Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Qureshi, Mudassar A. , Farid, M. , Aziz, A. and Ejaz, M.(1978) 'High Molecular Weight Pyridine Amines as Solvents for Uranium(VI) and Its Separation from Thorium', Separation Science and Technology, 13: 10, 843 — 868

To link to this Article: DOI: 10.1080/01496397808057134

URL: http://dx.doi.org/10.1080/01496397808057134

SEPARATION SCIENCE AND TECHNOLOGY, 13(10), pp. 843–868, 1978

High Molecular Weight Pyridine Amines as Solvents for Uranium(VI) and Its Separation from Thorium[*]

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Abstract

Three high-molecular-weight pyridine amines, 5-(4-pyridyl)nonane, 2-hexylpyridine, and diphenyl-2-pyridylmethane, have been studied as components of solvent extraction systems. Results are presented to show the dependence of the uranium extraction coefficient ($D_a^0 = [U_{org}]/[U_{aq}]$) on equilibrium concentrations of hydrochloric, nitric, and sulfuric acid solutions with and without thiocyanate ions. The optimal conditions for the extraction have been carefully selected from an extensive and critical investigation of the various factors involved; e.g., the effects of diluents, concentration of the mineral acids, thiocyanate ions, salting and complexing agents, and the concentration of the solvents. The extraction mechanism and composition of the extracted complexes of uranium have been studied from partition and slope-analysis data. The results obtained give an orderly picture of the mechanism of extraction of uranium thiocyanate complexes (partly in relation to the hydration and solvation of the compounds extracted). Anomalous extraction behavior was observed at solvent concentrations greater than 0.05 *M*. The results have been interpreted on the basis of the formation of micelles of the salt molecules of the solvents. It has been shown that these pyridines will extract the metal efficiently and reversibly from dilute acid chloride, nitrate, and sulfate solutions containing thiocyanate. Common salts have no depressing effect on extraction. Distribution coefficients and separation factors of several metal ions, with respect to uranium(VI), are reported for the three mineral acid systems, and a method for the separation of thorium-234 from uranium is also described.

[*] Dedicated to Prof. Dr. Khairat M. Ibn-e-Rasa on his 50th birthday.
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INTRODUCTION

Uranium is one of the most important raw materials for nuclear technology, and its separation and purification is of particular interest in processing and reprocessing of nuclear fuel. Its extraction separation may quite arbitrarily be said to start with the observation by Peligot (*1*) of the extractability of uranyl nitrate by ether in 1842. Since then there has been intense research for the development of new extractants for achieving better selectivity and completeness of extraction. In the search for new solvent extraction systems, the variable that has been most profitably exploited is the molecular configuration of the solvent extraction reagents themselves. Through the variation of molecular parameters such as the type of the functional group and molecular geometry, new and useful extractants have been developed. These include carbon- and phosphorus-bonded oxygen-donor solvents, high-molecular-weight amines, chelating compounds, and carboxylic and sulfonic acids. Recently we reported (*2, 3*) the results of our investigations on the utility of amine oxides as extractants for uranium(VI) and its fission products. The extensive amount of data presented in this paper deals with the use of high-molecular-weight pyridine amines as solvents for uranium(VI) from different mineral acid solutions with and without thiocyanate ions. Previous investigations have shown (*4–8*) that the high-molecular-weight pyridine amines are an interesting and versatile class of extractants and behave as liquid-anion exchangers and/or solvating reagents, depending on experimental conditions. In the present study we have used different types of substituted pyridines since the electron density on the nitrogen atom can be influenced by the nature of the organic group attached to the pyridine ring. For this purpose 5-(4-pyridyl) nonane, 2-hexylpyridine, and diphenyl-2-pyridylmethane were chosen. The results of the present investigation indicate that the extraction behavior of these pyridines is somewhat different from each other, and these differences have been explained on the basis of their basicity and accessibility of the active nitrogen atom. The data have been employed for the separation of thorium-234 (UX_1) from an old sample of uranium-238 employing hydrochloric acid solutions. From the point of view of solvent extraction-based separations, the data also suggest a number of other useful possibilities.

EXPERIMENTAL

Reagents

5-(4-Pyridyl)nonane (PyN) and 2-hexylpyridine (HPy) were obtained from K and K Laboratories, Plainview, New York. Diphenyl-2-pyridylmethane (DPPM) was obtained from Aldrich Chemical Co., Milwaukee, Wisconsin. The characteristics of these compounds are given elsewhere (*4*, *9*, *10*). Benzene solutions of the pyridines were used as organic phases in the solvent extraction experiments and were not preequilibrated with the acid solutions from which the extraction was carried out. The mineral acid solutions were generally prepared from B.D.H. volumetric solution ampules or were of Merck "Pro analysis" grade, and their solutions were standardized against solutions of sodium hydroxide of appropriate concentrations. NaOH solutions were freed from carbonate by preparing a standard solution of the alkali and passing it through De acedite FF, (OH^-) form, before dilution to the required volume. Standardization of the alkali solutions was done against *N*/5 potassium hydrogen phthalate solution prepared from the "Primary standard" grade sample of the salt after drying it at 110°C for 3 hr. Solutions of potassium thiocyanate were made by dissolving anhydrous chemically pure salt (B.D.H. AnalR) in demineralized double-distilled water. All other chemicals used in this study were AnalR grade or of the highest purity available.

Tracers

Uranium-233 used as a tracer in the present study was obtained from Radiochemical Centre, Amersham, England, and purified by extraction with diethyl ether to eliminate the extraneous alpha-activity probably due to the growth of daughter of uranium-232 which is generally contained in small quantity in the original supply. Thorium-234 and thorium-230 with a ^{230}Th:^{232}Th ratio of approximately 0.085 were isolated from an old sample of uranyl chloride (*11*) and a pitchblende mineral sample (*12*), respectively. ^{99m}Tc was separated from its parent 66.6-hr ^{99}Mo by solvent extraction according to the method of Faddeva et al. (*13*). Enriched ^{51}Cr was obtained (*14*) through Szilard-Chalmers reaction. ^{59}Fe, ^{65}Zn, $^{198+199}$Au, and ^{99}Mo were obtained by neutron activation of the respective reagent grade salts or the spec-pure metals in the research reactor PARR-1 of this institute. The radioisotopes ^{60}Co, ^{54}Mn, ^{63}Ni, and ^{144}Ce in chloride form, ^{95}Nb and ^{95}Zr (freed from its daughter ^{95}Nb before use) in the form of oxalate complexes in oxalic acid, and $^{110\mathrm{m}}$Ag in nitric acid solutions were obtained from Radiochemical Centre, Amersham, England. The radiochemical purity of the tracers was checked in most of the cases by γ-ray spectrometry and some times by β-ray absorption plots.

Radiochemical Assay and Instrumentation

For alpha-assay a Panex Reigate Series ARD-55/6 set up in conjunction with a windowless Alpha-Beta, 25 mm diameter Anthracene phosphor scintillation detector 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 a 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 a 7.5 × 7.5 cm thallium doped sodium iodide well-type gamma ray scintillation counter. γ-Spectra were taken with a Nuclear Data ND-4410 computer system 512/1024 multichannel analyzer, Model 2560. The detector used with this analyzer was 10 × 7.5 cm NaI(Tl) crystal.

