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M. Ejaz[a]
[a] NUCLEAR CHEMISTRY DIVISION, PAKISTAN INSTITUTE OF NUCLEAR SCIENCE AND TECHNOLOGY, RAWALPINDI, PAKISTAN

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Extraction Separation Studies of Uranium(VI) by Amine Oxides

M. EJAZ

NUCLEAR CHEMISTRY DIVISION
PAKISTAN INSTITUTE OF NUCLEAR SCIENCE AND TECHNOLOGY*
P.O. NILORE, RAWALPINDI, PAKISTAN

Abstract

The extraction of uranium(VI) by two amine oxides, 4-(5-nonyl)pyridine oxide and trioctylamine oxide has been studied. The extraction behavior of these two *N*-oxides is compared. The dependence of extraction on the type of amine oxide and acid, nature of organic diluent, and amine oxide concentration has been investigated. The influence of the concentration of the metal and salting-out agents is described. The possible mechanism of extraction is discussed in the light of the results of extraction isotherms, loading radiodata, and log-log plots of amine oxide concentration vs distribution ratio. The separation factors for a number of metal ions are reported, and the separation of uranium from some fission product elements has also been achieved.

INTRODUCTION

The utility of a variety of amine oxides as extractants has become a subject of general interest and some investigators have contributed papers to this topic (*1–10*). A substantial proportion of the investigations is, however, concerned with solutions of uranyl nitrate in nitric acid solutions using high molecular weight α-substituted pyridines. Although it has been shown that uranium can also be extracted from other mineral acids by amine oxides (*7*), little information can be found in the literature on the

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*A part of the work was done in the Department of Nuclear Chemistry, University of New South Wales, Australia.

mechanism of extraction and the effects of diluents, reagents, and extractable and inextractable salt concentrations on the extraction of uranium. These are herein described using a new symmetrical γ-substituted 4-(5-nonyl) pyridine oxide (heterocyclic amine oxide) and trioctylamine oxide (aliphatic amine oxide). The extraction behavior of these two *N*-oxides is compared. In very dilute nitric acid (0.1 to 1 *M*), 4-(5-nonyl)pyridine oxide appears to be a better extractant for uranium than trioctylamine oxide and tributylphosphate.

EXPERIMENTAL

Reagents

4-(5-Nonyl)pyridine oxide (NPyOx) and trioctylamine oxide (TOAO) were prepared and purified by reported methods (*8*) and their authenticity checked by means of elemental analysis, examination of their melting/boiling points, and IR spectra. Nitric, hydrochloric, and sulfuric acid solutions were generally prepared from B.D.H. Standard volumetric solution ampules. Uranyl nitrate and sulfate solutions were prepared by dissolving A.R. grade salts obtained from May and Baker Ltd., Dogenham, England. The uranyl chloride solutions were prepared by dissolving uranyl chloride hydrate obtained from Yokozawa Chem. Co. Ltd., Japan. All other chemicals were of analytical reagent grade.

Radioactive Nuclides

^{233}U(VI) was obtained from the Radiochemical Centre, Amersham, and was purified by solvent extraction (*11*) before use. (The concentration of uranium in the initial aqueous phases was $\sim 10^{-3}$ mole/liter.) ^{234}Th was milked from an old sample of uranyl chloride as reported (*9*). ^{99m}Tc was separated from its parent 66.6-hr ^{99}Mo by solvent extraction with 4-(5-nonyl)pyridine/benzene (*12*). $^{186+188}$Re was obtained by neutron irradiation of rhenium metal whereas ^{54}Cu, ^{198}Au, ^{99}Mo, and ^{187}W were obtained by neutron activation of the respective reagent grade salts, CuO, $AuCl_3$, MoO_3, and WO_3 in the research reactor of this Institute. Enriched ^{51}Cr (as $CrO_4{}^{2-}$) was prepared by the Szilard-Chalmers process using potassium chromate as the target material (unpublished data). The radioisotopes ^{60}Co, ^{59}Fe(III), ^{54}Mn, ^{63}Ni, ^{47}Sc, and ^{144}Ce in chloride form; ^{95}Nb, ^{95}Zr (freed from its daughter ^{95}Nb before use), and ^{182}Ta in the form of oxalate complexes; and ^{110m}Ag in nitric acid solution were obtained from the Radiochemical Centre, Amersham, and were pure enough to meet catalog specifications.

Radiochemical Assay and Instrumentation

For alpha assay an argon gas-flow proportional counter, Harwell type 3–7/11558, in conjugation with EKCO fast scaler type N 530F was used and also a Nuclear Chicago Corporation alpha scintillation counter Model DS-S serial 1709. Solid beta emitting samples were assayed with the aid of an end window Geiger assembly equipped with G.E.C. tube type EHM/2/S. Gamma ray count rates were determined using a Nuclear Chicago single channel analyzer, model 872, coupled with 3 in. × 3 in. thallium doped sodium iodide well-type gamma ray scintillation counter.

Extraction Procedure and Determination of Distribution Coefficients

The procedure for obtaining equilibrium partitions (the ratio of the equilibrium concentration of uranium in the organic phase to that in the aqueous phase) was as described previously (7). All data were obtained both by direct and reverse extractions.

RESULTS AND DISCUSSION

To find the appropriate diluent for the amine oxides, a number of diluents were tried. Nitric (0.1 *M*) and hydrochloric (6 *M*) acid solutions containing uranium-233 were extracted with 0.1 *M* NPyOx and 0.1 *M* TOAO, respectively, for 3 min, sufficient time for equilibration. The results are cited in Table 1. Benzene exhibited the maximum extraction but was not used because of its high vapor pressure. Xylene gave almost as efficient extraction as benzene and was favored for both of the amine oxides. Low partition coefficients were obtained when chloroform was employed in the

TABLE 1

Distribution Coefficients of Uranium from 0.1 *M* HNO_3 and 6 *M* HCl with 0.1 *M* NPyOx and 0.1 *M* TOAO, respectively

Diluents	Distribution coefficients NPyOx	Distribution coefficients TOAO
Benzene	9.23	10.2
Xylene	9.04	10.0
Toluene	9.00	9.89
Carbon tetrachloride	8.07	8.7
Methyl isobutyl ketone	5.4	8.9
Dibutylcarbitol	3.54	3.1
Chloroform	1.79	7.8

NPyOx system, probably because of its polar character and subsequent interaction through hydrogen bonding with the extractant, thus making the latter less available for the uranium species. Hydrogen-bond interaction has also been noted in the case of pyridine oxides (*13*) and TBP (*14*) with polar chloroform. However, in TOAO/chloroform no pronounced depression of the distribution coefficient was observed. A third phase was formed owing to the limited solubility of the solvate of uranyl nitrate with NPyOx when kerosene was used as a diluent. Under the experimental conditions the organic phase separated into two layers, one of which contained pure solvate and settled at the bottom of the aqueous phase and the other with a reduced concentration of the extractant.

