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 Shakir, Kamal and Beheir, Shokry G.(1980) 'Gel-Liquid Extraction and Separation of U(VI), Th(IV), Ce(lll), and Co(ll)', Separation Science and Technology, 15: 7, 1445 — 1458
To link to this Article: DOI: 10.1080/01496398008056096
URL: http://dx.doi.org/10.1080/01496398008056096

SEPARATION SCIENCE AND TECHNOLOGY, 15(7), pp. 1445–1458, 1980

Gel–Liquid Extraction and Separation of U(VI), Th(IV), Ce(III), and Co(II)

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Abstract

The gel–liquid extraction of U(VI), Th(IV), Ce(III), and Co(II) has been investigated in the 0.01 to 2 *M* HNO_3 range using a gel prepared by swelling styrene divinylbenzene with di-(2-ethylhexyl)phosphoric acid. Obtained results indicate that all of the tested cations can be extracted and that the extraction coefficients increase in the order Ce(III) < Co(II) < Th(IV) < U(VI) and generally decrease with acidity. Under suitable conditions, separation of Th(IV), Ce(III), or Co(II) from U(VI) or of Th(IV) from Ce(III) can be achieved. Kinetic studies indicate that the extraction process is controlled by a progressive shell sorption mechanism.

INTRODUCTION

Though liquid–liquid extraction has been widely used for metal ion separation and concentration, it sometimes suffers from problems of emulsification and losses of extractants to the aqueous solutions. To overcome these problems, it has been proposed (*1*, *2*) to gelatinize and pack the extractant in columns, thus replacing the conventional solvent extraction process by a flow process. Such a modification could both eliminate the emulsification and other extraction problems and combine, as well, the advantages of the solvent extraction technique and the countercurrent extraction process using fixed beds of adsorbents (*2*).

The extractant can be transferred to the gel phase either by allowing it to swell low cross-linkage polymer beads or by treating it with a suitable gelatinizing agent (*3*). The idea of using low cross-linkage copolymer beads swelled with an extractant for metal ions separation was patented in 1955 by Hale (*1*) and was introduced in 1961 by Small (*2*) who termed it gel–liquid extraction. Since then, only a few publications (*3–7*) have appeared in this field.

Investigations (*8*) have shown that the extraction of U(VI) with gels prepared by swelling styrene divinylbenzene (SDVB) with di(2-ethylhexyl)-phosphoric acid (HDEHP) or mixtures of HDEHP and either trioctyl phosphine oxide or tributyl phosphate is feasible. The aim of the present work was to throw some light on the extraction mechanism, to extend the investigation to the extraction of thorium(IV), cerium(III), or cobalt(II) from aqueous nitric acid solutions, and to attempt their separation from uranium(VI).

EXPERIMENTAL

Materials

The extractant, di-(2-ethylhexyl)phosphoric acid (HDEHP), was a Fluka product and was purified by a process involving partitioning between benzene and ethylene glycol (*9*).

Nitrobenzene was used as a diluent. It was purchased from Laborchemica Apolda and was purified by distillation (*10*).

The copolymer, styrene divinylbenzene, was provided by Serva Feinbiochemica Heidelberg in the form of beads of 80 to 150 μm diameter.

Stock solutions of uranyl nitrate, thorium nitrate, cerrous nitrate, and cobaltous nitrate were prepared from the corresponding "Analar" salts.

The radionuclides ^{144}Ce(III) and ^{60}Co(II) were obtained from the Radiochemical Centre, Amersham, and were used as tracers.

^{234}Th was obtained by separation from concentrated uranyl nitrate solutions by a solvent extraction process involving the use of tributyl phosphate (*11*).

