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Study of Mono-(2-ethylhexyl) Phosphoric Acid and Neutral Organophosphorus Synergists for Extraction of Uranium from Phosphoric Acid Solution

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Abstract

The distribution of uranium(IV) and uranium(VI) between phosphoric acid solution and mono-(2-ethylhexyl) phosphoric acid (H_2MEHP)–trioctyl phosphine oxide (TOPO), and mono-(2-ethylhexyl) phosphoric acid–dibutyl butyl phosphonate (DBBP) in kerosene diluent has been investigated. The effects of extractant composition, phosphoric acid concentration, temperature, uranium concentration, and shaking time on the uranium extraction have been examined. Reductive extraction and oxidative stripping processes for the separation and concentration of uranium from phosphoric acid solution with synergic systems of H_2MEHP–TOPO and H_2MEHP–DBBP are proposed and discussed.

INTRODUCTION

Wet-process phosphoric acid contains a significient amount of uranium, typically about 0.1 to 0.2 g/L. Apart from being economically favorable, recovery of uranium as a by-product of phosphate fertilizer production supplies part of the world's nuclear fuel resources and reduces environmental contamination. The recovery of uranium from phosphoric acid has been investigated by several workers (*1–7*), but the most promising processes are those based on solvent extraction separation using acidic and neutral organophosphorus compounds (*4–7*). Ordinary uranium extractants such as tributyl phosphate and long-chain alkyl amines cannot be used because they do not have enough extraction power to extract the very low concentration of uranium in the high concentration of phosphoric acid medium (4–6 *M*). Solvent extraction using mono-(2-ethylhexyl) phosphoric acid (H_2MEHP), $(C_2H_5 \cdot C_6H_{12}O)PO(OH)_2$, has been studied previously by Peppard (*8*) for extraction of M(III) lanthanides from HCl medium. Study of the separation of uranium from phosphoric acid solution with H_2MEHP and neutral organophosphorus synergists has not been reported. The object of this paper is to establish the basic extraction and separation conditions for the recovery of uranium from phosphoric acid solution with H_2MEHP–TOPO–kerosene and H_2MEHP–DBBP–kerosene synergist extraction systems.

EXPERIMENTAL

Purification and Identification of H_2MEHP

The mono-(2-ethylhexyl) phosphoric acid and di-(2-ethylhexyl) phosphoric acid mixture (58.61% HDEHP and 36.62% H_2MEHP) was obtained from Tokyo Kasei Kogyo Co. (Japan). A portion of the mixture was stirred with an equal volume of 2 *M* HCl at 80°C for 4 h. The aqueous hydrochloric acid phase was discarded and the cooled organic phase was washed with water to remove the major fraction of the HCl content. This washed mixture was then neutralized by the addition of 10% Na_2CO_3. The upper phase contained the major portion of the HDEHP and the lower phase contained the major portion of the H_2MEHP. The lower phase was acidified with HCl and then purified by extraction with diethyl ether.

The final product purity of H_2MEHP was >99% which was determined by titration with standard NaOH solution in a 80% ethanol–20% water medium using a Metrohm Herisau model E-512 titrator. U(IV) solution was prepared by zinc amalgam reduction of uranyl nitrate (*9*). All the other chemicals were analytical reagent grade.

Extraction Procedure

Equal volumes of aqueous and organic solution (10 mL each) were shaken in a 50-mL glass separating funnel or flasks with an electric shaker. After completion of the extraction period, the phases were allowed to settle. The uranium concentration in the equilibrium aqueous and organic phases were determined by spectrophotometry (*10*, *11*) and fluorometry (*12*). A thermostatted shaker was used to study the effect of temperature (20–70°C) on the extraction. The temperature fluctuation was within ±1°C. The experimental results are expressed in terms of extraction coefficient (*D*):

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

RESULTS AND DISCUSSION

Effect of Shaking Time on the Extraction of Uranium

The shaking time for the extraction of uranium(IV) and uranium(VI) from phosphoric acid solution was obtained with different extraction systems as shown in Figs. 1 and 2. The results indicate that the equilibrium uranium concentration in the aqueous and organic phases was obtained with 5 min of shaking. Five to eight minutes were required for separation of the two phases by gravity. This is about 2 to 3 min longer than the HDEHP extraction system. These values were maintained constantly throughout this investigation. A tendency toward formation of emulsions in the H_2MEHP extraction system has not been observed.

