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Ion Exchange of Th(IV), U(VI), and Pu(IV) on Macroreticular Resins in TBP–Shell Sol-T Solutions

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Abstract

Absorption of thorium, uranium, and plutonium by macroreticular cation and anion exchange resins from solutions of TBP in Shell Sol-T as a function of TBP and HNO_3 concentrations in the organic phase has been investigated. The absorption behavior is compared with that on conventional gel-type resins from TBP medium on the one hand and on macroreticular resins from aqueous nitric acid on the other.

INTRODUCTION

Ion-exchange behavior of several actinide elements from aqueous and mixed aqueous–organic media is extensively reported in the literature (*1*). However, information on the absorption of inorganic ions in general and of actinide elements in particular from purely nonaqueous media is quite scarce. From the fragmentary data available (*2–4*) on the ion exchange of actinides from nonaqueous media, it is difficult to derive any conclusions about the mechanism of absorption from such solvents.

Exchange of inorganic ions on conventional gel-type resins from nonaqueous solvents is not an easy proposition due to insufficient swelling of the resins in nonpolar media. Recent studies (*5*) have shown that it is possible to exchange metal ions on a macroreticular (MR) cation exchanger from solutions of 5 and 30% TBP in Shell Sol-T. Solutions of TBP in hydrocarbon diluents are essentially nonaqueous in nature, containing only traces of dissolved water (<2% w/v), and are now the generally accepted extractants for reprocessing of the spent nuclear fuels. These studies have led to the development of a few new ion-exchange methods for the separation of thorium, uranium, and plutonium in fuel reprocessing solutions (*7*, *8*). These separations were accomplished on a MR cation exchanger Amberlyst 15 (A15) in a TBP–Shell Sol-T–HNO_3 solvent system. Higher separation factors were obtained with this resin from organic medium than with gel-type resins from aqueous nitric acid medium. This and other advantages of using MR resins for absorptions from nonaqueous solvents have been discussed in an earlier report (*5*).

The above-mentioned studies were carried out mainly on A15, and only 5 and 30% solutions of TBP were considered. Effects of variations in the solvent concentrations and the organic phase acidities on the absorption behavior of the metal ions of the resin were not examined systematically. Though an attempt was also made to determine the distributions on a MR anion exchange resin, Amberlyst A26 (A26) (*5*), the results were discouraging and the data inconclusive. It was therefore felt necessary to carry out a systematic study on the absorption of metal ions on both types of MR resins as a function of varying TBP and organic phase acid concentrations in order

TABLE 1

Resins and Their Characteristics

Resin	Manufacturer	Type	Structure	Particle size (mesh size)	Capacity (meq/g dry)	Moisture content (%)
Amberlyst 15 (A15)	Rohm & Haas	Strong acid	Macroreticular	14–50	4.72	17.4
Dowex 50 × 8 (D 50)	Dow Chemicals Co.	Strong acid	Gel	50–100	4.95	18.8
Amberlite XE270 (XE270)	Rohm & Haas	Weak base	Macroreticular	14–50	4.20	2.0
Amberlyst A26 (A26)	Rohm & Haas	Strong base	Macroreticular	14–50	3.33	15.7
Dowex 1 × 4 (D 1)	Dow Chemicals Co.	Strong base	Gel	50–100	3.45	11.1

to have a better understanding of the absorption behavior. The present paper describes the determination of the distribution ratios (K_d) of thorium, uranium, and plutonium on MR cation and anion exchange resins from solutions of 5–50% TBP in Shell Sol-T containing varying concentrations of nitric acid in the organic phase. Higher TBP concentrations are not considered since they are not important from the fuel reprocessing point of view (*9*). The K_d values are compared with those obtained on typical gel-type resins under identical conditions and also with those obtained on MR resins from aqueous nitric acid medium. Separation factors are calculated from the distribution data and compared with similar data on MR resins from aqueous nitric acid medium. A possible explanation is provided to account for the high separation factors observed from organic phase exchanges.

