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Extraction of Uranium(IV) from Phosphoric Acid by Kerosene Solution of Mono-(2-ethylhexyl) Phosphoric Acid and Neutral Organophosphorus Synergists

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Extraction of Uranium(IV) from Phosphoric Acid by Kerosene Solution of Mono-(2-ethylhexyl) Phosphoric Acid and Neutral Organophosphorus Synergists

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Abstract

The extraction of uranium(IV) from phosphoric acid by mono-(2-ethylhexyl) phosphoric acid in kerosene has been investigated. The effects of extractant concentration, hydrogen ion concentration, temperature, and the synergistic effect of trioctyl phosphine oxide and dibutyl butyl phosphonate on this extraction system have been examined. Based on the extractant dependency and the acid dependency, an ion-exchange mechanism was generally observed and the extracted species were of the type, $UH_{8n-4}X_{4n}$, $UH_{8n-4}X_{4n}\cdot$TOPO, and $UH_{8n-4}X_{4n}\cdot$DBBP. The temperature effect for the extraction reaction has also been studied.

INTRODUCTION

Organophosphorus compounds have been recognized as efficient extractants for metals in solvent extraction processes. The extraction of a large number of metal ions with dialkyl phosphoric acids and other organophosphorous compounds has been reported previously (*1–3*). The extraction of UO_2^{2+} and other metal ions from acid solutions by di-(2-ethylhexyl) phosphoric acid (HDEHP), $[(C_2H_5\cdot C_6H_{12}O)_2PO(OH)]$, and di-(2-ethylhexyl) phosphoric acid-trioctyl phosphine oxide (TOPO), $[(n\text{-}C_8H_{17})_3PO]$, has been widely studied from the point of view of elucidating the mechanism of extraction and temperature effects as wel. as for practical metal extraction processes (*1, 3–7*). The extraction of metal ions with mono-(2-ethylhexyl) phosphoric acid, $[(C_2H_5\cdot C_6H_{12}O)PO(OH)_2]$, has not been studied as intensively as HDEHP extraction. Peppard et al. (*8*) studied the extraction of M(III) lanthanides from HCl with H_2MEHP–

toluene solutions. Synergistic and antagonistic effects on the extraction of M(III) lanthanides from HCl by toluene solutions of H_2MEHP–TOPO and H_2MEHP–TBP have been studied by Mason et al. (*9*). Peppard et al. (*10*) have also demonstrated the separation of actinides(III) from lanthanides(III) in HCl with H_2MEHP–toluene solutions. Observations on the extraction of U(IV) from phosphoric acid solution with H_2MEHP, H_2MEHP–TOPO, and H_2MEHP–DBBP solutions have not yet been reported. The object of the present work was to investigate mechanisms and temperature effects for extraction of tetravalent uranium from phosphoric acid by kerosene solution of H_2MEHP and neutral organophosphorus synergists.

EXPERIMENTAL

Reagent grade chemicals were used throughout. U(IV) solution was prepared by zinc-amalgam reduction of uranyl nitrate (*11*). The concentration of U(IV) was determined by measuring its absorbance at 660 nm (*12*). The mono(2-ethylhexyl) phosphoric acid and di-(2-ethylhexyl) phosphoric acid mixture (58.61% HDEHP and 36.62% H_2MEHP) were obtained from Tokyo Kasei Kogyo Co. (Japan). The H_2MEHP was separated from the mixture and purified according to the method of Laskorin (*13*) and Peppard (*14*). The purity of the separated H_2MEHP was >99% as determined by titration with standard NaOH solution in 80% ethanol–20% water medium using a Metrohm Herisau model E-512 titrator.