Gel Preparation

A known weight of SDVB beads, dried for 3 hr at 90°C, was soaked for 24 hr in 80% solution of HDEHP in nitrobenzene at a solid/liquid ratio of 1/4 (w/w). The excess solvent was removed by either centrifugation (Method 1) or suction filtration (Method 2). The first of these techniques, centrifugation, was adopted for the preparation of gels to be used in the batch technique. Suction filtration was used in the preparation of gels to be used in the column operation. In both cases the gels were well washed with nitric acid solution of the same concentration to be used in the experiment. Analyses indicate that the HDEHP remaining per gram of the plastic beads depends considerably on the method of removing the excess swelling mixture, being about 144 and 593 mg for gels subjected to suction filtration and centrifugation, respectively.

General Procedure of Extraction

Extraction was carried out by either the equilibration batch technique or the column operation technique. The batch technique was used for the determination of the distribution coefficients, E, and the separation factors, α, which can be defined by the equations:

$$E = C_r/C_{aq} \qquad \text{and} \qquad \alpha = E_1/E_2$$

where C_r is the concentration of the metal ion/g SDVB, C_{aq} is the concentration of the metal ion/mL of the aqueous phase after equilibration, and E_1 and E_2 are the distribution coefficients obtained under similar conditions for Metals 1 and 2, respectively.

In the gel batch technique, 1 g of dried SDVB beads was converted to gel by Method 1. The obtained gel (Gel 1) was then soaked for 24 hr in 20 mL solution of the cation under test. Preliminary experiments have shown that this time period was sufficient for equilibrium to be reached under our test conditions.

The second technique, column operation, was used for the separation of the metal ions from their mixtures. Unless otherwise stated, 4 g of SDVB was converted into a gel by Method 2 and the obtained gel (Gel 2) was then packed into glass columns similar to those used by Klement (*12*) for ion exchange processes. Each column consisted of (a) a reservoir of about 100 mL capacity, (b) the gel container which consists of a glass tube of about 1.1 cm i.d. and 8 cm height, and (c) a capillary tube containing the two aforementioned parts. The gel bed was pretreated with 50 mL of nitric acid solution of the same concentration to be used in the experiment (usually 0.05 *N* HNO_3). Solution mixtures of U(VI) and the metal ion to be separated from it were then percolated at a rate of 1 mL/min. In cases where the gel bed was saturated with the cations to be separated, the column was washed with a 50 mL solution of 0.05 *N* HNO_3 before passing the eluents solutions. The effluents were collected in 5 or 10 mL fractions for analysis.

The capacity of the gel for U(VI) was determined at aqueous nitric acid concentrations ranging from 0.05 to 2 *N*, and it was found that the gel capacity depends on the HDEHP content of the gel (and consequently it depends on the method of gel preparation). The average capacities of the gels used in the batch (Gel 1) and column (Gel 2) processes were found to be 0.92 mmole UO_2^{2+}/g plastic beads (~0.44 mmole UO_2^{2+}/mL gel) and 0.22 mmole UO_2^{2+}/g plastic beads (~0.16 mmole UO_2^{2+}/mL gel), respectively. The molar ratio of HDEHP:UO_2^{2+} in uranium-saturated gels was found to be close to 2:1, which is similar to that obtained (*13*) in the liquid–liquid extraction of U(VI) with HDEHP under saturation conditions. For thorium, the molar ratio of HDEHP: Th(IV) in the gel was found to be about 3:1, suggesting that, as in the case of the liquid–liquid extraction of thorium from nitric acid solutions (*14*), thorium most probably exists in the gel as $Th(NO_3)\cdot(HDEHP)_3$.

Analyses

Uranium(VI) remaining in the effluent solutions was determined spectrophotometrically using the thoron method (*15*). In cases where solution mixtures of U(VI) and another element were used, the cations were separated, before analysis, by the anion exchange procedure described by Korkisch et al. (*16*).

Thorium(IV), cerium(III), and cobalt(II) were determined radiometrically. When solutions mixtures of any of these cations and U(VI) were investigated, ^{234}Th-free uranium was used to avoid any interference of the radioactivity of ^{234}Th(IV) with the radiometric measurements.

^{234}Th was applied in only the batch technique where low solution volumes were used. Natural thorium was used in column operations, and in this case the metal ion was determined spectrophotometrically with the thoron method (*17*) after separation from U(VI) by the anion-exchange process (*16*).