Extraction Experiments

According to the common procedure of liquid–liquid extraction, uranium(VI) or the other test elements was extracted from its mineral acid (HCl, HNO_3, or H_2SO_4) solutions with or without thiocyanate into benzene containing the respective extractant (PyN, HPy, or DPPM); it was proved by the preliminary experiments that the shaking time of 5 min was enough to complete the extraction equilibrium. Throughout the present work the concentration of uranium in the initial aqueous phases was $<10^{-3}\ M$. Each experiment was run in duplicate and the average values are reported. All the extraction studies were done at the ambient temperature (24±2°C). The extraction coefficient D of each ion was determined by the ratio of radioactivity concentration of both phases and is defined as:

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

RESULT AND DISCUSSION

To find the appropriate diluent for the pyridine solvents, a number of diluents were tried. Table 1 shows the extraction data of uranium(VI)

TABLE 1

Effect of Diluents on the Distribution Coefficient of Uranium(VI) between a 0.1 *M* solution of NPy in a Diluent and an Aqueous Solution of 7 *M* HCl

Diluent	Dielectric constant	Dipole moment, μ (in debyes)	*D*
Benzene	0.284	0	16.8
Carbon tetra-chloride	2.238	0.0	0.09, third phase formation
Xylene	2.568	0.62	0.431
Chloroform	4.806	1.15	2.37
Nitrobenzene	34.8	3.99	0.24, third phase formation

from 7 *M* hydrochloric acid for various PyN–organic diluent systems. Some properties of the diluents, e.g, dielectric constant and dipole moment, are also given since it has been shown (*15*, *16*) that the dielectric constant and π-electrons of the diluent influence the extraction of acids and metal ion into the organic phase. It is seen that the partition coefficient decreases with an increase in diluent polarity. Benzene exhibited maximum extraction and was used as a diluent in subsequent experiments. In the case of carbon tetrachloride a loss of activity was recorded and precipitate appeared in the aqueous phase. The precipitation is probably due to the aggregation of the pyridine salts to such an extent that splitting of the organic phase occurs and the micelles of the salt molecules settle down into the aqueous phase. In the case of nitrobenzene, a diluent of relatively high dielectric constant which is expected to depress association, the loss of activity may be due to a third phase resulting from the partial miscibility of the uranium-amine complex in the organic phase or from the partial dissociation of the ion-pair.

The dependence of the partition values of trace ($<10^{-3}$ *M*) amounts of uranium on the hydrochloric acid concentration is shown in Fig. 1A for 0.1 *M* benzene solutions of PyN, DPPM, and HPy. In all cases the extraction increases with increasing concentration of the acid in the initial aqueous phases, attains maxima at around 7 *M* concentration where strong anionic chloride complexes of the metal exist, and then decreases. The decrease in extraction is evidently due to the competition of the acid for association with the free base or due to the formation of less extractable metal complexes. It is seen that the extraction in the PyN system is much greater than in DPPM and HPy systems. This cannot be explained by the basicity effect alone, and the discrepancy can also be ascribed to the steric effects of the bulky groups adjacent to the nitrogen atom and thus shield-

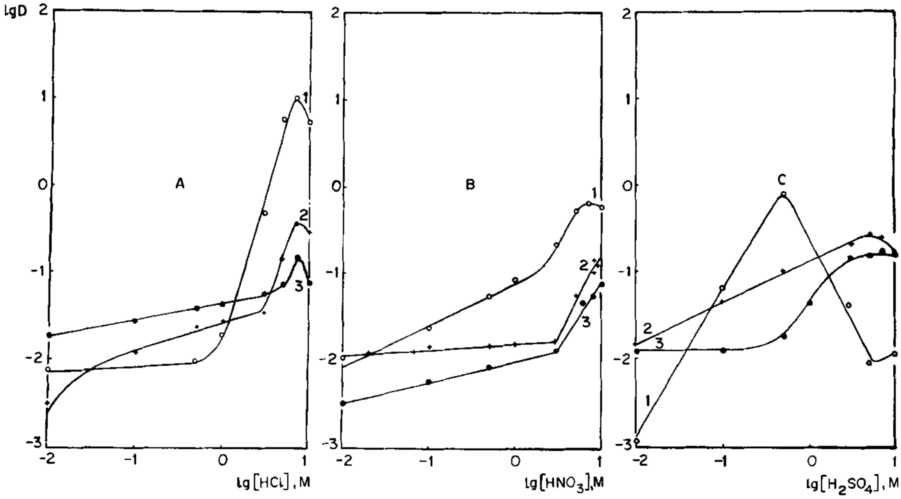
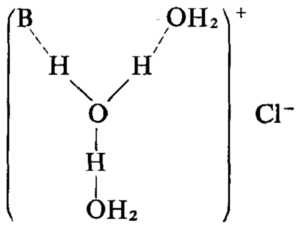


FIG. 1. Dependence of the distribution coefficient of uranium on the concentration of the mineral acid solutions using 0.1 *M* solvent/benzene. Curves: 1, PyN; 2, DPPM; 3, HPy.

ing the functional groups and retarding the complex formation. In the case of HPy and DPPM the extraction of uranium from the whole range of acid concentration is poor. This is perhaps because HPy and DPPM do not form stable cations of the type $(BH)^+$ through electrostatic interaction but instead lead to the formation of hydrogen bonded ions, $(B\text{--}H^+)$, which associate with the uranium anionic chloride species to give an unstable ion-pair. Another plausible explanation is that the acid is extracted via the hydrated proton, $(H_3O)^+$ (oxonium ion), because in aqueous solutions HPy and DPPM, due to their low basicity, do not compete favorably with water for the proton. A possible structure for the extracted species of hydrochloric acid is



and the hydrolyzed pyridine amine hydrochlorides result in the formation of unstable ionic associates, $B\cdot H_3O(H_2O)_n\cdot UO_2Cl_{2+n}^{n}$, through the anionic consequences. The above structure for the cationic portion indicates that solvation and hydration numbers are variable quantities, while the cationic portion as a whole is a quite labile structure. These results are in accordance with the previous observations (7) that anionic complexes (except those which form complex metal acids) are poorly extracted by these pyridines, especially HPy. Such a behavior makes these pyridines very selective for the separation of uranium from base metal ions such as Fe(III) and Cr(VI) which are quantitatively extracted as complex metal acids from moderate acid solutions.

The extraction isotherms of uranium(VI) from nitric acid solutions by 0.1 *M* benzene solutions of PyN, DPPM, and HPy are plotted in Fig. 1B. In the case of PyN the extraction isotherm shows a maximum at around 7 *M* acid concentration before decreasing at high acidities. The extracted uranium species is apparently the anionic nitrate complex whose extraction decreases as the acid competition increases. In the case of HPy and DPPM the extraction is less than for PyN, and there is no decrease in the partition value at relatively high acidities. This is probably because the acid competition for the reagent (– ve extraction effect) and the formation of less hydrolyzed (more extractable) species through the reduction of water activity (+ ve extraction effect) act in opposite directions, and the partition value does not decrease at 10 *M* acid as in the corresponding PyN system. The extraction of uranium in these systems is less than in the corresponding chloride systems because uranium does not form strong anionic nitrate complexes in nitric acid media.

In the sulfuric acid system (Fig. 1C), PyN shows maximum extraction at around 0.5 *M* acid concentration. The extracted uranium species are perhaps the neutral and/or anionic sulfate complexes whose extraction decreases as the sulfate/bisulfate ratio decreases. In the case of HPy and DPPM, unlike PyN, the extraction increases as the concentration of the acid in the aqueous phase increases. This can be explained similarly to the nitrate system.

The mechanism of the extraction of anionic chloride, nitrate, and sulfate complexes (excluding hydration) by the pyridines can be represented as

$$[UO_2X_{(m+n)}^{-m}]_{aq} + mBHX_{org} \rightleftarrows [(BH)_m \cdot UO_2X_{(m+n)}]_{org} + mX_{aq} \quad (1)$$

(where X is the anion of the acid and B is a molecule of the nitrogen-containing organic solvent) or through the mechanism of adduct formation, more properly described as

$$[UO_2X_n]_{aq} + mBHX_{org} \rightleftarrows [(BH)_m \cdot UO_2X_{(m+n)}]_{org} \quad (2)$$

However, the two systems are thermodynamically equivalent and are only different methods of arriving at the same end, and they lead to the identical predictions concerning the equilibrium condition. Since in acid media, except in acid-deficient regions, the anion-exchange mechanism plays a major role in extraction by the pyridines, the equilibrium constant from Eq. (1) can be represented as

$$K = \frac{[(BH)_m UO_2 X_{(m+n)}]_{org}[mX]_{aq}}{[UO_2 X^{-m}_{(m+n)}][BHX]^m_{org}}$$

and the partition coefficient

$$D = \frac{[(BH)_n UO_2 X_{(m+n)}]_{org}}{[UO_2 X^{-m}_{(m+n)}]_{aq}}$$

$$= K \frac{[BHX]^m_{org}}{[mX]_{aq}}$$

at constant aqueous ligand concentration

$$D \propto [BHX]^m_{org}$$

This treatment is only approximate and true only for dilute solutions. According to the law of mass action, the log-log plot of D vs [pyridines] at a constant aqueous ligand concentration should be equal to m, the pyridine association number. The effect of varying the PyN, DPPM, and HPy concentrations on the extraction of uranium from solutions which were 7 M with respect to HCl is shown in Fig. 2. The dependence of the distribution coefficient on the concentration of PyN, DPPM, and HPy from 7 M HCl shows that the slope of the linear parts of the curves is ~2, indicating that two molecules of the pyridines are being utilized per molecule of uranyl complex. This indicates that ion-pairs of the type $(UO_2Cl_4'')(BH)_2{}^+$ are extracted into the organic phase, and extraction occurs through the anionic consequences. Another plausible explanation is that the extraction of $UO_2Cl_3{}^-$ occurs through the formation of mixed quadrupoles formed by the association of free amine salts of the mineral acid with the uranium species to give $(BH^+)Cl^- \cdot BH^+ \cdot UO_2Cl_3{}^-$ either because of dipole-dipole head-to-tail association of $(BH^+)Cl^-$ with $BH^+ \cdot UO_2Cl_3{}^-$ or because two BH^+ cations are hydrogen bonded to one chloride anion.