Synergic Effect of Neutral Organophosphorus Compounds

The effect of adding dibutyl butyl phosphonate $[C_4H_9 \cdot (C_4H_9O)_2PO]$ and trioctyl phosphine oxide to 0.5 and 0.2 *M* H_2MEHP solutions on the

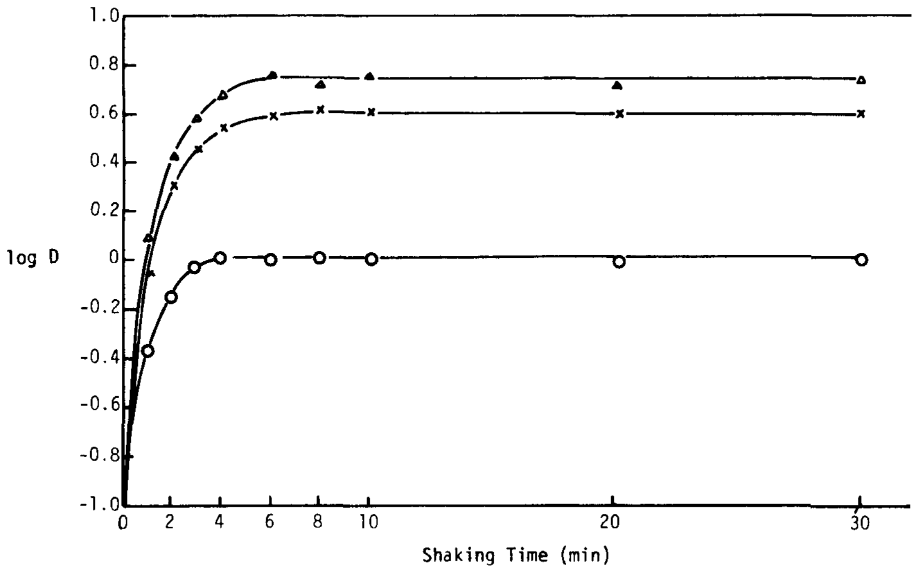


FIG. 1. Extraction coefficient as a function of shaking time on uranium(IV) extraction in different extraction systems. (▲) 0.5 *M* H_2MEHP–0.125 *M* TOPO–kerosene; (X) 0.5 *M* H_2MEHP–0.1 *M* DBBP-kerosene; (O) 0.5 *M* H_2MEHP-kerosene; uranium concentration: 4.2×10^{-4} *M*; phosphoric acid concentration: 6 *M*; temperature: 20 ± 1°C.

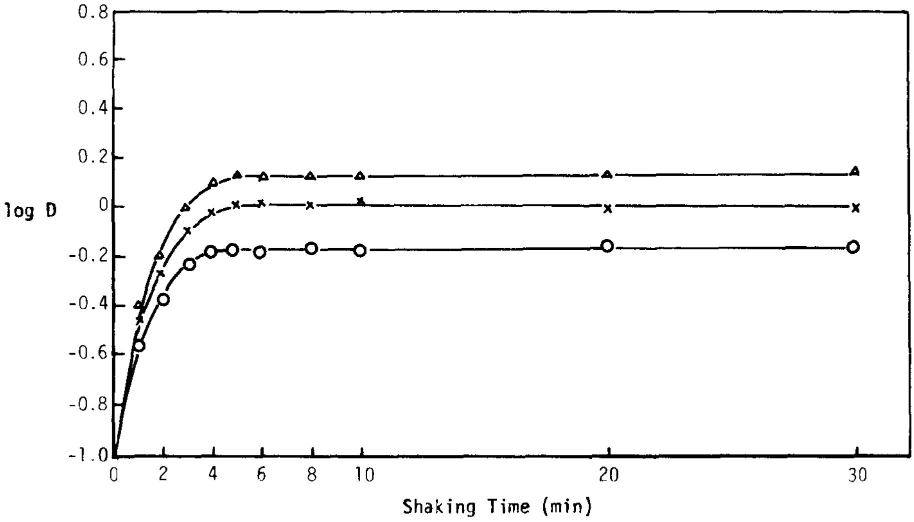


FIG. 2. Extraction coefficient as a function of shaking time on uranium(VI) extraction in different extraction systems. (▲) 0.5 *M* H_2MEHP–0.125 *M* TOPO–kerosene; (X) 0.5 *M* H_2MEHP–0.1 *M* DBBP–kerosene; (○) 0.5 *M* H_2MEHP–kerosene; uranium concentration: 4.2×10^{-4} *M*; phosphoric acid concentration: 6 *M*; temperature: 20 ± 1°C.