RESULTS AND DISCUSSIONS

Dependence of the Extraction Coefficients on the Aqueous Acidity

The dependencies of the distribution coefficients of U(VI), Th(IV), Ce(III), and Co(II) on the aqueous nitric acid concentration were investigated at different initial molar concentrations (C_M) of the metal ion in the aqueous phase as well as at different initial ratios (C_{HDEHP}/C_M) of mmoles of HDEHP in the gel/mmoles of the metal ion in the aqueous phase. Obtained data are plotted in Fig. 1 which shows that the distribution coefficients generally decrease with acidity, suggesting that cation exchange mechanisms are involved in the extraction. U(VI) and Th(IV) generally show higher extraction coefficients than those exhibited by Ce(III) or Co(II).

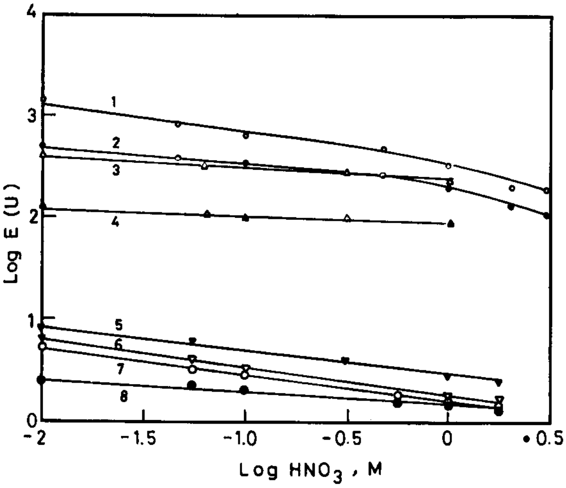

FIG. 1. Dependence of the distribution coefficients of U(VI), Th(IV), Co(II), and Ce(III) on the aqueous acidity. Technique, batch; gel type, 1; total HDEHP, 1.84 mmole.

Curve no.	1	2	3	4	5	6	7	8
Metal ion	U(VI)	U(VI)	Th(IV)	Th(IV)	Co(II)	Co(II)	Ce(III)	Ce(III)
C_M, M	1×10^{-3}	1×10^{-2}	1×10^{-5}	1×10^{-2}	1×10^{-5}	1×10^{-2}	1×10^{-5}	1×10^{-2}
C_{HDEHP}/C_M	92	9.2	9200	9.2	9200	9.2	9200	9.2

Dependencies of the Rate of Extraction on the Gel Particle Size, Temperature, Metal Ion Concentration, and the Rate and Period of Shaking

Rate data obtained for the extraction of U(VI) from 0.05 *N* HNO_3 solutions under different operating conditions are presented in Fig. 2a which shows that: (a) the rate of U(VI) extraction increases with the increase of the fineness of the gel particles (Curves 2 $\neq$ 3 and 4 $\neq$ 5 or $\neq$ 6), uranyl ion concentration (curves 2 $\neq$ 4 and 3 $\neq$ 6), temperature (curves 1 $\neq$ 4) or shaking rate (curves 6 $\neq$ 7); and (b) the rate of uptake is quite fast, particularly at the initial stages of extraction.

The above results suggest that the rate of extraction is controlled by diffusion and chemical processes. The latter process seems to be the rate-determining one at the initial stages of extraction while the diffusion process mostly controls the rate of uptake at the later stages. The existence of such a combination of chemical and diffusion control is usually met

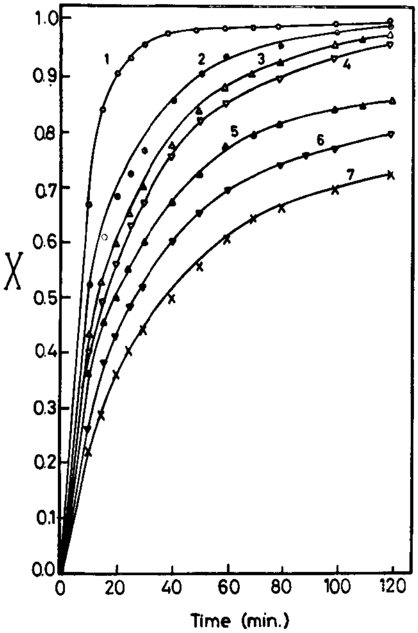

FIG. 2a. Kinetics of U(VI) extraction.

