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The Extraction of Uranium(VI) from Mineral Acid Solutions by Di-4-octylphenylphosphoric Acid (DOPPA)

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Abstract

The extraction of uranium(VI) from sulfuric, hydrochloric, nitric, and perchloric acid was studied using dioctylphenylphosphoric acid (DOPPA) in heptane as extractant. At low aqueous acid concentration, an ion-exchange mechanism was generally observed and the extracted species was of the type $UO_2A_4H_2$. Deviation from this behavior was observed at higher acid concentrations. From perchloric acid solutions, after an initial decrease, the extraction coefficient increased after 3 to 4 *N* acid. Some of the explanations offered in the literature for this behavior in the case of di-2-ethylhexylphosphoric acid (DEHPA) have been critically examined. Extraction of mineral acids, particularly HCl and HNO_3, was also observed with DOPPA but to a lesser extent than with DEHPA.

INTRODUCTION

Dialkylphosphoric acids have proved to be good extractants. Di-2-ethylhexylphosphoric acid (DEHPA) has been subjected to an intensive study both from the point of view of elucidating the mechanism of extraction as well as application to practical metal extraction problems. This is illustrated by the large number of reported studies on the extraction of uranium(VI) (*1–3*). Baes (*4*) discussed different aspects of the extraction of metallic species by dialkylphosphoric acids. In a study of the effect of the reagent structure, Ferraro and Peppard (*5*) found that with increasing electronegativity of the organo group the acid strength of the compound increases as well as the extraction capability. In comparing extraction of DEHPA and di-(*p*-1,1,3,3-tetramethylbutylphenyl) phosphoric acid (dioctylphenylphosphoric acid, DOPPA) in the case of actinium, Peppard and others (*6*) found that the latter reagent gave an extraction coefficient 10^7 fold greater than did DEHPA. In spite of this interesting observation, the phenylphosphoric acids have not been studied as metal extractants in any significant manner. In their study on the effect of reagent structure on the extraction of uranium(VI), Krosavec and Klofuter (*7*) employed a number of phenylphosphoric acids but not DOPPA. However, the extraction of calcium, barium, strontium (*8*), sodium (*9*), and thorium (*10*) by this reagent has been studied. In the present work the extraction of uranium(VI) from sulfuric, hydrochloric, nitric, and perchloric acids has been studied.

EXPERIMENTAL

Purification of DOPPA

For the preparation of DOPPA, the starting material was octylphenyl acid phosphate obtained from Mobil Chemicals, U.S.A. This material, consisting of approximately two parts by weight of dioctylphenylphosphoric acid (DOPPA) and three parts by weight of monooctylphenylphosphoric acid (MOPPA), was dissolved in kerosene and repeatedly extracted with monoethylene glycol to separate the monoester. On cooling (5°C) the kerosene layer, part of the diester crystallized out. Further purification of the DOPPA fraction was achieved by recrystallization from petroleum ether (b.p. 60 to 80°C). The product was checked for purity and the absence of MOPPA by titration with alkali in an ethanol medium.

Extraction Procedure

The extraction tests were made by equilibrating equal volumes of aqueous and organic phases of predetermined composition for 15 min, allowing the two layers to separate and analyzing both layers for uranium. Depending on the uranium concentration, a volumetric (*11*), spectrophotometric (*12*), or fluorimetric (*13*) method was employed for analysis. 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.

RESULTS AND DISCUSSION

Extraction from Sulfuric Acid Solutions

The extraction of uranyl sulfate from sulfuric acid solutions by DOPPA in heptane was studied at different acid concentrations. The results are shown in Fig. 1. To bring out the dependence of E_u on DOPPA concentration in the organic phase, values of E_u were taken from Fig. 1 and plotted in Fig. 2.

From the similarity in chemical nature of DOPPA, DEHPA, and other dialkyl phosphoric acids it can reasonably be assumed that the general mechanism of extraction of uranium(VI) by all these extractants will be the same. Therefore, based on the observations of Sato (*14*), Baes (*15*), and Hardy (*16*) in the case of dialkylphosphoric acids, the important features of the extraction system uranium–mineral acid–DOPPA–heptane can be summarized as (1) DOPPA exists as a dimer in a hydrocarbon diluent such as heptane, (2) the monoionized dimer complexes uranium (*17*), (3) for every UO_2^{2+} ion extracted two hydrogen ions are liberated, and (4) depending on the degree of loading in the organic layer, even polymeric uranium containing species can be present in this phase. Based on these assumptions, the extraction reaction can be represented as

$$UO_{2_a}{}^{2+} + 2(HA)_{2_o} \rightleftarrows UO_2A_4H_{2_o} + 2H_a{}^+ \qquad (1)$$

where A represents the anion of DOPPA, $(C_8H_{17}\cdot C_6H_4O)_2PO_2{}^-$, and a and o indicate the aqueous and organic phases, respectively. On the basis of Eq. (1), at low organic loading a plot of log E_u against log [acid] at different [DOPPA] must give a straight line with a slope of -2 and a plot of log E_u against log [DOPPA] must give a straight line with a slope of $+2$. The results in Figs. 1 and 2 confirm these expectations.

