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THE CHEMISTRY OF URANIUM
IN NONAQUEOUS SOLUTION

by

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PREFACE

The material in this report was written initially to be part of a chapter on "The Physical and Chemical Properties of Uranium" published in The Handbook of Experimental Pharmacology: New Series, Volume XXXVI, edited by H. C. Hodge, J. N. Stannard, and J. B. Hursh, and printed by Springer-Verlag, Heidelberg, in 1973. Because of space limitations, this portion of the chapter was omitted. There is, however, sufficient interest in this aspect of uranium chemistry to warrant publication of the omitted material as this separate report.

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ABSTRACT

This report reviews the chemistry of uranium in non-aqueous solution, exclusive of molten-salt solution. Chapters are included for the various oxidation states of uranium: III, IV, V, and VI. The last chapter treats separately the behavior of U(VI) in different types of extractants: ethers, ketones, and alcohols; organophosphorus compounds; long-chain amines; and chelating agents in organic diluents.

I. INTRODUCTION

This report describes the behavior of uranium in primarily organic solvents. The behavior of uranium in molten-salt solutions is not considered.

II. URANIUM(III)

The absorption spectrum of U(III) has been measured in anhydrous acetic acid (Jeżowska-Trzebiatowska, 1963; Alei et al., 1967) and methanol (Jeżowska-Trzebiatowska, 1963). The measured spectra are characterized by a large number of bands in the interval from 10,000 to 45,000 cm^{-1} and correspond closely to those measured for U(III) in aqueous perchloric acid solution (Stewart, 1952).

Alei et al. (1967) report that UCl_3 is sparingly soluble in anhydrous acetic acid, while UI_3 dissolves readily. Solutions of both have a deep wine-red color. These solutions are considerably more stable than aqueous solutions of U(III). However, solutions of U(III) in acetic acid sealed in Pyrex bulbs slowly lose their characteristic red color to form a light-green solution and a light-colored precipitate. Analyses have shown the solution to exhibit the spectrum of U(IV) and the precipitate to be uranium tetraacetate. About 1/2 mole of molecular hydrogen is evolved per mole of U(III) converted to U(IV). This corresponds to the net reaction

Conversion of U(III) to U(IV) in acetic acid is accelerated by the addition of sodium or potassium acetate, hydrochloric acid, or perchloric acid. Exposure to air or water also increases the rate of conversion to U(IV).

The reaction $\text{UCl}_3 + 4\text{AgClO}_4 \rightarrow \text{U}(\text{ClO}_4)_4 + \text{Ag} + 3\text{AgCl}$ is quantitative in pure acetic acid in the absence of oxygen (Alej et al., 1967). Neither U(IV) nor U(VI) react with AgClO_4 . In the presence of oxygen, there is further oxidation of U(IV) to U(VI). This reaction has been proposed as an analytical method for determining U(III) in the presence of other oxidation states.

The potential of the U(III)/U(IV) couple at the mercury electrode has been studied in acid solutions of water and of 30, 60, and 80% ethanol-water mixtures by Nolan and Amis (1964) and in dimethylformamide (DMF) and dimethylsulfoxide (DMSO) by Michlmayr et al. (1966). In water and 30% ethanol-water mixtures, evidence was obtained for a monochloride complex for both U(III) and U(IV) at low chloride concentrations. In 60 and 80% media, at all chloride concentrations, U(III) and U(IV) were observed to form the same type of chloride complex. In DMF, the U(IV) ions were found to be reversibly reduced to U(III), followed by the irreversible reduction to U(0). All electrode reactions of U(IV) ions in DMSO were found to be irreversible.

III. URANIUM(IV)

Absorption spectra of solutions of UCl_4 dissolved in a variety of organic solvents have been measured (Rohmer et al., 1952; Jeżowska-Trzebiatowska et al., 1958; Jeżowska-Trzebiatowska and Bukietyńska, 1961; Jeżowska-Trzebiatowska, 1963; Karracker, 1964; Alej et al., 1967). These spectra are characterized by narrow, sharp maxima and relatively low intensity. In the visible part of a spectrum, generally four groups of bands occur. The data of Jeżowska-Trzebiatowska and Bukietyńska (1961) show maxima in methanol at 16,000, 18,690, 19,800, and 22,220 cm^{-1} and in tri-n-butyl phosphate (TBP) at 14,930, 18,020, 20,200, and 21,980 cm^{-1} .

Conductivity measurements of UCl_4 in methanol (Jeżowska-Trzebiatowska et al., 1958) and ethanol (Roach and Amis, 1962) indicate that UCl_4 is dissociated to a certain extent:

The dissociation is increased by the addition of TBP (Jeżowska-Trzebiatowska et al., 1958). With water present, the UCl_4 is hydrolyzed and the conductivity of the solution is attributable to the $\text{U}(\text{OH})_2^{2+}$ or UOH^{3+} complex, depending on the water concentration (Roach and Amis, 1962). Further evidence for the dissociation of UCl_4 and existence of the UCl_3^+ complex in the lower alcohols comes from the isolation of compounds such as $\text{UCl}_3(\text{OC}_2\text{H}_5) \cdot 2\text{Bipy}$ and $\text{UCl}_3(\text{OC}_2\text{H}_5) \cdot 2\text{Phen}$ from ethanol solutions of UCl_4 by the addition of 2,2'-bipyridyl (Bipy) and o-phenanthroline (Phen) (Gans and Smith, 1964b). The

compound $\text{UCl}_3(\text{CN}) \cdot 4\text{NH}_3$ has been separated from a solution of UCl_4 in anhydrous liquid ammonia by the addition of NaCN or KCN . Analogous compounds are formed when KCN is added to UBr_4 or UI_4 dissolved in liquid ammonia (Bagnall and Baptista, 1970).

The ready formation in ethanol solutions of UCl_4 of hexachlorouranate(IV) compounds $(\text{BH})_2\text{UCl}_6$, where B is Bipy, Phen, or a number of tertiary phosphines, indicates the presence also of the UCl_6^{2-} complex (Gans and Smith, 1964a, 1964b). A species of this type is extracted from aqueous HCl solutions with organic solutions of tri-n-octylamine (Keder, 1962) and TBP (Vdovenko et al., 1965). Jørgensen (1963) has spectrophotometrically identified mixed chlorobromouranate(IV) complexes, UBrCl_5^{2-} , and $\text{UBr}_2\text{Cl}_4^{2-}$ in nitromethane solutions.