EXPERIMENTAL

Reagents and Chemicals

Various resins used in the present work and their general characteristics are listed in Table 1. The resins were repeatedly treated with 2–3 *M* HNO_3, washed extensively with demineralized water to remove extraneous acid, and finally rinsed with small volumes of alcohol and dried at 60°C for 24 h. The capacities and moisture contents of the treated resins were determined by standard methods and are given in Table 1.

Tri-*n*-butylphosphate (TBP) and Shell Sol-T (SST) were obtained from Bayer's Chemicals and Shell, Netherlands, respectively. Solutions containing known percent (v/v) of TBP and SST were prepared by diluting measured volumes of the former in volumetric flasks with the diluent. The solutions were then washed with a 2% solution of sodium carbonate followed by demineralized water to remove the degradation products of TBP and other impurities (*10*). Organic solutions containing the metal under study in the required concentrations (≤ 1 g/L) were prepared by extracting the metal from nitric acid. The acid concentration in the organic phase was varied by controlling the aqueous acidity before extraction.

Th(IV) and U(VI) solutions were prepared by dissolving the respective nitrates in dilute HNO_3. Plutonium(IV) nitrate (^{239}Pu) was initially purified by an anion exchange method (*11*) to remove cationic and other α-active impurities. To stablize the Pu(IV) oxidation state, small amounts of sodium nitrite (~0.03 mol/L) were added to its aqueous solutions.

All chemicals and reagents used were of AR grade.

Determination of the Distribution Ratios (K_d)

K_d was determined by equilibrating 0.5 g portions of the resin with 10 mL solutions containing known concentration of the metal ion for 6 h and analyzing the equilibrium solution for the respective metal. K_d was calculated from

$$K_d = \frac{\text{Concentration of the metal in the resin, mg/g}}{\text{Concentration of the metal in the solution, mg/mL}}$$

The separation factor, α_B^A, was calculated from

$$\alpha_B^A = K_d^A / K_d^B$$

Analytical Procedures

Plutonium in aqueous solutions was analyzed radiometrically by counting the α-activity of small volumes, usually less than 500 μL, dried on stainless steel planchettes, in a 2π gas flow (argon) proportional counter. Plutonium concentration in the organic solutions was assayed by α-scintillation counting (*12*). Thorium was analyzed by thoron (*13*) and uranium by dibenzoylmethane (*14*) methods. Nitric acid concentrations in both the aqueous and the organic solutions were determined by alkalimetric titrations to pH 7 in a neutral solution of potassium oxalate to prevent hydrolysis of the metal ions (*15*).

RESULTS AND DISCUSSION

Distribution Ratios

K_d of Th(IV), U(VI), and Pu(IV) on A15 and XE 270 from 5–50% TBP as a function of various organic acidities is given in Figs. 1 and 2, respectively.

The maximum nitric acid concentration that can be obtained in the organic phase depends on the concentration of TBP, since the acid exists as a 1:1 complex, $TBP \cdot HNO_3$ in the organic phase (*16*). Hence the range of acidities that could be varied in a given TBP concentration is different in each case.

The results in Fig. 1 show high absorption of Th(IV) and Pu(IV) in preference to U(VI) by A15 at all concentrations of TBP studied. At a fixed