In these respects the behavior of DOPPA is similar to that of DEHPA except that under all experimental conditions the extraction coefficients are higher than in the latter case by a factor of 5 to 6. The effect of diluent on the extraction coefficient was also similar to that observed by Sato (*18*), i.e., kerosene > heptane > cyclohexane > dichloroethane > carbon tetrachloride > benzene > toluene > chloroform.

Effect of Aqueous Uranium Concentration

The effect of increasing $[\text{uranium}]_a$ on the $[\text{uranium}]_o$ shows that the limiting uranium: DOPPA ratio is 1: 2 and not 1: 4 as indicated by Eq. (1). This suggests the presence of uranium complexes other than

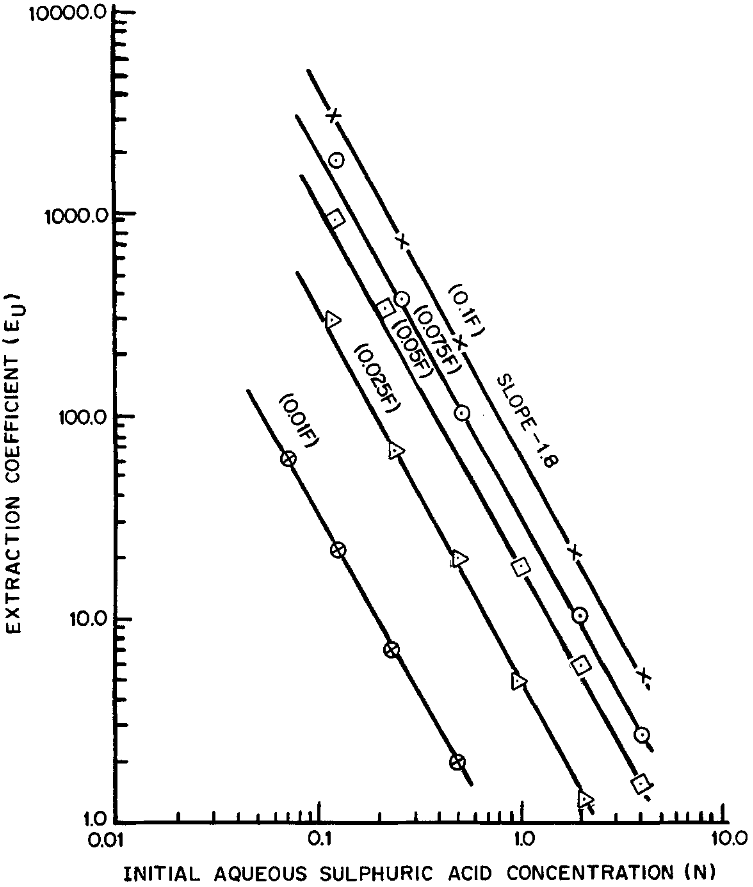

FIG. 1. Effect of sulfuric acid concentration on the extraction of uranium by DOPPA. Organic: DOPPA in heptane; figures in parentheses are DOPPA concentration (*F*); volume, 25.0 ml. Aqueous: Uranium, 0.0024 *M*; H_2SO_4, varying concentration; volume, 25.0 ml.