with in what is called the shell-progressive sorption mechanism (*18*). This mechanism is generally characterized by a sharp moving boundary between the unreacted shell and the shrinking unreacted core with each gel particle. The rate-determining process is the diffusion of the extracted ion through the reacted layer which depends not only on the particle size but also on the concentration of the ion to be separated from the solution.

That the extraction is controlled by the shell-progressive sorption mechanism could be confirmed by rate data analysis. As shown from Fig. 2b, the rate data obtained under the different operating conditions could be reasonably fitted into the kinetic equation given by Native et al. (*18*) for the shell-progressive sorption mechanism, viz.:

$$t = \frac{C_{s0}R^2}{6D_eC_{A0}} 1 - 3(1 - X)^{2/3} + 2(1 - X)$$

where t is the contact time, R is the radius of the sorbent bead, C_{s0} is the concentration of the sorbent, C_{A0} is the aqueous concentration of the ion A to be exchanged, D_e is the effective diffusion coefficient of A through a reacted layer, and X is the ratio between the measured and the maximum capacity and is determined experimentally.

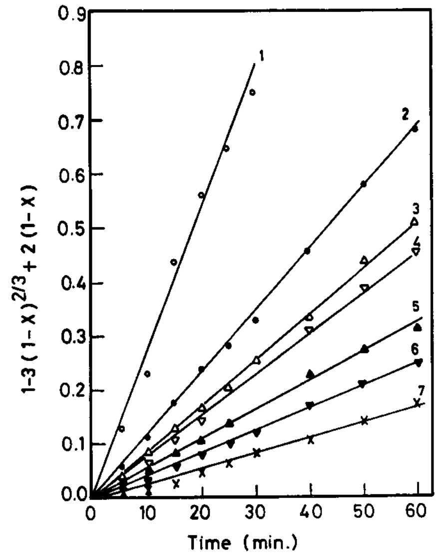

FIG. 2b. Test of the Native model for the kinetic data obtained for U(VI). Technique, batch; gel type, 1.

Curve no.	Temperature (°C)	Mesh size (μm)	U(VI) (M)	Shaking
1	60	75–90	0.02	Hard
2	22	75–90	0.1	Hard
3	22	120–140	0.1	Hard
4	22	75–90	0.02	Hard
5	22	80–150	0.02	Hard
6	22	120–140	0.02	Hard
7	22	120–140	0.02	Mild

Separation of Th(IV) from U(VI)

Figure 3 shows the results obtained for the elution of Th(IV) and U(VI) with HCl solutions of different acidities and indicates that, while 10 *N* HCl solution can quantitatively elute uranium, 12 *N* HCl solution strips only about 20% of the amount of thorium held on the gel. These findings suggest that thorium can be at least partially separated from U(VI) using 10 *N* HCl as eluent. This is illustrated in Fig. 4 which shows a profile for the separation of thorium(IV) from uranium(VI) on a thorium–uranium-saturated gel bed using 10 *N* HCl as eluent. As shown from the figure, uranium can be quantitatively eluted and its thorium contamination can be considerably reduced. Complete separation of the two cations from each other can be attained at low loading conditions; that is, at a high HDEHP/metal ions ratio on the gel. This is demonstrated in Fig. 5 which shows

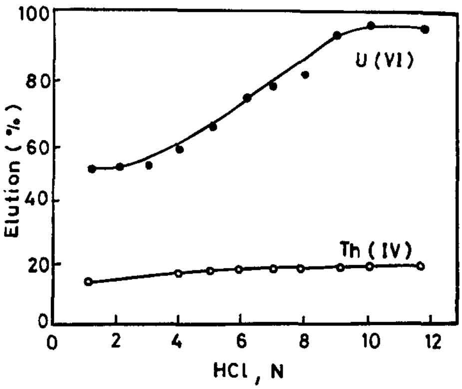

FIG. 3. Effect of HCl on the stripping of U(VI) and Th(IV) from loaded gel batches. Gel type, 1; shaking period, 24 hr.