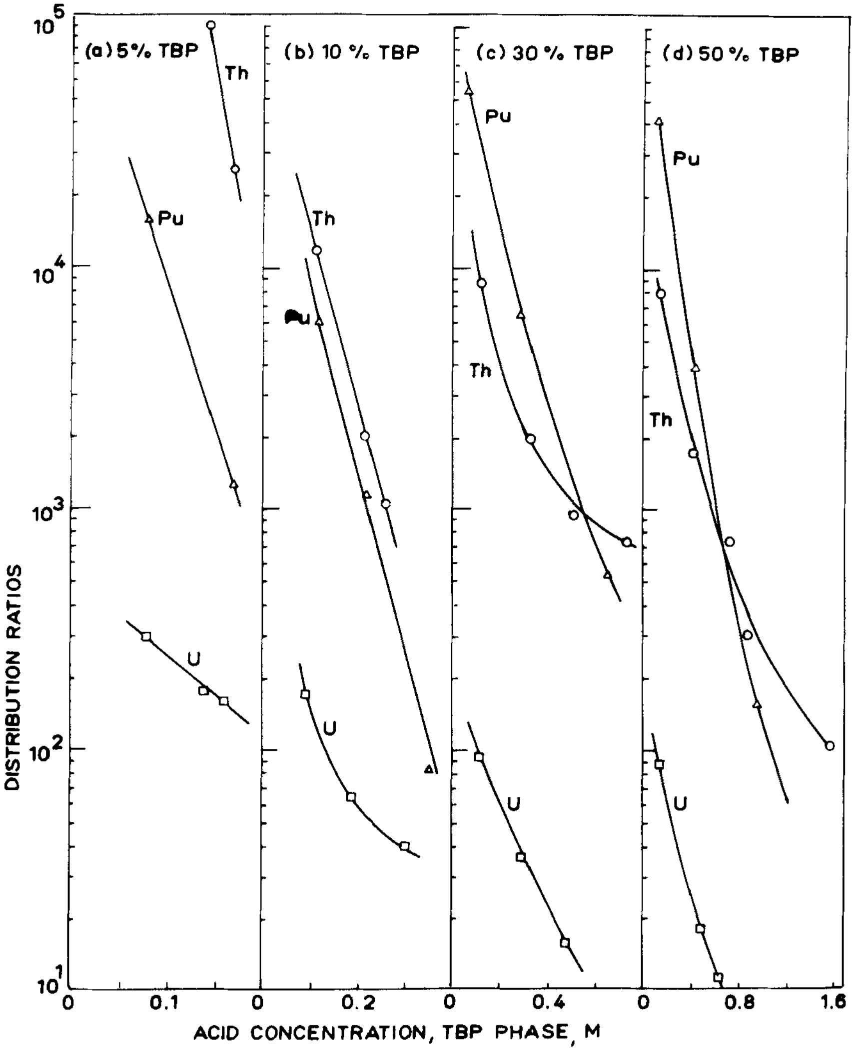

FIG. 1. Distribution ratios on Amerlyst 15 from TBP at various organic phase acidites.