extraction power for uranium in 6 *M* phosphoric acid at 20 ± 1°C was examined as shown in Figs. 3 and 4. An immediate increase in extraction ability or synergistic effect is observed when TOPO and DBBP are added with H_2MEHP in kerosene solution. The synergistic enhancement of extraction of U(IV) and U(VI) suggests the more stable complex formation between uranium–H_2MEHP–TOPO and uranium–H_2MEHP–DBBP. After reaching a maximum distribution coefficient, the antagonistic effects are observed. This is probably due to the competition reaction with adduct formation between TOPO–H_2MEHP and DBBP–H_2MEHP through hydrogen bond formation to reduce the concentration of effective extractant. Figures 3 and 4 show that the maximum distributions occur at TOPO/H_2MEHP and DBBP/H_2MEHP mole ratios equal to 1/4 and 1/5, respectively. For both U(IV) and U(VI) extraction the experimental results indicate that the synergistic effect of H_2MEHP–TOPO is larger than that of H_2MEHP–DBBP. This is due to the fact that the base strength of TOPO(R_3PO) is higher than the base strength of DBBP(R′(R′O)$_2$PO). This result is an agreement with Blake's report (*13*) for the dialkyl–phosphoric acid extraction system. Figures 3 and 4 also reveal that the synergistic extraction effect of H_2MEHP–TOPO and H_2MEHP–DBBP on U(IV) is larger than on U(VI). These results suggest that the recovery of uranium from phosphoric

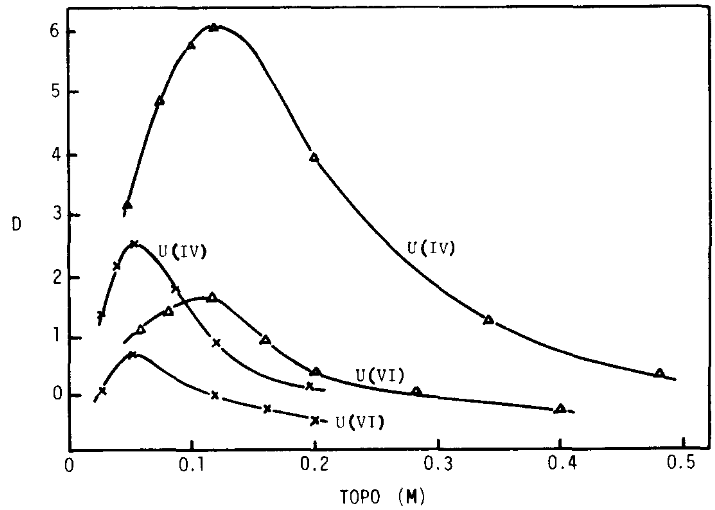


FIG. 3. Effect of TOPO/H_2MEHP ratio on uranium extraction. (▲) 0.5 *M* H_2MEHP–kerosene; (X) 0.2 *M* H_2MEHP; uranium concentration: 4.2×10^{-4} *M*; phosphoric acid concentration: 6 *M*; temperature: 20 ± 1°C.

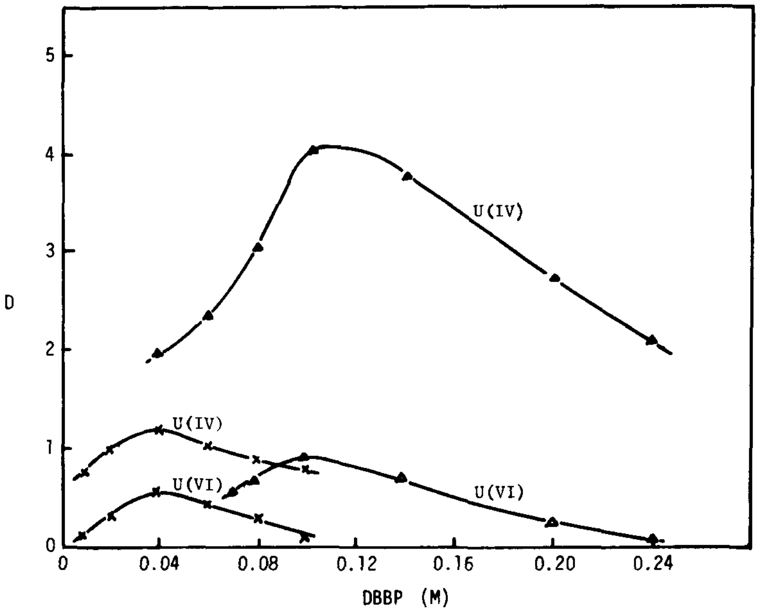


FIG. 4. Effect of DBBP/H_2MEHP ratio on uranium extraction. (▲) 0.5 *M* H_2MEHP–kerosene: (X) 0.2 *M* H_2MEHP; uranium concentration: 4.2×10^{-4} *M*; phosphoric acid concentration: 6 *M*; temperature: 20 ± 1°C.

acid by H_2MEHP–TOPO and H_2MEHP–DBBP extraction should be carried out in the U(IV) state.