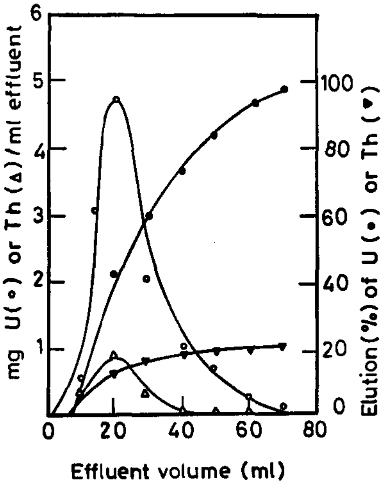

FIG. 4. Elution of Th(IV) and U(VI) on saturated gel bed using 10 *N* HCl as eluent. Gel type, 2; total HDEHP, 1.8 mmole; feed, 2.38 mg U(VI)/mL + 2.38 mg Th(IV)/mL; gel load (mmole), 0.43 U(VI) + 0.28 Th(IV).

the results obtained for the elution of uranium and thorium from a gel bed containing 7.36 mmole of HDEHP and loaded with 0.042 mmole of U(VI) plus 0.02 mmole of Th(IV). As shown in the figure, uranium could be quantitatively eluted with 10 *N* HCl while thorium was totally retained on the gel and could be eluted with a 0.01 *M* ethylenediaminetetraacetic acid (EDTA) solution.

The fact that uranium(VI) cannot form complexes with EDTA furnishes

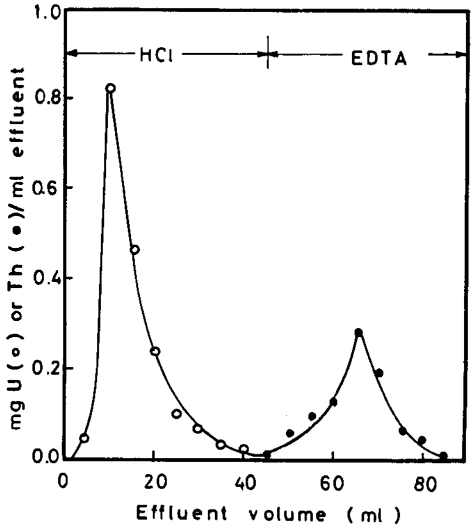

FIG. 5. Elution of U(VI) and Th(IV) on low-loaded gel bed using 10 N HCl and 0.1 M EDTA solutions as eluents. Gel type, 1; total HDEHP, 7.36 mmole; gel load (mmole), 0.021 Th(IV) + 0.042 U(VI).

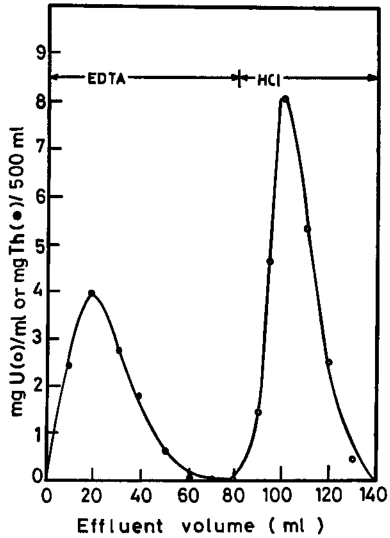

FIG. 6. Elution of Th(IV) and U(VI) on saturated gel bed using 0.1 M EDTA and 10 N HCl solutions as eluents. Gel type, 2; total HDEHP, 1.80 mmole; feed, 1.43 mg U(VI)/mL + 2.32 μg Th(IV)/mL; gel load (mmole), 0.889 U(VI) + 0.001 Th(IV).

another procedure for its separation from thorium, even on saturated gel beds. In this procedure, thorium is first eluted with an EDTA solution (Fig. 6). U(VI) is retained on the gel bed and can be eluted afterwards with 10 *N* HCl solution.