Extraction of Uranium(VI) by 0.1 *M* 4-(5-Nonyl)pyridine Oxide in Xylene at Different Acidities

The isotherms of distribution of uranyl salts between solutions of 0.1 *M* 4-(5-nonyl)pyridine oxide dissolved in xylene and aqueous phases of nitric, hydrochloric, and sulfuric acid solutions are shown in Fig. 1. In the nitrate system the degree of extraction decreases as the acid concentration is increased from 0.005 to 0.01 *M* and then attains a maximum in 0.1 to 0.5 *M* acid media before decreasing again at high acid concentrations. The extraction maximum in the acid range of 0.1 to 0.5 *M* is attributed to the extraction of uranyl nitrate, since high extraction of uranyl nitrate in this acidity range was also observed in the cases of 2-alkylpyridine oxides (*2*, *5*) and sulfoxides (*15*). The decrease in extraction above 0.5 *M* nitric acid can be explained, analogous to the 2-alkylpyridine oxide system (*3*), as due to the decrease in the concentration of free extracting agent with increase of acidity in the aqueous phase. Since uranyl ion is easily hydrolyzed in weakly acid media (*16*, *17*), it may be assumed that the ascending branch of the isotherm below 0.01 *M* nitric acid is mainly due to the extraction of products of the hydrolysis of uranium; e.g., uranyl hydroxide nitrate. In this acid region of high pH, the extraction of uranium as uranyl hydroxide nitrate has also been reported in the cases of 2-alkylpyridine oxides (*2*, *3*), *N*-oxides of amino substituted phosphine oxides (*18*), and sulfoxides (*19*). The extraction of uranyl chloride from hydrochloric acid solutions of low acidity is as efficient as from the corresponding nitric acid solutions, suggesting an identical type of mechanism. Therefore, it seems probable that the extraction of uranyl chloride, like that of uranyl nitrate, in weakly acid solutions is due to the extraction of uranyl chloride along with uranyl hydroxide chloride. A further increase in the equilibrium hydrochloric

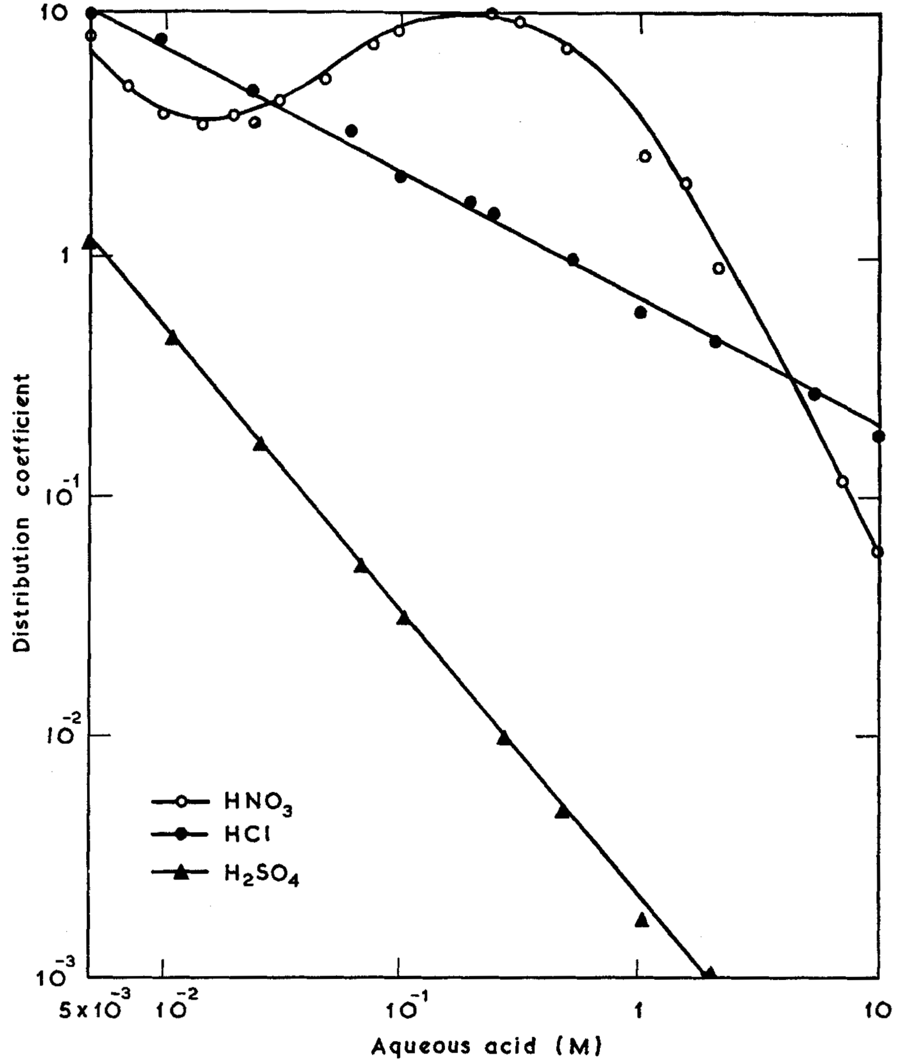

Fig. 1. Variation of distribution coefficient of uranium(VI) with concentration of aqueous acids for extraction by 0.1 *M* 4-(5-nonyl)pyridine oxide/xylene.

acid concentration of the aqueous phase leads to a decrease in the distribution coefficient. This is apparently due to the decrease in the products of the hydrolysis of uranium and a decrease in the concentration of the free extracting agent through its combination with the acid. In the sulfuric acid system the distribution coefficient falls much more rapidly than from nitrate or chloride media. At low sulfuric acid concentrations the extraction seems to be that of uranyl sulfate. The fall in distribution coefficient may be due to the formation of inextractable anionic sulfate complexes.

