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ANION-EXCHANGE BEHAVIOR OF
TRANSPLUTONIUM ELEMENTS AND
LANTHANIDES IN HYDROCHLORIC ACID-
ORGANIC SOLVENT MIXTURES

by

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ABSTRACT

The influence of 20 water-miscible organic solvents on the adsorption of tervalent transplutonium and rare-earth elements from hydrochloric acid media has been investigated using Dowex 1 as the exchange resin. From the distribution coefficients that were determined in various organic solvent-hydrochloric acid mixtures, the conditions most suitable for a group separation of the transplutonium elements from the lanthanides are indicated. The best separation possibilities exist in mixtures that consist of 75 or 60% acetone and 25 or 40% concentrated hydrochloric acid and are 2M in lithium chloride. Under these conditions, the separation factors of the pair americium-ytterbium have values of 28.8 and 21.5, respectively, the former being higher by about a factor of 4 than that obtained in pure aqueous lithium chloride media. So far, however, separation experiments conducted by using this fact have not produced satisfactory results because of a considerable tailing effect in the elution of ytterbium.

I. INTRODUCTION

From pure aqueous hydrochloric acid solutions in the entire range from 1 to 12M hydrochloric acid concentrations, the tervalent actinides and lanthanides and thorium are not at all or only very slightly retained by strongly basic anion-exchange resins.¹⁻⁴ Consequently groups of these elements as well as individual members cannot be separated in these media. Separation conditions are improved, however, if lithium chloride solutions of high concentrations (slightly acidified with hydrochloric acid) are used as eluents. By means of these media, the rare-earth elements can be eluted ahead of the transplutonium elements, thus making possible a group separation of these elements.^{2,5,6} For example, very effective

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separations of americium from europium have been achieved by preferential elution of the europium from a Dowex 1, X8 column with 10M lithium chloride at 87°C.⁵

This separation principle has been applied in this Laboratory for the separation of transplutonium elements from the lanthanides in an analytical scheme concerned with the processing of rock debris for transplutonium elements produced by underground nuclear detonations (Plowshare program).⁷ This group separation of trivalent actinides and lanthanides is possible because of the increased anionic chloride complex formation in these highly salted solutions, with the actinides more readily forming adsorbable anionic species than the lanthanides.

The adsorbability of the actinide and lanthanide ions decreased with increasing acidity and is highly dependent on the lithium chloride concentration. For practical use, superior actinide-lanthanide group separations are obtained in the medium mentioned above.⁵ Below 8M lithium chloride, the distribution coefficients of the elements of the two series tend to merge, and above 10M, the elution time becomes inconveniently long. Under optimum operating conditions (10M lithium chloride as eluent and at a flow rate of about 0.25-0.154 ml/cm²), the separation factor of the pair americium-lanthanum is about 19, while that of the pair americium-lutetium is about 6.2.⁵

Previous investigations carried out in mixed aqueous-organic solvent mixtures containing hydrochloric acid have shown that thorium and the rare earths are adsorbed on strongly basic resins from such media,^{8,9} although, as mentioned above, they are not retained from pure aqueous hydrochloric acid solutions. However, in most mixed aqueous-organic solvent systems, the extent of adsorption, although appreciable, is virtually the same for both thorium and the rare earths.⁸ Later investigations showed¹⁰ that this is not the case when a mixture used as eluent consists of 75% acetone and 25% concentrated hydrochloric acid, under which condition the rare earths can be eluted ahead of the thorium (separation factor of about 9).

Based on this observation, it seemed likely that by using this or similar eluents in the presence or absence of lithium chloride also, a group separation of the trivalent transplutonium elements from the lanthanides may be effected, as it is possible in the pure aqueous lithium chloride system mentioned above. Therefore the present investigations have been carried out using mostly acetone-hydrochloric acid solutions, but also 19 other solvents strongly acidified with hydrochloric acid.

II. EXPERIMENTAL PROCEDURE

A. Reagents and Solutions

1. Ion-exchange Resin

Air-dried Dowex 1 (Bio Rad AG1, X8; 100-200 mesh; chloride form) was used for the batch and column experiments. The same resin, but of 200-400 mesh size and also with the cross linkings of X4 and X10, has also been employed for separation studies.

2. Tracers

Hydrochloric acid solutions of the following radioactive tracers were used: Am^{241} , Cm^{244} , Cf^{252} , Yb^{169} , Ce^{144} , Sc^{46} , Pu^{239} , and Np^{239} . Standard counting methods were used for their measurements.

3. Organic Solvents

The solvents were used off the shelf, with no attempt at further purification. Most of them, including acetone, were of reagent-grade purity.

