. Deptula (*10*) and Laskorin and co-workers (*11*) investigated extraction of uranium with phosphine oxides and showed that at low aqueous acid concentration (1 *N* H_2SO_4) the species present in the organic phase is $UO_2SO_4 \cdot 2TOPO$ and at 5 *N* H_2SO_4 it is $UO_2SO_4 \cdot 2TOPO \cdot H_2SO_4$. We observed that E_u increased up to an aqueous sulfuric acid concentration of 8 *N* and decreased thereafter (Fig. 4). In 4 *N* H_2SO_4, E_u increased linearly as the second power of [TOPO] in the organic phase (Fig. 5). This observation cannot be used to distinguish between the two species $UO_2SO_4 \cdot 2TOPO$ and $UO_2SO_4 \cdot 2TOPO \cdot H_2SO_4$. To obtain better information, extractions were carried out from aqueous solutions, 6 *N* in H_2SO_4, containing varying concentration of uranium with 0.1 *F* TOPO in heptane. The organic phase in each case was analyzed for uranium, acid, and sulfate. The results, summarized in Table 1, show that with an increase in concentration of uranium in aqueous phase, the uranium concentration in the organic phase increased, the acid concentration remained nearly constant, and the sulfate concentration increased. These observations are in line with the findings of Laskorin and co-workers (*11*) that the organic phase species in the extraction of uranium from 5 *N* H_2SO_4 by TOPO is $(TOPOH^+)_2$-$UO_2(SO_4)_2{}^{2-}$. Saturating 0.1 *F* TOPO in heptane by repeated equilibration with 0.25 *M* uranium in 6 *N* H_2SO_4 and analyzing the resulting organic phase, it was found that $UO_2{}^{2+}:H^+:SO_4{}^{2-}:TOPO$ was 0.5:1:1:1, which agrees with the ion pair formula indicated above. This study has thus confirmed that TOPO itself can extract uranium from sulfuric acid solutions, and explains why in the $UO_2{}^{2+}$–DOPPA–TOPO system no marked antagonistic effect was observed even in the presence of excess TOPO.

Comparison of Synergism in DOPPA and DEHPA Extraction

From Figs. 1 and 2 it can be noted that the concentration of the synergistic agent to obtain a maximum value of ΔE_u depends on DOPPA concentration. In the case of TBP and DBBP the ratio DOPPA:TBP or

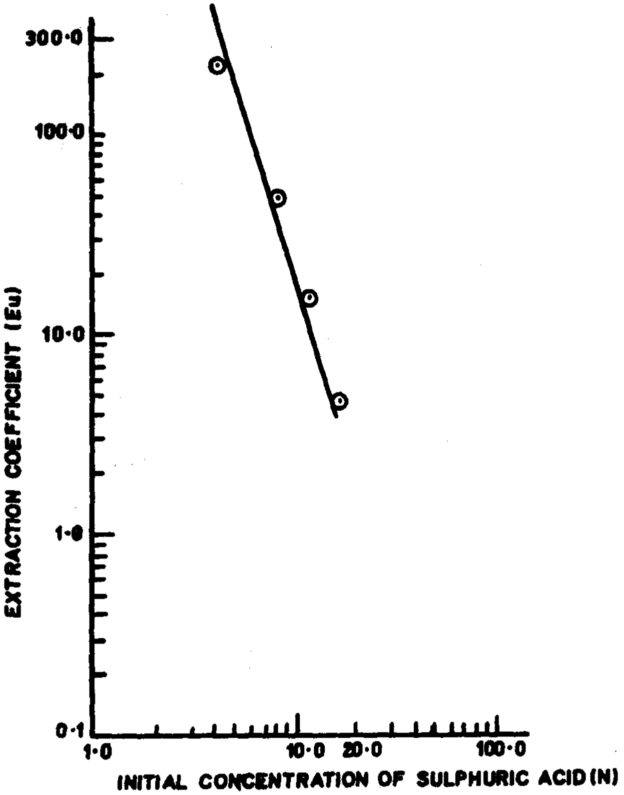

FIG. 4. Effect of sulfuric acid concentration on the extraction of uranium with TOPO. Organic: 25 ml 0.1 *F* TOPO. Aqueous: 25 ml 0.018 *M* uranium with varying concentrations of H_2SO_4.