Effect of Salting-out Agents on the Extraction of Uranium by 4-(5-Nonyl)pyridine Oxide

The results presented in Fig. 2 show the effect of aqueous nitrate, chloride, and sulfate ions on the extraction of uranium(VI) by 0.1 *M* NPyOx/xylene. It is seen that there is no marked change in the extractability when neutral salts are added to the aqueous nitric and hydrochloric acid solutions of 0.005 *M* each. It is possible that in these experiments sodium nitrate and chloride not only act as salting-out agents, but also suppress the hydrolysis of the uranyl ion. The suppression of hydrolysis of multicharged cations,when in a solution of alkali metal salts, with the increased tendency to form stable nitrato or chloro complexes, has been reported by Ivanov et al. (*20*) and Gevorkyan et al. (*21*). Therefore, it may be argued that the decrease in the products of hydrolysis of uranium, which are extracted by the reagent, results in the formation of the complexes which are no better extracted than the uranyl hydroxide nitrate and chloride. The addition of the neutral sulfate to the weakly sulfuric acid solution of 0.005 *M* first increases the distribution coefficient up to about 0.05 *M* but a further increase leads to a continuous slight decrease in the distribution coefficient. The addition of the sulfate ions in the weakly sulfuric acid media indicates that electrically neutral sulfate complexes are formed by the addition of sulfate ions, and when an excess is present the inextractable complexes start forming. The transfer of uranyl nitrate and chloride to the organic phase is increased in the presence of sodium nitrate and sodium chloride when the acidity of the aqueous phase is kept comparatively high at about 0.25 *M*, where hydrolysis does not occur. Such an increase is quite common and can be explained on the basis of common ion and salting-out effects and the absence of acid competition.

Dependence on Concentration of 4-(5-Nonyl)pyridine Oxide

The extraction of uranium using aqueous phase nitric, hydrochloric, and sulfuric acid solutions of constant composition and different concent-

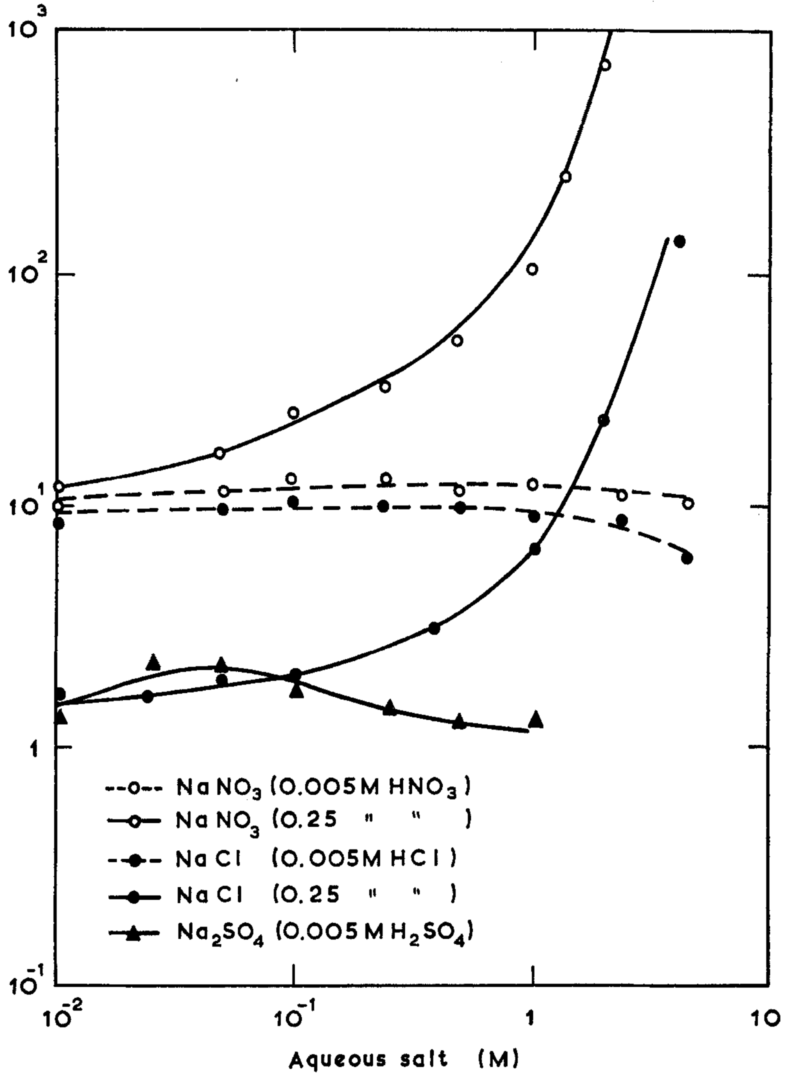

FIG. 2. Effect of salting-out agents on the extraction of uranium(VI) by 4-(5-nonyl)pyridine oxide.

rations of the amine oxide was investigated to find information concerning the extraction mechanism of uranyl salts. The results are shown in Fig. 3.

Assuming that the extraction mechanism of uranyl nitrate by NPyOx is analogous to TBP, the extraction reaction can be represented as

$$UO_{2_{aq}}{}^{2+} + 2NO_{3_{aq}} + y(NP_yO_x)_{org} \rightleftarrows UO_2(NO_3)_2 \cdot y(NPyOx)_{org}$$

with the equilibrium constant (extraction constant):

$$K_1 = \frac{[UO_2(NO_3)_2 \cdot y(NPyOx)]_{org}}{[UO_2{}^{2+}]_{aq}[NO_3{}^-]_{aq}{}^2[NPyOx]_{org}{}^y} \qquad (1)$$

