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URANIUM(VI) AND RUTHENIUM EXTRACTION BY DIALKYLDITHIO-PHOSPHORIC ACIDS

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ABSTRACT

Oxygen donors like dialkylphosphoric acids are good extractants for actinide ions, but little is known about their sulfur homologs. In this paper investigations of U(VI) and Ru extraction from various aqueous media are reported. This includes extraction of U(VI) from nitric, perchloric, and phosphoric acids by solutions of dialkyldithiophosphoric acids in dodecane or benzene. Extraction of U(VI) by synergistic mixtures, of which at least one of the components is a sulfur donor, has been investigated. The extracted species have been identified, and a comparison with the complexes obtained by extraction with the homologous oxygen donors is made. The sulfur-actinide bond is weaker than the oxygen-actinide one, but in some synergistic extractions the dialkyldithiophosphonates are more efficient than the oxygen donors. In addition to size effects, this behavior could be attributed to the weakness of the hydrogen bonds of the SH groups, which allows a greater variety of the ligands to enter the coordination sphere of the metal. Ruthenium, like the d-transition elements, gives strong bonds with the sulfur donors. However, its extraction from nitric acid is slow. We investigated the influence of several parameters on the distribution coefficients and found that the presence of a reagent which destroys nitrous ions is necessary to achieve quantitative extraction. The role of RuNO groups is also discussed.

INTRODUCTION

Dialkylphosphoric acids are known as good extractants for actinide ions in most of their valency states (1). The high affinity of these oxygen donors for the hard 5f ions is clearly understood in terms of charged hard sphere interactions.

The softer donor dialkyldithiophosphoric acids, in which two sulfur atoms replace the phosphoryl and hydroxyl oxygens, have not been considered as efficient actinide extractants, and investigations dealing with their behavior are rather scarce. However, it was found by Curtui et al. (2,3) that U(VI) can be extracted in organic phases containing dialkyldithiophosphoric acids. It has also been reported that actinide (4) or lanthanide dithiocarbamates (5) are stable under anhydrous conditions. These facts led us to investigate systematically the extraction of actinides and lanthanides by organosulfur donors. These ligands are reported to bond strongly with the d-transition ions, so that we undertook simultaneous investigations into their extractive properties toward the 4d transition element ions present in non-negligible amounts in irradiated nuclear fuels.

In this paper we report the results concerning U(VI) and Ru extraction and attempt to compare the extractive properties of dialkylphosphoric acid with those of their sulfur homologs.

MATERIALS AND METHODS

Reagents

The dialkyldithiophosphoric acids were synthesized by IRCHA (Vert le Petit) and were at least 95% pure. No impurities were detected by infrared (IR) or proton nuclear magnetic resonance (NMR) spectroscopy. The oxygen donors trioctylphosphine oxide (TOPO) and dihexylmethoxyoctylphosphine oxide (POX 11) were also supplied by IRCHA with the same degree of purity. Ruthenium-103 used as radioactive tracer was prepared by ISOTEC. (The process used to obtain the appropriate solutions for extraction is described below.) Uranium-233, also used as tracer, was provided by STU (Fontenay-aux-Roses). All the remaining reagents were analytical grade and were used without further purification.

Apparatus

Alpha (α) particle counting by an ionization chamber was used for U analysis. Purity was checked by α spectroscopy. Gamma (γ) and beta (β) counting were used for Ru analysis and purity was checked by γ spectroscopy. A Cary 17 spectrophotometer placed in a glove box was used to record UV and visible spectra. Raman spectroscopy was carried out on a LRT 800 CODERG triple monochromator spectrophotometer using a 164 Spectraphysics krypton laser light source. Infrared (IR) spectra were carried out on a Perkin Elmer 377 spectrophotometer using KBr window cells with 0.2-mm optical path length.