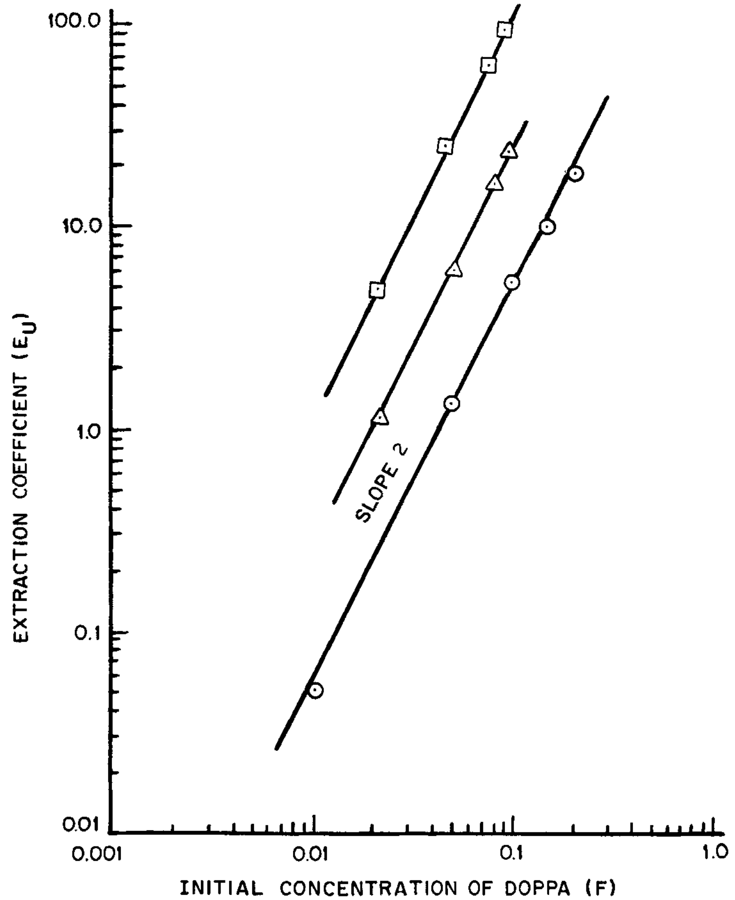

FIG. 2. Effect of DOPPA concentration on the extraction of uranium. Organic: Varying concentration of DOPPA (*F*) in heptane; volume, 25.0 ml. Aqueous: Uranium, 0.0035 *M*; H_2SO_4, 1 *N* (⊡), 2 *N* (△), 4 *N* (⊙); volume, 25.0 ml.

$UO_2A_4H_2$. In the case of DEHPA (*19*) it is now well known that near maximum loading of the organic phase, polynuclear complexes of the type $(NO_2)_nX_{(2n+2)}H_2$ are formed in the organic phase. Isopiestic measurements on a solvent consisting of 0.05 *F* DOPPA in heptane with varying uranium loadings showed that similar polynuclear complexes are formed with $n \simeq 4$.

Extraction from Hydrochloric Acid Solutions

The results of extraction studies using 0.025 to 0.1 *F* DOPPA in heptane from solutions of varying hydrochloric acid concentration are summarized in Fig. 3. E_u decreased with increasing acid concentration, but beyond 2 *N* the decrease is steep. In acid concentrations of less than 2 *N*, the slope of the curves with different [DOPPA] are ~ -2, as expected on the basis of a simple ion-exchange mechanism. The results, when replotted as log E_u vs log [DOPPA] with different initial acid concentrations, fall on a straight line with a slope of +2 which is also in line with this mechanism. The steep fall of E_u a bove 4 *N* acid is probably due to the formation of chloro complexes (*20*) such as UO_2Cl_2, $UO_2Cl_3^-$, and $UO_2Cl_4^{2-}$ which are not extractable by DOPPA.

There is an interesting comparison between DOPPA and DEHPA in regard to extraction of uranium from hydrochloric acid. From his studies with DEHPA, Sato (*21*) concluded that at less than 3 *N* acid, uranium is extracted essentially by the ion-exchange mechanism of Eq. (1), and when the acid concentration is above 7 *N* it is extracted by a combined ion-exchange solvation mechanism. The latter was shown as

$$UO_{2_a}^{2+} + 2Cl_a^- + (HA)_{2_o} \rightleftarrows UO_2Cl_2(HA)_{2_o} \qquad (2)$$

However, taking into account his observation that hydrochloric acid is extracted into the organic phase with UO_2Cl_2 when the aqueous acidity is high, it appears more reasonable to believe that uranium is extracted under these conditions by solvation of the halo acids HUO_2Cl_3 and $H_2UO_2Cl_4$ instead of by the neutral species UO_2Cl_2. These acids can be hydrogen bonded to the extractant molecule at the phosphoryl oxygen. The ability of DEHPA to solvate acids is confirmed by the extraction of hydrochloric acid (*22*) and nitric acid (discussed later). In contrast to DEHPA, the results with DOPPA (Fig. 3) show a steep fall of E_u at high acid concentrations, indicating that the halo acids are not extracted. This may be attributed to the fact that P → O group in this case is less basic.

