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CATION EXCHANGE BEHAVIOR OF LANTHANIDES AND TRIVALENT ACTINIDES IN ETHANOL-HYDROCHLORIC ACID

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S. F. Marsh, M. R. Ortiz, and J. E. Rein

ABSTRACT

Cation exchange in various organic solvent-hydrochloric acid media was studied for separating microgram levels of fission products from trivalent actinides. Ethanol provided the largest group separation factors. With either conventional or macroporous resins, equilibrations were too slow for useful column operation. The slow equilibration was caused by slow diffusion of the inorganic ions within the resin beads. A pellicular ion exchange resin, consisting of silica beads with a thin shell of resin, gave rapid and complete lanthanide-trivalent actinide separations.

I. SUMMARY

A cation exchange separation system was developed for the trivalent actinide and lanthanide groups. This separation is based on the formation of stronger trivalent actinide chloride complexes. This procedure combines an aqueous-organic mixed solvent, which is high in both ethanol and hydrogen chloride, and a pellicular ion exchange resin.

We evaluated various solvent compositions and ion exchange resins using europium and americium tracers to represent the two elemental groups. The largest distribution coefficient (K_d) differences were obtained when using ethanol as the organic component. Furthermore, the Eu/Am K_d ratios increased with increasing concentrations of both ethanol and hydrogen chloride. However, equilibration of the chloride complexes between the solvent and the resin was too slow in high ethanol to be useful with columns of microporous (conventional) or macroporous resin. Rapid equilibration was attained with pellicular cation exchange resin that consisted of solid silica beads coated with a thin layer of resin.

An effective separation uses 10% aqueous-ethanol-7.6M HCl to elute trivalent actinides from a column of pellicular cation exchange resin. The lanthanides are then eluted with 5M HCl, which is free of organic complexants or salts that usually in-

terfere in chemical assays. This separation will be incorporated into a procedure used to determine burnup in fast breeder reactor (FBR) fuels, using the fission product lanthanide group as the burnup monitor.

II. INTRODUCTION

Early investigations revealed similarities and regularities in the chemical and physical properties of transplutonium elements and the lanthanide elements, thus confirming an inner transition of the 5f electrons analogous to the 4f electron transitions of the lanthanides. Because the stable oxidation state of most transplutonium elements, like the lanthanides, is +3 makes their mutual group separation difficult. Group separations have been achieved by various ion exchange and solvent extraction systems, mainly by incorporating organic complexants^{1,2} or high concentrations of dissolved inorganic salts of a complexing anion^{3,4}.

When the objective of the separation is to obtain fractions for subsequent chemical assay, complexants or inorganic salts that invariably interfere in assay methods must first be destroyed or removed. The complexants are destroyed by rather harsh treatments, such as wet ashing or combustion. The

extent of the treatment depends on the stability of the particular compound. Equally tedious treatments are often required to remove large amounts of inorganic salts. Cation exchange in hydrochloric acid media⁵ is especially attractive because chloride is not a strongly interfering complexant in assay methods and can be removed, if desired, by simple volatilization. Figure 1 shows that the K_d value for +3 lanthanides, represented by the extreme group members lanthanum and lutetium, becomes minimum near 5M HCl, and thereafter increases with increasing hydrochloric acid concentration. However, the K_d value for the trivalent actinides, represented by Am^{3+} , continuously decreases with increasing hydrochloric acid concentration.

This tendency of trivalent actinides to form stronger chloride anionic complexes was used by Diamond and coworkers⁶ in 1952 to separate recently discovered americium from neutron-irradiated plutonium samples. A useful separation of americium from lanthanide fission products was attained using Dowex 50 cation exchange resin (of undesignated cross-linkage) in aqueous 13M HCl, which was prepared by saturating concentrated hydrochloric acid with hydrogen chloride gas. These same authors improved the separation by using a 20% ethanol solution saturated with hydrogen

chloride (Fig. 2). In the two decades since this work, many applications of the 20% ethanol-hydrochloric acid system have been reported in the literature. Surprisingly, we found no references extending the system to higher ethanol and higher hydrochloric acid concentrations at the time we began our investigations. Russian investigators⁷ recently evaluated mixed solvents incorporating high ethanol and high hydrochloric acid concentrations.