The hexanitratouranate(IV) complex $\text{U}(\text{NO}_3)_6^{2-}$ is extracted from nitrate solutions with organic solutions of tri-n-octylamine (Keder et al., 1961) and tricaprylmethylammonium nitrate (Koch and Schwind, 1966). Smirnov-Averin et al. (1963) have proposed that U(IV) is extracted with TBP as the $\text{U}(\text{NO}_3)_6^{2-}$ complex from aqueous solutions with nitric acid concentrations $>3\text{M}$. Woodhead and McKay (1965) report the existence of the $\text{U}(\text{NO}_3)_6^{2-}$ species in solutions of TBP containing lithium nitrate. However, in TBP solutions with nitric acid concentrations $>4\text{M}$, these authors believe the species to be the U^{4+} ion solvated with TBP and probably electrostatically associated with the nitrate in solution. The major species of U(IV) to be extracted into TBP from nitric acid solutions is $\text{U}(\text{NO}_3)_4 \cdot 2\text{TBP}$ (Smirnov-Averin et al., 1963; Woodhead, 1964; McKay and Streeton, 1965; Woodhead and McKay, 1965). Spectral evidence was found for this species in TBP solutions of U(IV) containing 0.2-1.5M nitric acid (Woodhead and McKay, 1965). With no added acid and with $\text{NO}_3/\text{U} = 4$, there is evidence that the U(IV) species in TBP solutions is $\text{UOH}(\text{NO}_3)_3 \cdot x\text{TBP}$ (Woodhead and McKay, 1965).

The species extracted into organic solutions of TBP from aqueous HCl solutions also depends on the acid and TBP concentrations. Under conditions close to saturation, the disolvated species $\text{UCl}_4 \cdot 2\text{TBP}$ is extracted (Shevchenko et al., 1961; Lipovskii and Yakovleva, 1964; Vdovenko et al., 1965; Lipovskii et al., 1965). $\text{UCl}_4 \cdot 3\text{TBP}$ is extracted with an increase in TBP concentration (Lipovskii and Yakovleva, 1964; Vdovenko et al., 1965). The UCl_6^{2-} complex mentioned previously is extracted with an increase in HCl concentration in the initial aqueous solution and an excess of TBP (Vdovenko et al., 1965). Similar solvated complexes $\text{UCl}_4 \cdot 2\text{S}$ and $\text{UCl}_4 \cdot 3\text{S}$ are found with other organophosphorus extractants: diisooamyl methylphosphonate (Shevchenko et al., 1961; Vdovenko et al., 1965; Lipovskii et al., 1965) and tributylphosphine oxide (Ellert et al., 1968). From solutions of UCl_4 in tributylphosphine oxide, compounds of the type $\text{UCl}_4 \cdot n\text{S}$ have been isolated where $n = 1.5, 2, 3.5, 4, 5$, or 8 (Ellert et al., 1968). The compound $\text{U}(\text{OH})\text{Cl}_3 \cdot 3\text{S}$ has been isolated also.

Coordination compounds of the type $\text{UCl}_4 \cdot 4\text{ROH}$ are obtained by the evaporation of solutions of UCl_4 in the lower alcohols, where R represents

the methyl, ethyl, n-propyl, or iso-propyl radical (Bradley et al., 1962). However, solvolysis occurs with the butyl alcohols. Replacement of the chloride in UCl_4 increases in the order n-butyl < sec-butyl < tert-butyl. A number of other U(IV) compounds of the type $\text{UX}_4 \cdot n\text{S}$ have been separated from organic solvents. For example, $\text{X} = \text{NO}_3^-$, $n = 2.5$, $\text{S} = \text{dimethylacetamide}$ (Bagnall et al., 1961); $\text{X} = \text{ClO}_4^-$, $n = 6$, $\text{S} = \text{dimethylacetamide}$ (Bagnall et al., 1962); $\text{X} = \text{SCN}^-$, $n = 4$, $\text{S} = \text{dimethylacetamide}$ (Bagnall et al., 1964); and $\text{X} = \text{Cl}^-$ or Br^- , $n = 4$, and $\text{S} = \text{acetonitrile}$ or ethyl acetate (Vdovenko et al., 1969). Alei et al. (1967) have proposed the solvolytic reaction

where $x + y = 4$, to explain the spectral changes observed by the introduction of HClO_4 into a solution of U(IV) in acetic acid.

Uranium(IV) in liquid-ammonia solution is oxidized by silver acetate to U(VI) within a few hours at room temperature (Kline and Kershner, 1966). In anhydrous liquid HF, UF_4 is oxidized by fluorine to UF_5 (Asprey and Penneman, 1967; see Sec. IV).

The rate of electron exchange between U(IV) and U(VI) ions in water-ethanol mixtures has been investigated by Mathews et al. (1959) and Indelli and Amis (1959). The polarographic studies involving the U(IV)/U(III) couple have been mentioned in Sec. II. Other polarographic studies have been made in acetic acid media as a means of determining the amount of uranium present (Fisher and Thomason, 1956; Číhalík et al., 1958).

IV. URANIUM(V)

Gritzner and Selbin (1968) have succeeded in measuring the absorption spectrum of UO_2^+ in the region of 6100-20,000 cm^{-1} in dry dimethylsulfoxide solutions. Disproportionation of the species into UO_2^{2+} and UO_2 occurred, but with a half-life of about 1 hr. The main peak in the spectrum occurred at 6620 cm^{-1} . Two other maxima with about 1/10th the intensity of the main peak were observed at 12,940 and 15,080 cm^{-1} .

Ryan (1968) has prepared the UCl_6^- and UBr_6^- complexes in dry nitromethane by oxidizing UCl_6^{2-} and UBr_6^{2-} with the respective free halogens. Salts of the U(V) complexes were crystallized from the solutions. Ryan (Selbin and Ortego, 1969) has also prepared salts of UI_6^- by condensing anhydrous liquid HI on the chloro salts and evaporating the mixture slowly and by reacting $\text{UO}_2\text{Cl}_4^{2-}$ salts with liquid HI.

UF_5 can be prepared from UF_4 by stirring a suspension of high-surface-area UF_4 in anhydrous liquid HF at 25°C under 10 psig of fluorine (Asprey and Penneman, 1967). The oxidation to UF_5 proceeds rather rapidly, but to UF_6 ,

fairly slowly. Compounds of MUF_6 , where M is cesium or rubidium, have been prepared by stirring a slurry of the alkali metal fluoride and UF_4 in liquid HF with fluorine at 10 psig and 25°C .

A number of other U(V) compounds including addition compounds and alkoxides have been separated from anhydrous liquid solvents. Their preparation has been reviewed by Selbin and Ortego (1969).

V. URANIUM(VI)

An excellent description of the behavior of uranyl salts in organic solutions based on investigations completed to the time has been given by Vdovenko (1960, 1964). This behavior may be classified according to the manner in which uranium is extracted from an aqueous solution into an organic solution or by the organic solvents or extractants in which a particular behavior is exhibited. Such extractants are (1) ethers, ketones, and alcohols, (2) organophosphorus compounds, (3) long-chain amines, and (4) chelates, such as β -diketones.

A. Ethers, Ketones, and Alcohols

Of all the uranium salts, uranyl nitrate appears to have the right combination of properties favorable for extraction into relatively nonpolar liquids with low dielectric constants. These properties are an appreciable complexing ability of the nitrate ion, low charge density on the anion in the complex, and sufficiently strong polarization of the hydrate water in the neutral complex (Vdovenko et al., 1968).