B. Determination of Distribution Coefficients

Two 1-g amounts of the resin were accurately weighed on an analytical balance into 60-ml polyethylene bottles for each determination. To each bottle, 20 ml of the mixed aqueous-organic solvent solution under investigation was added, followed by the addition of 5-10 μl of the tracer being studied. The mixtures were shaken for at least 2 hr on a shaking machine. Then the resin was filtered off, and the activity of 10 ml of the filtrate was measured (in the case of gamma counting). When the tracers used had to be determined by alpha counting (Cm, Cf, Pu, and Np), suitable aliquots were pipetted onto tantalum plates for counting. The number of counts of tracer going into the resin was calculated from the difference between the initial and final tracer concentrations of the mixed aqueous-organic solvent solutions, and the distribution coefficient (K_d values) were computed in the usual manner.⁸

C. Column Operations

Separation experiments were performed in the following manner:

1. 0.5 or 1 g of the resin was soaked in a few milliliters of a mixture 60 or 75 v/o in acetone, 40 or 25 v/o in concentrated hydrochloric acid, and 2M in lithium chloride (eluent solution). When freshly prepared, these mixtures have a yellow color, which, on standing for about one day, changes to a reddish brown. This coloration is caused by the reaction of

hydrochloric acid with acetone, whereby mesityl oxide and other condensation products are formed. Experiments conducted with a 2-day-old mixture showed that these colored products do not interfere with the column operations. In the preparation of the mixtures, the sequence of mixing the chemicals should be: first lithium chloride (anhydrous), then acetone, and finally concentrated hydrochloric acid.

2. The slurry was transferred quantitatively to an ion-exchange column of 0.5-cm inner diameter and 20-cm height, using further small portions of the eluent solution. In the column, the resin bed is supported by a pad of glass wool.

3. After the level of eluent solution had dropped to the upper part of the resin bed, 150 μ l of eluent solution containing the tracers (ytterbium and/or americium in 5- μ l and 10- μ l quantities, respectively, per 150-200 μ l of eluent solution) were added, and the collection of fractions was started.

4. After this sorption step, ytterbium was eluted by passing eluent solution through the resin bed, usually using a flow rate of 9-10 drops/min (50-60 drops correspond to one milliliter).

5. The adsorbed americium was eluted with a few milliliters of 5M hydrochloric acid.

III. RESULTS AND DISCUSSION

As the first step in investigating the anion-exchange behavior of some transplutonium and rare-earth elements, we have studied the effect of increasing acetone concentration on their adsorption on Dowex 1. Table I presents the results of these investigations. The distribution data

TABLE I. Distribution Coefficients of Transplutonium and Rare-earth Elements on Dowex 1 in Acetone-Hydrochloric Acid Mixtures

Volume Ratio of Acetone to Concentrated HCl	Metal Ions					
	Am(III)	Cm(III)	Cf(III)	Ce(III)	Yb(III)	Sc(III)
10:90	1.6	< 0.1	2.2	< 0.01	< 0.01	1.1
20:80	1.52	0.46	4.1	< 0.01	0.27	1.25
40:60	2.0	1.3	4.5	< 0.1	0.35	2.2
50:50	2.25	1.61	8.2	0.3	0.79	2.7
60:40	3.1	2.0	10.1	0.91	1.08	3.6
70:30	6.0	6.7	18.1	2.1	2.07	5.0
75:25	17.6	9.8	35	3.1	3.67	5.2
80:20	16.9	18.3	39.2	5.9	5.8	6.6
90:10	76	80.6	131	28.3	28.9	12.8
95:5	354	282	580	140	166	33

in Table I indicate that an increase of the volume ratio of acetone to concentrated hydrochloric acid generally increases the adsorption of all metal ions investigated. A comparison of the adsorption behavior of the trans-plutonium elements shows that, at all ratios of acetone and hydrochloric acid, californium is more strongly adsorbed than americium or curium. The adsorption data of the latter two elements in the various acetone-hydrochloric acid mixtures in relation to each other show that, at low acetone concentrations, curium is less strongly adsorbed than americium, but at high percentages of this solvent, the reverse is true. Exceptions are the distribution coefficients that were measured at volume ratios of 70:30 and 95:5.

In the rare-earth group, the adsorption of cerium, ytterbium, and scandium also steadily increases with an increase of the volume ratio of acetone to concentrated hydrochloric acid. The data in Table I show that the adsorbability of ytterbium (which has been selected as a representative of the "heavy" rare earths) is generally higher than that of cerium, and the difference between the distribution coefficients of these two elements is very small, becoming practically negligible at high percentages of acetone. In other words, individual lanthanides cannot be separated in any of the media listed in Table I. A separation of scandium from the lanthanides would, however, be feasible at very low and very high ratios of acetone to hydrochloric acid.