Procedures

All the uranium distribution coefficients were determined by routine laboratory techniques. Ruthenium extraction was performed in thermostatically regulated water jackets in which 20 ml of aqueous and organic phases were mixed by a rotating magnetic agitator. An emulsion (2 ml) was taken to measure the distribution coefficients of Ru. This was done after separation of the two phases by centrifuging and sampling of suitable aliquots for γ-ray analysis.

Preparation of the Ru Solutions

For the Ru data it was important for the ^{103}Ru tracers to be in the same chemical state as the inactive Ru carrier. The isotopic exchange reactions of Ru are generally slow, like its chemical reactions. In order to obtain solutions similar to nuclear reprocessing solutions containing ^{103}Ru and inactive isotope Ru carriers, we proceeded in the following manner. The ^{103}Ru initially in hydrochloric solution was added to a solid mixture of metallic Ru, KOH, and Na_2O_2 in a nickel crucible. By heating, the metallic Ru was dissolved in the alkaline melt. After cooling, the melt was dissolved in water. This solution was then added drop by drop to a concentrated solution of HNO_3

and $Na_2S_2O_8$ to oxidize the ruthenium to the Ru(VIII) tetraoxide RuO_4. This compound was extracted by several volumes of CCl_4 and the Ru finally transferred to a 2 N HNO_3 plus 0.1 M NH_2NH_2 aqueous solution by reductive reextraction. The latter solution was used as a mother liquor for distribution coefficient determinations.

RESULTS AND DISCUSSION

Uranium(VI) Extraction

Haiduc et al. showed that U(VI) is better extracted by dialkyldithiophosphoric acids when a neutral oxygen donor is present. This is illustrated by the enhancement of extraction when butanol is used as a diluent (3) or by the synergistic extraction of U(VI) in tributylphosphate dibutyldithiophosphate mixtures (6). In our laboratory, we undertook to study the mechanism of extraction of uranyl ion in the presence of dialkyldithiophosphoric acids. Figure 1 shows the variation in U(VI) distribution coefficient as a function of pH and extractant concentration. The dibutyldithiophosphoric acid (HDBDTP) was present in the organic phase as a monomer in a wide range of concentrations, and the two slopes close to 2 indicate that the extraction mechanism can be represented by the following equation:

$$(UO_2^{2+})_{aq} + 2(HDBDTP)_{org} \rightarrow 2(H^+)_{aq} + [UO_2(DBDTP)_2]_{org}. \qquad (1)$$

Slopes less than two were observed with extractants having short alkyl chains because both the ligand and the uranium complex solubilities in the aqueous phase are not negligible. The limited size of the $P{<}^{S}_{S}$ group and the expected long interatomic distance of the metal-sulfur bond suggest that the coordination of uranium in the organic phase is not saturated if Eq. (1) is correct. We titrated the water in the organic phase by the Karl Fisher method in the presence or absence of uranium and found that the difference corresponds to one water molecule per uranyl ion. The extracted species is thus $UO_2(DBDTP)_2H_2O$.

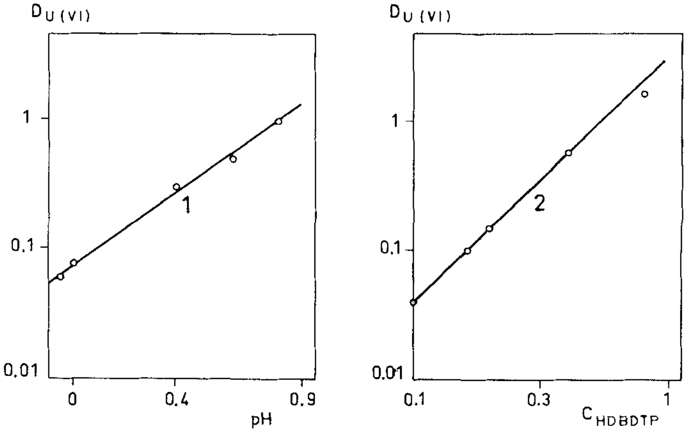


FIGURE 1. Extraction of U(VI) from perchloric acid solutions into dodecane-dibutyldithiophosphate solutions ($C_{U(VI)}$ before extraction 0.0002 M; ionic strength (μ) unity). (1) C_{HDBDTP} = 0.5 M, pH variable; and (2) pH = 0.43, C_{HDBDTP} variable.