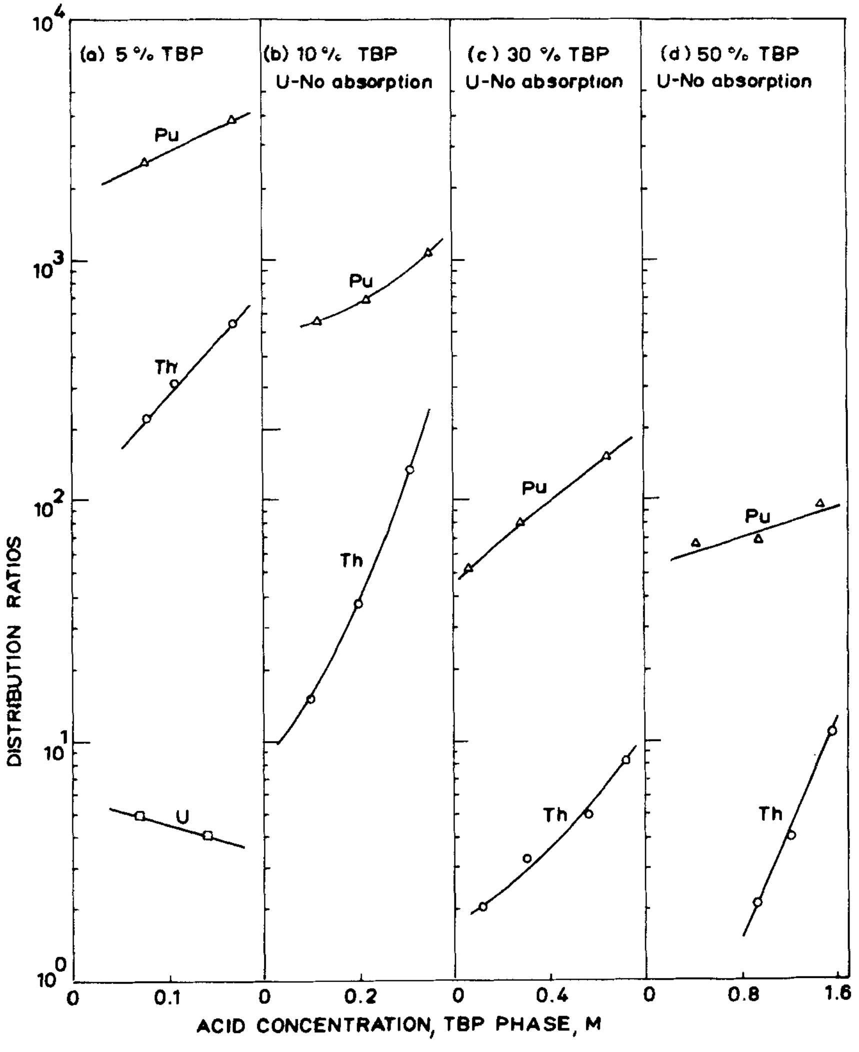

FIG. 2. Distribution ratios on Amberlite XE270 from TBP at various organic phase acidities.

TBP concentration, K_d decreases as the organic phase acidity increases. This is in agreement with the commonly observed behavior of cations on strong cationic resins with respect to the H^+ ion concentration in the aqueous phase. Low absorption of bivalent uranyl ions from all concentrations of TBP is also in conformity with its behavior on cation exchange resins from aqueous nitric acid solutions.

Figure 2 shows high absorption of Th(IV) and Pu(IV) in preference to U(VI) by MR anion exchanger XE270 from TBP medium. K_d is found to increase with organic phase acidity. A similar effect was seen in the absorption of Th(IV) and Pu(IV) by strong base anion exchange resins from aqueous nitric acid medium (*11, 17, 18*). This perhaps indicates that the mechanism of absorption by the anion exchange resin from both TBP and aqueous nitric acid media is the same, viz., exchange of anionic nitrate complexes like $M(NO_3)_6^{2-}$ from the solution phase with NO_3^- ions from the resin phase. The formation of a strongly preferred bivalent anionic nitrato complex increases with HNO_3 concentration in the solution phase, resulting in increased absorptions at higher acidities. While in aqueous medium the K_d-HNO_3 curves show a maxima between 7–7.5 *M* HNO_3, absorption from the TBP phase exhibits a continuous variation with acidity. It can also be seen that the distribution ratios considerably increase as the TBP concentration decreases. This may be due to a fall in the effective dielectric constant of the solution phase as the TBP concentration decreases (dielectric constants: TBP = 8.02, Shell Sol-T ≈ 2). In a medium of low dielectric constant and negligible water content (<0.5% w/v), solvation of ions will be low with a consequent increase in the interionic electrostatic interactions (*20*). This in turn could favor the formation of anionic nitrate complexes with metal ions more easily in lower concentrations than in higher concentrations of TBP. The same explanation holds good for the high absorption of metals by XE270 at very low organic phase acidities, as observed from the present studies, in contrast to the high concentrations of acid required for similar absorptions from aqueous medium. These results are also in agreement with most generally observed type of behavior in mixed solvent media of a large increase in K_d when organic solvents are substituted for water at a given ligand concentration, which is greater the less water present in the solvent mixture (*21*).