Effect of Phosphoric Acid Concentration

The effects of phosphoric acid concentration on U(IV) and U(VI) extraction with H_2MEHP, H_2MEHP–TOPO, and H_2HEHP–DBBP are shown in Figs. 5 and 6. The distribution ratio decreases very rapidly with increasing phosphoric acid concentration. The decrease of the distribution ratio for U(IV) and U(VI) at higher acidity exhibits the existence of more complex species, such as $U(H_2PO_4^{4-n})_n$ and $UO_2(H_2PO_4^{2-n})_n$, in the aqueous solutions. Similar results have been observed by Hurst (*6*) and Bunus (*14*) for the HDEHP–TOPO–kerosene extraction of U(VI). The experimental results show that the uranium distribution ratio is 1.25 and 0.8 for extraction of U(IV) and U(VI) from 6 *M* H_3PO_4 at 20°C with 0.5 *M* H_2MEHP. Figures 5

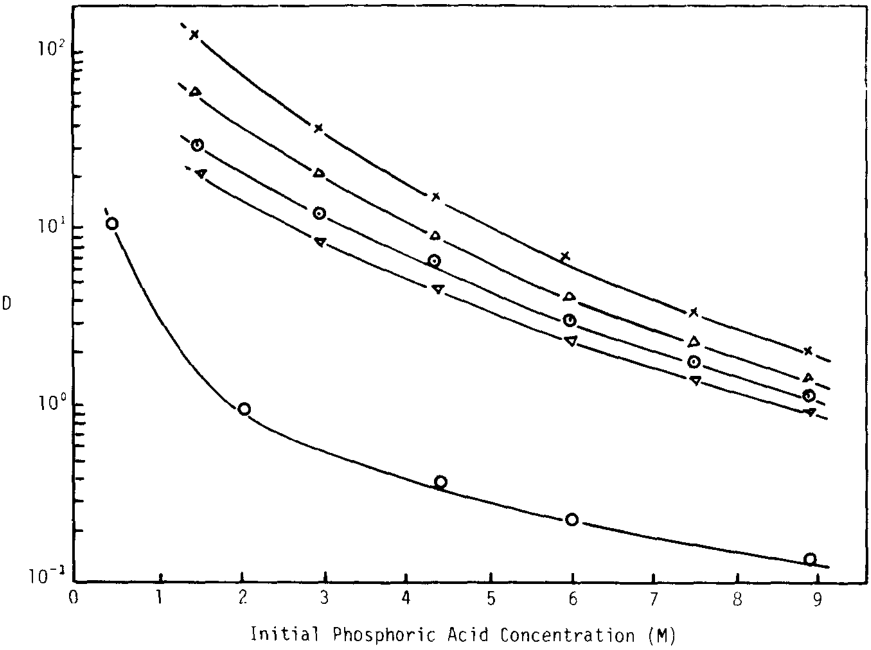


FIG. 5. Effect of H_3PO_4 concentration of uranium(IV) extraction in different extraction systems. (×) 0.5 *M* H_2MEHP–0.125 *M* TOPO–kerosene; (△) 0.5 *M* H_2MEHP–0.1 *M* DBBP–kerosene; (⊙) 0.2 *M* H_2MEHP–0.05 *M* TOPO–kerosene; (▽) 0.2 *M* H_2MEHP–0.04 *M* DBBP–kerosene; (○) 0.5 *M* H_2MEHP; uranium concentration: 4.2 × 10^{-4} *M*; temperature: 20 ± 1°C.