Equal volumes of aqueous and organic solution (10 mL each) were shaken in a 50-mL glass separating funnel or flask. The initial aqueous uranium concentration was always about 4.2×10^{-4} *M*. After completion of the extraction period, the phases were allowed to settle and to separate by gravity. The uranium concentration in the equilibrium aqueous and organic phases was determined by spectrophotometry (*15*) and fluorometry (*16*). A thermostatted shaker was used to study the effect of the temperature (20–70°C) on the extraction; the temperature fluctuation was within ±1°C. It was experimentally established that the equilibrium time for all the extraction was within 5 min. The experimental results are expressed in terms of distribution ratio (*D*), where

$$D = \frac{\text{Uranium concentration in the organic phase } (C_U)_o}{\text{Uranium concentration in the aqueous phase } (C_U)_a} \qquad (1)$$

RESULTS AND DISCUSSION

Dependence on H_2MEHP Concentration

Based on the cryoscopic determination of molecular weights, Peppard et al. (*8*, *9*, *14*, *17–19*) report that H_2MEHP is polymeric in a nonhydrogen bonding diluent, e.g., *n*-hexane and cyclohexane, dimeric in ketone, and monomeric in alcohol. It is believed that the polymerization in nonpolar solvents occurs because of hydrogen bonding. Therefore, H_2MEHP in kerosene may be represented as $(H_2X)_n$, in which X is $(C_2H_5 \cdot C_6H_{12}O)PO_3{}^{2-}$. The dependency of the extraction of uranium(IV) on H_2MEHP concentration was studied at different phosphoric acid concentrations (0.1, 0.5, 1 *M*). The plot of log *D* vs log $(C_{H_2MEHP})_o$ is linear as shown in Fig. 1. The curves in Fig. 1 have a slope of 4; the following reaction is assumed to occur between U(IV) in the aqueous phase and $(H_2X)_n$ in the organic phase.

$$U^{4+}{}_{(a)} + 4(H_2X)_{n(o)} \rightleftharpoons UH_{8n-4}X_{4n(o)} + 4H^+{}_{(a)} \qquad (2)$$

where the subscripts (*a*) and (*o*) refer, respectively, to mutually equilibrated

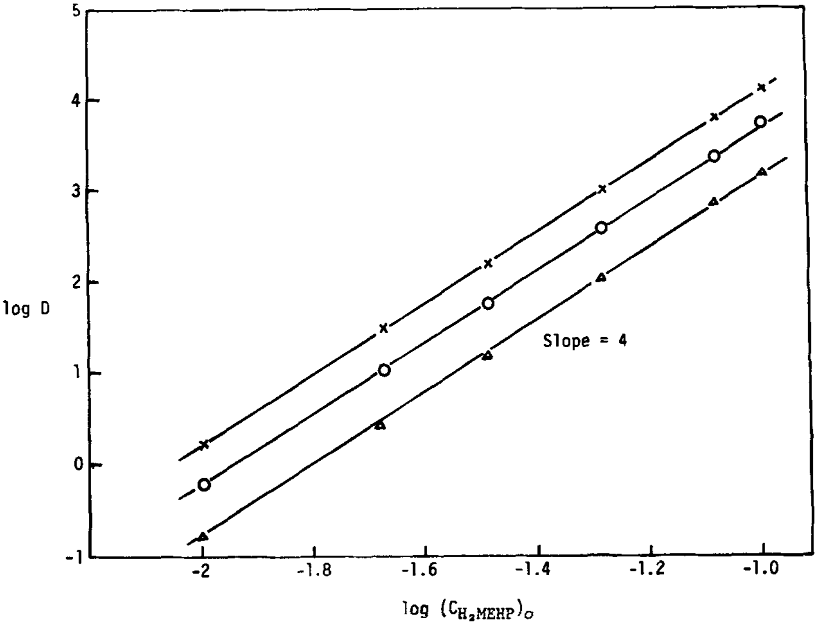

Fig. 1. Effect of H_2MEHP concentration on uranium(IV) extraction. U(IV): 4.2×10^{-4} *M*. H_3PO_4: 0.1 *M* (×), 0.5 *M* (○), and 1 *M* (△) at 20 ± 1°C.

aqueous and organic phases, and the formulation of the extracted species is empirical and not intended to imply any particular structure.