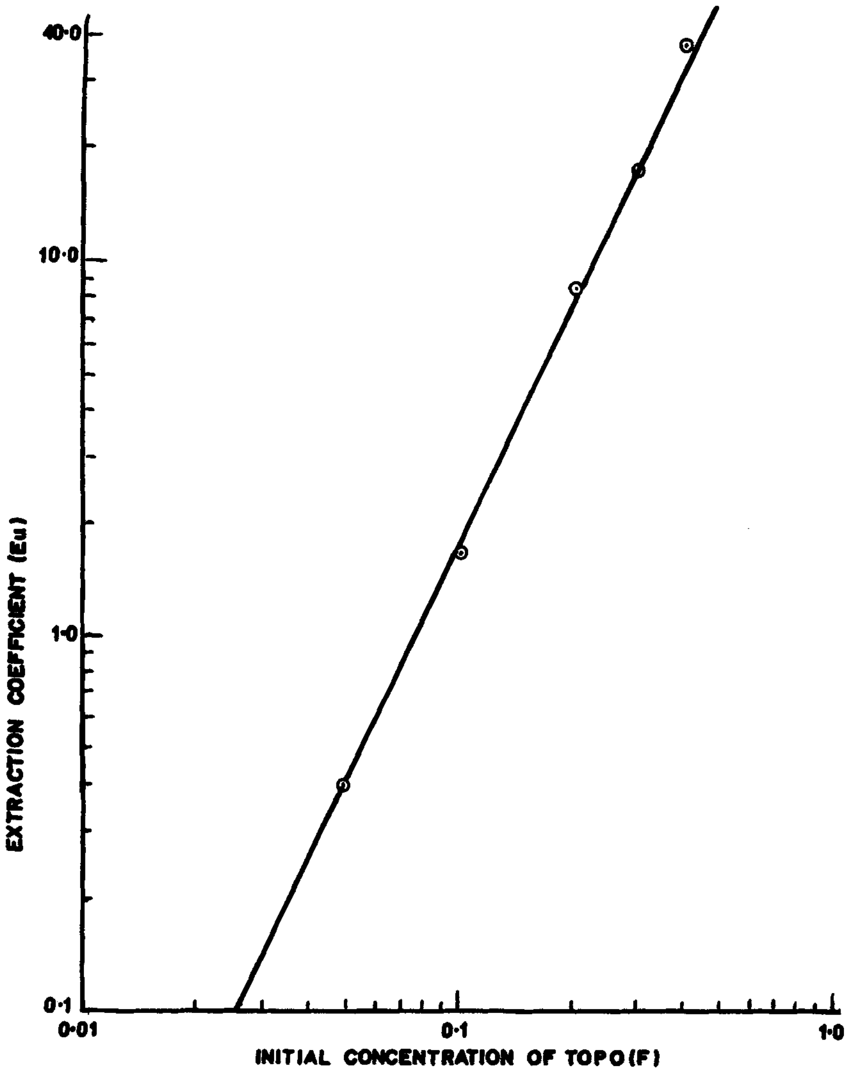

FIG. 5. Effect of TOPO concentration on the extraction of uranium. Organic: 25 ml of varying concentrations of TOPO. Aqueous: 25 ml 0.018 *M* uranium in 4 *N* H_2SO_4.

TABLE 1

Extraction of Uranium from Sulfuric Acid Solution by TOPO[a]

Initial aqueous U conc (M)	Concentration in organic phase			Excess $[SO_4^{2-}]$ over the acid conc, $[SO_4^{2-}]_T - \frac{1}{2}[H^+]$
	U (M)	H^+ (M)	SO_4^{2-}	
0.0	Nil	0.078	0.039	0.0
0.017	0.011	0.076	0.048	0.010
0.034	0.018	0.076	0.052	0.014
0.051	0.023	0.074	0.053	0.016
0.068	0.027	0.074	0.055	0.018
0.085	0.029	0.072	0.057	0.021

[a] Aqueous phase, 6 N H_2SO_4; organic phase, 0.1 F TOPO in heptane; aqueous: organic ratio, 1:1.