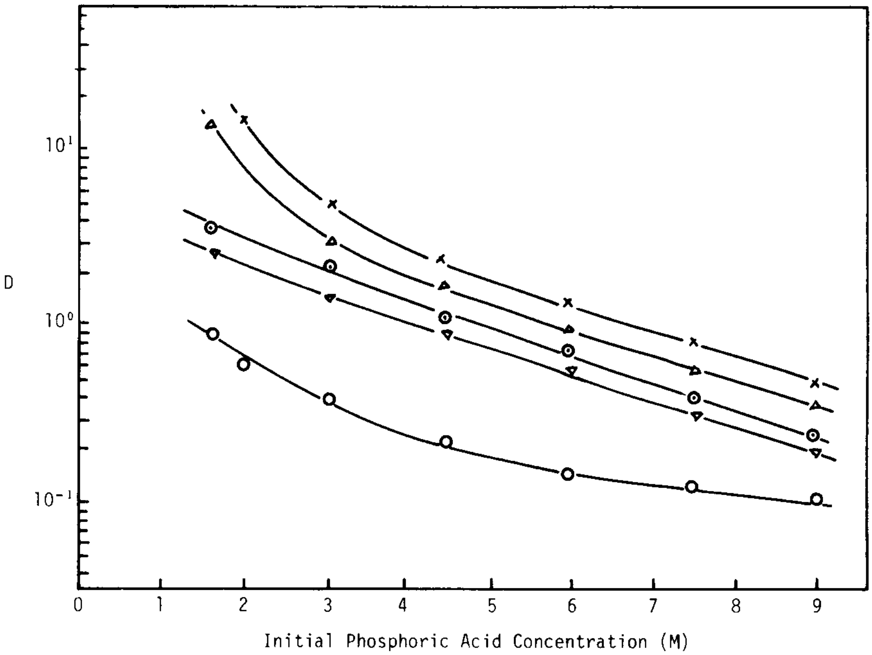


FIG. 6. Effect of H_3PO_4 concentration on uranium(VI) extraction in different extraction systems. (×) 0.5 *M* H_2MEHP–0.125 *M* TOPO–kerosene; (△) 0.5 *M* H_2MEHP–0.1 *M* DBBP–kerosene; (⊙) 0.2 *M* H_2MEHP–0.05 *M* TOPO–kerosene; (▽) 0.2 *M* H_2MEHP–0.04 *M* DBBP–kerosene; (○) 0.5 *M* H_2MEHP; uranium concentration: 4.2×10^{-4} *M*; temperature: 20 ± 1°C.

and 6 also indicate that the distribution ratio of U(IV) is higher than that of U(VI) at the same extraction condition. Figure 5 reveals that U(IV) in a phosphoric acid concentration of 4–6 *M* can be extracted to the organic phase with H_2MEHP–TOPO or H_2HEHP–DBBP. Figure 6 shows that the distribution ratio of U(VI) at higher acidity (>7 *M*) is less than 1. Therefore, based on the distribution ratio variation of uranium in different oxidation states and at different phosphoric acid concentrations, the U(IV) in the phosphoric acid solution can be extracted with H_2MEHP–TOPO or H_2HEHP–DBBP and stripped as U(VI) from the organic phase with concentrated phosphoric acid solution.

Effect of Temperature

Figures 7 and 8 show the temperature effect for the extraction of U(IV) and U(VI) from 6 *M* H_3PO_4 with 0.5 *M* H_2MEHP–0.1 *M* DBBP and 0.5 *M*

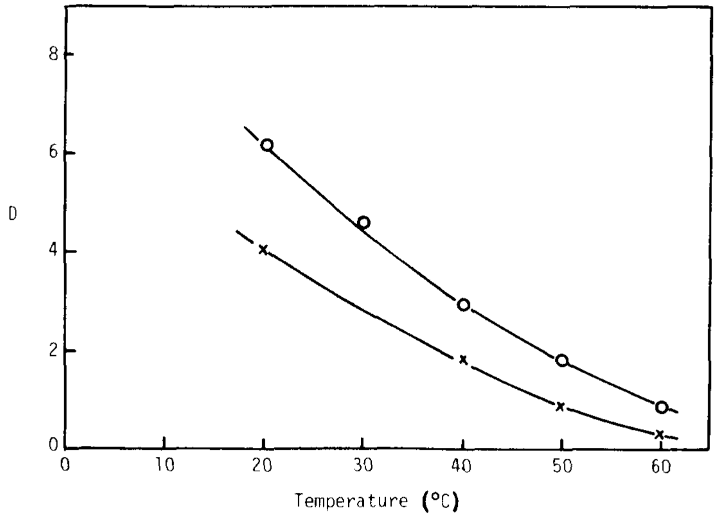


FIG. 7. Effect of temperature on uranium(IV) extraction from 6 *M* H_3PO_4 with different extraction systems. (○) 0.5 *M* H_2MEHP–0.125 *M* TOPO; (×) 0.5 *M* H_2MEHP–0.1 *M* DBBP; uranium concentration: 4.2×10^{-4} *M*.