The effect of neutral chloride ions on the extraction of uranium by 0.1 M PyN and 0.1 M DPPM in benzene was investigated, and the extraction efficiency was determined at different molarities of the chloride salts of Li^+, Mg^{2+}, and Al^{3+} while keeping the hydrochloric acid concentra-

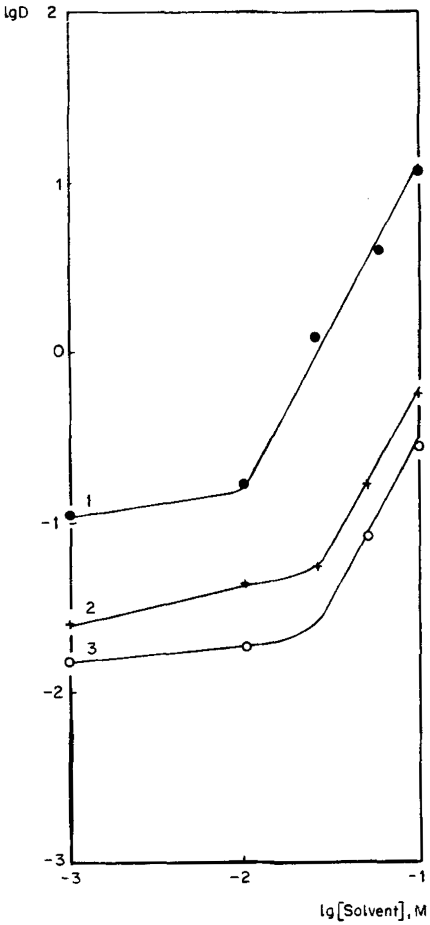


FIG. 2. Variation of the distribution coefficient of uranium with solvent concentration from 7 *M* HCl. Curves: 1, PyN; 2, DPPM; 3, HPy.

tion fixed at 0.1, 0.5, and 1 *M*. The extraction curves thus obtained are shown in Figs. 3 and 4, respectively. The results apparently suggest that once the pyridines are converted into their chloride salts, H^+ ions do not play a key role in the extraction, and also that the extraction depends only on the chloride ions. The extraction seems to increase in the order $AlCl_3 > MgCl_2 > LiCl$. This indicates the increasing aqueous hydration of these ions with increasing charge number. This is because a large charge number

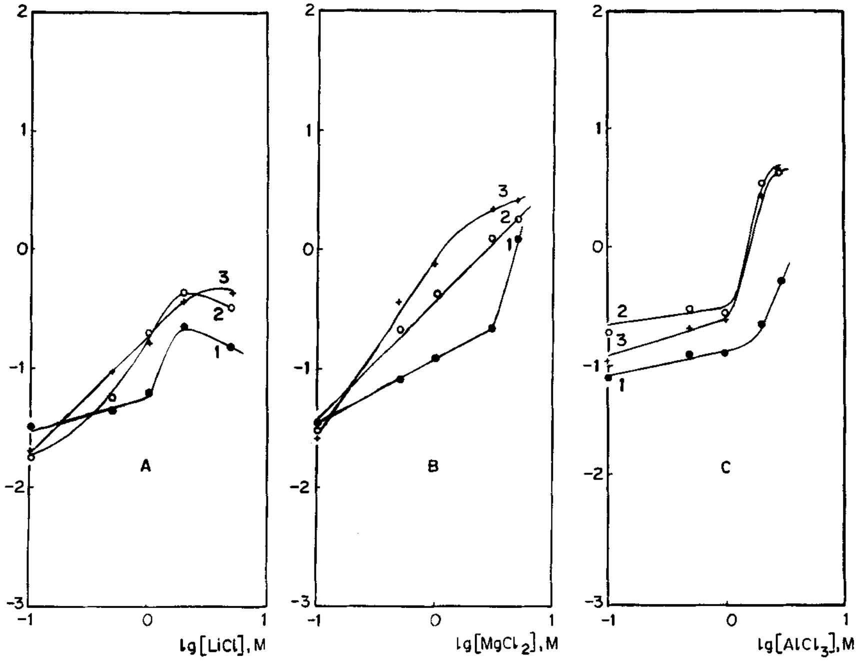


FIG. 3. Variation of the distribution coefficient of uranium as a function of the concentration of the chloride salts of lithium, magnesium, and aluminum from constant hydrochloric acid solutions by 0.1 *M* PyN/benzene. Curves: 1, 0.1 *M* HCl; 2, 0.5 *M* HCl; 3, 1 *M* HCl.

helps the ions to exert a high electrical potential (Ze/r) which acts on the dipoles of water molecules which rearrange themselves around the ions in different ways depending on their charge and radius, thereby affecting the structure of water and its activity to different extents.

We investigated the extraction of uranium from aqueous mineral acids containing 0.02 *M* potassium thiocyanate using 0.1 *M* solutions of the pyridines in benzene. Figure 5 shows the initial hydrochloric, nitric, and sulfuric acid concentrations and the extractability of uranium(VI). From this figure it is seen that in low acid concentrations the partition coefficients, with the addition of thiocyanate, are higher than in the simple chloride, nitrate, and sulfate systems. This is presumably because thiocyanate ions, unlike common acid anions of relatively higher electrical potential, do not coordinate the proton of the hydrated water in the aqueous sheath of the metal ion and get into the inner coordination sphere where

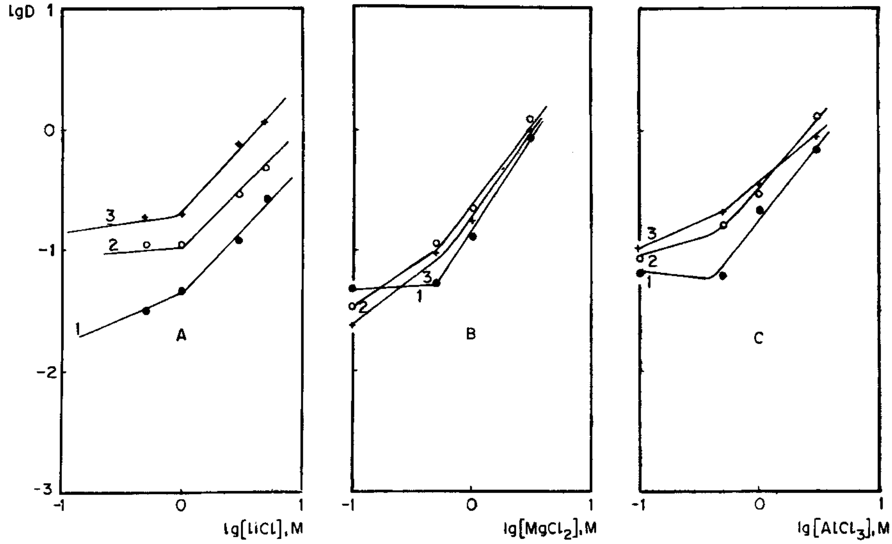


FIG. 4. Variation of the distribution coefficient of uranium as a function of the concentration of the chloride salts of lithium, magnesium, and aluminum from constant hydrochloric acid solutions by 0.1 *M* DPPM/benzene. Curves: 1, 0.1 *M* HCl; 2, 0.5 *M* HCl; 3, 1 *M* HCl.