DBBP is nearly 2.5:1 for ΔE_umax. For TOPO this ratio is 3:1. For a given concentration of DOPPA, say 0.1 F, ΔE_umax is 36 for TBP, 120 for DBBP, and 300 for TOPO when the aqueous solution was 4 N in H_2SO_4. This is in accordance with the reported relative efficiencies of these reagents as synergistic agents (*7*). In the case of DEHPA the variation of $E_{\max}$ with TBP, DBBP, and TBPO, and the ratio of DEHPA: neutral reagent at $E_{\max}$, was explained by Baes (*12*) in terms of the following equilibria:

$$M(HA_2)_{2(o)} + B_{(o)} \rightleftarrows M(HA_2)_2B_{(o)} \tag{3}$$

with

$$K_2 = \frac{[M(HA_2)_2B]_{(o)}}{[M(HA_2)_2]_{(o)} \cdot [B]_{(o)}}$$

$$H_2A_{2(o)} + B_{(o)} \rightleftarrows H_2A_2B_{(o)} \tag{4}$$

with

$$K_3 = \frac{[(H_2A_2B)]_{(o)}}{[H_2A_2]_{(o)} \cdot [B]_{(o)}}$$

$$H_2A_{2(o)} + 2B_{(o)} \rightleftarrows 2HAB_{(o)} \tag{5}$$

with

$$K_4 = \frac{[HAB]_{(o)}^2}{[H_2A_2]_{(o)} \cdot [B]_{(o)}^2}$$

According to these authors, $E_u$max occurs at lower concentrations of the neutral reagent with increasing K_3 values and its magnitude is nearly

TABLE 2

Concentration of Synergistic Agent Required for $E_{\max}$

Reagent	0.1 *F* DEHPA[a]	0.1 *F* DOPPA
TBP	0.16 *F*	0.04 *F*
DBBP	0.10 *F*	0.04 *F*
TOPO/TBPO	0.046 *F* (TBPO)	0.035 *F*

[a] From Fig. 1 of Ref. *12*.

proportional to K_2. The lower and nearly constant requirement of the synergistic agent in the case of DOPPA (Table 2) for obtaining $E_u$max (or ΔE_umax) is probably due to the high K_3 value in the case of all synergistic agents as compared to DEHPA. For DOPPA–TOPO, according to Zangen (*13*), K_3 is "too high" to be determined. The comparatively higher $E_u$max value for DOPPA than for DEHPA with any given synergistic agent is due to the higher K_2 values in the former case (*13*).

Effect of Uranium Loading in the Organic Phase

In a study of the synergistic effect of TBP in the extraction of uranium from H_2SO_4 solution using DEHPA, Sato (*14*) observed a change from synergistic to antagonistic behavior when uranium loading in the organic phase was greater than 0.25 mole/mole of HA, irrespective of acid and uranium concentration in the aqueous phase. He attributed this effect to the interference of TBP in the formation of polymeric complexes of the type $(UO_2)_nX_{2n+2}H_2$ (*15*). Since this observation was made only with DEHPA and one synergistic agent combination, it was felt that a study of the behavior of other synergistic agents (DBBP and TOPO) and comparison of the results with those using DOPPA would not only be interesting but might throw more light on the factors responsible for this behavior.

Figures 6, 7, and 8 summarize the extraction data with 0.1 *F* DOPPA + 0.05 *F* synergistic agent. The extraction coefficients were determined as a function of initial uranium and acid concentration in the aqueous phase. It can be seen that when the uranium concentration in the aqueous phase is $< 0.025\ M$, only a synergistic effect was observed, irrespective of the nature of the synergistic agent and the aqueous acid concentration. On the other hand, the synergistic behavior changed to antagonistic behavior beyond a certain uranium concentration, depending on the synergistic agent employed. Similar observations were made with DEHPA–synergistic agent systems. The results, summarized in Table 3, show that uranium