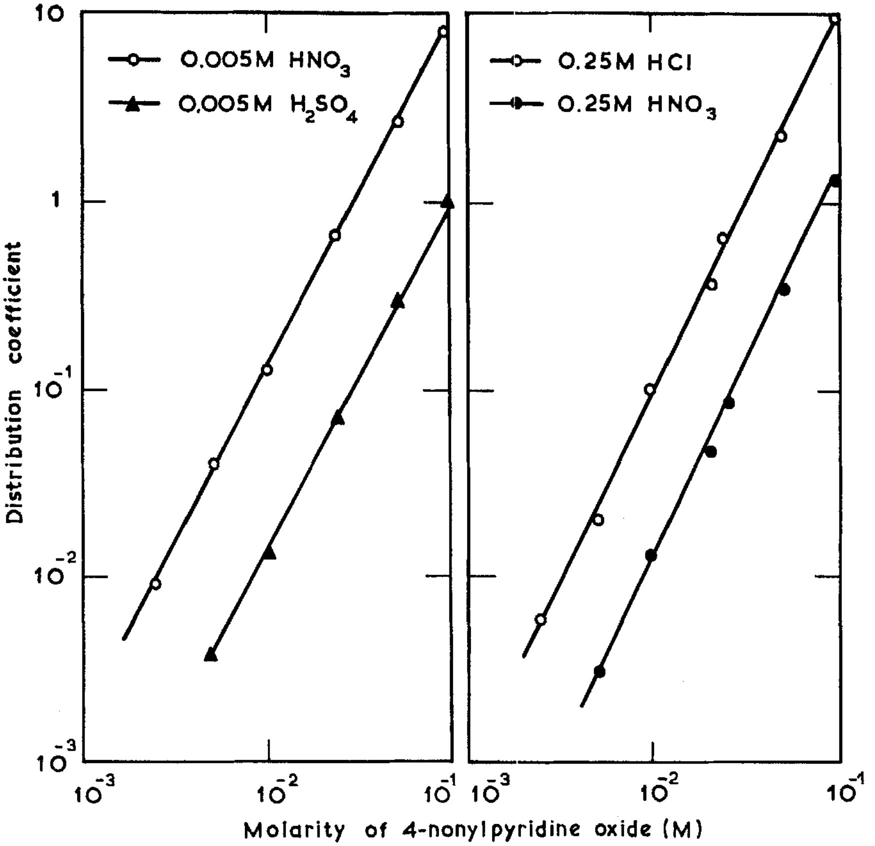

FIG. 3. Dependence of distribution coefficient of uranium(VI) on the concentration of 4-(5-nonyl)pyridine oxide.

Ideally, all the terms in brackets should be activities. In order to avoid complicated thermodynamic factors, the concentrations of the complexing agents are held low enough so that the concentration may be used instead of activities. Thus the metal distribution ratio would be defined as

$$D_1 = \frac{[UO_2(NO_3)_2 \cdot y(NPyOx)]_{org}}{[UO_2{}^{2+}]_{aq}} \tag{2}$$

$$D_1 = K_1[NO_3{}^-]_{aq}{}^2 \cdot [NPyOx]_{org}{}^y \tag{3}$$

At constant acid concentration, Eq. (3) can be written as

$$D_1 \propto [NPyOx]_{org}{}^y$$

i.e., the distribution coefficient is proportional to the power of [NPyOx] concentration corresponding to the number of NPyOx molecules attached to the extracted complex. This feature represents one method whereby the composition of the extracted complex can be determined. The slope of the line showing the dependence of the partition coefficient on the concentration of NPyOx in xylene from 0.25 M HNO_3 on bilogarithmic coordinates, as shown in Fig. 3, is close to 2, so that Eq. (3) can be written as

$$D_1 = K_1[NO_3{}^-]_{aq}{}^2 \cdot [NPyOx]_{org}{}^2 \tag{4}$$

For TBP the same equation may be written as

$$D_2 = K_2[NO_3{}^-]_{aq}{}^2 \cdot [TBP]_{org}{}^2 \tag{5}$$

For the extraction of uranium by NPyOx and TBP from aqueous solutions of the same ionic strength, the following relation can be written:

$$\frac{K_1}{K_2} = \frac{D_1}{D_2} \frac{[TBP]^2}{[NPyOx]^2} \tag{6}$$

for [TBP] = [NPyOx], Relation (6) can be written as

$$\frac{K_1}{K_2} = \frac{D_1}{D_2}$$

From Table 2 it is evident that in very dilute nitric acid solutions the extractability of 4-(5-nonyl)pyridine oxide exceeds that of TBP by 100 to 1000 times. The comparatively high extraction of uranyl nitrate as compared to TBP at low acidities is probably due to the fact that heterocyclic amine oxides are very polar compounds. From Table 3 it is clear that the oxygen atom in heterocyclic amine oxides is more polar than it is in other common oxodonors such as ethers, sulfoxides, and TBP.

TABLE 2

Comparative Evaluation of the Stability of the Complexes of Uranyl Nitrate with NPyOx and TBP

Concentration of HNO_3 (M)	D_1 (0.1 M NPyOx)	D_2 (0.1 M TBP)	K_1/K_2
0.15	9.5	0.0046	2065
0.3	10	0.018	555
0.6	7	0.04	175
1.05	3.5	0.12	29
2.0	1.3	0.25	5
3.0	0.6	0.43	1.4
5.0	0.25	0.65	0.38
6.0	0.15	0.7	0.214
7	0.1	0.5	0.200
8	0.08	0.42	0.19
9	0.06	0.22	0.272
10	0.05	0.14	0.3

TABLE 3

Dipole Moments of Some Oxygen Donor Compounds

	Compound	Dipole moment (Debye units)
1.	$C_5H_5N \rightarrow O$	4.24
2.	$(C_6H_5)_2S \rightarrow O$	4.00
3.	$(CH_3)_3N \rightarrow O$	5.03
4.	$(CH_3O)_3P \rightarrow O$	3.02
5.	$(CH_3)_2S \rightarrow O$	3.90
6.	$(CH_3)_2C{=}O$	2.89
7.	$(C_4H_9)_2S \rightarrow O$	3.93
8.	$(C_6H_5O)_3P \rightarrow O$	2.84
9.	$(n\text{-}C_4H_9O)_3P \rightarrow O$	3.05
10.	$(C_6H_5)_3As \rightarrow O$	5.54

This conclusion is supported by the dipole moment (*22–25*) and thermodynamic studies (*26*). The amine oxide, being more polar and an active solvent, displaces water from the inner sphere of uranyl ion and directly coordinates to the metal ion, whereas TBP needs the help of the acid or the salt to diminish the activity of water. Therefore 4-(5-nonyl)pyridine oxide is superior to tributylphosphate in its extraction ability in very dilute nitric acid as a result of stronger ligand properties and smaller interference from stearic hindrance. This order, however, is reversed in moderate acid media owing to stronger competitive extraction of the acid by the amine oxide due to its comparatively high basicity which is a function of polarity. From the logarithmic dependence of *D* on the reagent concentration, an amine oxide/uranium ratio of ~2 was also found in the organic phase from 0.25 *M* HCl and 0.005 *M* HNO_3 and H_2SO_4. The results are shown in Fig. 3.