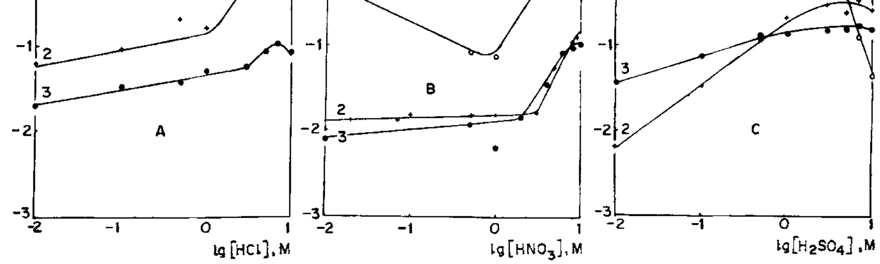


FIG. 5. The plot of the distribution coefficient of uranium vs the concentration of the mineral acid solutions containing 0.02 *M* KSCN by the solvent solutions in benzene. Curves: 1, PyN; 2, DPPM; 3, HPy.

the electrostatic interaction is supplemented by donor–accepter interaction, with the result that thiocyanate leads to the formation of larger and less hydrated complexes. However, in moderate and concentrated acid solutions, the partition values are not very much influenced by the addition of thiocyanate. This is because of the fairly high concentration of the anions of the supporting acids.

In order to examine the influence of thiocyanate concentration on the extraction of uranium, the dependence of the distribution ratio of uranium as a function of the thiocyanate concentration in the aqueous phase was investigated from constant acidity solutions. The log-log plots of the distribution ratios vs the concentrations of thiocynanate in the aqueous phases are presented in Fig. 6 for the hydrochloric acid system. The maximum extraction in the three bases occurs in the range of 0.1 to 1 *M* concentration of potassium thiocyanate. In acid-deficient systems (< 1 *M*

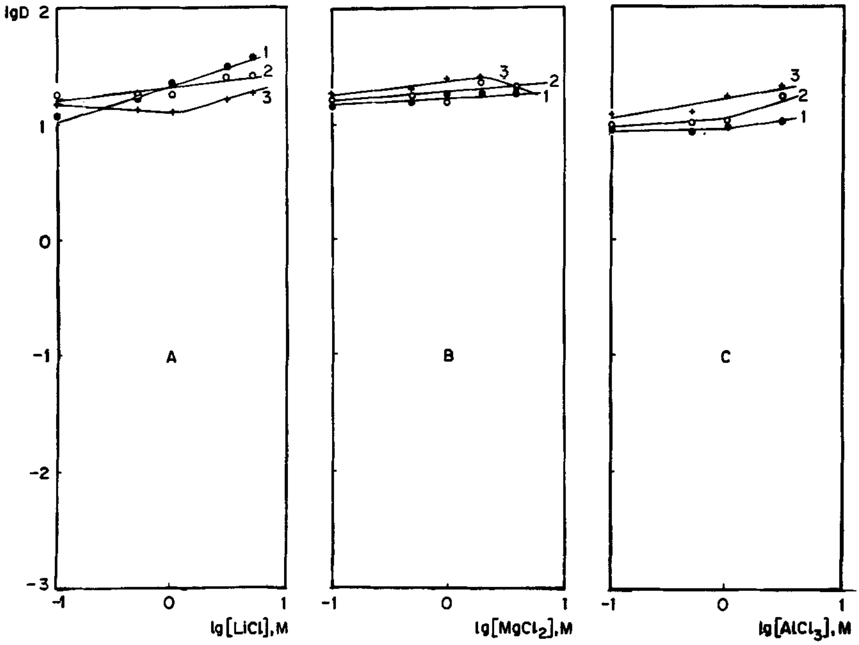


FIG. 6. Dependence of the distribution coefficient of uranium on the aqueous thiocyanate concentration for extraction by 0.1 *M* solvent solutions in benzene from hydrochloric acid media. A, PyN; B, HPy; C, DPPM. Curves: 1, 0.01 *M* HCl; 2, 0.1 *M* HCl; 3, 0.5 *M* HCl.

concentration) all the three nitrogen-bearing solvents can be considered to extract electrically neutral species by solvation. The general extraction reaction can be described as

$$UO_2X_2nH_2O + yB + zKSCN = UO_2(B)_y(SCN)_z + 2KX + nH_2O$$

In the case of PyN (Fig. 4A), the slope of the linear parts of the curves decreases from a value of +2 as the acid concentration increases from 0.1 to 1 *M*. This is believed to be due to the co-extraction of the acid, which cannot be ignored. Even though the same fraction of thiocyanate is utilized for extractable species, the slope would not necessarily indicate the true solvation number. In the case of HPy and DPPM, the partition values remain nearly constant up to 0.05 *M* thiocyanate, indicating that a hydrated uranium complex is extracted by these reagents which, because of their low basicity, cannot compete with water for coordination sites

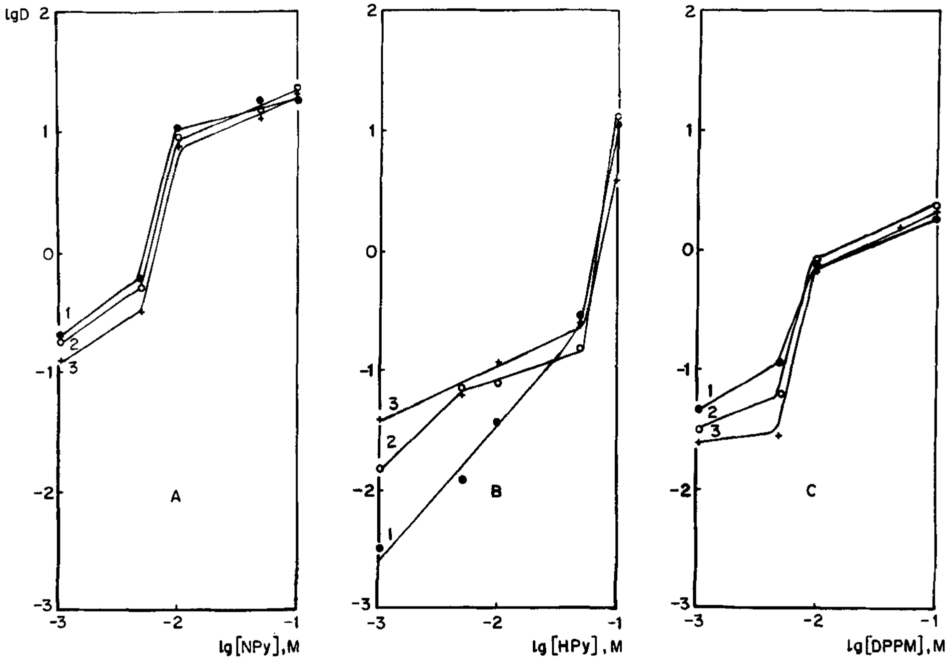


FIG. 7. Dependence of the distribution coefficient of uranium on the aqueous thiocyanate concentration for extraction by 0.1 *M* solvent solution in benzene from nitric acid media. Curves: 1, 0.01 *M* HNO_3; 2, 0.1 *M* HNO_3; 3, 0.5 *M* HNO_3.

of uranium. A certain amount of SCN^- is required to reduce the activity of water and give extractable complexes. Extraction in the PyN and HPy systems is quantitative in the range of 0.5 to 1 *M* KSCN, but DPPM extracts thiocyanate complexes less efficiently. Despite the similar extraction reaction, it is reasonable to distinguish between alkyl- and aryl-substituted pyridines. The most striking difference between the two types lies in the electron density at the nitrogen atom which influences the polarity, basicity, and coordination power of the extractant. In the case of DPPM, electron sinks, viz., phenyl groups, and from electrometric effects, it is expected to show less extraction capacity than PyN and HPy.

The influence of the concentration of thiocyanate ions on the extraction of uranium by 0.1 *M* benzene solutions of the pyridine from nitric and sulfuric acid media is shown in Figs. 7 and 8, respectively. The results are fairly similar to the corresponding hydrochloric acid system, indicating that the nature of the supporting acid does not greatly influence the nature of the extractable species. However, in the case of the PyN–sulfuric acid system, the partition values are fairly high at 1 *M* KSCN when the concentration of the acid is low. This is probably due to the formation and extraction of the metal as mixed sulfate-thiocyanate complexes.