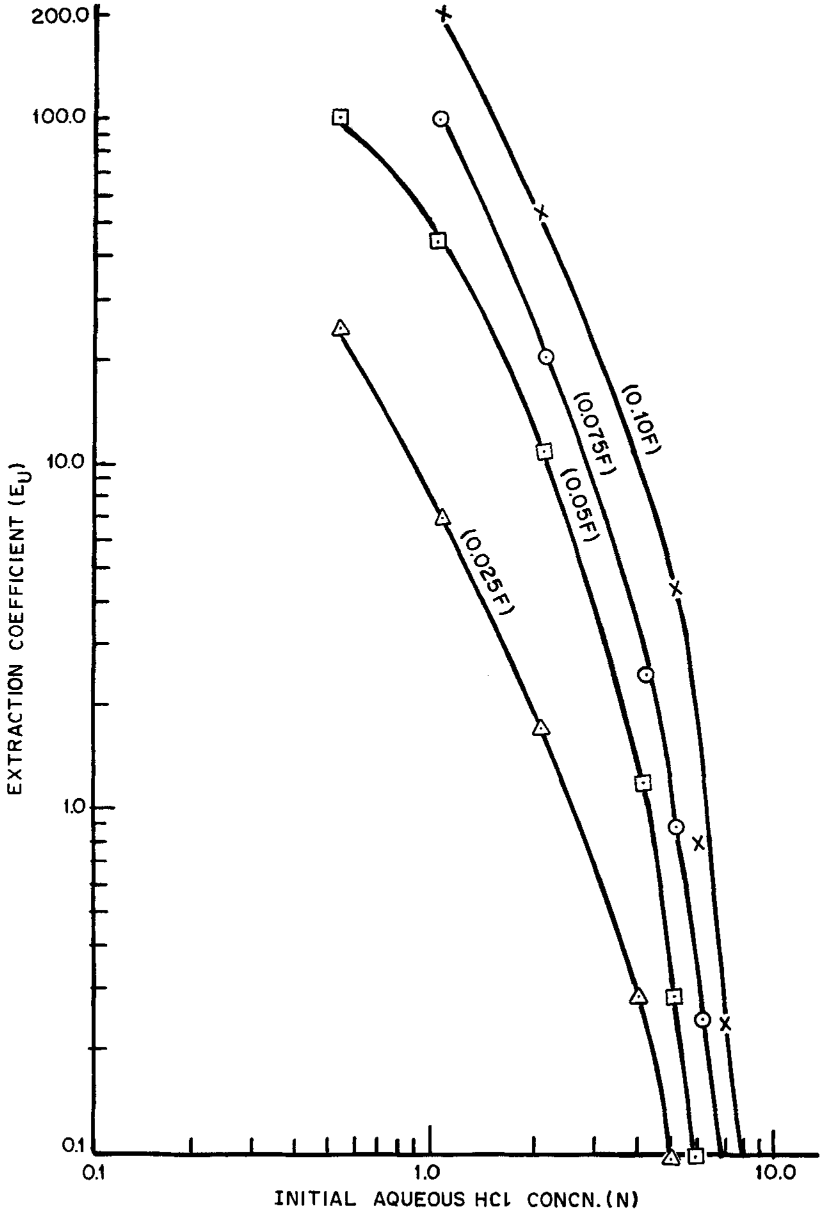

FIG. 3. Effect of hydrochloric acid concentration on the extraction of uranium. Organic: DOPPA in heptane; figures in parentheses are DOPPA concentration (*F*); volume, 25.0 ml. Aqueous: Uranium, 0.003 *M*; HCl, varying concentration; volume, 25.0 ml.

Extraction from Nitric Acid Solutions

Extraction of uranium(VI) from nitric acid solutions was studied and the results are compared with those reported for di-*n*-butyl phosphate (*23*) (DBP) and DEHPA (*24*) in Fig. 4. Up to 3 *N* acid, the decrease in E_u is on $[H^+]$ to the second power, which is in accordance with the normal ion-exchange mechanism (Eq. 1). From 3 to 7 *N* acid the decrease is more gradual, but beyond 7 *N* it is once again sharp. In contrast, DEHPA and DBP show a minimum in their extraction curves at 3 *N* acid, rising to about 7 *N*, and falling once again beyond that. The increase in E_u in the range 3 to 6 *N* acid in the case of DBP and DEHPA was explained by Healy (*23*) and Sato (*24*) in terms of a solvation mechanism (Eq. 2) forming $UO_2(NO_3)_2(HA)_2$ in the organic phase. The sharp fall in E_u beyond 7 *N* acid is attributed by them to a competing reaction with nitric acid:

$$(HA)_{2_o} + HNO_{3_a} \rightleftarrows HNO_3(HA)_{2_o} \qquad (3)$$

A different explanation was given by Nemodruk (*26*) for the increase in E_u at higher than 3 *N* acid. According to him, uranium is extracted as the UO^{4+} ion which can exist in highly acidic solutions as a result of the reaction

$$UO_2^{2+} + 2H^+ \rightleftarrows UO^{4+} + H_2O \qquad (4)$$

Apart from the absence of any direct evidence for the presence of UO^{4+} ion in solution, Vdovenko and Vavilov (*26*) rejected this hypothesis in favor of a combined ion-exchange solvation mechanism leading to synergistically extracted mixed complex of the type $(UO_2NO_3HA_2)_2 2HA$. In a more recent study, Rozen (*27*, *28*) confirmed the presence of such a mixed complex in the organic phase and attributed some of the incorrect conclusions on the composition of the complex as arising out of disregarding the variation in the activity coefficients of the species involved. From the results presented in Fig. 4, it appears that DOPPA shows much less tendency to form a solvated or a mixed complex than dialkylphosphoric acids. The steep fall in E_u at greater than 6 *N* acid can still be attributed to the competitive extraction of nitric acid. Separate experiments have shown that nitric acid extraction by DOPPA is comparable to that by DEHPA.

