

this difference was attributed to the large difference in flow rate in the two types of experiments.

5. Application of the transfer theory procedure to column desorption data was shown to be

possible. A dependence of the desorption rate on flow and on macro-component ion concentration was indicated.

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## Ion Exchange as a Separations Method. III. Equilibrium Studies of the Reactions of Rare Earth Complexes with Synthetic Ion Exchange Resins<sup>1</sup>

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### Introduction

From the early investigation of the column separations method,<sup>2</sup> it was apparent that the separation efficiency which could be achieved was dependent upon a number of factors (such as *pH* and concentration of the complexing agent, type of complexing agent, concentrations of cations being separated, ionic strength of the eluant, type of resin, resin particle size, flow rate of eluant, column diameter and column length). Some of these variables were studied by Tompkins, *et al.*, in a process development program whose purpose was the design of an all-column fission product factory.<sup>3</sup> During this same period, similar studies were undertaken by F. H. Spedding, *et al.*, in their application of this separations method to large scale rare earth separations.<sup>4</sup>

These empirical studies resulted in the solution of a very difficult problem (*i. e.*, the separation of rare earths), but the fundamental knowledge concerning the column process was not greatly increased. Being able to get good results was more of an art than a science. It had not been possible to study most of the variables over a wide range because of the long time required to make a column run. For this reason there was a tendency to arbitrarily fix one or more conditions, without studying each extensively, and then to study the effects of varying other factors and to choose those conditions which gave the best results. Because of the exceedingly long time required to study the effect of flow rate in the lower range, Spedding, *et al.*, after studying it down to  $\sim 2$  ml./sq. cm./min., arbitrarily chose this rate for their rare earth separations.<sup>4</sup> In the studies of Tompkins, *et al.*,<sup>3</sup> the flow rate was varied from 10 to 0.02 ml./sq. cm./min. The results of the latter investigation indicated the importance of operating columns as near to equilibrium conditions as possible.

The above considerations indicated the need for a more thorough understanding of the column

reactions. It appeared that the studies which needed to be undertaken were: (1) a determination of the effects of various factors (*i. e.*, the *pH* and concentration of the complexing agent, the type of complexing agent, the concentration of the cations being separated, the ionic strength of the eluant and the type of resin) on the equilibrium constants of the reactions involved in column separations; (2) development of a simple theory which would predict column behavior from a knowledge of these equilibrium constants; (3) a study of the kinetics of column reactions to determine the effect of non-equilibrium conditions on column separations.

Equilibrium studies of this type had already been completed by Boyd, *et al.*, for systems involving ion exchange in which no complexing agents were used.<sup>5</sup> They had shown that the distribution of a substance between the exchanger and any solution in equilibrium with it can be predicted from the mass law.<sup>5</sup>

At the time this work was initiated, ion-exchange techniques had been employed in the elucidation of some of the equilibria occurring when the alkaline and rare earth cations were adsorbed from citrate buffers by the resinous exchanger, Amberlite IR-1. Thus, by applying the mass law, Schubert and Richter<sup>6</sup> had obtained values for the dissociation constants of the strontium and barium citrate complex ions, and for the strontium tartrate complex which were in agreement with those determined by electrometric and by other methods. L. S. Myers<sup>7</sup> had measured the exchange adsorption from dilute acid solutions of the trivalent La, Ce and Y ions over the concentration range from 0.1 to  $10^{-9}$  *M*. Here it was observed that the distribution coefficient,  $K_d$ , became independent of rare earth concentration when the latter was less than  $10^{-6}$  *M*. A preliminary study of the nature of the predominant rare earth citrate complex ion in the *pH* range from 2.0 to 3.0 had indicated the yttrium complex to be appreciably more stable than that of lanthanum.<sup>8</sup>

The purpose of the investigation, described

(1) This document is based on work done under Contract W-35-059-eng-71 for the Atomic Energy Project, and the information contained therein will appear in Division IV of the National Nuclear Energy Series (Manhattan Project Technical Section) as part of the contribution of the Clinton Laboratories.

(2) E. R. Tompkins, J. X. Khym and W. E. Cohn, *THIS JOURNAL*, **69**, 2769 (1947).

(3) E. R. Tompkins, *et al.*, to be published.

(4) F. H. Spedding, *et al.*, *THIS JOURNAL*, **69**, 2777 (1947)

(5) G. E. Boyd, J. Schubert and A. W. Adamson, *THIS JOURNAL*, **69**, 2818 (1947).