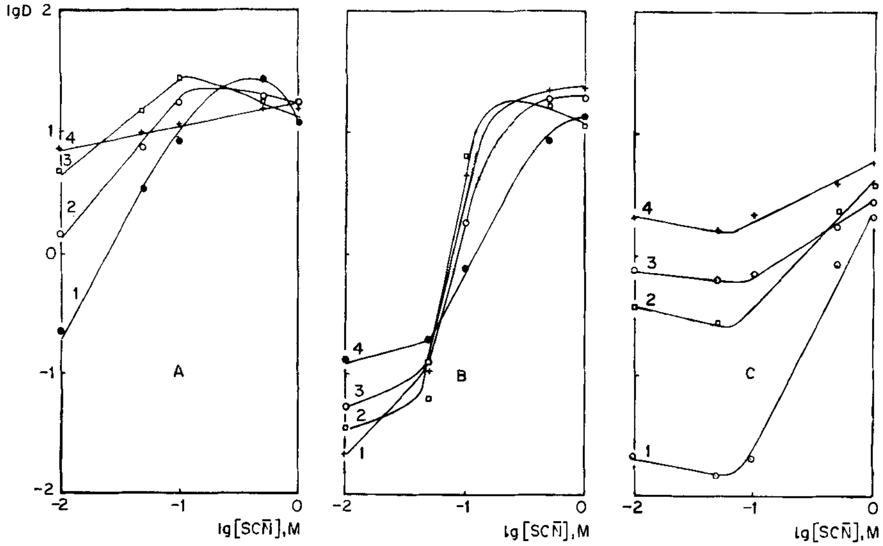


FIG. 8. Dependence of the distribution coefficient of uranium on the aqueous thiocyanate concentration for extraction by 0.1 *M* solvent solutions in benzene from sulfuric acid media. A, PyN; B, HPy; C, DPPM. Curves: 1, 0.01 *M* H_2SO_4; 2, 0.1 *M* H_2SO_4; 3, 0.5 *M* H_2SO_4; 4, 1 *M* H_2SO_4.

The composition of the extracted compounds in the pyridine systems was determined by diluting the extracting agents with benzene. Figure 9 shows such plots for PyN, HPy, and DPPM. In the PyN system, when the partition coefficients are plotted on a log scale against the solvent concentration also on a log scale (Fig. 9A), straight lines are not obtained. Instead, curves are obtained which can be resolved into three straight sections, a line with a slope of approximately unity for low pyridine concentrations in the vicinity of $\sim 10^{-3}$ M PyN/benzene, a second section with a slope of approximately 4 beginning at 5×10^{-3} M PyN, and a flat section with almost zero slope at $>10^{-2}$ M. The third sections with almost zero slope have also been reported in the case of aliphatic amines by certain authors who attribute the phenomenon to the aggregation of the amine salts into micelles in the organic phases, since the diluent is of low dielectric constant and does not reduce the electrostatic forces between neighboring PyN–HCl ion-pairs, thus increasing the tendency to polymerize at a

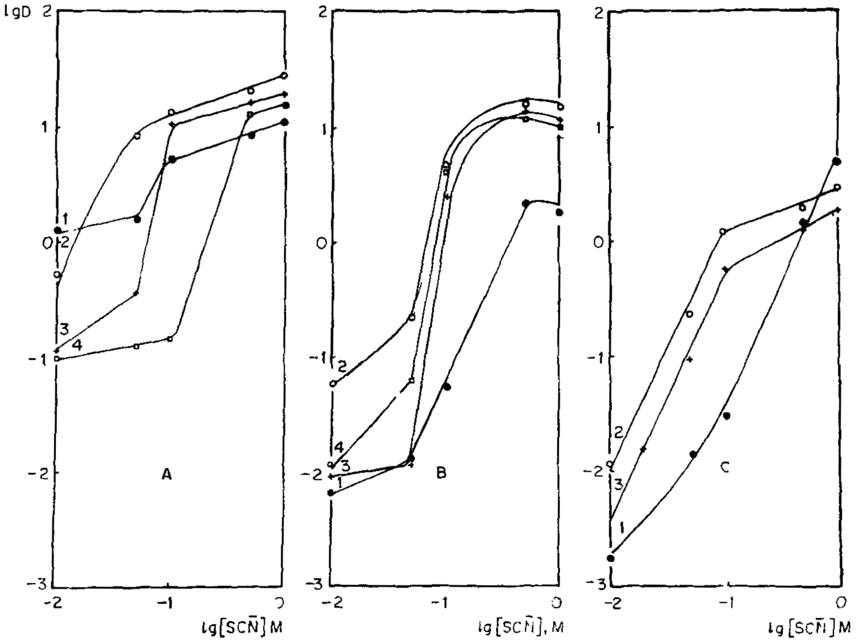


FIG. 9. Variation of the distribution coefficient of uranium as a function of solvent concentration in benzene from 0.1 M mineral acid solution containing 0.5 M KSCN. A, PyN; B, HPy; C, DPPM. Curves: 1, 0.1 M HCl; 2, 0.1 M HNO_3; 3, 0.1 M H_2SO_4.

particular concentration according to

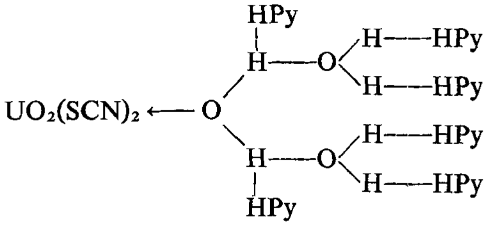
$$\mathrm{NPyH^+ + Cl^- \rightleftarrows NPyH^+Cl^- \rightleftarrows (NPyH^+Cl^-)_2}$$

$$\mathrm{(NPyH^+Cl^-)_{\it n} \rightleftarrows (NPyH^+Cl^-)_{micelles}}$$

The first section of the curves with slope ~1 indicates that at low reagent concentrations only one molecule of the extractant is involved in the extraction process, and as the concentration of the pyridine increases, more molecules become attached to the uranium complex (which is probably hydrolyzed). In the case of the PyN–HCl–SCN^- system (Fig. 9B), the slope of the linear parts of the curves in the reagent concentration range of 0.005 to 0.01 *M* is close to 4. At the same time, the plot of log of distribution ratios vs the log of thiocyanate ion concentration from low acid concentration indicates a slope of ~2. This shows the probable nature of extracted species to be $UO_2(SCN)_2(PyN)_4$. In the case of HPy at reagent concentrations greater than 0.05 *M*, the slope of the linear parts of the curves is close to 6. The solvation number 6, which is higher than that commonly found for halides and thiocyanates, seems reasonable because the concentration of the supporting acids is too low to expel the water molecules from the hydrate shell. Thus a large number of HPy are necessary to reduce the number of water molecules and give an effective extraction. It is also possible that a hydrogen bond is formed between the hydrogen atom of the water molecules directly coordinated with uranium since the water molecules entering the inner sphere are strongly deformed and acquire acidic properties, and the solvent molecules possessing the properties of a base can interact with the coordinated water. Water molecules may also be present in the second hydration layer, and as the ligand concentration increases, these organic molecules become attached to the hydration water to give a complex of the type

$$\mathrm{UO_2(SCN)_{\it n}(H_2O)_{\it n} \cdot (HPy)_6}$$

which can be structurally written as:



As the concentration of the supporting acids increases, the solvation number appears to decrease from this value. It is probable that the smaller the number of hydrating water molecules, the fewer the sites for the addition of solvent. Therefore, the solvation number will diminish with an increase in the equilibrium concentration of acid in the aqueous phase. It is seen that under similar conditions of extraction, the solvation numbers in these solvents are different from each other. This is because the degree of hydration of uranyl salts depends on the nature of the active solvent. Relatively active PyN is expected to displace water from the inner sphere of the uranyl ion and extract anhydrous uranyl thiocyanate by entering the positions usually occupied by two water molecules. However, uranyl thiocyanate appears to be extracted as the hydrated species in the case of HPy and DPPM. A possible explanation of this is that the substitution at α-positions of these pyridines creates steric hindrances whereby these pyridines cannot displace the water.