Extraction from Perchloric Acid Solutions

Extraction of uranium from solutions varying in perchloric acid concentration and 0.005 *M* and 0.05 *M* in uranium was studied. The results

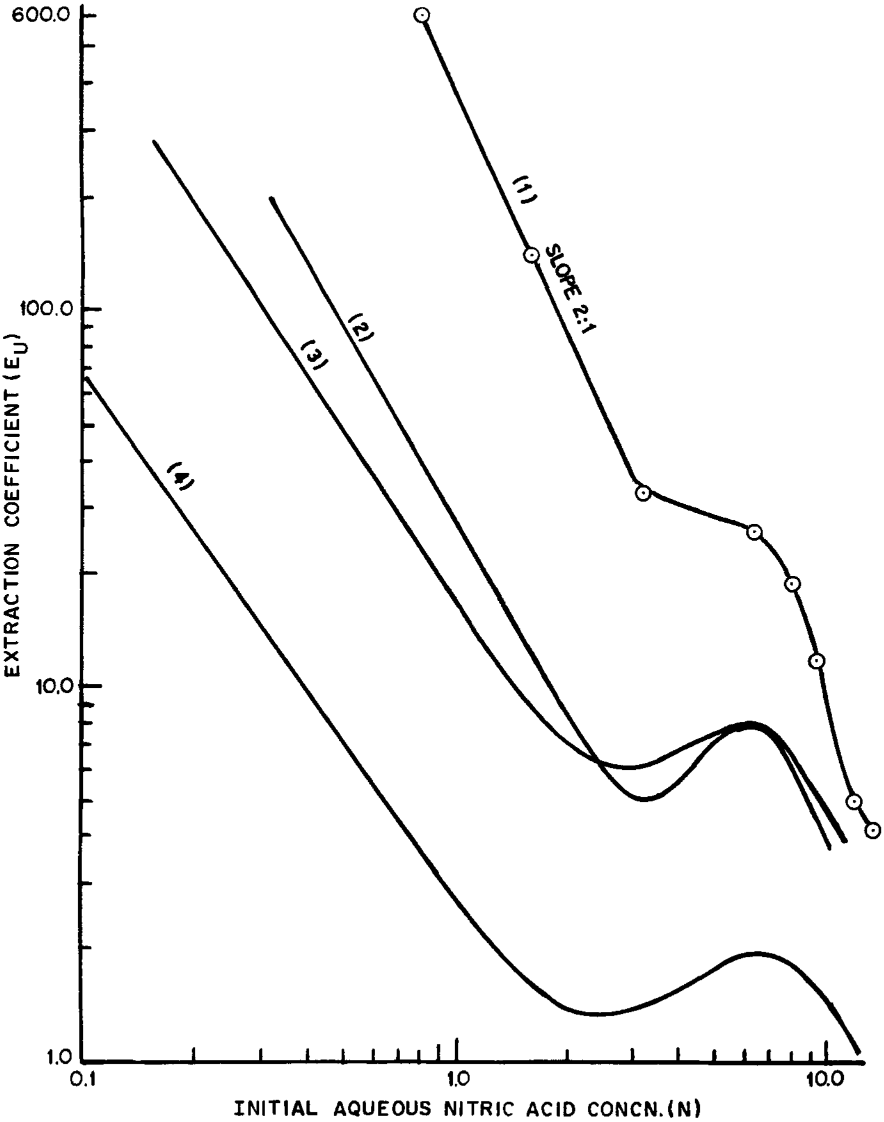

FIG. 4. Extraction of uranium from nitric acid by DOPPA and some dialkyl phosphoric acids. Curve 1: Experimental. Organic: 0.1 *F* DOPPA in heptane; volume, 25.0 ml. Aqueous: Uranium, 0.003 *M*; HNO_3, varying concentration; volume, 25.0 ml. Curve 2: 0.05 *F* DBP in toluene (*23*, *24*). Curve 3: 0.1 *F* DEHPA in kerosene (*23*, *24*). Curve 4: 0.05 *F* DEHPA in kerosene (*23*, *24*).

are shown in Fig. 5. Under conditions of low organic loading, e.g., extraction with 0.1 *F* DOPPA from 0.005 *M* aqueous uranium solution, the slope of the initial part of the curve is nearly −2. For comparison, one set of results with 0.05 *F* DEHPA is also given. In all cases E_u decreased with acid concentration up to 3 to 4 *N* and increased thereafter. In the case of DEHPA, Nemodruk (*29*) explained that behavior on the basis of a normal ion-exchange mechanism involving UO_2^{2+} ions in the low acid range and an ion-exchange behavior involving UO^{4+} ion in the higher acid range. This is an extension of his earlier hypothesis with regard to the extraction behavior from strong nitric acid solutions and suffers from the same limitations. Schmit and Pfanhauser (*30*), on the other hand, preferred a solvation mechanism with the formation of $UO_2(ClO_4)_2 \cdot 2DEHPA$ in the organic phase at high aqueous acidities. Vavilov (*31*) also accepted this explanation. However, no direct evidence for the simultaneous extraction of perchlorate, as needed in these explanations, has been provided by any of these authors.