(6) J. Schubert and J. W. Richter, May, 1945, to be published.

(7) L. S. Myers, Jr., July, 1945, to be published.

(8) B. H. Kettle and J. W. Richter, October, 1945, to be published.

here and in succeeding papers of this series, was to develop a simple method by which the column separation of any two substances could be predicted for any chosen set of conditions or, conversely, to be able, from the results of a few simple equilibrium and rate studies, to choose operating conditions which would result in any desired degree of separation. The first part of this study, the determination of the equilibrium constants of the reactions involved in the separations, is described below. In subsequent papers, the applications of the classical plate theory to near-equilibrium column operation and the effect of operating a column under conditions far removed from equilibrium, will be discussed.

### Experimental

**Method.**—In these experiments, known masses of resin were equilibrated with measured volumes of solutions of various compositions containing one or more radioactive rare earth elements in known concentrations. The resin and solution for each experiment were introduced into a cylindrical vial, 2.8 cm.  $\times$  9.0 cm., which was closed with a screw cap containing a dropper. A number of these vials were then shaken for forty-eight hours (twenty-four hours had been shown to give essentially complete equilibrium) on an International-type shaker in a constant temperature room maintained at  $25 \pm 1^\circ$ . These vials were then removed, the resin allowed to settle and an aliquot of the supernatant solution removed from each vial by means of the dropper and transferred to a beaker of 5 ml. capacity. The  $pH$ 's of these solutions were taken with a micro glass-electrode using a Beckman  $pH$  meter to compare them to a standard buffer.

Each beaker of solution was next placed in a centering cylinder which served to locate it accurately under a conventional, bell-type, mica window, Geiger-Mueller counter. When a beta-emitting element was being determined, care was taken to assure a solution depth greater than the range of the beta particles of that radioisotope. Thus, in these determinations the radioactivity measured by counting was proportional to the concentration of the beta emitter in the solution. This eliminated the need for accurate measurements of the aliquots to be counted. When gamma counts were used, the aliquots were measured more carefully since the activity measured was a function of the total quantity of the gamma emitter in the aliquot being counted. In experiments employing more than one rare earth in a single vial, elements with radioisotopes of widely differing radiation characteristics were chosen. This permitted an easy analysis of each rare earth in the presence of the other by a method similar to that described by Harris and Tompkins.<sup>9</sup>

After the  $pH$  and activity determinations had been made, the solutions were returned to the original vials as quantitatively as possible and the conditions varied as desired by the addition of one or more reagents in varying amounts. The vials were again shaken to equilibrium and the process repeated until the desired range had been studied. The errors introduced by the transfer of the solutions and by dilution due to the addition of reagents were negligible in most cases; in those cases in which the effect was appreciable, a correction was applied (e. g., the increase in  $NH_4^+$  when the effect of  $pH$  was being studied).

**Materials.**—The ion exchangers used in this study were synthetic resins of the types described in previous publications.<sup>9</sup> These were converted to the ammonium form by exhaustive treatment with ammonium chloride, washed well with water, and air-dried. In most of these studies, the resin, Dowex 50, was used. It has only one combining group, nuclear sulfonic acid, and thus its combining capacity was not affected by the  $pH$  of the solution. This

facilitated the interpretation of the results of these studies. The rare earths employed in the studies had been previously purified by column separation, as described by Harris and Tompkins<sup>9</sup> (with the exception of the Eu which was Hilger's spectroscopic standard). Their radioactive isotopes were produced by bombarding them in the chain reacting pile, except for Y, Ce, and 61 which were obtained from fission. The other reagents were C. P., analyzed grade. The compositions of the solutions used in these equilibrium studies are shown in the tables of results.

### Results

**Combining Capacity of Dowex 50.**—A carefully weighed sample of the air-dried ammonium compound of the resin was desiccated in an oven at  $120^\circ$  to constant weight. The loss in weight calculated on the air-dried basis was 8.57%. Another aliquot of the resin was converted to the lanthanum form, dried, ashed and the weight of the lanthanum oxide determined. From this, the combining capacity of the resin was calculated at 0.00543 equivalent per gram of ammonium resin (on the oven-dried basis). Thus, the ammonium resin used in these experiments had an equivalent weight of 184 g. (all weights of resin shown in subsequent tables were calculated to the oven-dried basis).