With respect to the separability of americium from ytterbium, the medium consisting of 75% acetone and 25% concentrated hydrochloric acid seemed to be the most interesting, because under these conditions the separation factor, i.e., $K_d \text{ Am}/K_d \text{ Yb}$, has a value of 4.8. Furthermore, the adsorption of americium is sufficiently high in this mixture.

To see if in organic solvents other than acetone this separation factor can be increased, we studied the adsorption of americium and ytterbium on Dowex 1 in 19 other organic solvent mixtures, which were prepared by mixing the organic solvent with concentrated hydrochloric acid in the volume ratio of 75:25. Table II presents the results of these investigations, with the solvents arranged in the order of decreasing separation factors ($K_d \text{ Am}/K_d \text{ Yb}$).

The adsorption data in Table II show that the separation factor is highest in the acetone mixture. Therefore the acetone system has been selected for further investigations. These investigations have first been directed toward the study of the effect of varying hydrochloric acid concentration on the adsorption of transplutonium and rare-earth elements. For this purpose, the distribution coefficients of these metal ions have been determined in 75 and 90% acetone mixtures containing 25 and 10%, respectively, of hydrochloric acid of varied molarity. Tables III and IV present the results of these investigations showing different adsorption patterns at the two selected acetone concentrations.

TABLE II. Distribution Coefficients (K_d) and Separation Factors (α)
for Am(III), as Compared to Yb(III), in Various Organic Solvents
(75%) Mixed with Concentrated HCl (25%) on Dowex 1, X8

Solvent	K_d Values		Separation Factors (α), Am/Yb
	Am(III)	Yb(III)	
Acetone	17.6	3.7	4.8
Acetic acid	1.5	0.39	3.8
Methyl ethyl ketone	16.7	5.7	2.9
1,2-Bis(2-methoxy-ethoxy)ethane	3.9	1.4	2.7
Tetrahydrofuran	5.2	2.1	2.5
Monoethylether of ethylene glycol	2.2	0.9	2.4
Methanol	1.1	0.48	2.3
Monomethylether of ethylene glycol	0.45	0.21	2.1
Pyridine	0.75	0.4	1.8
Ethanol	8.4	5.1	1.6
Isobutanol	15.3	10	1.5
Isopropanol	20.3	14	1.4
Monobutylether of ethylene glycol	2.8	1.9	1.4
Hexone	10	7.6	1.3
1-Butanol	12	10	1.2
Cyclohexanol	16.6	13	1.2
Ethylene glycol	<0.1	<0.1	-
Propylene glycol	~0.1	<0.1	-
Glycerol	<0.1	<0.1	-
Dimethylformamide	<0.1	<0.1	-

TABLE III. Distribution Coefficients on Dowex 1 in 75% Acetone Mixtures
Containing 25% of Hydrochloric Acid of Varied Molarity

Ion	HCl Concentration, M in 25 v/o Aqueous Phase				
	1.5	3.0	6.0	9.0	12
Am(III)	10.7	11.8	10.0	8.9	17.6
Cm(III)	9.76	8.1	6.8	7.51	9.8
Cf(III)	7.5	7.5	7.5	9.6	35
Ce(III)	11.5	9.0	6.6	4.17	3.1
Yb(III)	6.9	8.5	5.5	4.5	3.67
Sc(III)	4.51	4.8	4.1	4.12	5.2

TABLE IV. Distribution Coefficients on Dowex 1 in 90% Acetone Mixtures
Containing 10% of Hydrochloric Acid of Varied Molarity

Ion	Final HCl Concentration, M				
	0.15	0.3	0.6	0.9	1.2
Am(III)	617	246	101	46.6	76
Cm(III)	327	170	66.1	45.1	80.6
Cf(III)	287	137	59.4	63.8	131
Ce(III)	902	284	96.1	53.8	28.3
Yb(III)	276	141	57.4	32.4	28.9
Sc(III)	74	36.3	15.1	10.4	12.8

As shown in Table III, in the 75% acetone mixtures containing 25% of hydrochloric acid of a varied molarity, the dependence of the distribution coefficients on the hydrochloric acid concentration is rather irregular, and minimum K_d values are frequently observed at certain acidities. As a rule, the variation of the distribution coefficients when proceeding from lower to higher acidities (or vice versa) is relatively small. With regard to the adsorption behavior of the transplutonium elements, the adsorption sequence changes when the hydrochloric acid concentration is varied; in 1.5M or 3.0M hydrochloric acid, the order of increasing adsorption is $\text{Am} > \text{Cm} > \text{Cf}$. The same adsorption sequence has been observed in methanol-nitric acid mixtures,¹¹ but in the 12M acid, the order is $\text{Cf} > \text{Am} > \text{Cm}$ (see Table III). A similar reversal of the order of adsorption of these three elements is observed in the 90% acetone mixtures, as shown in Table IV.