In our experiments, when 0.1 *F* DOPPA was equilibrated with an equal volume of 9.4 *N* perchloric acid, we found that the concentration of perchlorate ion in the organic phase was negligible (<0.003 *M*). The perchlorate determination in the organic phase was carried out by spectrophotometry using Brilliant Green (*32*) after scrubbing the perchlorate from the organic phase with 8 *M* hydrochloric acid. To prevent interference from traces of DOPPA, the acid solution was repeatedly washed with heptane. Even after repeated contact with an aqueous phase 0.05 *M* in uranium and 9.4 *M* in perchloric acid, the organic phase (0.1 *F* DOPPA in heptane) showed no significant increase in perchlorate concentration although it was practically saturated with uranium (0.05 *M*). It was also observed that the saturated organic phase on separation, and after being kept at 0 °C for several days, deposited a yellow crystalline solid which on separation and analysis failed to show any significant concentration of perchlorate but corresponded to a stoichiometric composition of U:DOPPA = 1:2. Thus all attempts to find evidence of a solvated neutral complex of the type $UO_2(ClO_4)_2$ failed, indicating that the earlier theories were wrong.

There is a close similarity in the extraction behavior of uranium from perchloric acid by DEHPA and DOPPA and that of iron(III) and scandium(III) by dinonyl naphthalene sulfonic acid, a case studied by Whitney and Diamond (*33*). These authors explained the increase in extraction at high acid concentration by assuming that the low water activity in strong perchloric acid solutions leads to a partial dehydration of the metal ion,