Water can be replaced by a more lipophilic oxygen donor, and Fig. 2 shows that the presence of 2-methylpentanol enhances the distribution coefficients. The slope of the distribution curve indicates the coordination of 1 alcohol molecule per uranium atom. The slope of the distribution coefficient as a function of dibutyldithiophosphoric acid concentration at constant alcohol concentration remains equal to 2, and it can be concluded that the extracted species has the formula $UO_2(DBDTP)_2 \cdot ROH$.

Only slight synergistic extraction has been observed in the mixture dibutylphosphoric acid plus tertiary amine or quaternary ammonium salts for both U(VI)(7) or Pu(VI) (8). We investigated U(VI) extraction in trilaurylmethylammonium nitrate (TLMA-NO_3) plus dibutyldithiophosphoric acid in benzene. Uranium(VI) extraction coefficients as a function of HDBDTP:TLMA-NO_3 concentration ratio are shown in Fig. 3. A synergistic effect is observed, the maximum distribution coefficients occurring for a 2:1 ratio

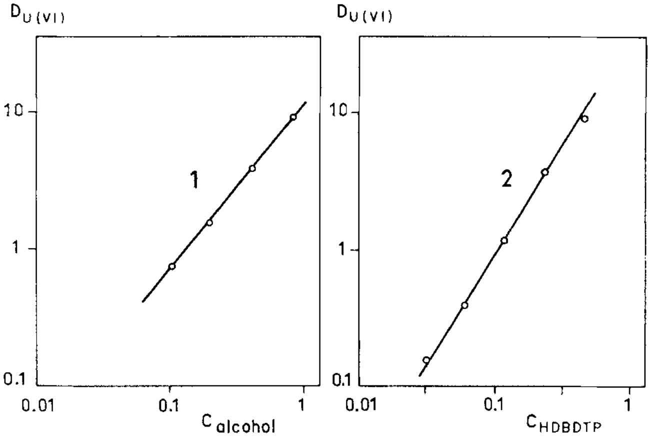


FIGURE 2. Effect of 2-methylpentanol concentration on the distribution coefficients of uranium: (1) C_{HDBDTP} = 0.1 M in benzene, pH = 0.6, $C_{U(VI)}$ = 0.0002 M, $C_{alcohol}$ variable; (2) $C_{alcohol}$ = 0.1 M, pH = 0.4, $C_{U(VI)}$ = 0.0002 M, C_{HDBDTP} variable.

of the organic reagents. The variation in U(VI) distribution coefficient as a function of the concentration of the possible species involved in the extraction equilibrium are plotted in Fig. 4. It can be inferred from the slopes that the extraction mechanism is:

$$(UO_2^{2+})_{aq} + (TLMA^+\ NO_3^-)_{org} + 2(HDBDTP)_{org} \rightarrow$$
$$2(H^+)_{aq} + [UO_2(DBDTP)_2\ NO_3^-\ TLMA^+]_{org}. \qquad (2)$$

This reveals a coordinated NO_3^- ion, contrary to what is observed with extraction by the equivalent synergistic mixtures containing the oxygen donor, where extracted species with the formula $UO_2(DBP)_3S$ were observed. (S^+ represents either the tetraalkylammonium or hydrogenotrialkylammonium cations.) This difference can be attributed to the higher affinity of U(VI) for the dialkylphosphate ion. Table 1 gives the values of the formation constants β_1 of the aqueous 1:1 complex of U(VI) with DBP^- and $DBDTP^-$ ions.