**Distribution Coefficient.**—The distribution coefficient is equal to the concentration of a cation in the resin phase divided by its concentration in the liquid phase, or

$$K_d = \frac{M_2/\text{mass of resin}}{M_1/\text{volume of solution}} = \frac{M_2}{M_1} \times \frac{\text{volume of solution}}{\text{mass of resin}} \quad (1)$$

in which  $M_2$  and  $M_1$  are the fractions of the cation,  $M$ , in the resin and the liquid phases, respectively, and  $K_d$  is the distribution coefficient at equilibrium. From equation (1) it can be seen that in studies where the quantity of resin and the volume of solution remain constant

$$K_d = k \frac{M_2}{M_1} = k \frac{M - M_1}{M_1} \quad (2)$$

where  $k$  is the ratio of the solution volume to the resin mass. The mass of the resin and the solution volume may, of course, be expressed in any units desired. For calculating the values of  $K_d$  given in this paper, the volume was expressed in milliliters and the resin mass in grams of oven-dried ammonium resin.

In determining the distribution coefficients under varying conditions,  $M$  and  $M_1$  were measured as described above,  $M$  being determined on an aliquot of the original solution and  $M_1$  on an equal volume of this solution after equilibrating it with the resin. In studies where  $K_d$  varied over a narrow range,  $k$  was kept constant. Since it is desirable, for the sake of accuracy, to adjust the ratio so that  $M_2/M_1$  will be in the range of one-half to two, it was not possible to maintain this ratio,  $k$ , constant when some variables were studied and still retain a high degree of precision.

Because it was necessary to change the ratio of resin mass to solution volume, a study was made

(9) Harris and Tompkins, *THIS JOURNAL*, **69**, 2792 (1947).

to determine the constancy of  $K_d$  when  $k$  was varied. Two rare earths, praseodymium and cerium, were used in this study. The volume of the solution remained constant at 10 ml., the mass of resin being varied from 0.686 to 12.526 g. The results of this study are shown in Table I. It will be noted that the variation is within experimental error.<sup>10</sup>

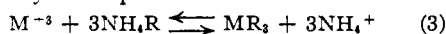
TABLE I

THE EFFECT OF THE RESIN TO SOLUTION RATIO ON THE DISTRIBUTION COEFFICIENTS OF Pr AND Ce

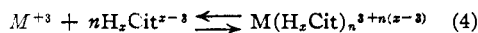
Solution: 10 ml., 0.23  $M$  in citrate, 0.50  $M$  in  $\text{NH}_4^+$ ,  $3 \times 10^{-4}$   $M$  in rare earth,  $\text{pH}$  2.8; resin, Dowex 50, ammonium form, 40-60 mesh.

Grams of resin (oven-dried basis)	$k$	$M_2/M_1$		$K_d$	
		Pr	Ce	Pr	Ce
0.686	14.57	1.24	2.26	18	33
1.371	7.29	2.6	5.1	19	37
2.743	3.65	4.9	9.6	18	35
5.486	1.822	10.4	19.2	19	35
12.526	0.798	...	27.1	..	34

**The Rare Earth Resin Compounds.**—The separation of rare earths by their elution from resin columns with complexing agents depends upon the competition between the citrate complexes of the rare earths and their resin compounds. These two competing reactions may be expressed by the equations



and



in which  $\text{M}^{+3}$  is the rare earth ion,  $\text{NH}_4\text{R}$  the ammonium resin,  $\text{MR}_3$  the rare earth resin compound,  $\text{H}_2\text{Cit}^{x-3}$  one of the citrate ions and  $\text{M}(\text{H}_2\text{Cit})_n^{3+n(x-3)}$  the rare earth citrate complex. As has been shown by Boyd, Schubert, and Adamson,<sup>5</sup> the exchange constant for reaction (3) may be written

$$K_1 = \frac{(\text{MR}_3)(\text{NH}_4\text{R})^3}{(\text{NH}_4\text{R})^3} \times \frac{(\text{NH}_4^+)^3}{(\text{M}^{+3})} \quad (5)$$

in which the activities of the solid phase components,  $\text{MR}_3$  and  $\text{NH}_4\text{R}$ , may be expressed in terms of their mole fractions for ideal solid solutions, and the thermodynamic activities of the ions in the solution,  $(\text{NH}_4^+)$  and  $(\text{M}^{+3})$ , are employed. When  $\text{M}^{+3}$  is present in very low concentrations,  $\text{NH}_4\text{R} \cong \text{NH}_4\text{R} + \text{MR}_3$  and

$$K_1 = \frac{(\text{MR}_3)}{(\text{NH}_4\text{R})} \times \frac{(\text{NH}_4^+)^3}{(\text{M}^{+3})} \quad (6)$$