Extraction by 0.1 *M* NPyOx/Xylene from Constant Acidity Solutions of HNO_3 and HCl with Variable Uranium Concentration

The saturation experiments were undertaken in order to find out whether the complexes $UO_2(NO_3/Cl)_2$. 2NPyOx are also formed at high loading of the organic phase by U(VI). The results presented in Fig. 4 imply that the limiting loading of 0.1 *M* NPyOx in xylene corresponds to the formation of

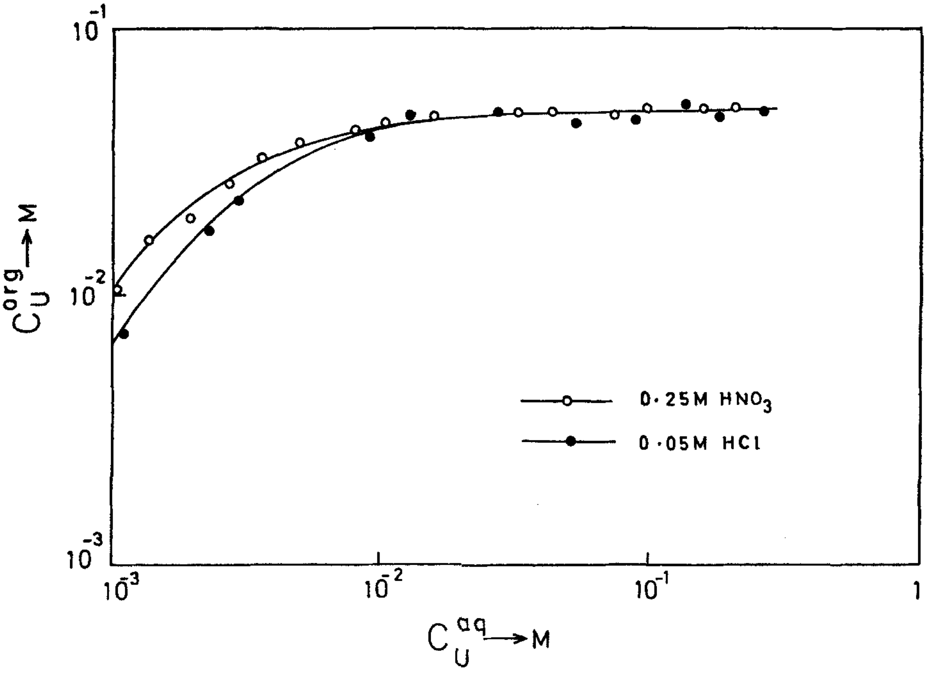

FIG. 4. Extraction by 0.1 *M* 4-(5-nonyl)pyridine oxide/xylene from constant acidity solutions with variable uranium concentration.

the extracted complexes $UO_2(NO_3/Cl)_2 \cdot 2NPyOx$. Analogous types of compounds with pyridine oxides and TBP have been prepared by Nikolaev et al. (*27*) and Healy and Mckay (*28*), respectively.

Extraction of Uranium(VI) by 0.1 *M* Trioctylamine Oxide in Xylene at Different Acidities

It is seen from Fig. 5 that uranium is extracted from mineral acid solutions in a variety of ways that reflect the complexity of aqueous solutions of uranium. The maximum extraction of uranium occurs from weakly acid solutions. The decrease in distribution coefficient is much less pronounced in sulfuric acid than in nitric and hydrochloric acid solutions which show minima between 0.1 to 0.5 *M* acid. The value of the minima in the case of uranyl nitrate is lower than in uranyl chloride. The extraction of the corresponding acids into the organic phase increases in the same sequence (*8*). The decrease in the distribution coefficient in the case of aqueous phase nitric and hydrochloric acid solutions has been attributed by Torgov et al. (*4*) to a decrease in the concentration of free extracting reagent and also due to the decomposition of the complexes of the amine oxide with the hydrolysis products of uranium. The decrease in the partition coefficient with increasing sulfuric acid concentration may be due to the sulfate and bisulfate competition.

Comparison of Trioctylamine Oxide with 4-(5-Nonyl)pyridine Oxide

The results of the present investigation show that the extraction behavior of TOAO (aliphatic amine oxide) is fairly different from that of NPyOx (heterocyclic amine oxide). Part of the reason for these differences in the extraction behaviour can be discerned by examination of the possibilities for resonance in these two classes of *N*-oxides. In TOAO there is no possibility for the delocalization of electrons, and the high polarity ($D \sim 5.4$) is representative of a pure coordinated covalent nitrogen to oxygen linkage. However, in the heterocyclic amine oxide there is a resonance which stabilizes the

$$\underset{\text{I}}{\geqslant N^+\!-\!O^-} \rightleftarrows \underset{\text{II}}{>N^+\!=\!O} \rightleftarrows \underset{\text{III}}{>N\!-\!O^-}$$

amine oxide structure and, second, because of the contribution of Structure II the polarity of heterocyclic amine oxides is less ($D \sim 4.2$) than of

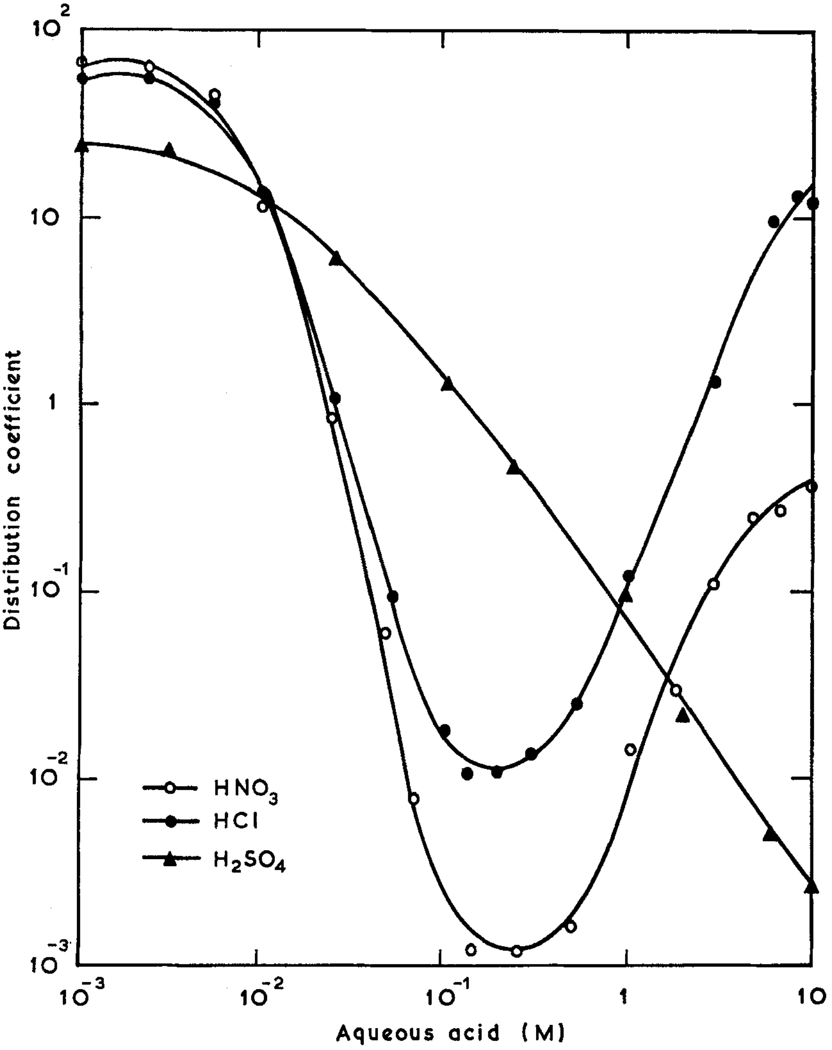

FIG. 5. Extraction of uranium(VI) by 0.1 *M* trioctylamine oxide in xylene at different acidities.