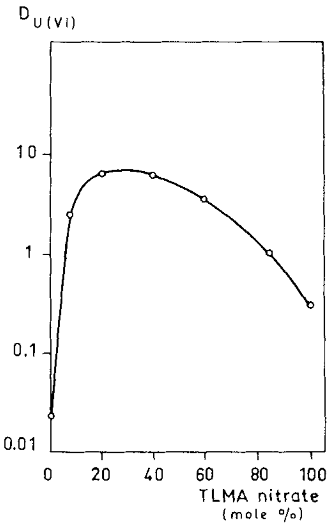


FIGURE 3. Distribution coefficients of U(VI) between mixtures of trilaurylmethylammonium nitrate plus dibutyldithiophosphoric acid in benzene and aqueous nitric acid solutions: $C_{TLMA-NO_3} + C_{HDBDTP} = 0.1$ M, where $\mu = 1$ and pH = 0.6.

The difference in U(VI) affinity for the two kinds of donors can be appreciated by the differences between these values. However, the preferential interaction of U(VI) with the alkylphosphate does not necessarily lead to higher distribution coefficients. This is illustrated by the higher extraction of U(VI) from concentrated phosphoric acid obtained by using sulfur donors. In Fig. 5, the distribution coefficients of uranium are plotted versus the composition of various synergistic mixtures containing di(2-ethylhexyl) dithiophosphoric acid (HDEHDTP) plus one neutral organophosphoric oxygen donor. The higher distribution coefficients are obtained by using a 1:1 mixture of POX 11 and HDEHDTP. The variation in distribution coefficients as a function of TOPO and HDEHDTP concentrations is plotted in Fig. 6. From Figs. 5 and 6, it

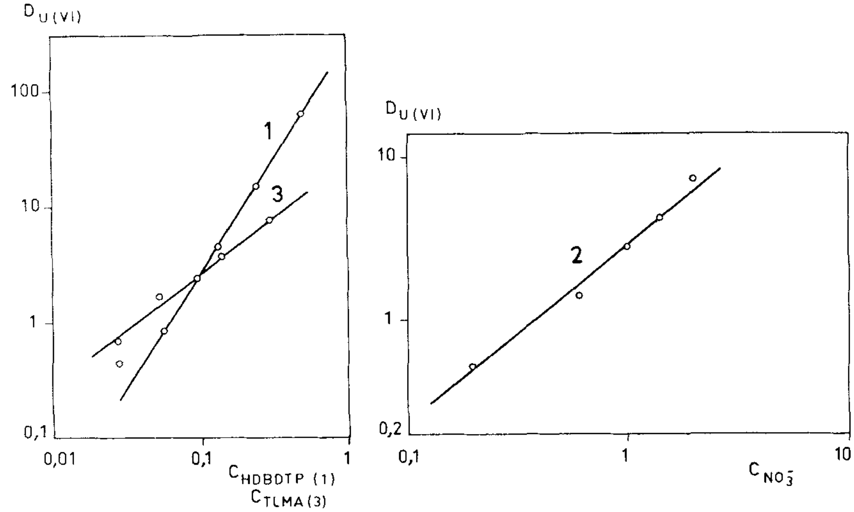


FIGURE 4. Variation of $D_{U(VI)}$ as a function of the concentration of the species which participate in the formation of the organic complex of U(VI): (1) $C_{TLMA-NO_3} = 0.01$ M, $C_{NO_3^-} = 1$ M, C_{HDBDTP} variable, pH = 0.6; (2) $C_{TLMA-NO_3} = 0.02$ M, $C_{HDBDTP} = 0.08$ M, $C_{NO_3^-}$ variable, pH = 0.6; (3) $C_{HDBDTP} = 0.01$ M, $C_{NO_3^-} = 1$ M, $C_{TLMA-NO_3}$ variable, pH = 0.6.