The results shown in Table IV indicate that in the 90% acetone-hydrochloric acid mixtures the K_d values of all metal ions increase considerably with a decrease of the final hydrochloric acid concentration. This behavior is contrary to observations usually made in pure aqueous hydrochloric acid media. In the latter media, the K_d values of many elements tend to decrease rather than increase with a decrease of the hydrochloric acid concentration.

With respect to a group separation of the transplutonium from the rare-earth elements, none of the adsorption characteristics shown in Tables III and IV are more suitable than those observed in the media containing up to 75% of acetone. In these mixtures, however, the separation factors of Am/Yb are relatively low; that is, they have maximum values ranging from about 2.8 to 5.7. Consequently, experiments have been carried out to increase these factors by the addition of lithium chloride to several of the acetone-hydrochloric acid mixtures. Table V shows the

TABLE V. Influence of Lithium Chloride Concentration on the Distribution Coefficients and Separation Factors of Americium and Ytterbium in Various Acetone-Hydrochloric Acid Mixtures

Volume Ratio of Acetone to Concentrated HCl	LiCl, M	Am(III)	Yb(III)	Separation Factors (α), Am/Yb
40:60	0	2.0	0.35	5.7
40:60	1	5.18	0.41	12.6
40:60	2	9.1	0.91	10.0
40:60	4	17.1	1.5	11.4
60:40	0	3.1	1.08	2.8
60:40	1	10.54	0.77	13.6
60:40 ^a	2	23.7	1.1	21.5
60:40	4 ^b	56	3.8	14.7
75:25	0	17.6	3.67	4.8
75:25	1	40.1	2.2	18.2
75:25	2	114	3.95	28.8
75:25	4 ^b	111	15	7.6

^aUnder the same experimental conditions, but using acetic acid in place of acetone, the K_d values of americium and ytterbium are 5 and 0.5, respectively, giving a separation factor of 10.

^bThese are saturated solutions in which the molarity of LiCl is not much less than 4.

results of these investigations, indicating that separation factors as high as 21.5 and 28.8 can be obtained in mixtures that are 2M in lithium chloride and in which the volume ratio of acetone to concentrated hydrochloric acid is 60:40 and 75:25, respectively. From a practical point of view of these two mixtures, the one that is 60% in acetone, 40% in concentrated hydrochloric acid, and 2M in lithium chloride would be more suitable for the separation of americium from ytterbium, because with it ytterbium is more readily eluted, so that the elution time does not become inconveniently long. In the same medium, the distribution coefficients of other actinides and rare earths such as Cm(III), Cf(III), Np(IV), Pu(IV), Ce(III), and Sc(III) had values of 21, 88.2, 414, 345, 1, and 5.8, respectively.

Separation experiments using the 60:40 mixture as the eluent showed that the bulk of ytterbium is rather rapidly eluted while, however, the last portion (about 20% of the ytterbium activity) of this element causes considerable tailing. This tailing is accompanied by an appreciable overlapping with the elution curve of americium so that no quantitative separation of these two elements could be achieved.

The same tailing effect and overlapping of elution curves was observed when using as eluent the mixture that consists of 75% acetone and 25% concentrated hydrochloric acid and is 2M in lithium chloride, although in this solution the separation factor $A_{m/Yb}$ is considerably higher (as shown in Table V). Several experiments to improve these separation conditions have been performed. Thus, the separation was tried in the presence of large amounts of the chlorides of magnesium or nickel. This should have served the purpose of displacing more rapidly the ytterbium from the resin by a mechanism of displacement chromatography and consequently reducing the tailing of this element.

These experiments were unsuccessful as were those in which we used Dowex 1, X8 of lower particle size, i.e., 200-400 mesh size and Dowex 1 of lower or higher crosslinking (X4 and X10). With Dowex 1, X4, even a less effective separation was achieved than with the X8 resin. This, in turn, proved to be much more suitable than Dowex 1, X10 (50-100 mesh) on which the K_d values were lower by a factor of 10.

The flow rates used in all this column work were of the order of 9-10 drops/min, which corresponds to about 0.2 ml/min. If the elution of ytterbium is performed at the much lower flow rate of 2 drops/min, the tailing effect is even more pronounced than at the high flow rates.

The same result is obtained if in the eluent solution 5% of the acetone is replaced by dimethylsulfoxide. This has been found to be an excellent agent for the anion-exchange separation of various metal ions when used as a mixture containing other organic solvents and hydrochloric acid.¹²

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