There have been a number of studies on the solubility of uranyl nitrate. The results of Yaffe (1949) are given in Table I for solvents in which uranyl nitrate hexahydrate is soluble to the extent of 0.1 g or more per 100 cc of solvent at 20°C . From studies such as this, it can be concluded that (1) uranyl nitrate dissolves in oxygen-containing liquids, (2) the solubility in alcohols and ketones is usually greater than in ethers and nitro-substituted hydrocarbons, (3) the solubility decreases with increasing chain length in a homologous series of a given class of solvents, and (4) the replacement of a methyl hydrogen by a halogen or phenyl group decreases the solubility. It has also been shown that the solubility of uranyl nitrate increases from the hexahydrate to the lower hydrates. However, anhydrous uranyl nitrate is only slightly soluble in ethers.

The solubility of UF_6 , UCl_6 , and other uranyl salts in organic solvents has been described elsewhere (see Gindler, 1973). The uranyl perchlorate-water-organic solvent system has been investigated by Vdovenko and co-workers (1963c, 1964, 1967a). The $\text{UO}_2(\text{ClO}_4)_2$ -water-diethyl ether system is interesting. If ether is added to the heptahydrate of $\text{UO}_2(\text{ClO}_4)_2$, the salt dissolves in a portion of the ether, the remainder of the ether forming a second phase with practically no uranium. If more $\text{UO}_2(\text{ClO}_4)_2$ in the form of the

monohydrate is added to this two-phase system, then the volume of the lower phase increases and, at a concentration of the components 25 wt % uranyl perchlorate, 5 wt % water, and 70 wt % ether, both phases merge into one. The solubility of the lower hydrates of $\text{UO}_2(\text{ClO}_4)_2$ in ethers is rather large. At the solubility maximum, when the precipitate contains the trihydrate, the mole ratio of $\text{UO}_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$:ether is 1:3:2.5 for diethyl ether and 1:1.7:3.3 for di-n-butyl ether. The solubility of uranyl chloride hydrates in simple ethers is very low. The anhydrous uranyl chloride is practically insoluble.

TABLE I. Solubility of Uranyl Nitrate Hexahydrate (UNH) in Various Organic Solvents at 20°C^a

Solvent	Solubility, gUNH per 100 cc Solvent	Solvent	Solubility, gUNH per 100 cc Solvent	Solvent	Solubility, gUNH per 100 cc Solvent
<u>Ethers</u>		<u>Esters</u>		<u>Ketones</u>	
diethylcellosolve	102	β -ethoxyethyl acetate	125	cyclohexanone	105
dimethyldioxan	92	ethyl acetylglucolate	110	methyl ethyl ketone + 15% xylene	100
diethyl ether	74	ethyl acetate	82	diethyl ketone	76
ethylhexylcellosolve	68	butylcellosolve acetate	77	methyl isobutyl ketone	75
dibutylcellosolve	49	butyl acetate	68	methyl n-amyl ketone	68
dibutylcarbitol	44	isopropyl acetate	64	diisopropyl ketone	41
pelargonic ether	17	sec-butyl acetate	61	<u>Aldehydes</u>	
n-butyl ether	16	amyl formate	56	acetaldehyde	42
xanthyl ether	14	n-butyl propionate	55	citronellal	34
amyl ether	11	isoamyl acetate	55	anisaldehyde	27
hexyl ether	9	isobutyl acetate	50	n-butyraldehyde	22
isopropyl ether	9	ethyl sebacate	48	<u>Substituted Hydrocarbons</u>	
dichloroisopropyl ether	5	amyl acetate	46	nitromethane	64
<u>Alcohols</u>		butyl adipate	40	triglycol dichloride	57
dibutoxytetraethylene glycol	90	n-butyl sebacate	37	1-nitropropane	8
isobutylcarbinol	57	n-amyl propionate	37	2-nitropropane	4
diethylcarbinol	57	β -phenyl ethyl acetate	35	nitrobenzene	1.5
n-amyl alcohol	55	methyl phenyl acetate	33	tetrabutylurea	6.0
2-ethyl butyl alcohol	49	isobutyl propionate	31		
methyl amyl alcohol	43	vinyl acetate	31		
n-heptyl alcohol	43	isoamyl propionate	27		
capryl alcohol	37	amyl succinate	25		
geraniol	36	amyl butyrate	25		
β , γ -dibromopropyl alcohol	32	isoamyl formate	24		
undecanol	27	amyl valerianate	21		
tetradecanol	13	geraniol acetate	16		
		n-butyl oxalate	9		
		isoamyl n-caporate	7		

^aYaffe (1949).

Conductivity measurements of hydrated and anhydrous uranyl nitrate in organic solvents and water by Jeżowska-Trzebiatowska and co-workers (Jeżowska-Trzebiatowska and Chmielowska, 1961; Jeżowska-Trzebiatowska and Ernst, 1964, 1966; Ernst and Jeżowska-Trzebiatowska, 1966) have shown that uranyl nitrate behaves as a very weak electrolyte in organic solvents of moderate or low dielectric constant. Some of their results are given in Table II. The stability or association constants have been calculated for the equilibrium reaction

and are based on measurements made at 25°C. In general, the extent of association increases with decreasing dielectric constant of the solvent. A comparison of the association constants of uranyl nitrate in alcohols and ketones

indicates considerably more association in ketones than in alcohols of the same dielectric constant, notably acetone and propanol. This suggests that the specific chemical properties of the solvent affect the equilibrium more than they do the dielectric properties.

TABLE II. Limiting Molar Conductivities and Association Constants of Hexahydrate, Dihydrate, and Anhydrous Uranyl Nitrate Solutions in Organic Solvents^a

Solvent	Dielectric Constant (25°C)	UO ₂ (NO ₃) ₂ ·6H ₂ O		UO ₂ (NO ₃)·2H ₂ O		UO ₂ (NO ₃) ₂	
		Λ ₀	log K ₂ ^b	Λ ₀	log K ₂ ^b	Λ ₀	log K ₂ ^b
<u>Alcohols</u>							
Methanol	32.63	245.8	3.21	264.2	3.45	255.5	3.67
Ethanol	24.30	82.20	4.16	136.9	4.25	127.6	4.47
Propanol	20.1					40.7	5.59
<u>Ketones</u>							
Acetone	20.7	200	5.70			200	6.36
Methylethyl ketone	18.5 (20°)	153.8	6.02			153.8	6.52
Methylisobutyl ketone		107	6.39			107	6.93
Heptanone-2						75.6	6.64

^aData are from Jeżowska-Trzebiatowska and Ernst (1964, 1966) and Ernst and Jeżowska-Trzebiatowska (1966).

^bK₂ refers to the equilibrium reaction $\text{UO}_2\text{NO}_3^+ + \text{NO}_3^- \rightleftharpoons \text{UO}_2(\text{NO}_3)_2$ at 25°C.