Surprisingly, absorption by the strong base anion exchanger Amberlyst A26 (A26) from TBP medium was found to be negligible. K_d of Pu(IV) at the optimum absorption conditions was found to be around 20, though the behavior of the resin in aqueous medium was according to expectations. This is perhaps due to the doubtful quality of A26 as a MR resin. After drying at 60°C for 24 h, as described in the experimental section, the physical appearance of A26 was found to have changed to that of a typical gel-type resin. It is probable that A26 has lost its macroreticular character as a result of the disappearance of most of the pore liquid during drying. Martinola and Meyer (*22*) have reported the occurrence of such an eventuality in MR resins of low cross-linking and porosity.

Absorption of Th(IV), U(VI), and Pu(IV) by both the gel-type resins, D50 and D1, from TBP–Shell Sol-T medium was found to be negligible, irrespective of TBP and acid concentrations ($K_d < 2$). This behavior, however, is easy to understand. It is well known that gel-type resins do not swell appreciably in nonpolar solvents (*23*) and that the presence of water *either in the resin (preswollen) or in the liquid phase is a prerequisite for these* resins to have exchange properties in nonpolar organic solvents (*24–26*). The moisture contents of the gel-type resins used in the present studies (Table 1) as well as the dissolved water in the TBP–Shell Sol-T solutions are too low to swell the resins to any significant extent.

K_d of Th(IV), U(VI), and Pu(IV) on all the gel and MR resins, determined independently from aqueous nitric acid solutions, were found to be in agreement with the literature data (*11, 17, 18, 27, 28*).

In TBP–SST medium the selectivity order on MR cation exchanger A15 was found to decrease as Th(IV) > Pu(IV) > U(VI) and that on MR anion exchanger XE270 was found as Pu(IV) > Th(IV) > U(VI). The same selectivity behaviors have been observed in aqueous nitric acid solution on both MR and gel-type resins.

Separation Factors

The separation factors $\alpha_{\mathrm{U}}^{\mathrm{Th}}$ and $\alpha_{\mathrm{U}}^{\mathrm{Pu}}$ on A15 and 5–50% were calculated at various organic phase acidities and compared with those obtained on this resin from 1–8 *M* nitric acid. In general, the separation factors were found to be higher in the organic medium exchange than in the aqueous. In 50% TBP, which is the most polar of all the concentrations studied, the separation factor versus acidity curves exhibit striking similarity with those in aqueous medium, as can be seen from Fig. 3. In the former case the maximum separation factors were obtained between 0.2–0.3 *M* acidity while in the latter case the maximum occurred at 1 *M* nitric acid. This may be due to the difference in the degrees of dissociation of HNO_3 in the two media because of a wide difference in the dielectric constants. In 5–30% TBP the separation factors exhibited a regular decrease wtih an increase in the acid concentrations and did not show any maxima.

The separation factors on XE270 from TBP as well as from aqueous media are compared in Fig. 4. Values in 5% TBP are shown in this figure since the absorptions were found to be the highest in this concentration. In