We required a lanthanide-trivalent actinide group separation to quantitatively isolate a lanthanide fraction that will serve as the fission monitor in a chemical method to determine burnup in mixed uranium-plutonium FBR fuels. For this application the lanthanide fraction must be (1) essentially free of other elements, especially the trivalent actinides that are particularly abundant in irradiated FBR fuel, and (2) in a medium free of complexants or salts that would interfere with chemical assay methods.

III. EXPERIMENTAL AND DISCUSSION

A. Selection of Ethanol for the Mixed Solvent

We first evaluated mixed solvents containing acetone, methanol, ethanol, n-propanol, and

Fig. 1.

Sorption of lanthanum, lutetium, and americium on cation exchange resin from aqueous HCl.

Fig. 2.

Sorption of promethium and americium on cation exchange resin from 80% aqueous-ethanol-hydrogen chloride mixtures.

isopropanol, with the aqueous portion ranging from 50 to 90%,* for the group separation of lanthanides and trivalent actinides using conventional, microporous cation exchange resin. The initial experiments involved batch contacts of many mixed solvent combinations with AG50W-X4 cation exchange resin using radiotracers of $^{152,154}\text{Eu}$ and ^{241}Am under essentially static conditions. It was later determined that equilibrium was not attained under these near-static conditions, nonetheless, useful trend information was obtained indicating that ethanol gave the largest Eu-Am Kd differences of any organic solvent and that this difference increased with increasing ethanol content. We therefore selected ethanol for further investigation.

B. Evaluation of Aqueous-Ethanol-Hydrogen Chloride Mixed Solvent Composition and Ion Exchange Resin Properties

Values of Kd for europium and americium were measured for various aqueous-ethanol-hydrogen chloride compositions using a conventional microporous cation exchange resin (AG50W-X4). The experiments involved 18-h batch contacts with vigorous mechanical agitation, a 10-ml liquid volume, and 0.1 g of dried resin.

The definition of Kd as used in this report is

$$K_d = \frac{\text{total activity on resin}}{\text{total activity in solution}} = \frac{[c]_i - [c]_f}{[c]_f}$$

*Because the composition of mixed solvents may be expressed in many ways, the opportunity for ambiguity is great. The format used in this report is "X"% aqueous-organic solvent. "Y" M HCl. "X" milliliters of 12 M HCl is added to a 100-ml volumetric flask. The organic solvent is added to the volume mark, waiting for temperature equilibration before final volume adjustment. A measured volume of this mixture is transferred to a larger flask (dissolution of hydrogen chloride substantially increases the solution volume), and the hydrochloric acid concentration is increased by bubbling hydrogen chloride into the solution, while cooling in an ice bath, until the approximate "Y" HCl molarity is reached. The actual hydrochloric acid concentration is determined by titration with standard sodium hydroxide to a phenolphthalein end point.

where

$[c]_i$ = initial concentration of radioisotope in solution, and

$[c]_f$ = final concentration of radioisotope in solution.

The Kd values calculated by this relationship are about 100 times smaller than would result from experiments using equal amounts of resin (grams) and solvent (milliliters).

Figure 3 shows the measured Kd values for europium and americium and their ratio for the aqueous-ethanol-hydrogen chloride mixture with the HCl molarity varying from 5 to 10 M. Figure 4 shows the Kd ratio data for aqueous-ethanol-hydrogen chloride compositions with varying levels of both the HCl molarity and the aqueous-ethanol composition. The value of the Eu-Am Kd ratio is shown to be dependent on both the HCl molarity and the aqueous-ethanol composition, attaining a maximum value of about 100 for 9 M HCl over the range of 5 to 25% aqueous composition.