A comparison of association constants of the hexahydrate, dihydrate, and anhydrous uranyl nitrate shows the association to increase as the number of water molecules decreases. This may be interpreted on the basis of the structure of uranyl nitrate and its hydrates. The most probable structure of uranyl nitrate hexahydrate is a linear uranyl ion surrounded in the equatorial plane by two nitrate ions bidentately attached and two water molecules, filling the coordination sphere. The four remaining water molecules are in the outer coordination sphere of the uranyl ion (Vdovenko et al., 1967b). The formulas for the hexahydrated, dihydrated, and anhydrous uranyl nitrate can then be written, respectively, as

The coordination sphere of the latter is unsaturated. In organic solvents, it is filled by two molecules of the solvent. The nitrate ion is bound coordinately more strongly in the $[\text{UO}_2(\text{NO}_3)_2\text{S}_2]$ sphere than in the $[\text{UO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ sphere, largely as a result of the lower basicity of the solvents in comparison with water.

A comparison of the conductivities of the three forms of uranyl nitrate in alcoholic solutions in Table II shows that it is the lowest for the hexahydrate. This can be explained by the participation of water molecules in the solvation layers of uranyl nitrate hexahydrate to produce a larger cation. With the

dihydrated and anhydrous species, the ion and its coordination sphere are surrounded only by alcohol molecules. Since these molecules are less basic than water, they form weaker hydrogen bonds. In effect, the ions are then smaller than the hexahydrated ion (Ernst and Jeżowska-Trzebiatowska, 1966). The small increase in conductivity from anhydrous to dihydrate is attributed to the former being coordinated only to alcohol molecules, while the latter retains its water and is therefore somewhat smaller.

Ernst and Jeżowska-Trzebiatowska (1969) have also measured the conductivity of uranyl chloride monohydrate and the anhydrous form in several organic solvents. Some of their results are given in Table III. The association constants refer to the equilibrium reaction

at 25°C. For a given organic solvent, these constants are smaller for the monohydrate and the anhydrous uranyl chloride than for any of the hydrated forms of uranyl nitrate (Table II). This indicates that uranyl chloride dissociates to a greater extent in organic solvents than does uranyl nitrate and is therefore a stronger electrolyte than uranyl nitrate in these solvents. The association constants of uranyl chloride exhibit a dependence opposite to that of uranyl nitrate on the number of water molecules associated with the salt. Anhydrous uranyl chloride dissociates more than the monohydrate. These two observations confirm the above conclusion that organic solvent molecules are less strongly coordinated than water molecules in the hydrates. In uranyl nitrate, this gives rise to an increase in strength of the nitrate coordination bond by chelation or by additional π -bonds. The simple chloride ion does not form additional bonds, and a water molecule in the coordination sphere of the uranyl ion only weakens the coordination of organic molecules. It is therefore easier for a chloride ion to penetrate the coordination sphere (Ernst and Jeżowska-Trzebiatowska, 1969).

TABLE III. Limiting Molar Conductivities and Association Constants of Monohydrate and Anhydrous Uranyl Chloride in Organic Solvents^a

Solvent	Dielectric Constant (25°C)	UO ₂ Cl ₂ ·H ₂ O		UO ₂ Cl ₂	
		Λ ₀	log K ₂ ^b	Λ ₀	log K ₂ ^b
<u>Alcohols</u>					
Methanol	32.63	111.9	1.90	98.10	1.84
Ethanol	24.30	40.40	2.30	31.31	2.21
n-Propanol	20.1	0.972 ^c	3.80	0.922	3.64
n-Pentanol	13.9	0.145 ^c	4.93		
Acetone	20.7	13.4 ^c	4.96		

^aData from Ernst and Jeżowska-Trzebiatowska (1969)

^bK₂ refers to the equilibrium reaction $\text{UO}_2\text{Cl}^+ + \text{Cl}^- \rightleftharpoons \text{UO}_2\text{Cl}_2$ at 25°C.

^cMinimal value Λ_{min} .

In solutions of anhydrous uranyl chloride and its hydrate in n-propanol, n-pentanol, and acetone, Ernst and Jeżowska-Trzebiatowska (1969) observed

that the K_2 equilibrium reaction did not adequately describe the concentration dependence of the molar conductivity. It was therefore assumed that complexes of the type $\text{UO}_2\text{Cl}_3 \cdot \text{S}^-$ may be formed. Association constants K_3 calculated for such a reaction gave values on the order of 10 for the two alcohols and several hundred for acetone. Evidence for the trinitratouranylate complex has been found by Jeżowska-Trzebiatowska and Chmielowska (1961) in the molar-conductivity-versus-concentration data of uranyl nitrate hexahydrate in acetonitrile, ethanol, acetylacetone, methylethyl ketone, methylisobutylketone, and TBP. Kaplan et al. (1956) and others have determined the existence of the $\text{UO}_2(\text{NO}_3)_3^-$ complex in nonaqueous solutions in the presence of another soluble nitrate of the type RNO_3 . The stability of the complex depends on the nature of R, the character of the organic solvent, and the presence of water in the solvent. The general order of the solvents with respect to the stability of the trinitratouranylate complex is ketone > ether > alcohol > water.

A number of investigations (e.g., Katzin and Sullivan, 1951; McKay and Mathieson, 1951) on the distribution of uranyl nitrate between an aqueous phase and an organic phase of alcohol, ester, ether, or ketone have shown that the water content of the organic phase increases with uranyl nitrate concentration. The relationship between water content M_W and uranyl nitrate content M_U may generally be expressed by a linear function

$$M_W = M_W^0 + hM_U,$$

where M_W^0 is the solubility of water in the pure solvent and h is a constant. The coefficient h is interpreted as the average number of water molecules bound to a salt molecule. The value of h is close to four for a large number of solvents, although other numbers exist. This has been interpreted as evidence for the existence of uranyl nitrate tetrahydrate in solution. This hydrated form of uranyl nitrate is not isolated, however, as a solid.

Infrared absorption spectra of hydrated uranyl nitrate dissolved in various organic solvents, including ethers and ketones, indicate that two water molecules are strongly bound to the uranyl nitrate (Ryskin et al., 1959a, 1959b; Vdovenko and Suglov, 1960). If more than two water molecules are present, as appears from distribution studies, they are more weakly bound and compete with solvent molecules in the outer coordination sphere. This is in agreement with the conclusions drawn from conductivity measurements.

A number of uranyl nitrate solvates have been isolated from solution. The composition of these complexes can be represented by the general formula $\text{UO}_2(\text{NO}_3)_2 \cdot x\text{H}_2\text{O} \cdot y\text{S}$, where S represents a solvent molecule. The sum of $x + y$ is generally four, but is often less, and rarely greater than four (Vdovenko, 1960, 1964). The ability of solvents to displace water decreases generally in the order: alcohols > ethers > ketones (Katzin and Sullivan, 1951). This order is in agreement with the decreasing basicity of the solvent molecules. It is opposite to the solvent order with respect to the stability of the trinitratouranylate complex ion.

B. Organophosphorus Extractants

Many organophosphorus compounds have been developed and investigated as possible extractants for uranium. These compounds may be classified generally as neutral or acidic organophosphorus compounds. The neutral compounds include the alkyl phosphates, phosphonates, phosphinates, and phosphine oxides. They are described by the general formulas $(RO)_3PO$, $(RO)_2RPO$, $(RO)R_2PO$, and R_3PO , respectively. The alkyl groups R are not necessarily the same for a given compound. The acidic organophosphorus compounds include the di- and mono-alkylphosphoric acids, the alkyl phosphonic acids, and the dialkyl phosphinic acids. These compounds have the general formulas $(HO)(RO)_2PO$, $(HO)_2(RO)PO$, $(HO)_2RPO$, and $(HO)R_2PO$, respectively.