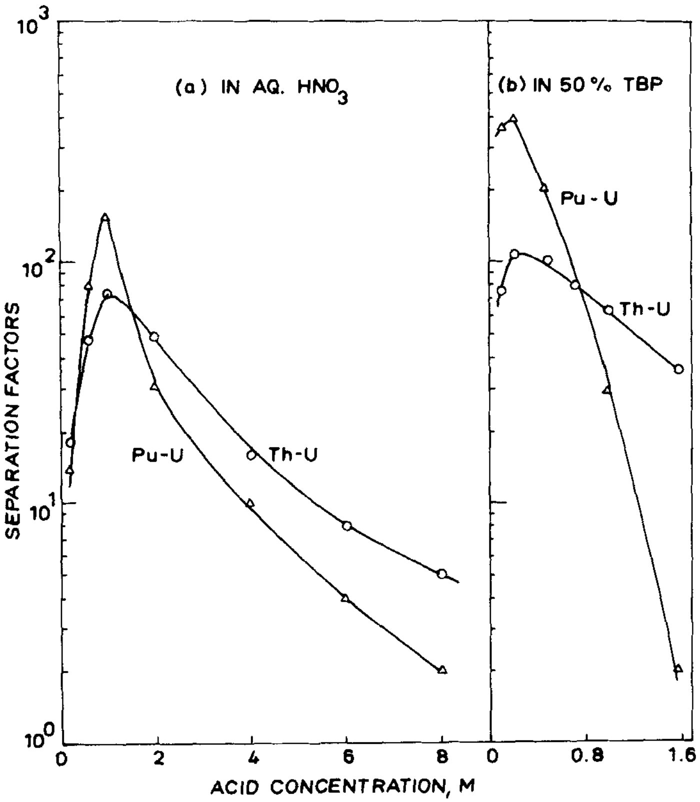

FIG. 3. Separation factors on Amberlyst 15 at various acidities.

both media the separation factors were found to increase with acid concentrations though this dependence is rather poor beyond a certain acid range in the Pu-U system in aqueous medium. The latter effect is due to the formation of poorly absorbed metal species beyond this range of acidity (*11*). The results show the interesting possibility of carrying out anion exchange separations of plutonium and thorium from uranium on XE270 in TBP-SST medium in much the same way as on any anion exchanger from aqueous nitric acid solutions. In the former case the separations could be much better because of the higher separation factors.

A logical interpretation of the higher separation factors obtained in the TBP phase in comparison to those in the aqueous phase could be given as follows.

The extractability of the metals in TBP from nitric acid decreases as U(VI) > Pu(IV) > Th(IV) (*9*). The selectivities from aqueous nitric acid solutions

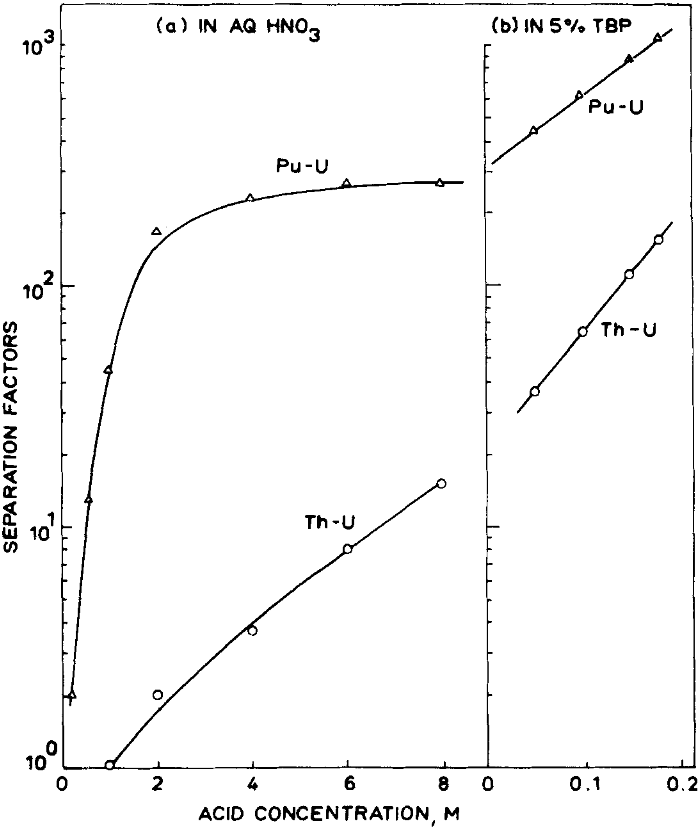

FIG. 4. Separation factors on Amberlite XE270 at various acidities.

on the cation and the anion exchange resins follow the orders Th(IV) > Pu(IV) > U(VI) and Pu(IV) > Th(IV) > U(VI), respectively. Thus it can be seen that while uranium has the highest affinity for TBP, it has the lowest affinity for both the resins. The net result of these two effects will be a considerable reduction in the absorption of uranium by the resins from TBP medium. Since both plutonium and thorium have high affinity for the resins, exchange of these metals from TBP medium is not affected to the same extent. Thus the enhanced separation factors observed from organic medium may be due to a combined effect of selective extraction and selective ion exchange.

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