If in the equation for the distribution coefficient (1),  $M_2$ ,  $M_1$  and the mass of resin are expressed in moles and the volume of solution in liters, a constant,  $K_d'$ , may be expressed as

$$K_d' = \frac{M_{\text{MR}_3}}{M_{\text{NH}_4\text{R}}} \times \frac{V_s}{M_{\text{M}^{+3}}} = \frac{M_{\text{MR}_3}}{M_{\text{NH}_4\text{R}}} \times \frac{1}{(\text{M}^{+3})} \quad (7)$$

in which  $M$  is the moles of the various reactants shown in (3),  $V_s$  is the volume of solution in liters,

(10) The precision of analyses based on radioactivity determinations are limited by the counting errors.

and  $(\text{M}^{+3})$  is the ionic concentration of the rare earth (which in trace concentrations of  $\text{M}^{+3}$  and solutions of constant ionic strength is nearly proportional to its activity). Substituting in (6)

$$K_1 = K_d' \times (\text{NH}_4^+)^3 \quad (8)$$

for cases in which the concentration of  $\text{M}^{+3}$  is very low as compared to the ammonium ion concentration.

In the experiments reported here, the ammonium form of Dowex 50 and IR-1 resins was equilibrated with solutions containing rare earths in concentrations from  $\sim 10^{-10}$   $M$  to  $10^{-1}$   $M$  and 0.5  $M$  to 0.75  $M$  ammonium perchlorate. The results of these experiments are shown in Table II and Fig. 1. It may be seen that the  $K_1$ 's for the ex-

TABLE II

COMPARISON OF THE  $K_1$ 's FOR EQUILIBRATION OF  $\text{NH}_4\text{R}$  WITH  $\text{Ce}^{+3}$ ,  $\text{Pr}^{+3}$  AND  $\text{Y}^{+3}$

Solution, 10 ml., composition as shown; resin, Dowex 50, ammonium form, 40-60 mesh, 11.9 mg.

Rare earth concn., $M$	$\text{NH}_4\text{ClO}_4$ concn., $M$	$\text{pH}$	$K_d'$			$K_1$		
			Ce	Pr	Y	Ce	Pr	Y
$3 \times 10^{-4}$	0.5	1.75	1000	730	420	125	91	53
$3 \times 10^{-4}$	.75	1.75	260	...	108	32.5	..	13.5
$3 \times 10^{-4}$	.75	1.10	245	...	104	30.6	..	13.0
$10^{-3}$	.75	1.10	18	...	13	2.3	..	1.9

change reactions with the resin compounds of these three rare earths vary appreciably. The  $\text{pH}$  has little effect on  $K_d$  but the rare earth concentration affects it in concentrations above  $3 \times 10^{-4}$   $M$  for Dowex 50 and  $4 \times 10^{-7}$  for IR-1.

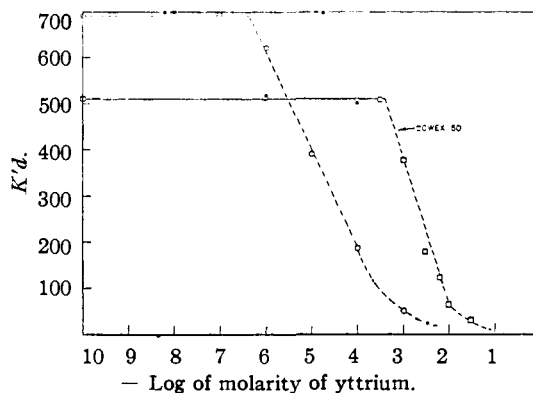


Fig. 1.—Variation of  $K'd$  with concentration of rare earth.