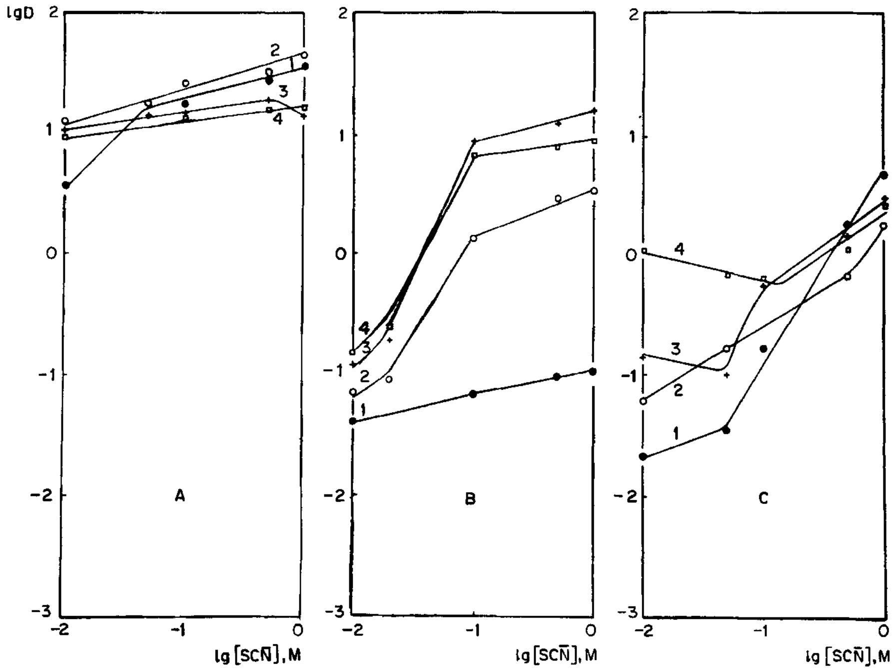


FIG. 10. Variation of the distribution coefficients of uranium as a function of concentration of chloride salts of lithium, magnesium, and aluminium by 0.1 *M* PyN/benzene from constant hydrochloric acid solutions containing 0.5 *M* KSCN. A, LiCl; B, $MgCl_2$; C, $AlCl_3$. Curves: 1, 0.1 *M* HCl; 2, 0.5 *M* HCl; 3, 1.0 *M* HCl.

We investigated the extraction of uranium from thiocyanate solutions as a function of the concentration of LiCl, $MgCl_2$, and $AlCl_3$ in aqueous solutions. The data obtained are given in Fig. 10. In all cases the extraction is quantitative over the whole region of the concentration of the salts, showing that high salt concentrations do not depress extraction.

The extraction of uranium was also investigated as a function of the concentration of different anions added to the constant acidity solutions of hydrochloric, nitric, and sulfuric acid containing optimal concentration of potassium thiocyanate by 0.1 *M* PyN, HPy, and DPPM solutions in benzene. The results are presented in Figs. 11, 12, and 13, respectively. In the case of PyN (Fig. 11), sulfate, nitrate, and ascorbate ions have no

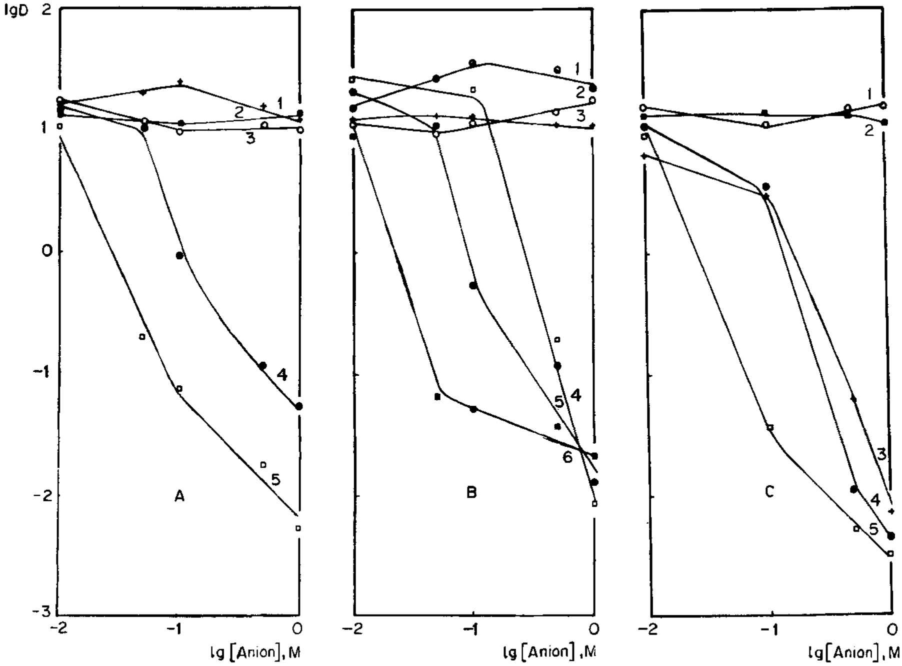


FIG. 11. The effect of the addition of some anions on the extraction of uranium with 0.1 *M* PyN/benzene. A, Initial aqueous solutions: C_{HCl}, 0.1 *M*; C_{SCN^-}, 0.5 *M*. Curves: 1, sulfate; 2, nitrate; 3, ascorbate; 4, oxalate; 5, acetate. B, Initial aqueous solutions: C_{HNO_3}, 0.1 *M*; C_{SCN^-}, 0.5 *M*. Curves: 1, chloride; 2, ascorbate; 3, sulfate; 4, acetate; 5, oxalate; 6, citrate. C, Initial aqueous solutions: $C_{H_2SO_4}$, 0.1 *M*; C_{SCN^-}, 0.5 *M*. Curves: 1, ascorbate; 2, chloride; 3, oxalate; 4, citrate; 5, acetate.

effect in concentrations up to 1 *M* in the initial aqueous solutions which were 0.1 *M* with respect to hydrochloric acid. Oxalate and acetate ions suppress the extraction. In the correspond ingnitric acid system, chloride, sulfate, and ascorbate ions have no effect whereas acetate, oxalate, and citrate ions prevent extraction almost completely at around 1 *M* concentration. Oxalate, citrate, and acetate also decrease extraction of uranium when the supporting medium is sulfuric acid. This indicates that the extractable uranium complex is independent of the nature of the supporting acid, and that oxalate, citrate, and acetate ions can be successfully used for the back-extraction of the metal. The results for the corresponding HPy and DPPM systems, plotted in Figs. 12 and 13, respec-

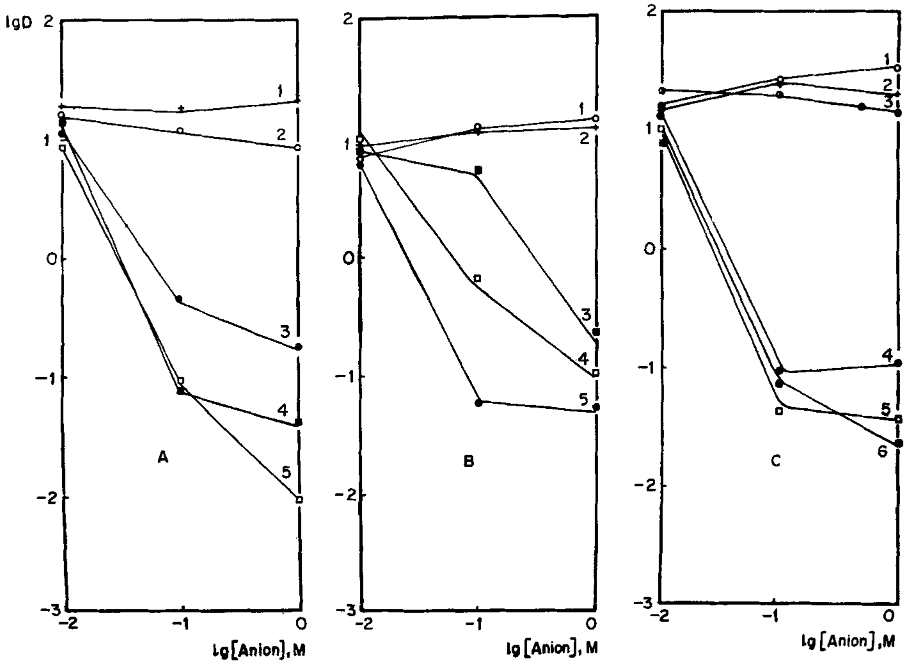


FIG. 12. The effect of the addition of some anions on the extraction of uranium with 0.1 *M* HPy/benzene. A, Initial aqueous solutions: C_{HCl}, 0.1 *M*; C_{SCN^-}, 0.5 *M*. Curves: 1, sulfate; 2, nitrate; 3, citrate; 4, oxalate; 5, acetate. B, Initial aqueous solutions: $C_{H_2SO_4}$, 0.1 *M*; C_{SCN^-}, 0.5 *M*. Curves: 1, nitrate; 2, chloride; 3, acetate; 4, oxalate; 5, citrate. C, Initial aqueous solutions: C_{HNO_3}, 0.1 *M*; C_{SCN^-}, 0.5 *M*. Curves: 1, chloride; 2, sulfate; 3, ascorbate; 4, citrate; 5, acetate; 6, oxalate.