The equilibrium constant for Reaction (2) can be written

$$K_1 = \frac{(C_U)_o(C_{H^+})^4{}_a}{(C_U)_a(C_{H_2X})^4{}_o} = D\frac{(C_{H^+})^4{}_a}{(C_{H_2X})^4{}_o} \qquad (3)$$

in which $(C_U)_o$ is the uranium concentration in the organic phase, $(C_U)_a$ the uranium concentration in the aqueous phase, $(C_{H^+})_a$ the aqueous acidity, and $(C_{H_2X})_o$ the H_2X concentration in the organic phase. Equation (3) indicates the following relationship must hold:

$$\log D = \log K_1 + 4 \log (C_{H_2X})_o - 4 \log (C_{H^+})_a \qquad (4)$$

At constant acidity, a plot of $\log D$ vs $\log (C_{H_2X})_o$ is a straight line with slope 4 (Fig. 1). Similar stoichiometry has been suggested by Kiwan and Amin (*20*) for the extraction of U(IV) from H_2SO_4 by HDEHP–CCl_4 solutions. In contrast, first power H_2MEHP dependence and third power HDOϕP (di[para-(1,1,3,3-tetramethyl butyl)phenyl] phosphoric acid) dependence have been reported by Peppard et al. (*8*, *21*) for the extraction of Am(III) and Pm(III) from $HClO_4$ and Th(IV) from $HClO_4$, HCl, and HNO_3 solutions.

Dependence on Hydrogen Ion Concentration

The extraction of uranium(IV) from phosphoric acid solution by H_2MEHP in kerosene was studied at different hydrogen ion concentrations. The ionic strength was adjusted to 1.0 with NaH_2PO_4. The results in Fig. 2 indicate that a plot of $\log D$ vs $\log (C_{H^+})_a$ is linear with a slope equal to -4 at constant extraction concentration (0.01 ~ 0.1 *M*). The experimental results also confirm that the cation exchange extraction mechanism follows Eq. (2). The extraction may, therefore, be regarded as a U(IV) ion–hydrogen ion exchange reaction. The increase of hydrogen ion in the aqueous phase decreases the extent of extraction as shown in Fig. 2. All the data support the conclusion that the complex formed in the organic phase of H_2MEHP–kerosene is $UH_{8n-4}X_{4n}$. Peppard et al. (*8*) have reported that the distribution ratio of M(III) lanthanides and Am(III) from HCl and $HClO_4$ with H_2MEHP-toluene is inversely third-power dependent upon the hydrogen ion concentration in the aqueous phase. Kiwan and Amin (*22*) have reported that for the extraction of U(IV) from HCl medium with HDEHP, the distribution ratio is inversely fourth-power dependent upon aqueous phase hydrogen ion concentration.