**The Rare Earth Citrate Complexes.**—When citrate is added to a solution of ammonium perchlorate containing trace quantities of a rare earth, and in contact with the resin, the distribution of the rare earth between the resin and solution is changed because of the formation of its citrate complex. From a knowledge of  $K_1$  for reaction (3) (which can be calculated from the distribution of the rare earth without citrate present (8) and the distribution of the rare earth in the presence of citrate) it is possible to calculate the dissociation constants of the rare earth

citrate complexes.<sup>6</sup> From equation (4), it can be seen that this constant may be expressed as

$$K_2 = \frac{(M^{+3})(A)^n}{(MA_n)} \quad (9)$$

where the quantities in parentheses represent the thermodynamic activities of the rare earth ions, citrate ions (A) and complex (MA<sub>n</sub>) (A and MA<sub>n</sub> being substituted for the previous designations for the sake of simplicity). From (7) and (8), the concentration of rare earth ions in equilibrium with ammonium resin can be expressed as

$$(M^{+3}) = \frac{M_{MR_4} (NH_4^+)^3}{M_{NHR} K_1} \quad (10)$$

in which *M* represents the moles of the reactants and (NH<sub>4</sub><sup>+</sup>) the thermodynamic activity of the ammonium ion. Substituting this value for (M<sup>+3</sup>) in (9) gives

$$K_2 = \frac{M_{MR_4}}{M_{NHR}} \times \frac{(NH_4^+)^3}{K_1} \times \frac{(A)^n}{(MA_n)} \quad (11)$$

When the concentration of citrate is much greater than that of the rare earth, (A) is nearly equal to the total citrate ion concentration and since the dissociation constant of the complex is small, (MA<sub>n</sub>) is nearly equal to the total concentration of rare earth in solution. Thus if (A) is varied, either by changing the total citrate concentration or the pH (which varies the portion of the citric acid that is ionized), it is possible to solve for the value of *n*. If all other factors (*i. e.*, resin weight, solution volume, rare earth, and ammonium ion concentrations) are held constant, from (7) and (11) it can be seen that

$$K_2 = K_3(A)^n \quad (12)$$

where *K*<sub>3</sub> is a constant combining the constant terms of (11). In Table III, the distribution coefficients for terbium between ammonium resin and solutions at several pH's containing citrate, ammonium perchlorate and terbium, in the concentrations shown, are listed. Also given are the values for *K*<sub>d</sub>, calculated for *n* equal to 1, 2, 3, 4, and 6. From this table, it can be seen that *n* equals 3 for reaction (4) at low pH's.

TABLE III

RELATIONSHIP OF THE DISTRIBUTION COEFFICIENT TO pH  
Solution: 10 ml., 0.23 *M* in citrate, 0.50 *M* in NH<sub>4</sub>ClO<sub>4</sub>, Tb<sup>+3</sup> < 10<sup>-6</sup> *M*, pH as tabulated; resin, Dowex 50, ammonium form, 40-60 mesh, 0.3657 g.

pH	Molarity of H <sub>2</sub> Cit <sup>-2</sup>	Found	Distribution coefficients ( <i>K</i> <sub>d</sub> ) calculated for <i>n</i> of				
			1	2	3	4	6
2.59	0.0327	14.2	29.3	18.0	14.5	11.2	6.6
2.73	.0423	7.1	20.8	10.7	6.8	4.1	1.4
2.89	.0566	3.0	14.8	6.0	3.0	1.4	0.3

\* Calculated from the dissociation constants of citric acid as determined by Bjerrum and Unmack, *Det. Kg. Danske Videnskab. Mat. fys. Medd.*, 9, 1 (1929).

In Table IV, the effect of varying the total citrate concentration and the pH on the distribution of europium between the resin and solution, is shown. From this table, it may be noted that *K*<sub>d</sub> varies inversely with the third power of the citrate

concentration at any given pH. The evidence shown in Tables III and IV indicates that the formula for the rare earth complex at pH's below 3.2 is M(H<sub>2</sub>Cit)<sub>3</sub>.

TABLE IV

THE EFFECT OF CITRATE CONCENTRATION ON *K*<sub>d</sub>  
Solution: 10 ml., 5 × 10<sup>-6</sup> *M* in Eu, citrate and ammonium ion concentration and pH as shown; resin, Dowex 50, ammonium form, 40-60 mesh, 0.4572 g.