Fig. 3.

Sorption of europium and americium on cation exchange resin from 5% aqueous-ethanol-hydrogen chloride mixtures.

Fig. 4.

Eu-Am Kd ratios on cation exchange resin from aqueous-ethanol-hydrogen chloride mixtures.

This relatively large K_d ratio indicated that a column of the microporous resin would retain only the rare earth fraction, thereby providing an effective group separation. This did not happen. Not only was the separation inadequate, but neither europium nor americium could be completely eluted. The elution behavior was as if two different complex species of each element were present, one eluting in a normal manner and the other eluting at a much slower rate. In an attempt to explain this unusual behavior, the elution of europium was measured from columns containing three (2X, 8X, and 12X) cross-linked cation exchange resins with 5% aqueous-ethanol-8.5M HCl mixed solvent. Table I shows that the initial elution rate is slower and that the later elution rate is faster for low cross-linked resin. A plausible explanation is that the more open structure of low cross-linked resin provides faster equilibration, hence both faster sorption and desorption rates.

Reaction rates between inorganic ions and ion exchange resin often are decreased in mixed solvents due to higher solvent viscosity and reduced resin pore size caused by bead swelling. A macroporous cation exchange resin, AGMP-50, with its larger pores and increased surface area, was therefore evaluated. The column elution behavior for americium using 15% aqueous-ethanol-8.6M HCl, (Fig. 5), showed little improvement when compared with the conventional resin. We conducted an experiment with this resin to measure the sorption of europium as a function of time for three solvent compositions with the aqueous content ranging from 40 to

TABLE I

CROSS-LINKAGE EFFECT ON ELUTION OF EUROPIUM FROM AG50W CATION EXCHANGE RESIN (50-100 MESH)

Effluent Increment (ml)	Percent of Europium Eluted in Increment		
	2X	8X	12X
1	9.8	17.1	34.6
2	8.1	9.5	10.2
3	6.8	6.4	5.7
4	5.6	5.3	4.0
5	4.6	4.0	3.1
6	3.8	3.2	2.5
7	3.3	2.7	2.1
8	2.8	2.3	1.8
9	2.7	2.1	1.5
10	2.3	1.8	1.3
Totals	49.8	54.4	66.8

100%. The experiment involved a series of batch contacts using vigorous mechanical agitation and $^{152,154}\text{Eu}$ as the tracer. Aliquots of the supernatant liquid were withdrawn periodically and the $^{152,154}\text{Eu}$

Fig. 5.

Elution of americium from a column of macroporous cation exchange resin with 15% aqueous-ethanol-8.6M HCl.

activity measured. Figure 6 shows that equilibrium was attained within 15 min for 100% aqueous-12M HCl, but was not attained in 22 h with either 60% aqueous-ethanol-10.7M HCl or 40% aqueous-ethanol-9.8M HCl.

We evaluated the effect of the macroporous resin mesh size on Kd using a 5% aqueous-ethanol-8.4M HCl mixed solvent and both $^{152,154}\text{Eu}$ and ^{241}Am tracers. Figure 7 shows that the sorption of europium increased with decreasing mesh size, whereas the sorption of americium remained nearly constant. This indicates a trend toward larger group separation factors for the lanthanides and trivalent actinides with finer mesh resin.

C. Successful Application of Pellicular Ion Exchange Resin

Our major conclusion from the above results is that an effective ion exchange separation of the lanthanide and trivalent actinide groups, using the aqueous-ethanol-hydrogen chloride system, requires a cation exchange resin where the exchange reaction is limited to the bead surface. Pellicular ion exchange resin, which was developed for high-pressure liquid chromatography, is such a resin. Each bead of this resin is a solid silica sphere of about 40- μm diam, coated with a 1- to 2- μm layer of ion exchange resin. Batch-contact experiments, similar to those done with the macroporous resin, were con-

Fig. 6.

Effect of ethanol on europium equilibration with macroporous cation exchange resin from aqueous-ethanol-hydrogen chloride mixtures.