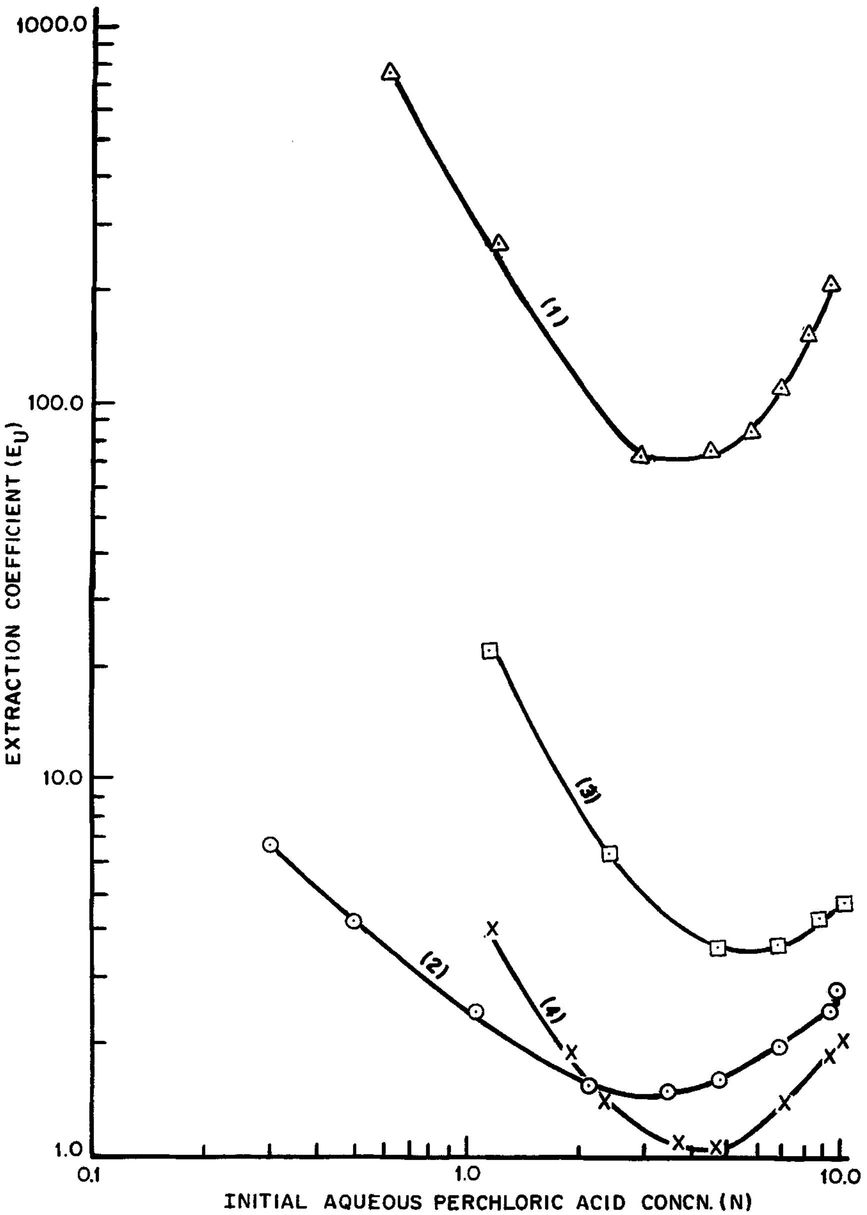

FIG. 5. Effect of perchloric acid concentration on the extraction of uranium by DOPPA and DEHPA. Organic: (△) 0.1 *F* DOPPA; (⊙) 0.1 *F* DOPPA; (⊡) 0.06 *F* DOPPA; (×) 0.05 *F* DEHPA. Aqueous: (△) uranium, 0.005 *M*; (⊙) uranium, 0.05 *M*; (⊡) uranium, 0.01 *M*; (×) uranium, 0.01 *M*; $HClO_4$, varying concentration, volume, 25.0 ml.

thereby facilitating the solvation of these ions by the anion of the extractant itself, and resulting in enhanced extraction. The case of uranium extraction from >4 *N* perchloric acid by both DOPPA and DEHPA can perhaps be better explained by the same mechanism. Evidence for the decrease in activity of water with increasing perchloric acid concentration is provided by a study of the distribution of water between 0.1 *F* DOPPA and an aqueous phase with varying acid concentration. The results (Fig. 6) show that beyond 2.5 *N* acid the water content of the organic phase decreased regularly with acid concentration in the aqueous phase. Apart from the cases mentioned above, the uranium distribution may be governed by more complex factors such as the variation of uranyl ion activity itself in the aqueous phase.

Extraction of Mineral Acids by DOPPA

It was observed that while perchloric and sulfuric acids were extracted to a negligible extent by DOPPA, hydrochloric and nitric acids were reasonably well extracted. The variation of log $[\text{acids}]_o$ with log $[\text{DOPPA}]_o$ for extraction from solutions of different initial concentration was linear with a slope +1, indicating that the extracted species was of the type $DOPPA \cdot HX$ ($X = Cl^-$, NO_3^-). However, under comparable aqueous acid concentration, nitric acid was better extracted than hydrochloric acid. In a comparative study of DOPPA and DEHPA it was found that the former was a poorer extractant of acids, showing the weaker donor property of the phosphoryl oxygen in this compound. The results are indicated in Fig. 7 where the variation of the water content of the organic phase with the aqueous HNO_3 concentration is also shown. The increase in H_2O extraction with increasing acid concentration in the organic phase is in line with the observations of Kertes, Beck, and Habouska (*34*) and Mikhailichenko and Valchenkova (*35*) that, in the case of DBP and DEHPA, the organic phase contains solvates of the type $(HA \cdot H_2O)_2 \cdot HNO_3$ and $(HA \cdot H_2O)_2 \cdot 2HNO_3$.

Influence of Acid Type on Extraction of Uranium

Extraction of uranium by DOPPA from H_2SO_4, HCl, HNO_3, and $HClO_4$ has been discussed above. It was noted that at comparable hydrogen ion concentrations in the aqueous phase, E_u decreased in the order $HClO_4 > HNO_3 > HCl > H_2SO_4$. The effect is brought out more clearly by calculating the apparent equilibrium constants (K_{eq}) for the extraction