Citrate, g.	pH	(H <sub>2</sub> Cit <sup>-</sup> )	(NH <sub>4</sub> <sup>+</sup> )	<i>K</i> <sub>d</sub>	(H <sub>2</sub> Cit <sup>-</sup> ) <sup>3</sup> × 10 <sup>6</sup>	(NH <sub>4</sub> <sup>+</sup> ) <sup>3</sup> × 10 <sup>6</sup>	<i>K</i> <sub>d</sub> × (NH <sub>4</sub> <sup>+</sup> ) <sup>3</sup> × (H <sub>2</sub> Cit <sup>-</sup> ) <sup>3</sup> × 10 <sup>6</sup>
0.25	3.21	0.0460	0.126	472	97	2.00	92
.25	3.36	.0564	.149	159	179	3.31	94
.25	3.50	.0644	.173	66	267	5.18	92
.50	2.90	.0580	.173	92	195	5.18	93
.50	3.08	.0777	.218	18.8	469	10.4	92
.50	3.25	.0966	.265	5.2	901	18.6	89
1.00	2.72	.0832	.264	8.5	576	18.4	90
1.00	2.79	.0944	.294	4.4	841	25.4	94
1.00	2.85	.1056	.321	2.4	1174	33.1	93

Tables V and VI show the effect of pH on the distribution coefficients of several rare earths. Comparison of the values of *K*<sub>d</sub> for pairs of these elements, shown in Table V, indicates the relative difficulty of separating them by the column method. Table VI shows the effect of increasing the pH on the ratios of the distribution coefficients of europium and element 61. It may be noted that as the pH is raised, thus increasing the proportion of the citrate in the HCit<sup>-2</sup> and Cit<sup>-3</sup> forms, the separation decreases, approaching the separation expected by the resin alone (see Table II). It appears that the H<sub>2</sub>Cit<sup>-</sup> ion is the only citrate ion effective in the separation of rare earths. Thus, the operation of separation columns at pH's above 3.5 will appreciably decrease their efficiencies.

In Table VII, the dissociation constant, *K*<sub>2</sub>, for each of several rare earth citrates are given. These were calculated from the values of *K*<sub>d</sub> given in Tables II and V.

**The Effect of Ammonium Ion Concentration on *K*<sub>d</sub> in the Presence of Citrate.**—The presence of citrate in a solution greatly decreases the rare earth ion concentration. For this reason it is possible to study the effect of the ammonium ion concentration over a wider range than when citrate is not present, since the errors in the determinations may be minimized. In Table VIII, the relationship between the distribution of cerium between Dowex 50 and citrate solutions, with varying ammonium ion concentrations, are shown. The distribution seems to depend upon the third power of the ammonium ion concentration times its activity coefficient.

**The Effect of Rare Earth Concentration on the Distribution Coefficient.**—In separating rare earths in concentrations greater than trace

TABLE V

THE EFFECT OF pH ON  $K_d$  OF Ce, Pr, 61, Tb, Y AND Tm

Solution: 10 ml., 0.23 M citrate, 0.5 M  $\text{NH}_4\text{ClO}_4$ , rare earth  $<10^{-6}$  M, pH as tabulated; resin, Dowex 50, ammonium form, 40-60 mesh, 0.3657 g.

Ce		Pr		61		Tb		Y		Tm	
pH	$K_d$	pH	$K_d$	pH	$K_d$	pH	$K_d$	pH	$K_d$	pH	$K_d$
2.88	21.6	2.80	15.0	2.88	3.8	2.89	3.0	2.88	3.6	2.58	4.1
2.68	56	2.72	23.2	2.72	10.4	2.73	7.1	2.59	12.0	2.41	12.3
2.53	126	2.67	27.9	2.49	36.9	2.59	14.2	2.41	31.4	2.17	50.6
2.44	189	2.34	156	2.22	150	2.42	33.9	2.17	115	...	...
2.21	615	...	...	...	...	2.18	128	...	...	...	...

TABLE VI

## EFFECT OF pH ON THE RATIO OF THE DISTRIBUTION COEFFICIENTS OF EUROPIUM AND ELEMENT 61

Solution: 10 ml.,  $5 \times 10^{-6}$  M in Eu,  $<10^{-6}$  M in 61;  $\text{NH}_4^+$ , citrate concentration and pH as shown; resin, Dowex 50, ammonium form, 40-60 mesh, 0.4572 g.