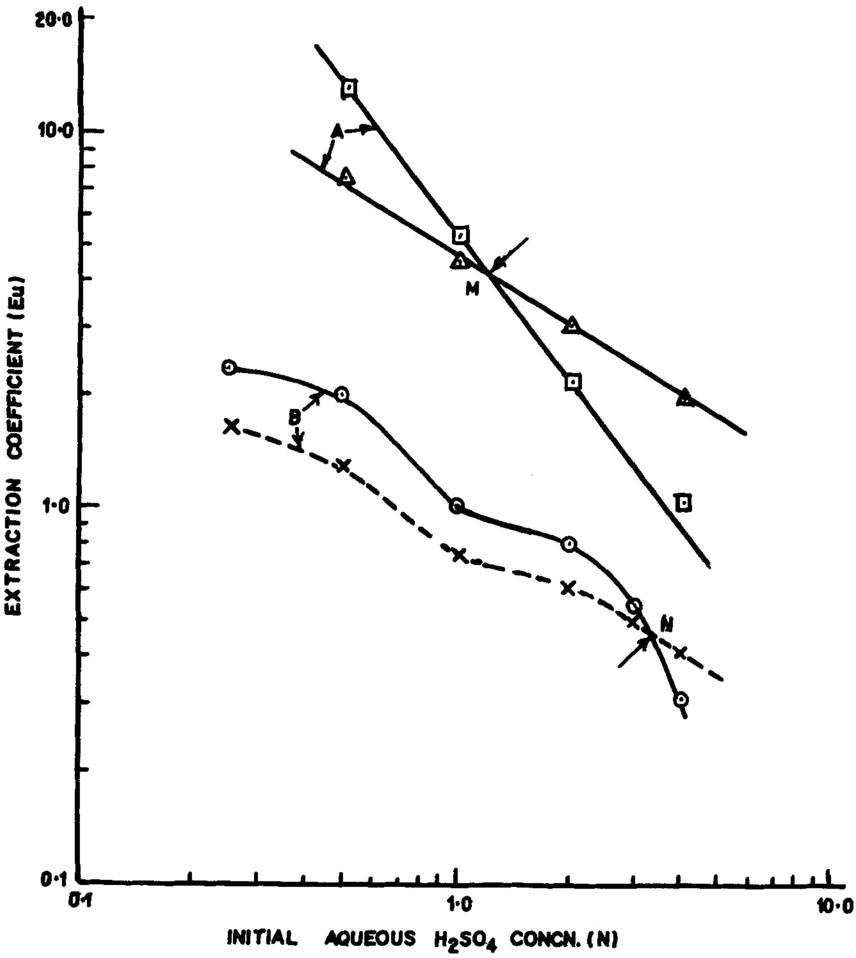

FIG. 6. Effect of uranium loading on the synergism of the DOPPA–TBP system. In all cases, organic 25 ml and aqueous 25 ml with varying [H_2SO_4]. (A) Organic: 0.1 *F* DOPPA (⊡), 0.1 *F* DOPPA + 0.05 *F* TBP (△); aqueous: 0.0312 *M* uranium. (B) Organic: 0.1 *F* DOPPA (◉), 0.1 *F* DOPPA + 0.05 *F* TBP (×); aqueous: 0.085 *M* uranium.