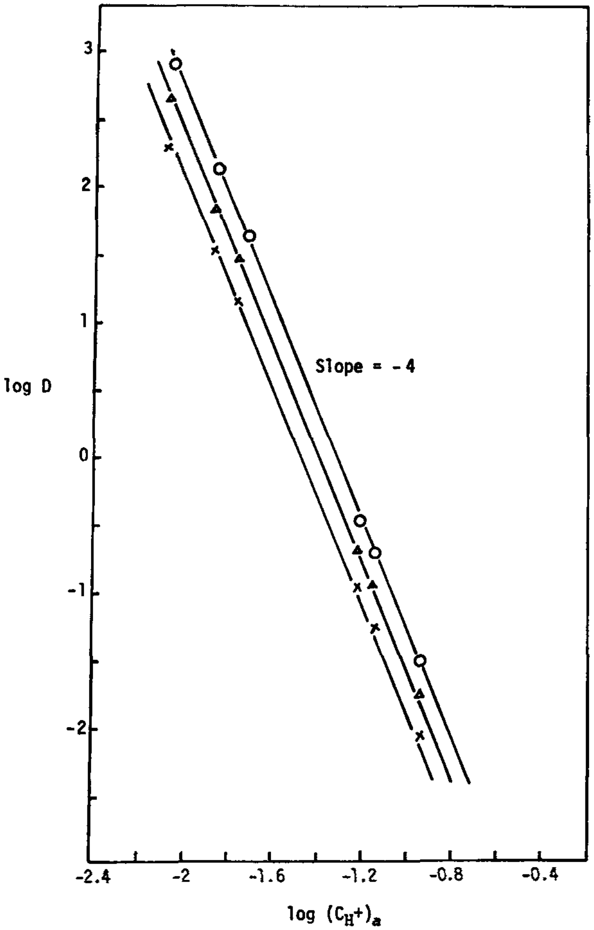

FIG. 2. Effect of hydrogen ion concentration on uranium(IV) extraction. Ionic strength = 1 in $H_3PO_4 + NaH_2PO_4$. U(IV): 4.2×10^{-4} *M*. C_{H_2MEHP}: 0.1 *M* (○), 0.05 *M* (△), and 0.01 *M* (×) at 20 ± 1 °C.

The Effect of Temperature on the Extraction Reaction

The effect of temperature on the distribution ratio for Reaction (2) was also studied at different phosphoric acid concentrations (0.1 ~ 1 *M*). The results indicate that the distribution ratio for the extraction reaction decreases with increasing temperature as shown in Fig. 3. The same results have been observed by Sato (*5*) for the extraction of U(VI) from H_2SO_4 by HDEHP–kerosene. The vant Hoff's equation in the form given by Eq.

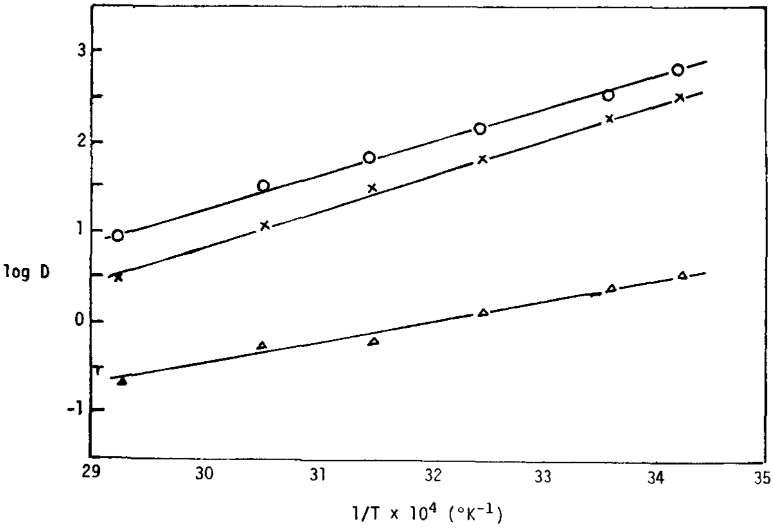

FIG. 3. Effect of temperature on uranium(IV) extraction by 0.05 *M* H_2MEHP–kerosene. U(IV): 4.2×10^{-4} *M*. H_3PO_4: 0.1 *M* (○), 0.5 *M* (×), and 1 *M* (△).

(5) can be used to calculate the enthalpy change, $\Delta H°$, associated with the extraction process:

$$\log D = \frac{-\Delta H°}{2.303RT} + C \qquad (5)$$

where C is a constant. The experimental plots of $\log D$ vs $1/T$ are linear as shown in Fig. 3, in agreement with expectation from Eq. (5). The value of $\Delta H°$ is equal to $-2.303 \times R \times$ slope. The enthalpy change (kcal/mol) is estimated to be -1.83 in 1 *M* H_3PO_4, -1.90 in 0.5 *M* H_3PO_4, and -2.48 in 0.1 *M* H_3PO_4, showing that the extraction of U(IV) by H_2MEHP–kerosene solution is an exothermic process. The stability of the extracted complex is higher at lower acidity.