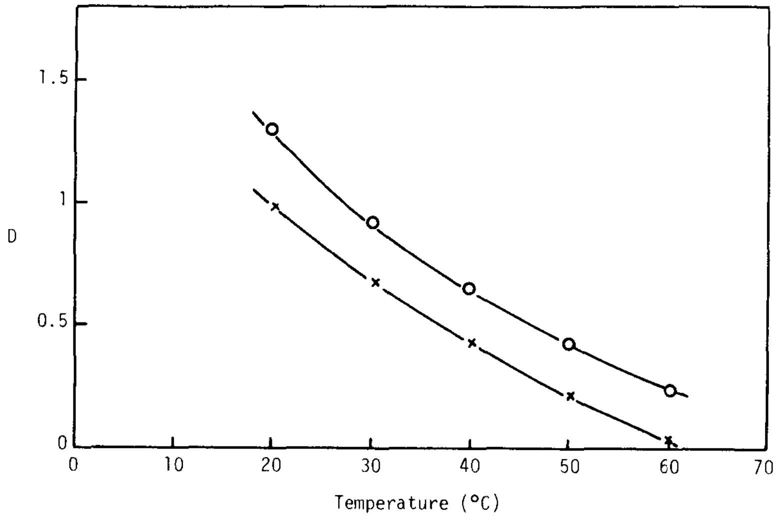


FIG. 8. Effect of temperature on uranium(VI) extraction from 6 *M* H_3PO_4 with different extraction systems. (○) 0.5 *M* H_2MEHP–0.125 *M* TOPO; (×) 0.5 *M* H_2MEHP–0.1 *M* DBBP; uranium concentration: 4.2×10^{-4} *M*.

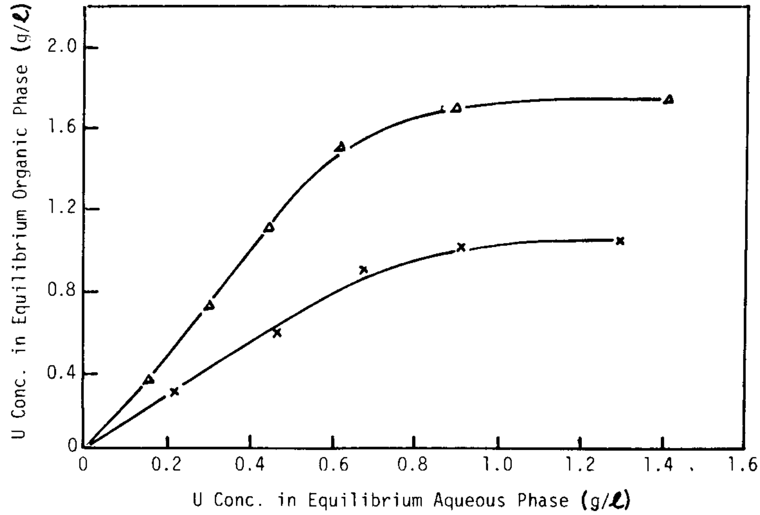


FIG. 9. Isotherms of U(IV) extraction with H_2MEHP-TOPO-kerosene. (△) 0.5 *M* H_2MEHP-0.125 *M* TOPO-kerosene; (×) 0.2 *M* H_2MEHP-0.05 *M* TOPO-kerosene; phosphoric acid concentration: 6 *M*; temperature: 20 ± 1°C.

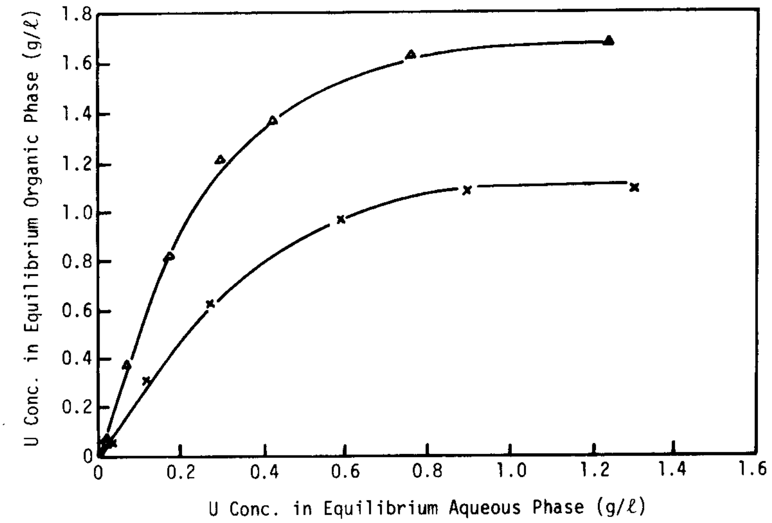


FIG. 10. Isotherms of U(IV) extraction with H_2MEHP-DBBP-kerosene. (▲) 0.5 *M* H_2MEHP-0.1 *M* DBBP-kerosene; (×) 0.2 *M* H_2MEHP-0.04 *M* DBBP-kerosene; phosphoric acid concentration: 6 *M*; temperature: 20 ± 1°C.