TABLE 1

Formation Constant of the U(VI), 1:1 Aqueous Complex with Dibutylphosphate or Dialkyldithiophosphate Ions

Complex	β_1	Method of Investigation	Reference
UO_2DBP^+	$10^{4.3}$	Solubility	(9)
UO_2DMDTP^+	0.8	Raman spectroscopy	(10)
UO_2DEDTP^+	1.2	Raman spectroscopy	(10)
	1.0	UV spectroscopy	(10)

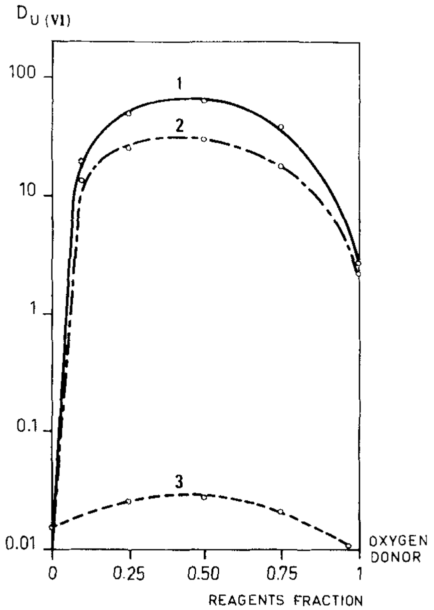


FIGURE 5. Distribution coefficients of U(VI) between 5 M aqueous phosphoric acid and a mixture of HDEHDTP plus neutral oxygen donors in dodecane as a function of the extractants concentration ratio: (1) 0.5 M (HDEHDTP + POX 11), (2) 0.5 M (HDEHDTP + TOPO), (3) 0.5 M (HDEHDTP + TBP).

appears that the species extracted in these mixtures is a mixed complex with the formula $UO_2(H_2PO_4)(DEHDTP)(TOPO)$.

The introduction of an $H_2PO_4^-$ ion in the coordination sphere of uranium is necessary for two reasons: the balance of charges and the saturation of the equatorial coordination of UO_2^{2+} to 5. Hence it appears that the replacement of di(2-ethylhexyl) phosphoric acid (HDEHP) by HDEHDTP completely alters the extraction mechanism. Several authors agree that the extraction data of U(VI) from concentrated phosphoric acid (11) or other aqueous media (12-14) is consistent with the following mechanism:

$$(UO_2^{2+})_{aq} + 2[(HDEHP)_2]_{org} + (TOPO)_{org} \rightarrow 2(H^+)_{aq} + [UO_2(DEHP)_2(HDEHP)_2TOPO]_{org}. \qquad (3)$$

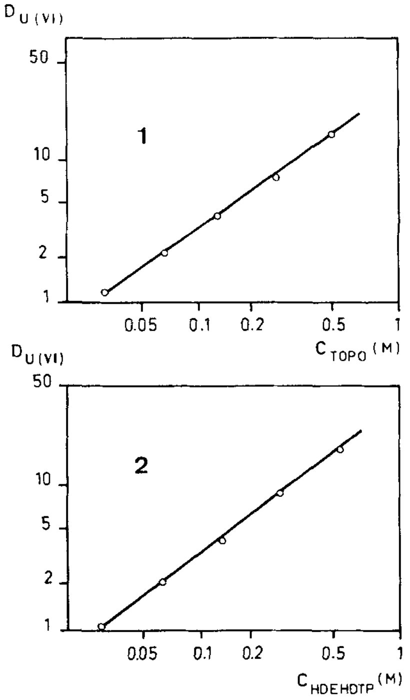
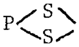


FIGURE 6. Distribution coefficients of U(VI) between 5 M aqueous phosphoric acid and mixtures of HDEHDTP plus TOPO in dodecane: (1) 0.01 M HDEHDTP, C_{TOPO} variable; and (2) 0.01 M TOPO, $C_{HDEHDTP}$ variable.

The maximum distribution coefficient occurs for the ratio (HDEHP)/(TOPO) equal to 4. There is no indication of the presence of $H_2PO_4^-$ ions in the organic phase. Contrary to what we observed (Fig. 6), the distribution coefficients of uranyl ions decrease when the neutral oxygen donors are present in excess (13,14). This drop has been attributed to the competition between U(VI) and TOPO for the coordination site of $(HDEHP)_2$.