Synergistic Effect of TOPO on Uranium(IV) Extraction

It is known that in some instances a neutral phosphate ester added to a HDEHP solution enhances the extraction (*1*, *3*) of metal ions. Studies were performed, therefore, to determine the effect adding TOPO to H_2MEHP on the extraction of U(IV). Figure 4 shows the experimental results for the synergistic effect of TOPO on uranium(IV) extraction by H_2MEHP–kerosene solution. At 0.5 and 1 *M* phosphoric acid, $\log D$ vs $\log (C_{\mathrm{TOPO}})_o$ is linear with a slope equal to 1. Based on the previous

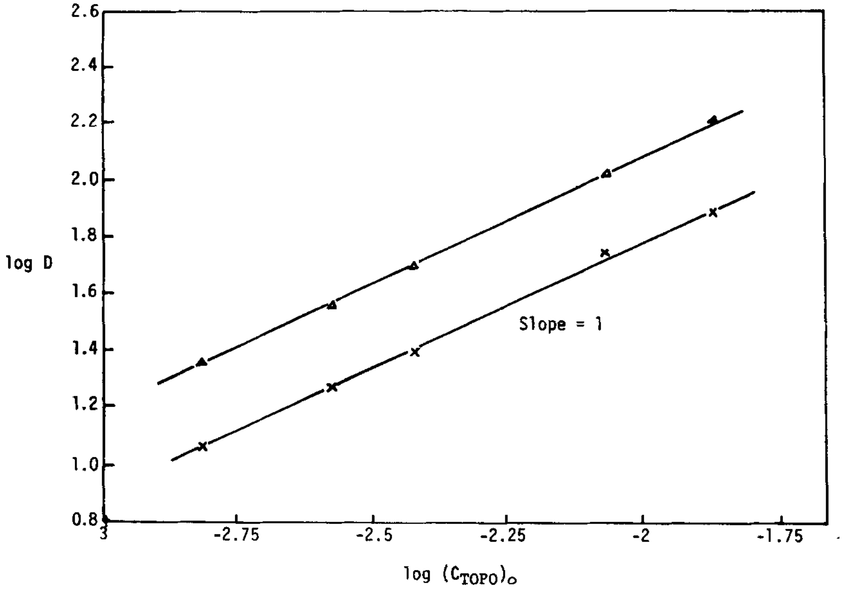

FIG. 4. Synergistic effect of TOPO on uranium(IV) extraction. U(IV): 4.2 × 10^{-4} *M*. Organic: 0.05 *M* H_2MEHP–TOPO in kerosene. Aqueous: 0.5 *M* H_3PO_4 (△) and 1 *M* H_3PO_4 (×) at 20 ± 1°C.

results and Fig. 4, the equilibrium involved in H_2MEHP–TOPO extraction of U(IV) is

$$U^{4+}{}_{(a)} + 4(H_2X)_{n(o)} + TOPO_{(o)} \rightleftharpoons UH_{8n-4}X_{4n}\cdot TOPO_{(o)} + 4H^+{}_{(a)} \quad (6)$$

The equilibrium constant for Reaction (6) can be written:

$$K_2 = \frac{(C_{U'})_o(C_{H^+})^4{}_a}{(C_U)_a(C_{H_2X})^4{}_o(C_{TOPO})_o} = D\frac{(C_{H^+})^4{}_a}{(C_{H_2X})^4{}_o(C_{TOPO})_o} \quad (7)$$

in which $(C_{U'})_o$ is the uranium concentration in the organic phase. Equation (7) suggests the following relationship must hold:

$$\log D = \log K_2 + \log (C_{TOPO})_o + 4 \log (C_{H_2X})_o - 4 \log (C_{H^+})_a \quad (8)$$

At constant H_2MEHP and hydrogen ion concentration, a plot of log *D* vs log $(C_{TOPO})_o$ should be linear with a slope equal to 1. The experimental results demonstrate that the adduct formation increases the distribution ratio at different phosphoric acid concentrations. In contrast, Peppard et al. (*10*) have reported that antagonistic effects have been observed for the extraction of Np(IV), Th(IV), and $UO_2{}^{2+}$ from aqueous H_2SO_4 into H_2MEHP–TBP–toluene solutions.