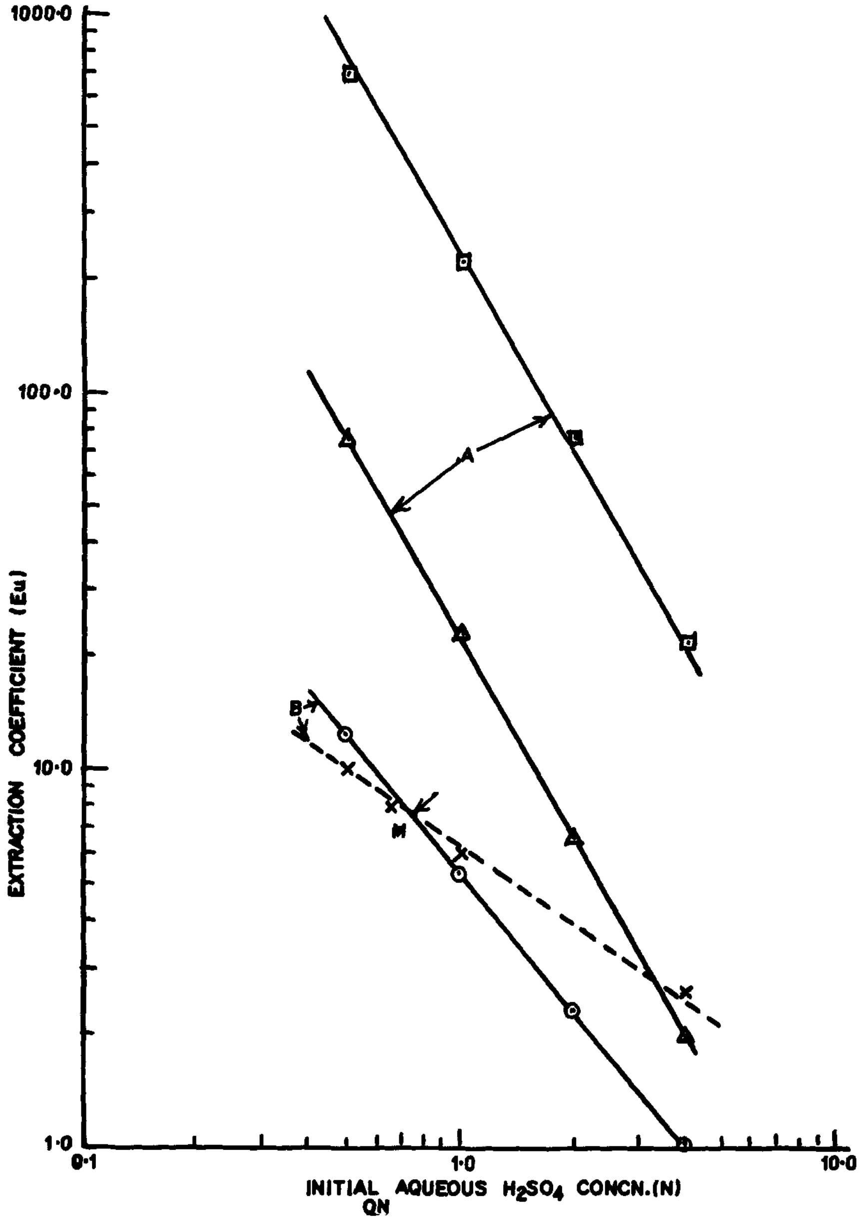

Fig. 7. Effect of uranium loading on the synergism of the DOPPA–DBBP system. In all cases, organic 25 ml and aqueous 25 ml with varying [H_2SO_4]. (A) Organic: 0.1 *F* DOPPA (△), 0.1 *F* DOPPA + 0.05 *F* DBBP (☐); aqueous: 0.02 *M* uranium. (B) Organic: 0.1 *F* DOPPA (◉), 0.1 *F* DOPPA + 0.05 *F* DBBP (×); aqueous: 0.036 *M* uranium.