The excess of neutral donors causes a net decrease in the activity of the acidic $(HDEHP)_2$ ligand. Consequently, it can be concluded that despite the higher affinity of uranyl ion for dialkylphosphoric acid, higher distribution coefficients are obtained with their sulfur homologs because (a) the weaker hydrogen bonds formed by  groups do not cause decreases in ligand activity and (b) the weaker S-to-metal bond allows an ion present in the aqueous phase to participate in the formation of the organic complex and probably to fit the uranyl ion (15).

Ruthenium Extraction

Ruthenium extraction has not been studied extensively probably because of the slow kinetics of ligand substitution. In nuclear fuels reprocessing, Ru is a source of trouble at different stages of the process, and solvent extraction methods may help to eliminate it. Furthermore, it is present in weighable amounts in the fission products, possibly constituting a non-negligible source of platinoids. In principle, dialkyldithiophosphates that have two sulfur donor atoms are good ligands for soft uranium ions. It is well known that dithiocarbamate bonds strongly with Ru to form the hexacoordinated complexes: $Ru(S_2CNR_2)_3^+$, $Ru(S_2CNR_2)_3$ and $Ru(S_2CNR_2)_3^-$, where R is an alkyl radical (16). Dithiocarbamate ions (DTC^-) are not stable in acidic solutions, so that it appeared interesting to investigate the extraction of Ru with dialkyldithiophosphates. In all the experiments described below, we used a Ru solution prepared as mentioned previously. The metal concentration was 0.0026 M. It was found that in the absence of an antinitrite reagent such as hydrazine or sulfamic acid, Ru is not extracted to a significant extent in 0.5 M HDEHDTP solutions in dodecane from 3 N HNO_3 solutions. Temperature is an important factor in the extraction. This fact shows that, as predicted, the kinetics of extraction is slow. The Ru distribution coefficients are plotted in Fig. 7 as a function of time, at different temperatures. The effect of sulfamic acid is also shown on the same figure. (Figure 8

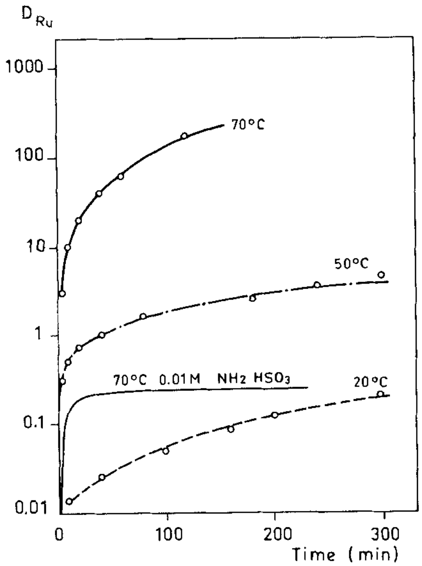


FIGURE 7. Effect of temperature and sulfamic acid concentration on the distribution coefficients of Ru as a function of the mixing time: organic phase, 0.5 M HDEHDTP in dodecane; and aqueous phase, HNO_3 3 M, sulfamic acid 0.25 M.

shows the effect of hydrazine.) Increased aqueous phase acidity is accompanied by a drop in the distribution coefficients. This is shown in Fig. 9. In the conditions used to extract Ru, the species U(VI), Pu(IV), and Np(IV) or Np(V) are not extracted, hence dialkyldithiophosphoric acids appear to allow rather easy separations of ruthenium from acidic nitrate solutions. As the extraction is governed by kinetics factors, investigations of possible extraction catalysts are particularly desirable. Because of the slow extraction kinetics it was not possible to deduce the extraction mechanism from extraction data. However, considering the nature of the aqueous Ru complexes which have the formula $Ru(NO)(NO_2)_x(NO_3)_y(H_2O)_z^{(3-x-y)+}$ (17) and the well-known stability of Ru NO^{3+} species, it can be assumed that in the organic