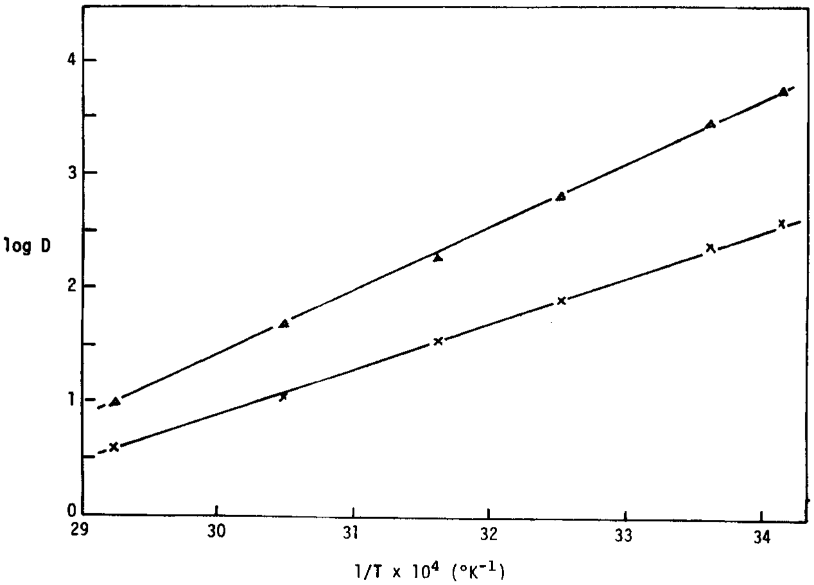

FIG. 5. Effect of temperature on uranium(IV) extraction by 0.05 *M* H_2MEHP–0.0125 *M* TOPO–kerosene. U(IV): 4.2×10^{-4} *M*. H_3PO_4: 0.5 *M* (△) and 1 *M* (×).

The temperature dependency for the extraction reaction with 0.05 *M* H_2MEHP–0.0125 *M* TOPO at 0.5 and 1 *M* phosphoric acid conditions is shown in Fig. 5. Over the temperature range 20–70°C, a plot of log *D* vs $1/T$ is a straight line. The distribution ratio decreases with increasing temperature. Based on Eq. (5), $\Delta H°$ values for extraction Reaction (6) at 1 and 0.5 *M* phosphoric acid concentration are calculated to be -7.57 and -8.76 kcal/mol, respectively. Compared to the previous system, the $\Delta H°$ values reveal that extracted $UH_{8n-4}X_{4n}\cdot$TOPO is more stable than $UH_{8n-4}X_{4n}$ in the organic phase. Bunus (*23*) reported that $\Delta H°$ values are -8.6 (0.3 *M* HDEHP) and -10 kcal/mol (0.9 *M* HDEHP) for the extraction of U(VI) from 4.3 *M* H_3PO_4 with HDEHP–TOPO–kerosene solutions.

Synergistic Effect of DBBP on Uranium(IV) Extraction

Figure 6 presents data for the synergistic extraction of U(IV) with H_2MEHP–DBBP at 0.5 and 1 *M* phosphoric acid concentration; log *D* vs log $(C_{\text{DBBP}})_o$ plots are linear with slope equal to 1. The experimental results indicate that the extraction equilibrium involved is