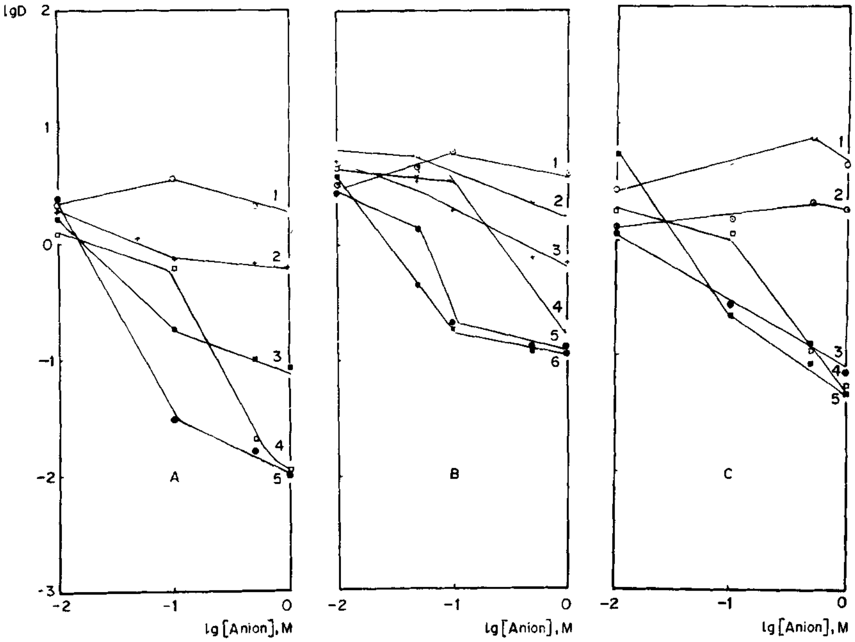


FIG. 13. The effect of the addition of some anions on the extraction of uranium employing 0.1 *M* DPPM/benzene. A, Initial aqueous solutions: C_{HCl}, 0.1 *M*; C_{SCN^-}, 0.5 *M*. Curves: 1, ascorbate; 2, sulfate; 3, citrate; 4, acetate; 5, oxalate. B, Initial aqueous solutions: $C_{\mathrm{HNO_3}}$, 0.1 *M*; C_{SCN^-}, 0.5 *M*. Curves: 1, chloride; 2, ascorbate; 3, sulfate; 4, acetate; 5, oxalate; 6, citrate. C, Initial aqueous solutions: $C_{\mathrm{H_2SO_4}}$, 0.1 *M*; C_{SCN^-}, 0.5 *M*. Curves: 1, ascorbate; 2, chloride; 3, oxalate; 4, acetate; 5, citrate.

tively, indicate that the effect of the anions is similar to that of the PyN system. The only difference to be noted is that the decrease of the partition values with the addition of oxalate, citrate, and acetate ions is relatively more pronounced in the case of PyN than in the corresponding HPy and DPPM systems.

The selectivity of the extraction of uranium by 0.1 *M* PyN/benzene from 7 *M* hydrochloric acid was evaluated. The results are shown in Table 2. In addition, the selectivity of the extraction was also investigated under optimal conditions from thiocyanate solutions by 0.1 *M* benzene solutions of PyN, HPy, and DPPM. The results obtained for the thiocyanate systems are presented in Tables 3, 4, and 5 respectively. From Table 2 it is seen that thorium can be quantitatively separated from uranium by

TABLE 2

Distribution Coefficients and Separation Factors of Different Metal Ions between 0.1 *M* PyN/Benzene–7 *M* Hydrochloric Acid Extraction Systems

Metal ions	Concentration (mole/l)[a]	Distribution coefficients	Separation factor
Tc(VII)	C.F.	2.350	4.340
Cr(VI)	C.F.	0.400	25.500
Mo(VI)	10^{-5}	1.050	9.714
Mo(V)	10^{-5}	2.153	4.744
Hf(IV)	10^{-7}	0.0077	1.3×10^3
Th	C.F.	$>10^{-3}$	$>10^4$
Ru(IV)	10^{-6}	0.0391	2.6×10^2
Au(III)	10^{-6}	12.90	7.9×10^{-1}
Fe(III)	10^{-4}	19.350	5.2×10^{-1}
Ce(III)	10^{-8}	$>10^{-3}$	$>10^4$
Cr(III)	C.F.	$>10^{-3}$	$>10^4$
Y(III)	10^{-8}	$>10^{-3}$	$>10^4$
Ir(III)	10^{-5}	$>10^{-3}$	$>10^4$
Zn(II)	10^{-5}	0.978	10.429
Hg(II)	10^{-7}	3.600	2.833
Sr(II)	10^{-8}	0.0051	2.04×10^3
Cu(II)	10^{-5}	0.106	96.226
Ag(I)	10^{-8}	0.0100	1.0×10^3

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

using 7 *M* hydrochloric acid solutions. The separation of uranium from thorium is of great importance in respect of the process occurring in breeder reactors and also for the isolation of ^{234}Th tracer which occurs in the decay series of ^{238}U that disintegrates with the following steps:

$$^{238}\mathrm{U} \xrightarrow[4.51 \times 10^{9}\ \mathrm{yr}]{\alpha} {}^{234}\mathrm{Th(UX_1)} \xrightarrow[24.1\ \mathrm{day}]{\beta^-} {}^{234}\mathrm{Pa(UX_2)} \xrightarrow[1.18\ \mathrm{min}]{\beta^-}$$

$$^{234}\mathrm{U} \xrightarrow[2.48 \times 10^{5}\ \mathrm{yr}]{\alpha}$$

The third product, uranium-234, has a half life of 2.48×10^5 years. Thus any uranium compound obtained from a chemical supplier will, in effect, contain ^{238}U and equilibrium quantities of UX_1 and ^{234}U. Since 1 g-atomic weight of uranium produces an equilibrium amount of 3.5×10^{-3} μg of UX_1, the separation of a submicro quantity of thorium from macroamounts of uranium by the following procedure can provide an

TABLE 3

Distribution Coefficients and Separation Factors of Different Metal Ions between 0.1 *M* PyN/Benzene–Mineral Acids (0.5 *M* with respect to KSCN) Extraction Systems