aliphatic amine oxides ($D \sim 5.4$). The ability to extract mineral acids, a function of basicity, is also related to the bond polarity and is less in heterocyclic *N*-oxides (*4*) ($pK_{BH^+} \sim 1.02$) than in aliphatic amine oxides ($pK_{BH^+} \sim 5.2$). Thus the difference in the extraction properties is presumably due to the comparatively high stability of the aliphatic amine oxide ion of the type $(R_3NOH)^+$, the formation of which is favored at comparatively high acidities. Consequently the hydrolyzed and/or nonhydrolyzed uranyl complexes are extracted in the high pH range where the acid competition is negligible. In high acid solutions, however, the strong bonding of the nitrogen bonded oxygen to the proton brings about a decrease in the effective electronegativity of the oxygen atom because of the importance of structure of the type $(R_3NOH)^+$. This makes the amine oxide behave as an amine rather than forming coordinated compounds through the nitrogen bonded oxygen at high acid concentrations. Rozen and Nikolotova (*34*) have also reported that the considerable change of extraction mechanism in the case of TOAO (*3*) from other neutral oxygen donor extractions is due to the comparatively high basicity of the oxygen. An analogous conclusion was drawn by Blair and Michael (*29*) who reported that the extraction ability of tri-*n*-octylarisine oxide, due to its comparatively high basicity, is comparable to trilaurylamine.

Effects of Salting-out Agents on the Extraction of Uranium by Trioctylamine Oxide

The addition of sodium nitrate and sodium chloride in weakly acid solutions (0.005 *M*) of nitric and hydrochloric acid does not increase the distribution coefficient of uranium (Fig. 6). Though the distribution coefficients of uranium at comparatively high salt concentrations are almost of the same order as those obtained in the case of the NPyOx system, it can be seen that the lowering of distribution coefficients with the addition of the salts is more pronounced in this case. This possibly indicates that the addition of neutral salts decreases the hydrolysis of uranium and hence the amount of extractable hydrolysis products, and that the stable chloride or the nitrate complexes formed are not as efficiently extracted by trioctylamine oxide as the products of the hydrolysis of uranium. The addition of the neutral chloride to hydrochloric acid solutions of comparatively high acidity (0.25 *M*) gives rise to high distribution coefficients (Fig. 6). This is due to the fact that when alkali metal chloride is the supporting electrolyte rather than the acid, a fraction of uranium is in the form of $UO_2Cl_3^-$ (*30*) which is probably extracted by an ion pair mechanism. Even though only

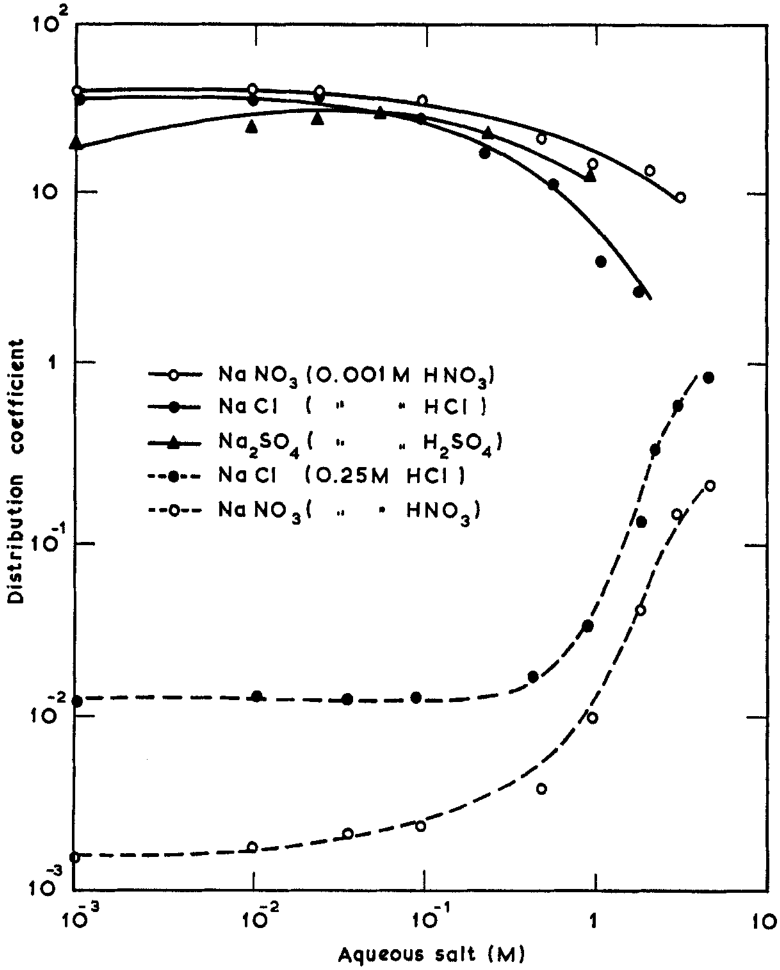

Fig. 6. Effect of salting-out agents on the extraction of uranium(VI) by trioctylamine oxide.

a small fraction of the uranyl ion may exist as an anion complex in solution, its removal by the extraction will result in a comparatively large amount being extracted by the solvent as the equilibrium concentration is continuously re-established. Similarly, the addition of the sodium nitrate in 0.25 *M* nitric acid increased the distribution coefficient, which is in conformity with published information that the anionic nitrate complexes are formed with the addition of sodium nitrate to dilute nitric acid solutions (*31*, *32*).

In sulfuric acid solutions of low acidity the addition of sodium sulfate (Fig. 6) produces results almost similar to the corresponding NPyOx system.

Determination of the Composition of the Extracted Compounds

The composition of the compounds extracted were determined by dilution and maximum saturation methods.