Fig. 7.

Equilibration of europium and americium with macroporous cation exchange resin from 5% aqueous-ethanol-8.4M HCl mixtures as a function of resin mesh size.

ducted for a pellicular cation exchange resin*. Equilibration was attained within 15 min for a 10% aqueous-ethanol-8.6M HCl medium (Fig. 8), contrasted to more than 22 h for the macroporous resin with a mixed solvent of even lower ethanol content of 60% aqueous-ethanol-10.7M HCl (Fig. 6).

The small bead size of the pellicular resin, however, resulted in a very slow flow rate, even in short columns. Flow rate was increased to a satisfactory level of 0.12 ml/min for a 6-mm-i.d. by 20-mm resin bed by applying a slight positive air pressure of 0.034 atm (0.5 psi) to the column. The column design in Fig. 9 includes a solvent reservoir and a convenient connection for the air pressure line. Figure 10 shows the separation of europium and americium using this column. Americium is >99% eluted with 5 ml of 10% aqueous-ethanol-7.6M HCl with no elution of europium. Europium then is completely eluted with 5 ml of aqueous 5M HCl.

An adequate separation of americium from as much as 210 μg of fission-product-distributed lanthanides was obtained on the 6- by 20-mm resin bed column shown in Fig. 9. This quantity of

*HC-Pellionex-SCX, H. Reeve Angel and Company.

Fig. 8.

Equilibration of europium on pellicular cation exchange resin from 10% aqueous-ethanol-8.6M HCl.

lanthanides represents a thirtyfold excess over the amount needed for the intended burnup determination.

Pellicular resins were observed in our laboratory and elsewhere⁸ to undergo physical degradation of the ion exchange surface, particularly in corrosive solvents such as ethanol-hydrochloric acid mixtures. Nonetheless, we have satisfactorily reused pellicular resin up to ten times, which tends to offset the current high cost of nearly \$10/g.

After we completed this work, an English translation of a paper by Guseva and Tikhomirova⁷ reported studies with mixed solvents of methanol-hydrochloric acid and ethanol-hydrochloric acid for lanthanide-trivalent actinide separations with conventional cation exchange resin. Similar to our findings, equilibration rates were observed to be unacceptably slow for high alcohol-content solvents. At equal percentage, methanol gave faster equilibration than did ethanol, and the recommended solvent for the separation was 40% aqueous-methanol-8M HCl. Because this conflicted with our finding that ethanol-containing solvents give superior separations, the use of methanol was reevaluated for conventional cation exchange. Figure 11 shows that the maximum Eu/Am K_d ratio was only 16, about one-seventh that obtained with ethanol mixed

Fig. 9.

Pressurized ion exchange column used with pellicular resin.

Fig. 10.

Separation of americium and europium on a column of pellicular cation exchange resin.

Fig. 11.

Sorption of europium and americium on conventional cation exchange resin from aqueous-methanol-hydrogen chloride mixtures.

solvents (Fig. 3). This does not imply that methanol-hydrochloric acid solvents do not provide faster equilibrations in combination with conventional ion exchange resin, but it does justify our selection of ethanol-hydrochloric acid solvents in combination with pellicular ion exchange resin.

IV. CONCLUSIONS

The lanthanide and trivalent actinide groups show large differences in their affinity for cation exchange resin from aqueous-ethanol-hydrogen chloride solvents. The normally slow equilibration of cations between resin and high organic content mixed solvent becomes rapid when pellicular ion exchange resin is substituted for conventional resin. Effective group separations can be achieved within a wide range of aqueous-ethanol-hydrogen chloride compositions. The separation system was demonstrated by selectively eluting trivalent actinides from a column of pellicular cation exchange resin while retaining the lanthanides; the lanthanides were then eluted with 5M HCl. This separation, which provides a lanthanide solution free of organic complexants or salts, is being incorporated into a method to determine nuclear fuel burnup using the fission product lanthanide group as the burnup monitor.

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