Citrate, M	pH	$(\text{H}_2\text{Cit}^-)$	$(\text{HCit}^-)$	$(\text{NH}_4^+)$	Europium		Element 61		$K_{d61}/K_{dEu}$
					$K_d$	$\frac{10^4 \times K_d}{(\text{NH}_4^+)^4 \times (\text{H}_2\text{Cit}^-)^4}$	$K_d$	$\frac{10^4 \times K_d}{(\text{NH}_4^+)^2 \times (\text{H}_2\text{Cit}^-)^2}$	
0.46	2.40	0.0460	0.0001	0.154	2600	93	4000	144	1.52
.46	2.72	.0832	.0008	.264	85	90	125	133	1.47
.46	2.85	.1056	.0014	.321	2.4	93	35	136	1.46
.23	3.08	.0777	.0016	.218	18.8	92	27.1	132	1.44
.23	3.25	.0966	.0028	.265	5.2	89	7.3	122	1.40
.115	3.63	.0713	.0043	.195	260	70	360	94	1.33
.115	3.90	.0805	.0115	.235	80	54	95	65	1.18
.018	4.25	.0126	.0038	.046	74	0.14	86	0.16	1.16
.018	4.73	.0085	.0085	.058	5.0	0.001	5.7	0.001	1.14

TABLE VII

COMPARISON OF  $K_d$ 's FOR THE EQUILIBRIUM OF  $\text{H}_2\text{Cit}^-$  WITH  $\text{Ce}^{+3}$ ,  $\text{Pr}^{+3}$ , AND  $\text{Y}^{+3}$ 

Solution: 10 ml., 0.23 M citrate, 0.5 M  $\text{NH}_4\text{ClO}_4$ , rare earth  $3 \times 10^{-4}$  M, pH 2.60; resin, Dowex 50, ammonium form, 40-60 mesh, 0.3657 g.

	$K_1$	$(\text{NH}_4^+)^4$	$\frac{M_{\text{NH}_4^+}}{\times 10^4}$	$(A)^4$	$\frac{M_{\text{MR}_4}}{\times 10^4}$	$(MA_2)$	$\frac{K_2}{\times 10^4}$
Ce	125	0.140	1.99	3.73	2.25	0.75	6.3
Pr	91	.140	1.99	3.73	1.82	1.18	4.4
Y	53	.140	1.99	3.73	0.92	2.08	2.3

TABLE VIII

THE EFFECT OF  $(\text{NH}_4^+)$  ON  $K_d$  OF CERIUM

Solution: 10 ml., 0.23 M in citrate,  $M_{\text{NH}_4^+}$  as tabulated, pH 2.8,  $3 \times 10^{-4}$  M  $\text{Ce}^{+3}$ ; resin, Dowex 50, ammonium form, 40-60 mesh, 1.371 g.

$K_d$	$M_{\text{NH}_4^+}$	$\gamma_{\text{NH}_4^+}$	$(\text{NH}_4^+)$	$\frac{K_d}{(\text{NH}_4^+)^2}$	$\frac{K_d}{(\text{NH}_4^+)^4}$	$\frac{K_d}{(\text{NH}_4^+)^4}$
530	0.168	0.82	0.138	10.1	1.40	0.19
310	.201	.82	.165	8.4	1.38	.23
178	.245	.81	.198	7.0	1.38	.27
131	.268	.81	.217	6.2	1.34	.29
94	.300	.81	.243	5.5	1.34	.33
53	.368	.79	.291	4.5	1.31	.38
12.6	.668	.70	.468	2.7	1.29	.60
3.9	1.168	.59	.689	1.8	1.28	.87

\* Heydweiller, *Z. anorg. allgem. Chem.*, 116, 42 (1921).

amounts, the effect of the rare earth concentration may be an important factor.<sup>2,3</sup> Table II and Fig. 1 show that the effect on the equilibrium constant,  $K_1$ , is appreciable for rare earth concentrations greater than  $3 \times 10^{-4}$  M. In Fig. 2, the effect of cerium concentration on  $K_d$ , when ammonium resin is equilibrated with solutions of

citrate, is shown. As will be noted, the rare earth concentration does not affect  $K_d$  in concentrations up to about  $6 \times 10^{-3}$  M under conditions similar to those used in the column separations. It seems probable that the effect of the rare earth concentration on the exchange reaction is one of the major limiting factors in determining the highest rare earth concentrations at which separations columns may be operated efficiently.