Dilution Method. The dependence of the distribution coefficient on the amine oxide concentration from aqueous nitric and hydrochloric acid solutions of 3 *M* concentration shows a slope of about unity (Fig. 7), indicating that one molecule of the amine oxide is being utilized per molecule of uranyl complex.

This indicates that ion pairs of the type $(UO_2A_3)^-(TOAOH)^+$, where A is a nitrate or chloride ion, are extracted into the organic phase and the extraction reaction can be represented as

$$H_{aq}^+ + UO_{2aq}^{2+} + 3A_{aq}^- + R_3NO_{org} \rightleftarrows (R_3NOH)^+(UO_2A_3)_{org}^-$$

In this region the results of the present investigation coincide with the results of Kennedy and Perkins (*1*), Torgov et al. (*4*), and Maksimovic and Puzic (*6*).

Extraction from Constant Low Acidity Solutions

In the weakly acid media of nitric, hydrochloric, and sulfuric acids (10^{-3} *M*), the slope of the curves characterizing the relationship between the distribution coefficients and the amine oxide concentration in the organic phase is close to 2 (Fig. 8). This shows that from weakly acid solutions a compound with approximately two molecules is formed during uranium extraction.

Maximum Saturation Method. The results obtained for the extraction of uranium (VI) from 0.001 *M* HNO_3, HCl, and H_2SO_4 with 0.1 *M* solutions

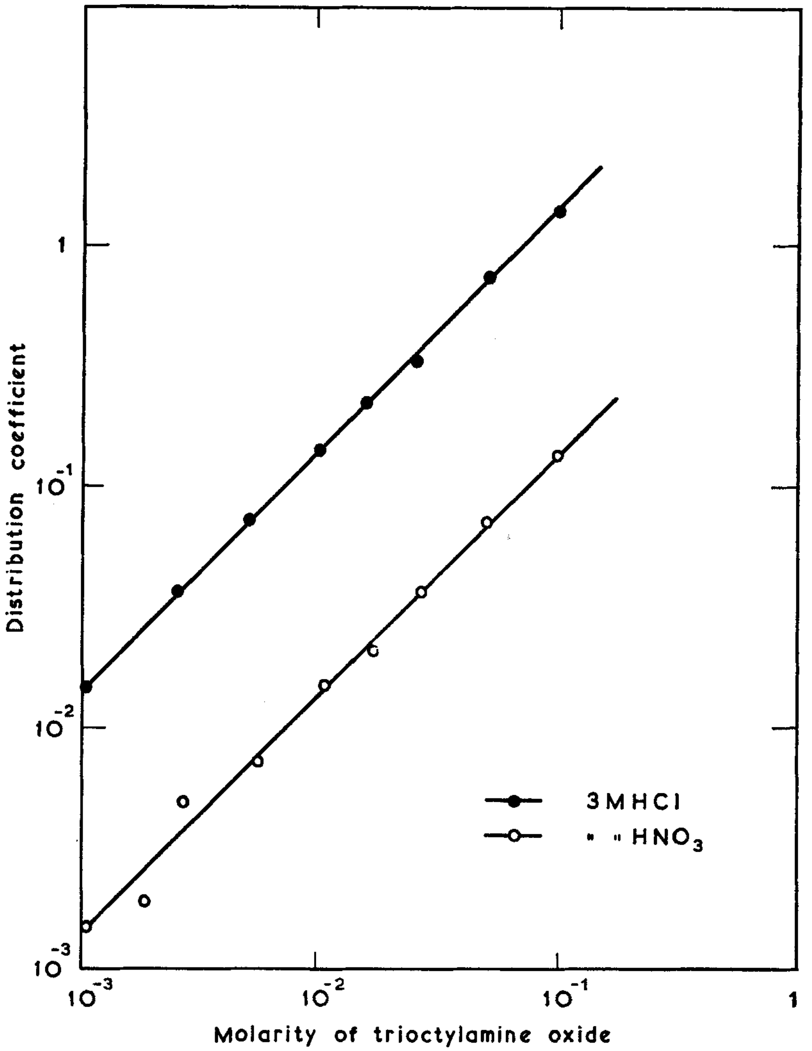

FIG. 7. Variation of distribution coefficient of uranium(VI) with concentration of trioctylamine oxide from constant high acidity solutions.

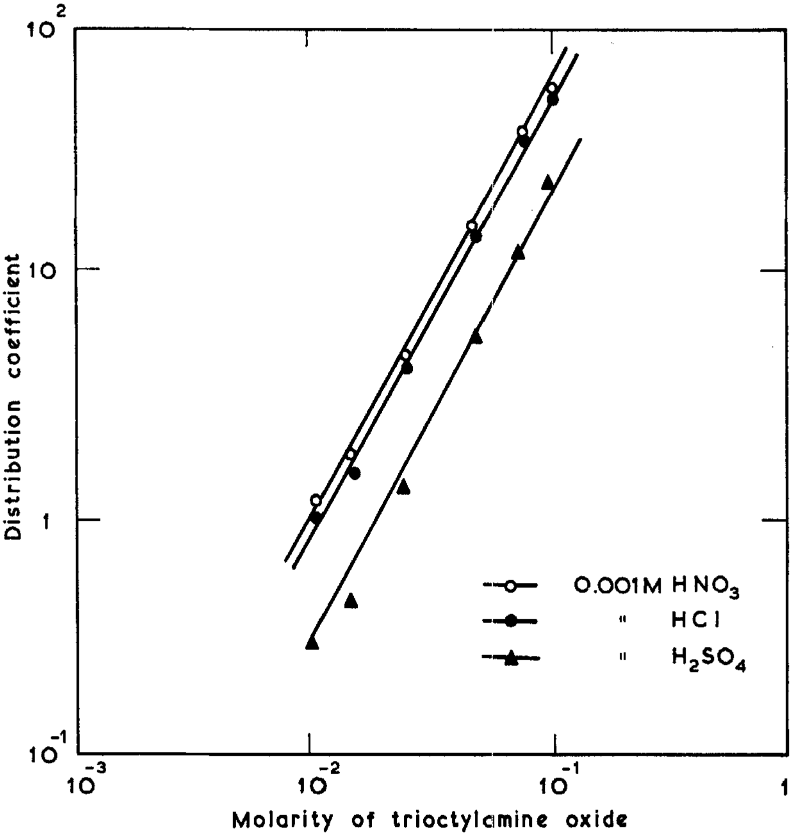

FIG. 8. Variation of distribution coefficient of uranium(VI) with concentration of trioctylamine oxide from constant low acidity solutions.