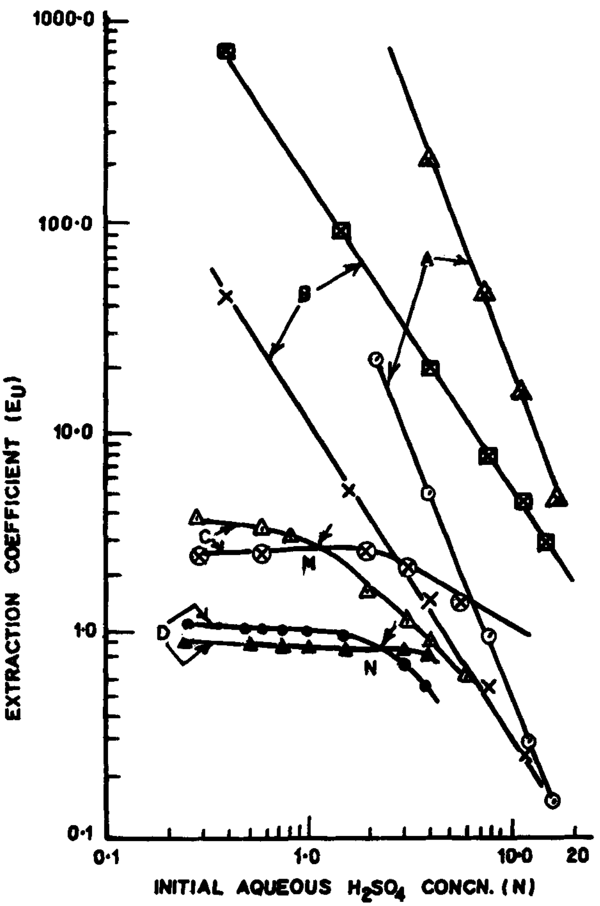

FIG. 8. Effect of uranium loading on the synergism of the DOPPA–TOPO system. In all cases, organic 25 ml and aqueous 25 ml with varying [H_2SO_4]. (A) Organic: 0.1 *F* DOPPA (◉), 0.1 *F* DOPPA + 0.05 *F* TOPO (◬); aqueous: 0.0028 *M* uranium. (B) Organic: 0.1 *F* DOPPA (×), 0.1 *F* DOPPA + 0.05 *F* TOPO (⊠); aqueous: 0.0256 *M* uranium. (C) Organic: 0.1 *F* DOPPA (⊗), 0.1 *F* DOPPA + 0.05 *F* TOPO (◬); aqueous: 0.0511 *M* uranium. (D) Organic: 0.1 *F* DOPPA (●), 0.1 *F* DOPPA + 0.05 *F* TOPO (▲); aqueous: 0.039 *M* uranium.

TABLE 3

Effect of Synergistic Agent and Uranium Loading on Synergism

HA	Neutral reagent	Conc of uranium at synergistic to antagonistic behavior	Mole ratio U:HA
DEHPA (0.1 *F*)	TBP (0.05 *F*)	0.025	0.25
DOPPA (0.1 *F*)	TBP (0.05 *F*)	0.025[a]	0.25
DEHPA (0.1 *F*)	DBBP (0.05 *F*)	0.031	0.31
DOPPA (0.1 *F*)	DBBP (0.05 *F*)	0.033[a]	0.33
DEHPA (0.1 *F*)	TOPO (0.05 *F*)	0.04	0.40
DOPPA (0.1 *F*)	TOPO (0.05 *F*)	0.038[a]	0.38

[a] Points M/N in Figs. 6, 7, and 8.

loading in the organic at which synergism changes to antagonism is dependent on the synergistic agent and not much on the extractant (DEHPA or DOPPA) used. With TBP, U: extractant was 0.25: 1 at this point, while with TOPO it was 0.4: 1. If the explanation offered by Sato (*14*) is to be accepted, it is difficult to explain the situation since TOPO, with its better coordinating ability, is expected to interfere more seriously in the formation of polymeric UO_2–DOPPA/DEHPA complexes and the uranium-to-extractant mole ratio would not have exceeded 0.25: 1. On the other hand, the change in behavior between TBP and TOPO can be explained satisfactorily based on a change in the mechanism of synergism itself, i.e., from an addition to a substitution mechanism. In the case of TBP the extracted complex may be of the type $(UO_2H_2A_4)B$ (addition mechanism), while in the case of TOPO it may be closer to the type UO_2A_2-$B_{1 or 2}$ (substitution mechanism). From their studies, Liem and co-workers (*16–18*) concluded that in dialkyl phosphoric acid–neutral organophosphorous extraction systems, both addition and substitution types of uranyl species may be formed depending on the extraction conditions and the nature of the neutral component. For example, in the UO_2^{2+}–DBP (dibutyl phosphoric acid)–TBP system they found, at low concentrations of TBP, evidence for the presence of complexes of the type $UO_2(HA_2)_2B$ only. When the P=O group in the neutral compound is more basic than in TBP, as in TOPO, their analysis revealed only substitution-type compounds like $UO_2A_2(HA)B$ and $UO_2A_2B_2$. Similar behavior in the DOPPA–TOPO system can be expected, in which case the synergistic effect should be noticed up to a UO_2^{2+} : DOPPA mole ratio of 0.5: 1.0 (in the case of UO_2A_2B). In an ideal case, therefore, there should be no change to antagonistic behavior. The observed behavior with TOPO is that the change takes place at UO_2^{2+}:DOPPA = 0.4:1.0. This result can be interpreted as arising out of the essentially substitution mechanism of the synergistic action with only a minor contribution from the addition mechanism. On the other hand, the change to the antagonistic behavior taking place with TBP when UO_2^{2+}:DOPPA is as low as 0.25:1.0 is evidence for a predominantly addition mechanism. The behavior of DBBP where the change takes place at UO_2^{2+}:DOPPA = 0.33:1.0 is to be attributed to the simultaneous action by both mechanisms. This is in line with the general observation of Liem and co-workers mentioned above. Therefore, the changes in the synergistic behavior observed with the three neutral organophosphorous compounds provide a reasonably good picture of the synergistic mechanism and they cannot be attributed to interference in the formation of polymeric species, as hinted by Sato.

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