H_2MEHP–0.125 *M* TOPO in kerosene. The experimental results indicate that the distribution ratio decreases rapidly with increasing temperature from 20 to 60°C. Figures 7 and 8 suggest that the uranium extracted in the organic phase can be easily stripped out at higher temperature. Figure 8 shows that at 50°C the distribution ratios for extraction of U(VI) from 6 *M* H_3PO_4 with H_2MEHP–TOPO and H_2HEHP–DBBP are 0.42 and 0.20, respectively. The above experimental results show that U(IV) in the phosphoric acid can be extracted with the synergistic extractant of H_2MEHP–TOPO or H_2HEHP–DBBP in kerosene and that U(VI) can be stripped from the organic phase with a high concentration of phosphoric acid (e.g., >8 *M*) at high temperature (e.g., 50°C).

Isotherms and Separation of Uranium from Phosphoric Acid Solution

Figures 9 and 10 show some of the typical extraction isotherms for U(IV) with H_2MEHP–TOPO and H_2HEHP–DBBP in kerosene, and Fig. 11 shows the stripping McCabe diagram for U(VI) with concentrated phosphoric acid. Based on the previous experimental results, a reductive extraction and oxidation stripping process for the recovery of uranium from phosphoric acid solution has been proposed as shown in Fig. 12. The synergistic extractants of H_2MEHP–TOPO or H_2MEHP–DBBP in kerosene are used. With the experimental data and McCabe-Thiele's graphical method, the extraction and stripping parameters for the proposed process can be summarized as shown in Table 1. The number of required reductive extraction stages are 5 and 9 for 98% uranium extraction recovery with 0.5 *M* H_2MEHP–0.125 *M* TOPO and 0.5 *M* H_2MEHP–0.1 *M* DBBP at 0.1 g/L uranium feed concentration. The number of required oxidative stripping stages are 4 and 3 for 98% uranium stripping recovery with 12 *M* H_3PO_4 from 0.5 *M* H_2MEHP–0.125 *M* TOPO and 0.5 *M* H_2MEHP–0.1 *M* DBBP in kerosene. In this extraction and stripping operation the feed uranium in the 6 *M* phosphoric acid is separated and concentrated about 210 times. The uranium concentration changes from 0.1 to 20.16 g/L. This product uranium solution can be further purified with a second purification cycle in the D_2T process as suggested by Hurst (*6*). For practical application of the proposed flow sheets, further laboratory batch and bench scale experiments have to be performed with wet-process phosphoric acid from a phosphoric acid plant.