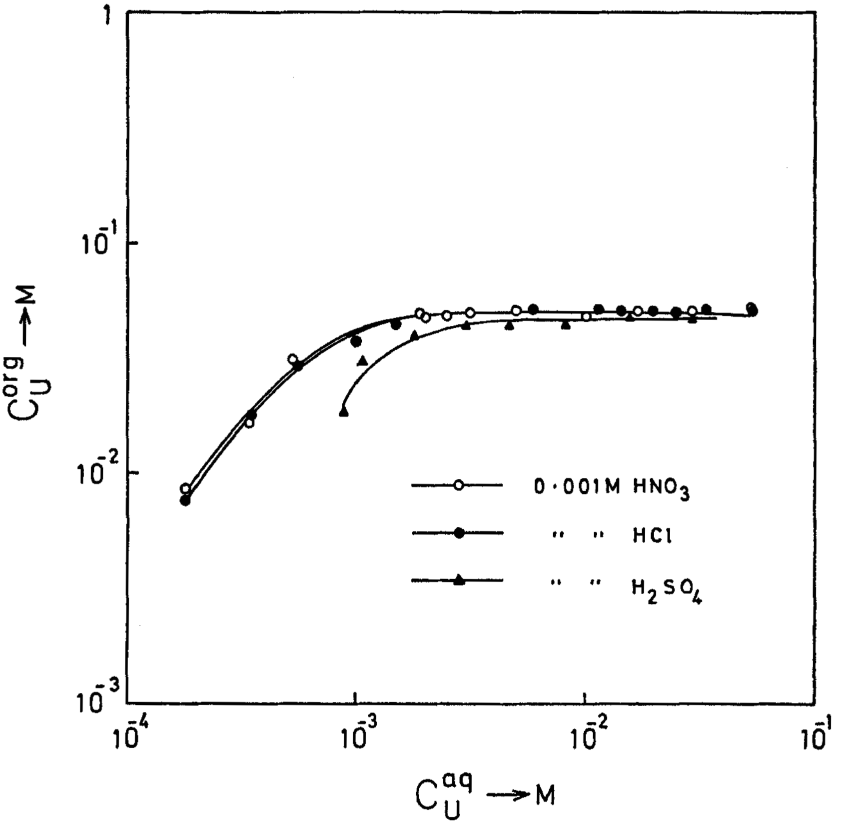

FIG. 9. Extraction by 0.1 *M* trioctylamine oxide/xylene from constant acidity solutions with variable uranium concentration.

of TOAO in xylene are shown in Fig. 9. The TOAO/U ratio in the saturated solutions was ~2 in all cases, as with NPyOx. The compounds of uranyl salts with two molecules of TOAO have been isolated by Nikitina and Liposkii (*33*).

Back Extraction of Uranium

Since uranium extraction from 1 *M* H_2SO_4 in the NPyOx system and from 0.25 *M* HNO_3 and 0.25 *M* HCl in the TOAO system is very poor, these solutions can efficiently be employed to strip uranium from the organic phases.

Separation of Uranium from Fission Product Elements

To find the selectivity of the extraction separation of uranium with 0.1 *M* NPyOx and 0.1 *M* TOAO solutions in xylene from 0.5 *M* HNO_3 and 5 *M* HCl, respectively, the behavior of a number of metal ions, including important fission products, was examined. The data presented in Table 4 show that it is possible to obtain almost complete separation of macroamounts of uranium from the important fission products by both of the amine oxides, since the separation coefficient would improve considerably when the extraction process was carried out in a manner such that there would be a high degree of saturation of the organic phase with uranium.

0.1 *M* NPyOx/Xylene–0.5 *M* HNO_3 System

The extraction of 20 mg of uranium in the presence of fission products was carried out from 0.5 *M* nitric acid +0.1 *M* ascorbic acid. In order to check the behavior of the fission products, the radioisotope of the corresponding element was added to the solution before extraction. The behavior of the fission products was checked on the basis of beta and gamma counts, while the percentage extraction of uranium was estimated gravimetrically by precipitation with oxine after its back extraction from the organic phase by 1 *M* sulfuric acid. The experiment gave 95 ± 2% extraction of uranium, but less than 0.1% extraction of Tc(VII), Nb(V), Ce(III), Y(III), In(III), Zn(II), Ba(II), Sr(II), and Cs.

0.1 *M* TOAO/Xylene–5 *M* HCl

In this system the extraction of 20 mg of uranium gave 95 ± 2% extraction of uranium, but less than 0.1% extraction of Ta(V), Zr(IV), Ce(III), Y(III), Ba(II), Sr(II), and Cs.

TABLE 4

Separation Factors for Various Metal Ions in 0.1 M NPyOx/Xylene and TOAO/Xylene Systems Using 0.5 M HNO_3 and 6 M HCl, respectively

Ion	Concentration (mole/liter)[a]	Separation factors D_U/D_M	
		NPyOx	TOAO
Tc(VII)	C.F.	0.95	0.7
Cr(VI)	5×10^{-2}	1	—
Mo(VI)	10^{-5}	1.02	8
W(VI)	10^{-7}	1	9
Nb(V)	C.F.	2.5×10^{2}	3.3×10^{2}
Ta(V)	10^{-9}	20	5×10^{2}
HF(IV)	10^{-9}	6.6	8×10^{3}
Zr(IV)	10^{-9}	5	5.5×10^{3}
Th(IV)	10^{-9}	1.25	2.4×10^{4}
Ce(IV)	10^{-8}	11	10^{4}
Fe(III)	10^{-5}	50	1
Au(III)	10^{-8}	0.025	10^{-3}
Y(III)	C.F.	1.5×10^{4}	1.1×10^{3}
Ce(III)	10^{-8}	1.6×10^{4}	—
In(III)	10^{-9}	2×10^{3}	0.5
Sr(II)	C.F.	1.3×10^{3}	$\sim 10^{4}$
Ba(II)	10^{-9}	1.2×10^{3}	$\sim 10^{4}$
Zn(II)	10^{-8}	5×10^{4}	—
Co(II)	10^{-9}	4.5×10^{4}	$\sim 10^{6}$
Mn(II)	10^{-4}	2×10^{5}	$\sim 10^{5}$
Cs	10^{-8}	1.7×10^{5}	$\sim 10^{5}$
Ag	10^{-7}	2×10^{3}	—

[a] C.F. = carrier-free.

CONCLUSION

4-(5-Nonyl)pyridine oxide appears to be a better extractant for uranium in low acid concentrations than tri-*n*-butyl phosphate. This is because of its comparatively high polarity, which is not as high as that of aliphatic *N*-oxides and arsine oxides (*29*) where the extraction mechanism changes from solvation to ion association.

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