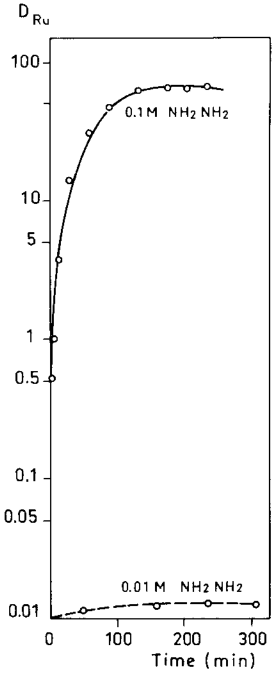


FIGURE 8. Effect of aqueous hydrazine concentrations on the distribution coefficients of ruthenium as a function of the mixing time: organic phase, 0.5 M HDEHDTP in dodecane; aqueous phase, HNO_3 3 N; and temperature, 70°C.

phase, Ru complexes probably have the formula: $Ru(NO)(DEHDTP)_3$ or $Ru(DEHDTP)_3$. The presence of these species is also substantiated by the successful synthesis and the stability of $Ru(NO)(DTC)_3$ and $Ru(DTC)_3$. In $Ru(NO)(DTC)_3$, the $Ru(NO)^{3+}$ linear ion is surrounded by five sulfur atoms of three dithiocarbamate ions, one being monodentate and the others bidentate. In $Ru(DTC)_3$, Ru is surrounded by six sulfur atoms (18). The acceleration of extraction kinetics by addition of hydrazine or sulfamic acid is probably due to the destruction of NO_2^- and (or) NO^+ ions which allows the dialkyldithiophosphate ions to enter more

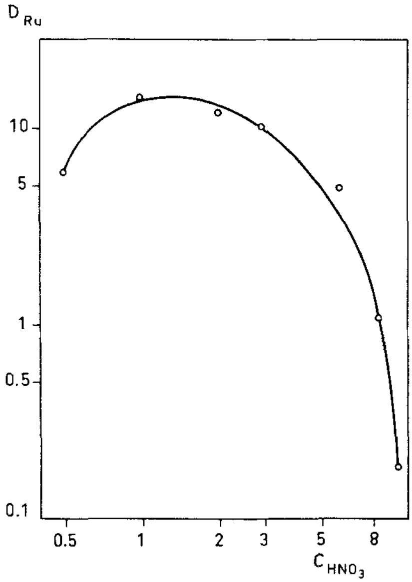


FIGURE 9. Effect of aqueous nitric acid concentration on the distribution coefficients of Ru: organic phase, 0.5 M HDEHDTP in dodecane; aqueous phase, C_{HNO_3} variable plus 0.25 M sulfamic acid; temperature 50°C, mixing time 300 min.

rapidly into the coordination sphere of Ru. Infrared spectra of the organic phases were taken in order to determine whether or not the presence of $Ru(NO)^{3+}$ ions [for which the ν_1 (NO stretching) vibration is intensively IR active (19)] could be detected. No absorption was found in the region 1700 to 2000 cm^{-1}. This suggests that the extracted species is $Ru(DEHDTP)_3$.

CONCLUSIONS

This study showed that dialkyldithiophosphoric acids extract U(VI) by mechanisms totally different from the more familiar dialkylphosphoric acids. In spite of the lower affinity of the sulfur donors for U(VI), they can participate in the formation of mixed complexes in the organic phases, giving higher extraction coefficients than their oxygen homologs.

Dialkyldithiophosphoric acids are good extractants for Ru contained in acidic nitrate solutions, but the extraction kinetics is very slow in the absence of antinitrites. Quantitative extraction is achieved at 70°C after 30 min of mixing of an organic phase [0.5 M di(2-ethylhexyl) dithiophosphoric acid] with a 3 N HNO_3 plus 0.1 M hydrazine aqueous phase. The extracted species is most likely the tris dialkyldithiophosphate Ru(III).

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