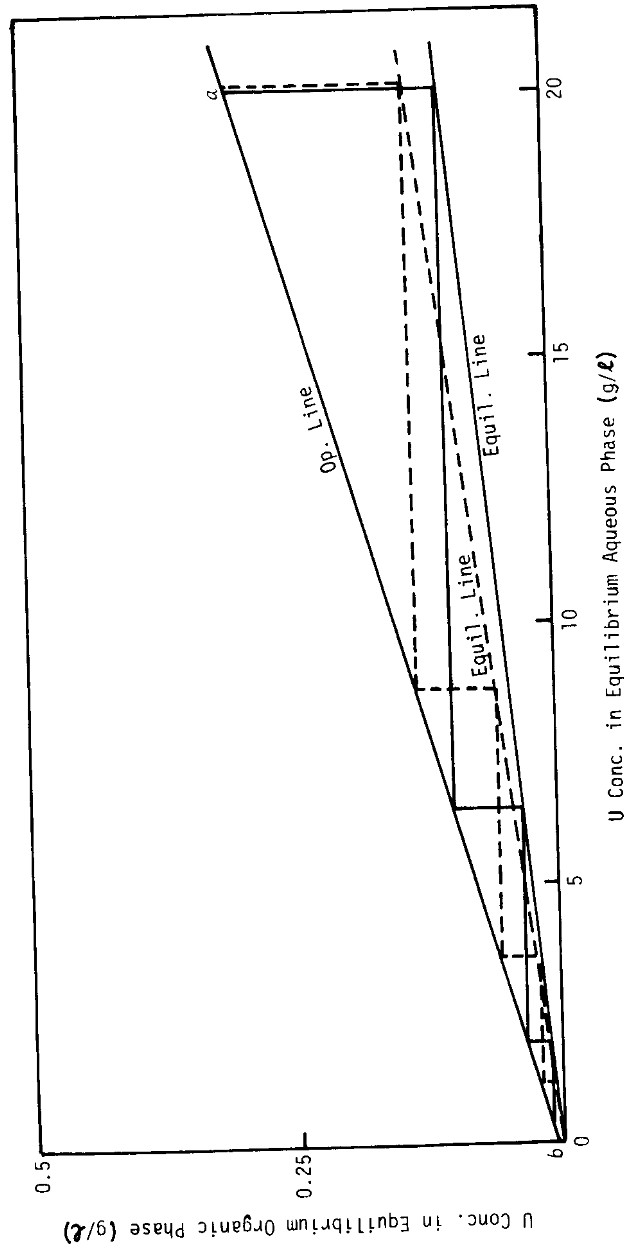
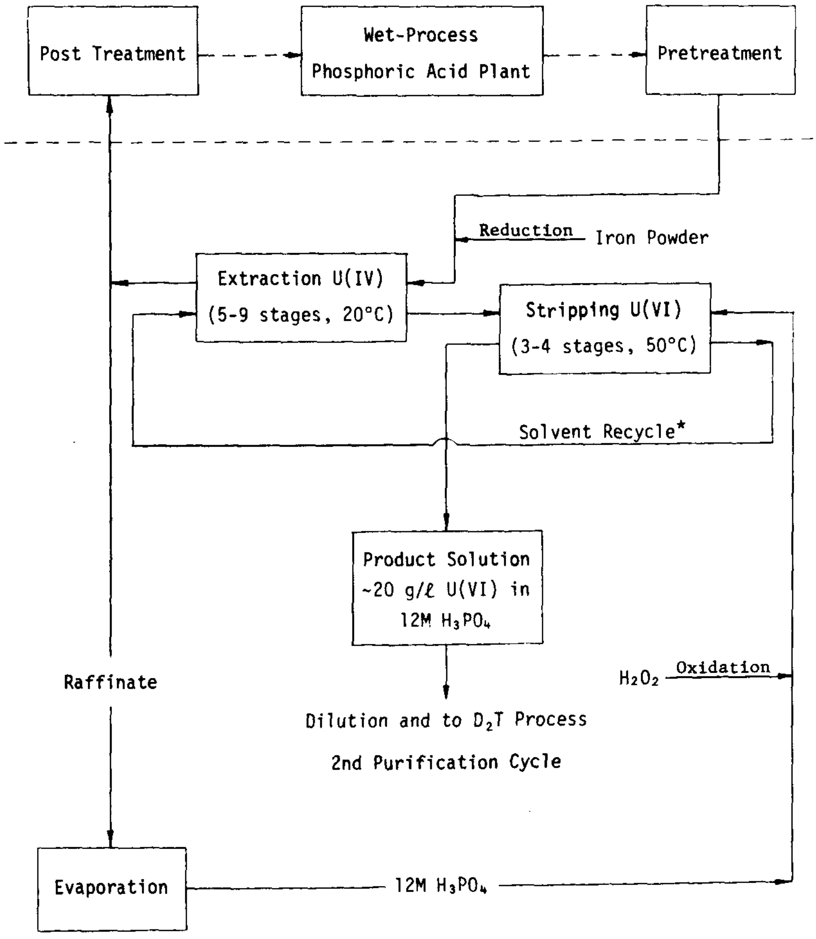


FIG. 11. McCabe-Thiele diagram for uranium(IV) stripping with 12 *M* H_3PO_4: (— —) 0.5 *M* H_2MEHP–0.1 *M* DBBP; (- -) 0.5 *M* H_2MEHP–0.125 *M* TOPO; temperature: 50°C; *a*: (20.16, 0.294); *b*: (0, 0.006); $V_a/V_0 = 70$; slope of operation line = 1/70.

TABLE 1

Summary of Extraction and Stripping Parameters

Type of operation	Extractant	Distribution coefficient at $V_0/V_a = 1$	No. of stages required	V_a/V_0	H_3PO_4 conc (M)	Operation temperature (°C)	Uranium recovery (%)
Extraction	0.5 M H_2MEHP–0.125 M TOPO	6.25	5	3	6	20	98
	0.5 M H_2MEHP–0.1 M DBBP	4.10	9				
Stripping	0.5 M H_2MEHP–0.125 M TOPO	6.6×10^{-3}	4	70	12	50	98
	0.5 M H_2MEHP–0.1 M DBBP	4.6×10^{-3}	3				



* (1) 0.5M H_2MEHP-0.125M TOPO-Kerosene

(2) 0.5M H_2MEHP-0.1M DBBP-Kerosene

FIG. 12. Proposed reductive extraction and oxidative stripping process for the recovery of uranium from phosphoric acid solution.

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