Separation of Ce(III) from U(VI)

On comparing the distribution coefficients obtained for U(VI) with those for cerium(III) (Fig. 1), it becomes evident that the extraction tendency of Ce(III) is much less than that of U(VI). The separation factors, α(U/Ce), obtained at different conditions are given in Table 1 which shows that separation factors >16 can be obtained. This suggests that chromatographic separation of the two concerned cations may be possible under suitable conditions.

TABLE 1[a]

Variation of $\alpha(U^{6+}/Ce^{3+})$ with the Aqueous Acidity at an Initial Metal Ion Concentration (C_M) of 1×10^{-2} *M*

HNO_3, *M*	0.01	0.05	0.1	0.5	1.0
α	20.3	16.2	17.3	18.6	12

[a] Technique, batch; gel type, 1; total HDEHP, 1.84 mmole; C_{HDEHP}/C_M, 9.2.

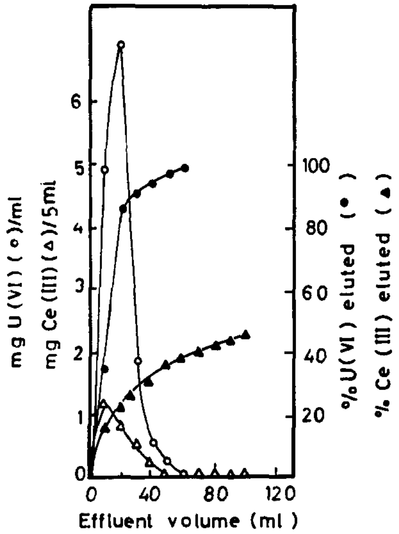

FIG. 7. Elution of U(VI) and Ce(III) on nearly saturated gel bed using 10 *N* HCl solution as eluent. Gel type, 2; total HDEHP, 1.80 mmole; feed, 2.35 mg U(VI)/mL + 1.41 mg Ce(III)/mL; gel load (mmole), 0.62 U(VI) + 0.14 Ce(III).

As shown from Fig. 7 which summarizes the results obtained for the separation of uranium and cerium on a gel bed nearly saturated with the two cations, uranium can be partially separated from cerium(III) by the use of a 10 *N* HCl solution as an eluent. As expected, complete separation of the two cations from each other could be attained (Fig. 8) by operating at low loading conditions and using the appropriate concentrations of nitric and hydrochloric acid solutions. Quantitative separation of Ce(III) from U(VI) could also be attained (Fig. 9) by first eluting Ce(III) with 0.1 *M* EDTA solution and then eluting U(VI) with 10 *N* HCl.

The relatively low extraction coefficients of Ce(III) in comparison with those of Th(IV) suggest that they can be separated from each other by the use of HDEHP–SDVB gel beds. The separation factors, α(Th/Ce), obtained at different conditions of acidity and of initial metal ion concentrations are presented in Table 2.

Separation of Co(II) from U(VI)

As shown from Fig. 1, the coefficients of distribution of Co(II) between HDEHP–SDVB gel and aqueous nitric acid solutions are generally low

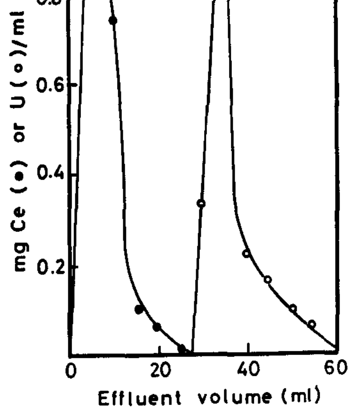

FIG. 8. Elution of Ce(III) and U(VI) on low-loaded gel bed using 1 *N* HNO_3 and 10 *N* HCl solutions as eluents. Gel type, 1; total HDEHP, 7.36 mmole; gel load (mmole), 0.042 U(VI) + 0.07 Ce(III).