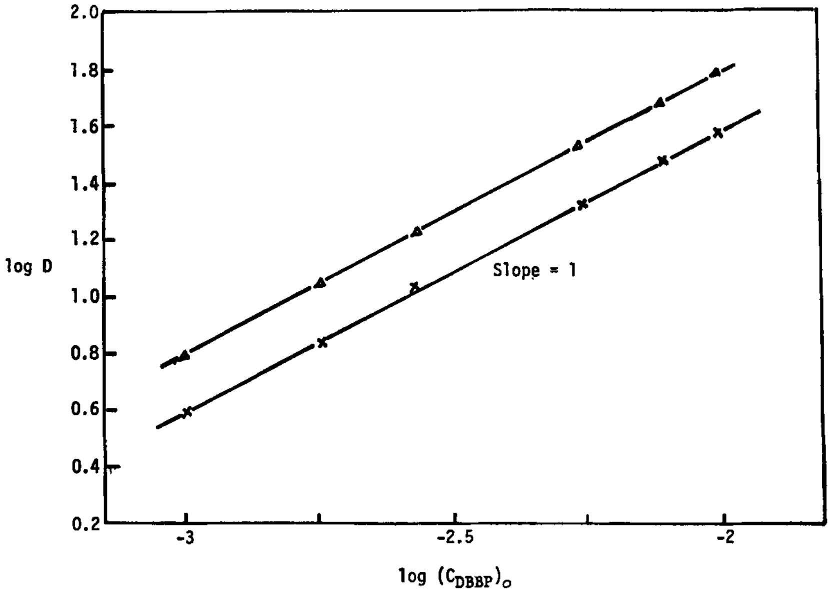

FIG. 6. Synergistic effect of DBBP on uranium(IV) extraction. U(IV): 4.2 × 10^{-4} *M*. Organic: 0.05 *M* H_2MEHP–DBBP in kerosene. Aqueous: 0.5 *M* H_3PO_4 (△) and 1 *M* H_3PO_4 (×).

$$U^{4+}{}_{(a)} + 4(H_2X)_{n(o)} + DBBP_{(o)} \rightleftharpoons UH_{8n-4}X_{4n}\cdot DBBP_{(o)} + 4H^+{}_{(a)} \quad (9)$$

The corresponding expression for the equilibrium constant, K_3, is

$$K_3 = \frac{(C_{U''})_o(C_{H^+})^4{}_a}{(C_U)_a(C_{H_2X})^4{}_o(C_{DBBP})_o} = D\frac{(C_{H^+})^4{}_a}{(C_{H_2X})^4{}_o(C_{DBBP})_o} \quad (10)$$

where $(C_{U''})_o$ is the uranium concentration in the organic phase. From Eq. (10) the following relationship must hold:

$$\log D = \log K_3 + \log(C_{DBBP})_o + 4\log(C_{H_2X})_o - 4\log(C_{H^+})_a \quad (11)$$

Equation (11) indicates that $\log D$ vs $\log(C_{DBBP})_o$ plots are straight lines with a slope equal to 1 at constant H_2MEHP and acidity concentration. At the same conditions the synergistic effect of DBBP on H_2MEHP for extraction of U(IV) is lower than that of TOPO. This is because the basicity of TOPO ($R_3P{=}O$) is higher than that of DBBP ($R'(R'O)_2P{=}O$).

Figure 7 shows the effect of temperature on H_2MEHP–DBBP extraction of U(IV) from 0.5 and 1 *M* phosphoric acid solutions; $\log D$ vs $1/T$ plots are linear. The extraction reaction is also an exothermic process; the distribution ratio decreases with increasing temperature. $\Delta H°$ values for

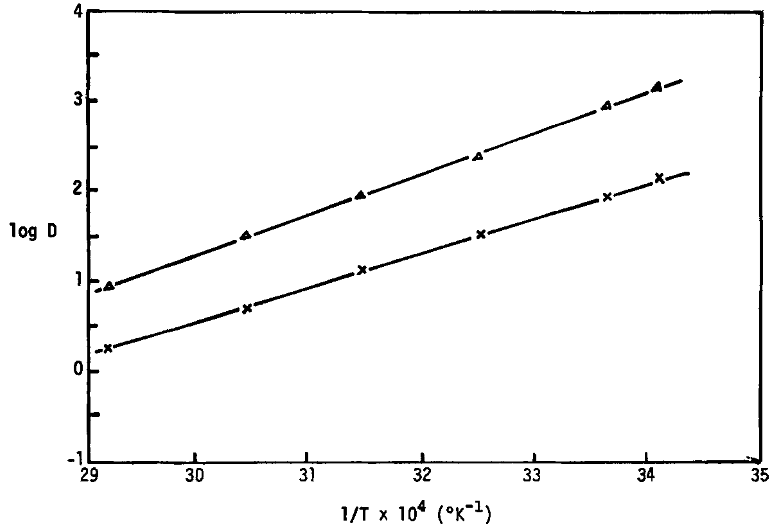

FIG. 7. Effect of temperature on uranium(IV) extraction by 0.05 *M* H_2MEHP–0.01 *M* DBBP–kerosene. U(IV): 4.2×10^{-4} *M*. H_3PO_4: 0.5 *M* (△) and 1 *M* (×).

the extraction Reaction (9) are calculated with vant Hoff's equation. At 0.5 and 1 *M* phosphoric acid, $\Delta H°$ values are -8.05 and -7.12 kcal/mol, respectively. The results indicate that the stability of $UH_{8n-4}X_{4n}\cdot$DBBP is lower than that of $UH_{8n-4}X_{4n}\cdot$TOPO, but it is higher than that of $UH_{8n-4}X_{4n}$.