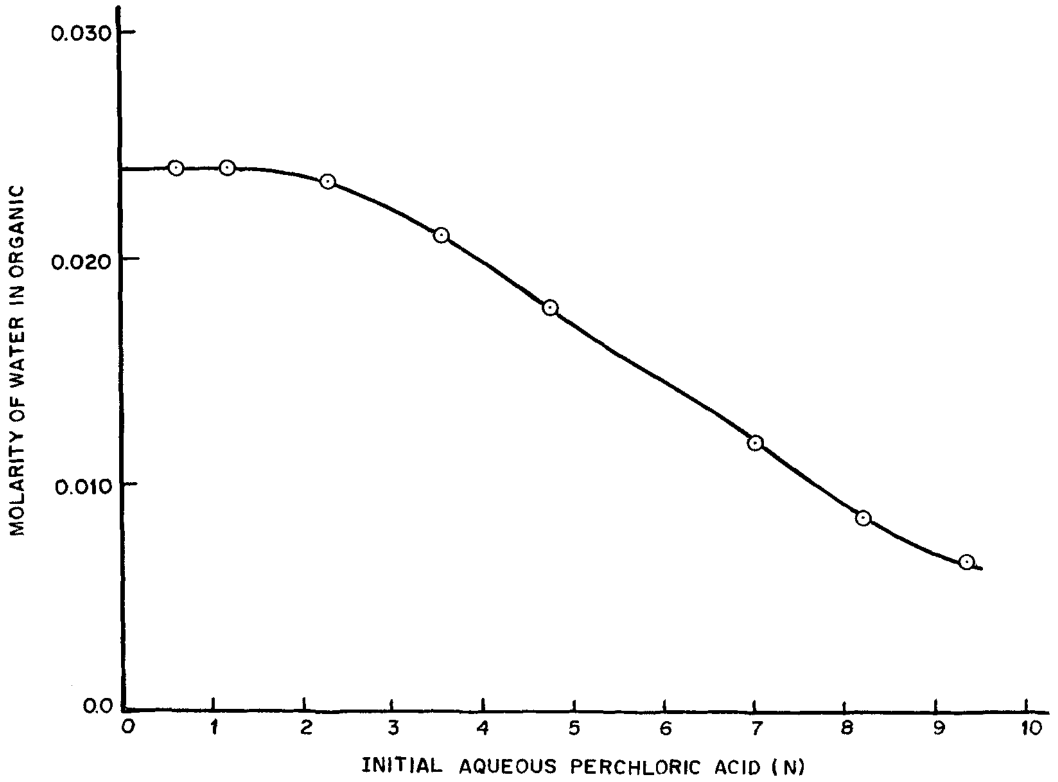

FIG. 6. Effect of perchloric acid concentration on the extraction of water with DOPPA. Organic: 0.1 *F* DOPPA in heptane; volume, 25.0 ml. Aqueous: Uranium, 0.005 *M*; $HClO_4$, varying concentration; volume, 25.0 ml.

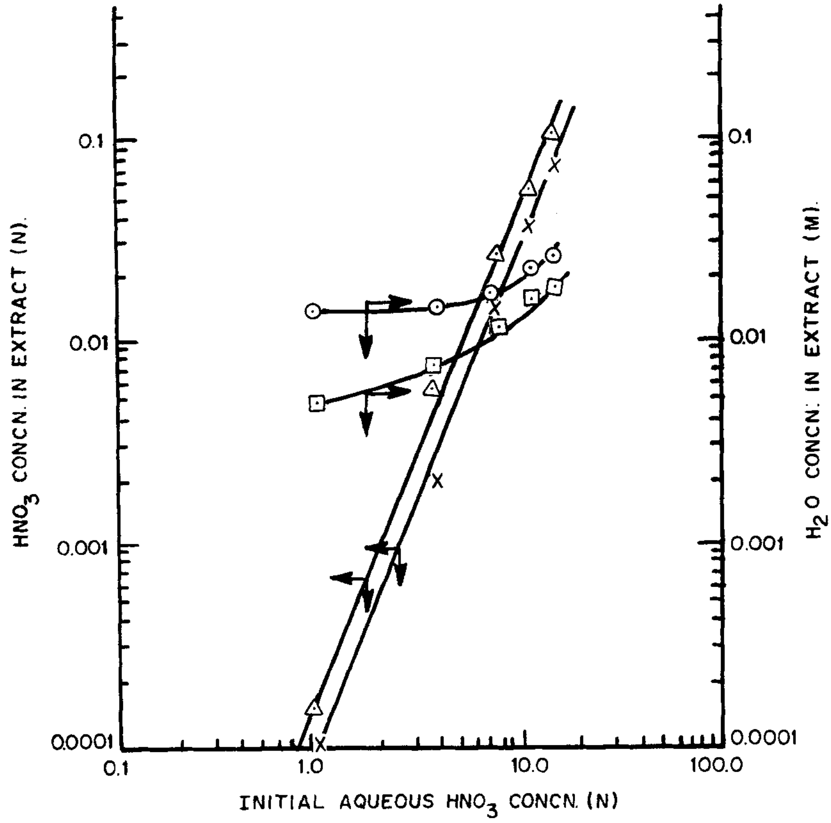

FIG. 7. Extraction of nitric acid and water by DEHPA/DOPPA: effect of nitric acid concentration. Organic: (△) 0.1 *F* DEHPA; (×) 0.1 *F* DOPPA; (⊡) 0.1 *F* DEHPA; (⊙) 0.1 *F* DOPPA. Aqueous: HNO_3, varying concentration; volume, 25.0 ml.

reaction (Eq. 1) under conditions of low uranium loading

$$K_{eq} = \frac{E_u[H^+]_a^2}{\left(\frac{C_S - 4C_u}{2}\right)_o^2}$$

where C_S is the initial DOPPA concentration in the solvent phase expressed as monomer, and C_U is the equilibrium uranium concentration in the organic phase. The calculated values for $HClO_4$, HNO_3, HCl, and H_2SO_4 are 1.9×10^5, 1.7×10^5, 0.93×10^5, and 3.3×10^4, respectively. The variation can be qualitatively explained in terms of the relative complexing (*36*) ability of the anions concerned. It is observed from the reported values for DEHPA (*37–39*) and DBP (*40*) that for any given acid medium, K_{eq} values for DOPPA are 5 to 6 times the corresponding values with these extractants.

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