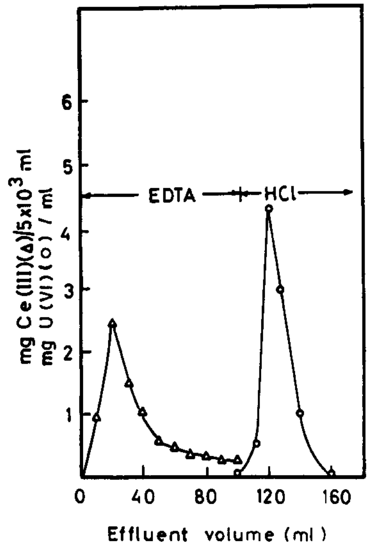

FIG. 9. Elution of U(VI) and Ce(III) on nearly saturated gel bed (≡2 g SDVB) using 0.1 M EDTA and 10 N HCl solutions as eluents. Gel type, 2; total HDEHP, 0.90 mmole; feed, 1.65 mg U(VI)/mL + 0.0046 mg Ce(III)/mL; gel load (mmole), 0.38 U(VI) + 0.0001 Ce(III).

TABLE 2[a]

HNO_3, M	0.01	0.05	0.1	0.5	1.0
α (1)	5.0	8.0	7.2	5.8	5.15
α (2)	25.10	25.04	25.76	19.36	11.80

[a] Technique, batch; gel type, 1; total HDEHP, 1.84 mmole. (1) C_M: 1×10^{-2} M, C_{HDEHP}/C_M: 9.2. (2) C_M: 1×10^{-5} M, C_{HDEHP}/C_M: 9200.

TABLE 3[a]

Variation of $\alpha(U^{6+}\ Co^{2+})$ with Aqueous Acidity

HNO_3, M	0.01	0.05	0.1	0.5	1	2
α	71.5	60.5	51.4	54.6	33.9	13.9

[a] Technique, batch; gel type, 1; total HDEHP, 1.84 mmole; C_M: 1×10^{-2} M; C_{HDEHP}/C_M: 9.2.

and slightly decrease with acidity. The separation factors of uranium(VI)/cobalt(II) at different HNO_3 concentrations are given in Table 3 which suggests that the separation of U(VI) from Co(II) may be satisfactorily achieved. Successful separation of the two cations could also be attained

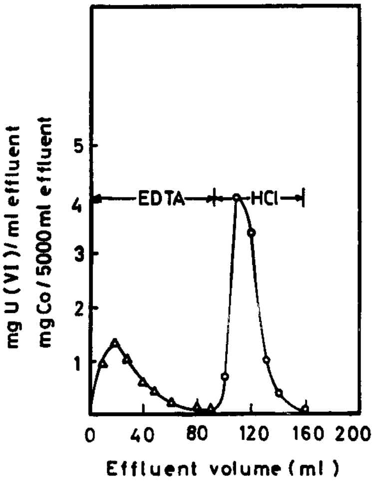

FIG. 10. Elution of U(VI) and Co(II) on nearly saturated gel bed (≡2 g SDVB) using 0.1 *M* EDTA and 10 *N* HCl solutions as eluents. Gel type, 2; total HDEHP, 0.90 mmole; feed, 1.19 mg U(VI)/mL + 0.6 μg Co(II)/mL; gel load (mmole), 0.40 U(VI) + 0.0005 Co(II).

by first eluting cobalt(II) with 0.1 *M* EDTA solution and then eluting uranium(VI) with 10 *N* HCl (Fig. 10).

Acknowledgment

The authors wish to thank Professor Dr. M. R. Zaki, Nuclear Chemistry Department, Nuclear Research Centre, A.E.E., for helpful discussion on the kinetic study.

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Received by editor July 12, 1979