Of the neutral organophosphorus compounds, tri-n-butylphosphate (TBP) has been studied most extensively. Healy and McKay (1956) have shown that a saturated solution of uranyl nitrate hexahydrate in TBP corresponds closely to the formula $UO_2(NO_3)_2 \cdot 2TBP$. Nemodruk (1967) has reported that when uranyl nitrate is extracted by undiluted TBP from aqueous solutions containing solid uranyl nitrate, it passes into the organic phase, both in the form of the disolvate $UO_2(NO_3)_2 \cdot 2TBP$ and as the monohydrate-monosolvate $UO_2(NO_3)_2 \cdot H_2O \cdot TBP$. The fraction of the latter is observed to increase with temperature. When an extract obtained under these conditions is allowed to cool from 100°C to room temperature, uranyl nitrate trihydrate separates as a crystalline deposit (Nemodruk et al., 1969). In this case, the mother solution contains an insufficient number of TBP and H_2O ligands to saturate the coordination spheres of the uranyl ions. As a result, polymeric complexes are formed. Nemodruk et al. (1969) have proposed the formation of the uranium dimer $2UO_2(NO_3)_2 \cdot 3TBP$ with the possibility of higher polymers being formed.

Healy and McKay (1956) found no evidence for the $UO_2(NO_3)_3^-$ complex when nitric acid was dissolved in TBP saturated with $UO_2(NO_3)_2 \cdot 6H_2O$. However, Woodhead (1964, 1965) has reported that the trinitratouranylate species may account for several percent of the uranium present in "wet" TBP with nitric acid present. The formation of the trinitratouranylate species is facilitated by the presence of other metal cations in the order

Woodhead (1965) has estimated that, with 1M $LiNO_3$ in TBP, 58% of the uranium is present as the trinitratouranylate complex.

Tributylphosphate is a rather viscous, nonvolatile, colorless liquid with a specific gravity of 0.97. To reduce its viscosity and to improve its separation from aqueous solutions, it is generally diluted with lighter liquids such as kerosene, benzene, xylene, dibutyl ether, and other diluents. Nemodruk and Glukhova (1963) and others have shown that the extraction of uranyl nitrate

is influenced by the nature of the diluent. For example, with a concentration of $2M$ TBP in various diluents, the distribution coefficients D for uranyl nitrate extracted from an aqueous nitrate solution decrease in the diluent order

benzene > toluene > xylene > carbon tetrachloride

> 1,2-dichloroethane > chloroform.

The ability of neutral organophosphorus compounds to extract U(VI) from aqueous nitrate solutions generally increases in the order

phosphate < phosphonate < phosphinate < phosphine oxide.

This is illustrated by the coefficients D determined by Burger (1958) for the distribution of U(VI) between an aqueous solution originally $0.2M$ in uranyl nitrate and $0.5M$ solutions of tributyl phosphate, dibutyl butyl phosphonate, butyl dibutyl phosphinate, and tributyl phosphine oxide in carbon tetrachloride. They are 0.19, 1.03, 3.9, and 23 for the respective compounds. The distribution coefficients of the different organophosphorus compounds are correlated with the $P=O$ stretching frequencies. An increase in the electronegativity of the phosphoryl group is associated with an increase in extractive ability. Nikolaev and Shubina (1961) have shown that complex formation with uranyl nitrate occurs through the phosphoryl group. A similar coordination occurs with uranyl bromide, chloride and acetate (Komarov and Pushlenkov, 1961a, 1961b). The composition of the uranyl nitrate complex with the different neutral organophosphorus compounds appears to be essentially the same as the disolvated TBP complex, that is, $UO_2(NO_3)_2 \cdot 2S$, where S is a neutral organophosphorus molecule (Blake et al., 1958; Burger, 1958; Healy and Kennedy, 1959). A similar complex $UO_2X_2 \cdot 2S$ is extracted from aqueous solutions of the anion X^- , where X^- represents perchlorate (Hesford and McKay, 1960), acetate, bromide, or chloride (Komarov and Pushlenkov, 1961a, 1961b; Shevchenko et al., 1961) ions. A more detailed study of the solvation of uranyl chloride by organophosphorus compounds by Vdovenko et al (1963d, 1963e, 1965) has shown that uranyl chloride not only forms the disolvated complex $UO_2Cl_2 \cdot 2S$ with TBP, dibutyl butyl phosphonate, and butyl dibutyl phosphinate diluted in CCl_4 , but as the concentration of the organophosphorus compound is increased, the complex $UO_2Cl_2 \cdot 3S$ is formed. With an increase in the initial HCl concentration of the aqueous phase and with an excess of TBP, evidence for a complex $(UO_2Cl_3 \cdot nTBP)^-$ is observed.

Healy and Kennedy (1959) have found that by saturating benzene solutions of organophosphorus compounds containing two phosphoryl groups [bis-(di-*n*-butoxyphosphinyl)-ethane, bis-(di-*n*-butoxyphosphinyl)-methane, or tetra-*n*-butyl pyrophosphate] with $UO_2(NO_3)_2 \cdot 6H_2O$, they could obtain 1:1 ligand-metal complexes, $UO_2(NO_3)_2 \cdot S$. Viscosity measurements indicated that polymers of the type $[UO_2(NO_3)_2 \cdot L]_n$ may be formed, where L represents the

coordinated ligand of the organophosphorus molecule. The extractive abilities of the two phosphinyl compounds were found to be somewhat greater than that of TBP; that of the pyrophosphate compound was considerably less than that of TBP. Mrochek et al. (1963) have shown that bis(di-n-hexylphosphinyl)-methane forms a polymeric-like complex with uranyl compounds in nonpolar diluents. Polymers can be prevented from forming by use of a polar diluent such as 1,2-dichlorobenzene. Further studies of the interaction between uranyl nitrate and bis-(disubstituted-phosphinyl)-alkanes have been made by Banks and co-workers (Parker and Banks, 1965; Mrochek and Banks, 1965; Mrochek et al., 1965) and Gorlov et al. (1967). The monosolvated complexes $\text{UO}_2(\text{NO}_3)_2 \cdot \text{S}$ are readily formed. Higher solvates may be formed also with the displacement of one or both nitrate groups from the coordination sphere. In the case of bis-(di-n-hexylphosphinyl)-methane (HDPM) and -ethane (HDPE), it appears that disolvates are formed in which all four phosphoryl groups are bonded symmetrically to the uranyl ion. There is evidence for the formation of the other complexes with other phosphinyl compounds. Experiments with uranyl perchlorate and HDPM and HDPE indicate the formation of disolvated complexes. Mikulski and Vetulani (1967) have found evidence for the monosolvated tetrabutylpyrophosphate complex $\text{UO}_2(\text{NO}_3)_2 \cdot \text{S}$ in extraction and infrared studies.