Metal ions	Concentration (mole/l)[a]	Distribution coefficients			Separation factors		
		0.1 *M* HCl	0.1 *M* HNO_3	0.1 *M* H_2SO_4	0.1 *M* HCl	0.1 *M* HNO_3	0.1 *M* H_2SO_4
Tc^{7+}	C.F.	6.17	4.7	5.6	2.917	3.617	3.928
Cr^{6+}	10^{-3}	2.32	2.58	0.351	7.758	6.589	62.67
Mo^{6+}	10^{-5}	0.230	1.002	4.697	78.26	16.968	4.690
Mo^{5+}	10^{-5}	18.759	110.438	15.91	9.6×10^{-1}	1.5×10^{-1}	1.387
Ru^{4+}	10^{-6}	0.096	0.466	0.075	1.8×10^{2}	36.480	2.9×10^{2}
Hf^{4+}	10^{-7}	0.266	1.220	1.431	67.669	13.934	15.384
Cr^{3+}	C.F.	0.043	0.110	0.116	4.1×10^{2}	1.5×10^{2}	1.8×10^{2}
Y^{3+}	10^{-8}	1.114	1.030	1.173	16.157	16.504	18.803
Ce^{3+}	10^{-8}	0.004	0.001	0.003	4.5×10^{3}	1.5×10^{4}	6.8×10^{3}
Na^{3+}	10^{-8}	0.14	0.014	0.025	1.2×10^{2}	1.1×10^{3}	8.7×10^{2}
Fe^{3+}	10^{-6}	7.00	2.041	16.974	2.571	8.333	1.296
La^{3+}	10^{-6}	0.050	0.046	0.267	3.6×10^{2}	3.7×10^{2}	82.397
Cr^{3+}	10^{-8}	0.010	0.004	0.002	1.8×10^{3}	4.2×10^{3}	8.4×10^{3}
Pm^{3+}	10^{-7}	0.002	0.000	0.002	6.6×10^{3}	2.8×10^{4}	7.8×10^{3}
Ir^{3+}	10^{-7}	0.060	0.022	0.035	3.0×10^{2}	7.5×10^{2}	6.2×10^{2}
Zn^{2+}	10^{-5}	119	243	104	1.5×10^{-2}	6.9×10^{-2}	2.1×10^{-2}
Co^{2+}	10^{-5}	204	359	119	8.8×10^{2}	4.7×10^{2}	1.8×10^{-1}
Cu^{2+}	10^{-6}	47	39	30	3.8×10^{-1}	4.3×10^{-1}	7.3×10^{-1}
Cs^{+}	10^{-8}	0.000	0.000	0.000	9.0×10^{4}	5.6×10^{4}	7.3×10^{4}

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

TABLE 4

Distribution Coefficients and Separation Factors of Different Metal Ions between 0.1 *M* HPy/Benzene–Mineral Acids (0.5 *M* with respect to KSCN) Extraction Systems

Metal ions	Concentration (mole/l)[a]	Distribution coefficients			Separation factors		
		0.05 *M* HCl	0.25 *M* HNO_3	0.05 *M* H_2SO_4	0.05 *M* HCl	0.25 *M* HNO_3	0.05 *M* H_2SO_4
Cr(VI)	C.F.	0.142	0.050	0.085	92.253	3.6×10^2	17.647
Mo(VI)	10^{-5}	1.19	896	228	11.00	2.0×10^{-2}	6.5×10^{-3}
Mo(V)	10^{-5}	73.8	13.4	13.7	1.7×10^{-1}	1.343	1.09×10^{-1}
Hf(IV)	10^{-7}	0.028	0.036	0.003	4.6×10^2	5.0×10^2	5.0×10^2
Ru(IV)	10^{-6}	0.244	0.280	0.214	53.688	64.285	7.009
Au(III)	10^{-6}	45.0	189	156	2.9×10^{-1}	9.5×10^{-2}	9.6×10^{-3}
Fe(III)	C.F.	0.007	0.004	0.005	1.8×10^3	4.5×10^3	3.0×10^2
Ce(III)	10^{-8}	0.012	0.003	0.005	1.09×10^3	6.0×10^3	3.0×10^2
Cr(III)	C.F.	0.016	0.018	0.011	8.18×10^2	1.0×10^3	1.3×10^2
Y(III)	10^{-8}	0.016	0.008	0.002	8.1×10^2	2.2×10^3	7.5×10^2
Ir(III)	10^{-5}	0.002	0.028	0.007	6.5×10^3	6.4×10^2	2.1×10^2
Zn(II)	10^{-5}	160	198	593	8.1×10^{-2}	9.0×10^{-3}	2.5×10^{-3}
Hg(II)	10^{-7}	94	405	341	1.3×10^{-1}	4.4×10^{-2}	4.3×10^{-3}
Sr(II)	10^{-8}	0.011	0.008	0.02	1.1×10^3	2.2×10^3	75.00
Cu(II)	10^{-5}	41	112	132	3.1×10^{-1}	1.6×10^{-1}	1.13×10^{-2}
Cs(I)	10^{-9}	0.000	0.000	0.000	1.3×10^6	2.2×10^4	1.66×10^3
Ag(I)	10^{-8}	1.18	9	8.2	11.100	2.00	1.82×10^{-1}
Br(I)	10^{-4}	0.012	0.015	0.034	1.09×10^3	1.2×10^3	44.117

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

TABLE 5

Distribution Coefficients and Separation Factors of Different Metal Ions between 0.1 *M* DPPM/Benzene–Mineral Acids (0.2 *M* with respect to KSCN) Extraction Systems

Metal ions	Concentration (mole/l)[a]	Distribution coefficients			Separation factors		
		0.1 *M* HCl	0.1 *M* HNO_3	0.1 *M* H_2SO_4	0.1 *M* HCl	0.1 *M* HNO_3	0.1 *M* H_2SO_4
Tc(VII)	C.F.	1.05	1.20	1.68	7.6×10^{-1}	6.2×10^{-1}	1.8×10^{-1}
Cr(VI)	C.F.	0.72	0.58	0.62	1.110	1.293	5.0×10^{-1}
Mo(VI)	10^{-5}	254.0	186.0	31.0	3.1×10^{-3}	4.0×10^{-3}	1.0×10^{-2}
Mo(V)	10^{-5}	20.0	10.60	4.10	4.0×10^{-2}	7.1×10^{-2}	7.6×10^{-2}
Hf(IV)	10^{-7}	0.800	0.020	0.017	1.000	37.500	18.235
Zr(IV)	10^{-5}	0.760	0.020	0.015	1.052	37.500	20.666
La(III)	10^{-7}	0.090	0.032	0.048	0.888	21.428	6.597
Ce(III)	10^{-8}	0.004	0.003	0.001	2×10^{2}	2.5×10^{2}	3.1×10^{2}
Cr(III)	C.F.	0.004	0.032	0.008	1.86×10^{2}	23.437	38.750
Fe(III)	10^{-4}	2.43	1.60	1.00	3.2×10^{-1}	4.6×10^{-1}	3.1×10^{-1}
Au(III)	10^{-}	83.00	75.00	107.00	9.6×10^{-3}	1.0×10^{-2}	2.8×10^{-3}
Nd(III)	10^{-7}	0.310	0.047	0.027	2.580	15.957	11.481
Pm(III)	10^{-7}	0.000	0.000	0.000	1.6×10^{3}	3.7×10^{3}	3.1×10^{3}
Sr(II)	10^{-8}	0.003	0.001	0.001	2.6×10^{2}	4.6×10^{2}	3.1×10^{2}
Co(II)	10^{-7}	1.18	1.23	1.10	6.7×10^{-1}	6.0×10^{-1}	2.8×10^{-1}
Hg(II)	10^{-7}	15.0	80.0	52.0	5.3×10^{-2}	9.3×10^{-3}	5.9×10^{-3}
Br(I)	10^{-5}	0.256	0.450	0.760	3.125	1.666	4.0×10^{-1}
Cs(I)	10^{-8}	0.000	0.000	0.000	4.0×10^{3}	9.3×10^{2}	7.7×10^{2}

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

excellent method for the isolation of ^{234}Th from moderately concentrated hydrochloric acid solutions.

PROCEDURE

Twenty milligrams of a several month old sample of uranium were extracted with 0.1 *M* NPy/benzene from 7 *M* HCl in four successive cycles. All the foregoing contact times were 3 min. ^{234}Th remaining in the aqueous phase was freed of traces of uranium by passing it through a cation exchange column (Dowex 50 × X8), 100 mesh in $^{+}$H form (capacity 1 ml). The column was washed with 2 to 3 *M* HCl, and then ^{234}Th was eluted with oxalic acid solution. The oxalate was destroyed with nitric acid and hydrogen peroxide, and the ^{234}Th solution in nitric acid was transferred to a planchet. The aliquots from the aqueous phase were evaporated to dryness. In each case the sample was covered with an aluminum absorber of 32 mg/cm^2 thickness which served to screen out all soft radiations, including that of UX_1 itself, so that only the strong beta emission of the UX_2 was registered. Decay of beta activity showed that thorium-234 separated by this procedure was more than 99% pure.

Some other practical applications arise from the results presented in Tables 2, 3, 4, and 5.

(1) The removal of rare-earth nuclear poisons from uranium, which is one of the most important separation problems in reactor chemistry, can be achieved from 7 *M* HCl alone and also from very dilute acid solutions containing 0.5 *M* potassium thiocyanate.

(2) Uranium can also be separated from a number of fission products including ruthenium, strontium, and cesium from dilute mineral acid solutions containing potassium thiocyanate.

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Received by editor March 31, 1978