Effect of Phosphoric Acid Concentration on the Distribution Ratio of U(IV)

The extracting ability of H_2MEHP, H_2MEHP–TOPO, and H_2MEHP–DBBP solution was studied at different phosphoric acid concentration as shown in Fig. 8. The distribution ratio decreases very rapidly with increasing phosphoric acid concentration. At lower acidity, U^{4+} is clearly the predominate species in the phosphoric acid solution as seen in Fig. 2. At higher acidity, the value of *D* for U(IV) is much lower, showing the existence of more complex species in the aqueous phase. The reaction of U(IV) with phosphoric acid might be as follows:

$$U^{4+} + nH_2PO_4^- \overset{\beta_n}{\rightleftharpoons} U(H_2PO_4^{4-n})_n \qquad (12)$$

The total uranium(IV) concentration in the aqueous phase is

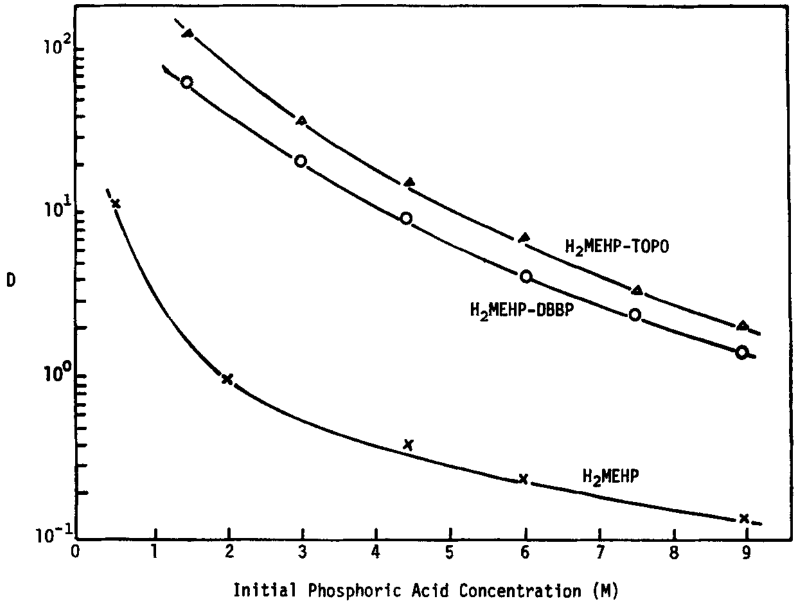

FIG. 8. Effect of H_3PO_4 concentration on uranium(IV) extraction. U(IV): 4.2×10^{-4} *M*. (△): 0.5 *M* H_2MEHP–0.125 *M* TOPO, (○): 0.5 *M* H_2MEHP–0.1 *M* DBBP, (×): 0.5 *M* H_2MEHP at 20 ± 1°C.

$$(C_{U(t)})_a = (C_{U^{4+}})_a + \sum_n [U(H_2PO_4{}^{4-n})_n] = (C_{U^{4+}})_a[1 + \sum_n \beta_n(H_2PO_4{}^-)^n] \tag{13}$$

As shown in Eqs. (2), (6), and (9), if only uncomplexed U^{4+} is extracted, then

$$D = \frac{(C_U)_o}{(C_{U(t)})_a} = \frac{(C_U)_o}{(C_{U^{4+}})_a[1 + \sum_n \beta_n(H_2PO_4{}^-)^n]} \tag{14}$$

Equation (14) shows that *D* decreases with increasing H_3PO_4 concentration. Figure 8 also reveals that U(IV) in phosphoric acid (4–6 *M*) can be extracted with either H_2MEHP–TOPO or H_2MEHP–DBBP. Therefore, the experimental results suggest that these extractants might be used to recover uranium from wet process phosphoric acid.

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