Uranium is efficiently extracted by acidic organophosphorus compounds. The ability to extract uranium within a given class of compounds tends to decrease with an increase in branching of the alkyl chain near the phosphate group (Blake et al., 1958). The acidity of compounds decreases roughly in the same order. Where comparisons can be made for the same alkyl group between classes of extractant, the extraction coefficient D of U(VI) increases in the order

dialkyl phosphoric acid < dialkyl phosphinic acid

< monoalkyl phosphoric acid.

This order is demonstrated by the 3,5,5-trimethylhexyl alkyl group in the extraction of U(VI) from an initial aqueous solution containing 0.004M U(VI) and 0.5M SO_4^{2-} at pH1 with a 0.1M solution of the extractant in CCl_4 . The distribution coefficients for the acids given in the above order are 40, 120, and >1000 (Blake et al., 1958). The choice of diluent affects the extraction of U(VI) . For dialkylphosphoric and dialkylphosphinic acids, D generally decreases as the dielectric constant of the solvent increases. For monoalkyl phosphoric acids, a reverse trend is observed (Blake et al., 1958).

The mechanism of extraction by dialkylphosphoric acids has been investigated rather extensively (e.g., see Nemodruk and Glukhova, 1967). These extractants are often associated in organic diluents as dimers (Baes et al., 1958). At low uranium concentrations, Baes et al. (1958) have suggested that U(VI) is extracted from aqueous perchlorate solutions into n-hexane solutions

of di-(2-ethylhexyl)-phosphoric acid (HL) as the $\text{UO}_2(\text{HL})_2\text{L}_2$ complex. A chelate structure has been proposed for this complex. At higher uranium concentrations in the organic phase, isopiestic and viscosity measurements indicate that polymerization occurs. Dyrssen and Krašovec (1959) have observed similar results in the distribution of U(VI) between aqueous perchlorate solutions and dibutylphosphate (HK) in chloroform and hexone. In addition, evidence for the species UO_2K_2 was observed in hexone at lower concentrations of dibutylphosphate. Evidence for both types of complexes UO_2L_2 and $\text{UO}_2(\text{HL})_2\text{L}_2$ has been reported by Mason et al. (1964) and Ul'yanov et al. (1966) in the extraction of U(VI) by di-(2-ethylhexyl)-phosphoric acid in n-decanol and in n-octane, respectively. Krašovec and Klofutar (1965) have reported the extraction of U(VI) by a number of different diarylphosphoric acids in chloroform. The data have demonstrated the presence of the $\text{UO}_2(\text{HL})_2\text{L}_2$ complex in the organic phase.

Healy and Kennedy (1959) have measured the distribution coefficient D for U(VI) between aqueous nitric acid solutions and dibutylphosphoric acid (HL) dissolved in benzene as a function of nitric acid concentration. A sharp decrease in D from 0.1 to 3M HNO_3 was attributed to the reaction

For $D > 10$, $x > 1$. For $x = 1$, the species $\text{UO}_2(\text{HL})_2\text{L}_2$ is present. The shape of the curve D versus nitric acid concentration from 3 to 10M is similar to that obtained with TBP, and the TBP extraction mechanism was therefore assumed:

The decrease in D at $> 7\text{M}$ HNO_3 was assumed to be caused by the competing reaction

Nemodruk and Glukhova (1967) have since proposed that U(VI) is not extracted by dialkyl phosphoric acids from aqueous solutions $> 5\text{M}$ HNO_3 by a solvate mechanism, but by an ion-exchange mechanism in which uranium participates in the form of the UO_4^{4+} ion. A similar mechanism was suggested by Nemodruk (1969) for the extraction of U(VI) from 8M HClO_4 solutions with di-(2-ethylhexyl) phosphoric acid. According to this concept, the species extracted from aqueous solutions high in acidity is the UOL_4 complex.

Krutikov and Solovkin (1970) have determined the compositions of the compounds that were separated from mixtures of uranyl nitrate and dibutyl phosphate in 0.2 and 6M aqueous nitric acid. A solid, amorphous, pale-yellow precipitate with the composition UO_2L_2 was found to separate from 0.2M HNO_3 .

Dark-yellow viscous liquids separated from 6M HNO_3 . After these had been washed in water, they were converted in air to a vitreous mass with the composition $\text{UO}_2(\text{NO}_3)(\text{HL}_2)$, $\text{UO}_2(\text{NO}_3)(\text{HL}_2)(\text{HL})_2$, or their mixtures.

The extraction mechanism of dialkyl phosphinic acids is expected to be similar to that of dialkyl phosphoric acids. The former are often found as dimers in organic diluents and the distribution coefficient of U(VI) exhibits a dependence on the concentration of the extractant at low uranium levels similar to that of dialkyl phosphoric acids (Blake et al., 1958). Evidence for the extraction of the $\text{UO}_2(\text{HL})_2\text{L}_2$ complex with "wet" di-n-octyl phosphinic acid in benzene has been reported by Peppard et al. (1965).

The distribution coefficient of U(VI) varies as the first to second power in extractions by monoalkyl phosphoric and phosphonic acids. This indicates that the extracted complexes have at least as many organophosphorus groups as the aggregates of the unreacted organophosphoric acid. Since the monoalkyl acids (H_2L) are associated more as polymers than are the dialkyl acids, this indicates that the extracted complex is not a simple UO_2L or $\text{UO}_2(\text{HL})_2$ species, but must contain additional extractant molecules (Blake et al., 1958).

Dialkyl phosphonic acids, in combination with neutral organophosphorus compounds, provide a synergistic enhancement of the U(VI) distribution coefficient. That is, the distribution coefficient obtained with the combined extractants is greater than the sum of the distribution coefficients obtained with the extractants individually. This is demonstrated by the extraction of U(VI) from an initial aqueous phase containing 0.5M SO_4^{2-} , 0.004M U(VI) at pH1 with di-(2-ethylhexyl) phosphoric acid (D2EHPA) and with TBP, each 0.1M in kerosene, and in synergistic combination. The measured distribution coefficients are 135 for D2EHPA, 0.0002 for TBP, and 470 for the combination (Blake et al., 1958). The synergistic enhancement observed with other neutral organophosphorus compounds and D2EHPA shows an increasing effect in the order

trialkyl phosphate < alkyl dialkyl phosphonate < dialkylalkyl phosphinate
< trialkyl phosphine oxide.

The n-butyl derivatives of these compounds increase the distribution coefficients obtained for the extraction of U(VI) with D2EHPA under the aforementioned conditions by factors of about 4, 12, 25, and 50, respectively (Blake et al., 1958).

It has been proposed that the observed enhancement in the distribution of U(VI) into the organic phase is caused by the addition of the neutral extractant S to the uranyl-dialkylphosphate complex $\text{UO}_2\text{L}_2(\text{HL})_2$ through hydrogen bonding (Blake et al., 1958). Dyrssen and Kuča (1960) have concluded from distribution studies that, in the concentration ranges of 0.003-0.06M dibutyl phosphate and 0-1M TBP in CCl_4 , the complex species $\text{UO}_2\text{L}_2(\text{HL})\text{S}$ is present

as well as the species $\text{UO}_2\text{L}_2(\text{HL})_2$. Kennedy and Deane (1961) have examined the uranyl species formed with dibutyl phosphate and tri-n-octyl phosphine oxide by infrared spectrometry. As a result of their studies, they have proposed that the uranyl ion is extracted from aqueous solutions by combinations by the acidic and the neutral organophosphorus reagents according to the reactions

and

Further investigations of the synergistic effect exhibited by acidic and neutral organophosphorus compounds for U(VI) have been made by Shevchenko et al. (1962), Zangen (1963a,b), Hahn and Vander Wall (1964), Vdovenko and Vavilov (1969a-c), Bykhovtsev and Melikova (1969), and others.

C. Long-chain Amines

Amines have been investigated as possible extractants for uranium. Investigations completed to 1958 have been summarized by Coleman et al. (1958). The extractive abilities of several amines in various organic diluents as determined by Coleman et al. (1958) are given in Table IV. It is readily

TABLE IV Distribution Coefficients of Uranium(VI) with Various Amines and Organic Diluents^a

Amine	Diluent			Amine	Diluent		
	Kerosene	Benzene	Chloroform		Kerosene	Benzene	Chloroform
<u>Primary amines</u>				<u>Tertiary amines</u>			
Primene JM-T ^b	3	10	90	Methyl-di-n-decylamine	T	50	50
Amine 21F81 ^c	25	40	50	Tri-n-octylamine	30	150	5
<u>Secondary amines</u>				Tris(tridecylamine) ^f	140	60	0.3
Di-n-decylamine	T	90	150	Tris(tridecyl B ^h) amine	7	1	0.1
Di(tridecylamine) ^d	80	120	40	Tris(2-ethylhexylamine)	0.1	0.2	<0.1
Amine S-24 ^e	110	20	2	Dibenzylaurylamine	0.3	2	2
N-benzylheptadecylamine	8000	2000	100	<u>Dialkylaurylamines</u>			
N-benzyltetradecylamine	1000	>1000	300	Laurylamine	P	<0.1E	(1)E
N-benzoyldodecylamine	1000	>1000	150	Dimethylaurylamine		<0.1	7
N-(2-naphthylmethyl)-dodecylamine	~500	~1000	125	Diethylaurylamine		<0.1	20
N-(α-methylbenzyl)dodecylamine	T	<1	0.2	Dibutylaurylamine	T	95	10
N-benzyl-n-tetradecylamine	T	400	250	Dihexylaurylamine	T	110	6
N-(cyclohexylmethyl)heptadecylamine	25	100	3	Trilaurylamine	70	140	4
N-(trimethylcyclohexylmethyl)-heptadecylamine	130	25	1	<u>Alkylidilaurylamines</u>			
N-n-decylododecylamine	150	100	25	Dilaurylamine	T	80	100
N-(γ-phenylpropyl)-n-tetradecylamine	T	75	250	Methylidilaurylamine	6	70	40
N-(α-methylbenzyl)-2-ethylhexylamine	T	80	2	Butyldilaurylamine		140	7
				Benzylidilaurylamine	15	50	4
				(2-Hydroxyethyl)dilaurylamine	2	5	2

^aData from Coleman et al. (1958)

Experimental conditions: 1M SO_4^{2-} , pH 1.0, 0.004M U(VI), 0.1M amine in given diluent, phase ratio ≈ 1:1, T third liquid phase separated, P precipitation, E emulsion, probably caused by precipitation

^bTrialkylmethylamine homologous mixture 18-24 carbon atoms

^c1-(3-Ethylpentyl)-4-ethyloctylamine

^dMixed C13 alkyls from tetrapropylene

^eBis-(1-isobutyl)-3,5-dimethylhexylamine

^fMixed C13 alkyls from tetrapropylene

apparent from the table that the n-benzyl-branched-alkyl secondary amines are the most efficient extractants of U(VI) of those amines tested. The efficiency of these amines is greater in kerosene and benzene than in chloroform.

The extraction mechanism has been outlined by Coleman et al. (1958). In general, an organic solution of an amine extracts acid from an aqueous solution to form an alkylammonium salt,

The amine salt in the organic phase can exchange its anion X^- for another Y^- in the aqueous phase,

The order of preference for anions in the organic amine solution (Coleman et al., 1958) is $ClO_4^- > NO_3^- > Cl^- > HSO_4^- > F^-$. In this anion-exchange representation, metals are extracted from aqueous solutions in which they are present as anions or anionic complexes. For U(VI), this infers reactions of the type

However, this mechanism is indistinguishable from one in which a neutral complex UO_2X_2 is extracted through a solvation process,

The distribution of U(VI) into the organic phase is dependent on the concentrations of the uranium, acid, and common or foreign anions in the aqueous phase; the concentration of the amine in the organic phase; the nature of the amine (R); the nature of the organic diluent; and the temperature of the system.

Coleman et al. (1958) have implied that the uranyl species extracted from aqueous sulfate solutions is $(R_3NH)_2UO_2(SO_4)_2$ in which the amine:uranyl:sulfate ratio is 2:1:2. However, species in which the amine:uranyl:sulfate ratio is 6:1:4 (McDowell and Baes, 1958; McDowell and Coleman, 1967) and 4:1:3 (Boirie, 1958; Sato, 1963, 1964a,b,d; Lipovskii and Kuzina, 1965; Deptuła and Minc, 1967b) have been reported. Kuzina and Lipovskii (1970) have attributed a decrease in the distribution coefficient of U(VI) with sulfuric acid concentration between 2 and 3M to the formation of the complex $(R_3NH)_4UO_2(SO_4)_2(HSO_4)_2$.

Evidence for various species extracted from nitric acid media have also been reported. Keder et al. (1961) have suggested that the trinitro-uranylate complex is present in the organic phase. Evidence for similar species in which the amine:uranyl:nitrate ratio is 1:1:3 has been reported by

Vdovenko et al. (1961a,b, 1963f,g) and Baroncelli et al. (1962). Lloyd and Mason (1964) have accounted for the extraction of U(VI) from nitrate solutions by considering the extracted species to be $(R_3NHNO_3)_2UO_2(NO_3)_2$ and $[(R_3NHNO_3)_2]_2UO_2(NO_3)_2$. Sato (1964c) has proposed that the $(R_3NH)_2UO_2(NO_3)_4$ species is extracted.

Most investigators agree that the uranyl complex extracted from hydrochloric acid solutions exists in the amine:uranyl:chloride ratio of 2:1:4 (Bizot and Trémillon, 1959; Keder, 1962; Sato, 1966; Vdovenko et al., 1966a). Vdovenko et al. (1962) have reported the formation of both the $R_3NHUO_2F_3$ and $(R_3NH)_2UO_2F_4$ complexes in amine-fluoride systems.

Kuzina and Lipovskii (1968) have investigated the extraction of U(VI) from aqueous oxalate solutions with trioctylamine. They have determined that the species extracted from neutral solutions is the $(R_3NH)_2UO_2(C_2O_4)_2 \cdot 2H_2O$ complex. With an increase in oxalic acid concentration, the distribution coefficient decreases with the extraction of the $(R_3NH)_3UO_2(C_2O_4)_2(HC_2O_4)$ complex. In the presence of fluoride in the form of $R_3NH F$, the extracted species are the $(R_3NH)_3UO_2(C_2O_4)_2 F$ and $(R_3NH)_3UO_2(C_2O_4)F_3$ complexes (Lipovskii and Nikitina, 1969). The extraction of U(VI) from solutions having a constant oxalic acid concentration (0.42M) but a varying nitric acid concentration has been explained by Lipovskii and Kuzina (1969) by the formation of the different complexes $(R_3NH)_3UO_2(NO_3)(C_2O_4)_2$ at $<0.5M$ HNO_3 , $(R_3NH)_2UO_2(NO_3)_2(C_2O_4)$ at $\sim 0.5M$ HNO_3 , and $(R_3NH)_2(UO_2)_2(NO_3)_4(C_2O_4)$ at $>0.5M$ HNO_3 .

Deptuła and Minc (1967a) have reported a synergistic effect in the extraction of U(VI) from aqueous sulfate solutions with a mixture of tri-n-octylamine and di-n-butyl phosphoric acid or di-(2-ethylhexyl) phosphoric acid (HL). The ratio of $UO_2SO_4:HL:R_3N$ of the extracted complex was determined to be 1:1:1.

Vdovenko and co-workers, in a series of experiments, have identified a number of complexes formed between U(VI) and tetradecylammonium salts in benzene solutions. Some of these complexes are listed in Table V. In general, these species are not simple monomers, but involve chain or island polymeric structures.

D. Chelating Agents in Organic Diluents

Morrison and Freiser (1957) have described the principles of solvent extraction by the use of chelating agents. The uranyl chelate is a type of coordination compound in which the uranyl ion combines with a polyfunctional base capable of occupying two or more positions of the coordination sphere of the uranyl ion to form a heterocyclic ring structure. Chelating agents having acidic groups, such as the phenolate or carboxylate, function as bases by loss of a proton and react as the anion. In effect, a chelating agent suitable for use in the solvent extraction of uranium reduces the affinity of the uranyl ion

TABLE V. Some Complexes Identified in the Reaction between
Uranyl and Tetradecylammonium Salts in Benzene^a

<u>R₄NClO₄-UO₂(ClO₄)₂^b</u>	<u>R₄NF-UO₂F₂^e</u>
R ₄ NUO ₂ (ClO ₄) ₃	R ₄ NUO ₂ F ₃
(R ₄ N) ₂ UO ₂ (ClO ₄) ₄	(R ₄ N) ₃ UO ₂ F ₅
<u>R₄NCl-UO₂Cl₂^c</u>	(R ₄ N) ₃ UO ₂ F ₃ Cl ₂
R ₄ NUO ₂ Cl ₃	(R ₄ N) ₃ UO ₂ F ₃ (CH ₃ CO ₂) ₂
(R ₄ N) ₂ UO ₂ Cl ₄	R ₄ NUO ₂ F ₃ (TBPO) _x , x = 1 or 2
R ₄ NUO ₂ Cl ₃ L	<u>R₄N SCN-UO₂(SCN)₂^f</u>
L = TBPO, TBP, acetone	R ₄ NUO ₂ (SCN) ₃
(R ₄ N) ₂ UO ₂ Cl ₃ A	(R ₄ N) ₂ (UO ₂) ₃ (SCN) ₈
A = Br ⁻ , I ⁻ , NO ₃ ⁻	(R ₄ N) ₃ UO ₂ (SCN) ₅
(R ₄ N) ₂ (UO ₂) ₃ Cl ₇ (OH)	R ₄ NUO ₂ (SCN) ₃ L ₂
<u>R₄NCl-UO₂Br₂^d</u>	L = TBPO, TBP
R ₄ NUO ₂ Br ₃	(R ₄ N) ₂ UO ₂ (SCN) ₃ (NO ₃)
(R ₄ N) ₂ UO ₂ Br ₄	<u>(R₄N)₂SO₄-UO₂SO₄^g</u>
R ₄ NUO ₂ Br ₃ L	(R ₄ N) ₂ UO ₂ (SO ₄) ₂
L = TBPO, TBP, (C ₄ H ₉) ₂ O, CH ₃ SCN, CH ₃ CN	(R ₄ N) ₈ UO ₂ (SO ₄) ₅
(R ₄ N) ₂ UO ₂ Br ₃ A	(R ₄ N) ₂ UO ₂ (SO ₄) ₂ (TBPO)
A = Cl ⁻ , I ⁻ , SCN ⁻ , NO ₃ ⁻ , ClO ₄ ⁻	(R ₄ N) ₃ UO ₂ (SO ₄) ₂ A
	A = Cl ⁻ , NO ₃ ⁻

^aR = C₁₀H₂₁, TBPO = tributyl phosphine oxide, TBP = tributyl phosphate.

^bVdovenko et al. (1964a).

^cVdovenko et al. (1966a).

^dBelyaev et al. (1967).

^eVdovenko et al. (1968b).

^fVdovenko et al. (1967c).

^gVdovenko et al. (1968a).

for water and increases its affinity for an organic solvent. Gindler (1962) has reviewed the use of chelating agents for the solvent extraction of U(VI). The agents reviewed include the β -diketones: acetylacetone, benzoylacetone, 2-acetoacetylpyridine, dibenzoylmethane, and thenoyltrifluoroacetone; substituted 1-phenyl-3-methyl-4-acyl-pyrazolones-5; 8-hydroxyquinoline (oxine) and substituted quinolinols; 1-nitroso-2-naphthol; cupferron; n-benzoylphenylhydroxylamine; 1-(2-pyridylazo)-2-naphthol (PAN); sodium diethyl dithiocarbamate; disalicylethylenediimine; and tropolone.

Irving and Edgington (1960) have observed a synergistic enhancement of the uranium distribution coefficient with TBP or TBPO and thenoyltrifluoroacetone (HTTA) mixtures. They determined the formulas of the extracted species to be $\text{UO}_2(\text{TTA})_2 \cdot \text{TBP}$ and $\text{UO}_2(\text{TTA})_2 \cdot 3\text{TBPO}$. Ferraro and Healy (1962) have determined that the extracted species have the general formula $\text{UO}_2(\text{TTA})_2 \cdot \text{S}$, where S represents TBP, TBPO, and a number of other neutral extractant molecules. The species $\text{UO}_2(\text{TTA})_2 \cdot 3\text{TBPO}$ was also isolated. Further investigations of the synergistic effect include those of Milich et al. (1964), Li et al. (1965), Batzar et al. (1967), and Kononenko and Burtненко (1968).

Laskorin et al. (1965) have reported the extraction of U(VI) from carbonate solutions by quaternary phosphonium and arsonium bases after the addition of 8-hydroxyquinoline to the solvent mixture.

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