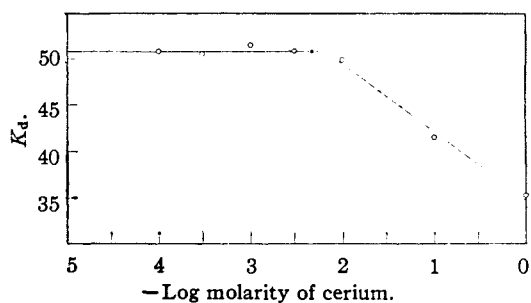


Fig. 2.—Variation of  $K_d$  with concentration of rare earth, in 0.23 M citrate.

**Absence of Hysteresis Effects with Dowex 50 and Citrate.**—Boyd, Schubert and Adamson<sup>5</sup> reported a hysteresis effect between the results obtained by approaching equilibrium from two directions when Amberlite IR-1 resin in one form was equilibrated with a solution containing the other ion being studied. This effect became greater as the charge on the ion increased, being rather appreciable for the rare earths. Subsequent work on IR-1 at lower pH, however, has

shown that the equilibrium was reversible.<sup>7</sup> For this reason, it appeared that Dowex 50 should be tested to see if it showed such characteristics. In the experiments whose results are shown in Table IX, two series were set up, one starting at a high pH so that most of the rare earth was in the solution, and the other starting at a low pH, with a larger percentage of the rare earth adsorbed on the resin. The pH's of these solutions were adjusted stepwise, the first series downward and the latter upward,  $K_d$  being measured at several pH's for each series. The results of these experiments, corrected for variations in the ammonium ion concentration, show that there is no detectable hysteresis in this system.

TABLE IX

COMPARISON OF VALUES FOR  $K_d$  OBTAINED BY APPROACHING EQUILIBRIUM FROM BOTH DIRECTIONS

Solution: 10 ml., 0.23 M citrate, 0.5 M in  $\text{NH}_4\text{ClO}_4$ , rare earth concentration and pH as shown; resin, Dowex 50, ammonium form, 40-60 mesh, weights as shown.

pH	Distribution coefficients ( $K_d$ )					
	0.3657 g. resin pH decreased			1.3715 g. resin pH increased		
	Ce	Pr	Y	Ce	Pr	Y
2.2	680	330	98	630	330	103
2.4	232	115	33	230	115	36
2.6	82	41	12	82	41	12
2.8	30	15	4.6	33	14	5.5

Comparisons between Several Resins as to their Efficiency for the Rare Earth Separations.—In Table X, a comparison of several resins as to their separations efficiency is shown. As will be noted, the Amberlite IR-1 gives the poorest results, on the basis of the equilibrium experiments, while Duolite C appears to be the best. Actually, a number of other factors such as the ratio of solution volume to resin mass in the column (*i. e.*, bed density), the combining capacity of the resin and the rate at which equilibrium is approached are important in column operation, particularly when large concentrations of rare earths are being separated. Further column tests will be necessary before this comparison is complete.

TABLE X

COMPARISON OF THE EFFICIENCIES OF SEVERAL RESINS FOR RARE EARTH SEPARATIONS

Solution: 10 ml., 0.23 M citrate,  $5 \times 10^{-6}$  M Eu and  $<10^{-6}$  M 61; pH as tabulated;  $(\text{NH}_4^+)$  required to adjust pH; resin, ammonium form, 40-60 mesh.

Dowex 50			Dowex 30		
pH	$K_d$ Eu	$K_d$ 61/ $K_d$ Eu	pH	$K_d$ Eu	$K_d$ 61/ $K_d$ Eu
2.90	92	1.45	2.61	118	1.56
3.08	18.8	1.44	2.82	13	1.57
3.25	5.2	1.41	..	..	..
Duolite C			Amberlite IR.1		
pH	$K_d$ Eu	$K_d$ 61/ $K_d$ Eu	pH	$K_d$ Eu	$K_d$ 61/ $K_d$ Eu
2.40	230	1.65	2.42	39	1.32
2.55	85	1.60	2.58	19	1.34
2.80	27	1.62	2.85	8.3	1.30
3.00	3.1	1.52			

It will also be desirable to test a number of other exchangers, both organic and inorganic.

**Comparison between Several Complexing Agents.**—The choice of citrate as the complexing agent for the rare earth separations was made as a result of the demonstration of its applicability for separating rare earth fission products. Citrates and tartrates were introduced in this process as a means of separating alkaline earth fission species. The discovery of their application for the rare earth separations was made when a mixture of the fission products was eluted and it was noted that several of the rare earth fission products were fractionated.<sup>2</sup>

A systematic study of various classes of compounds to determine the relative dissociation constants of their rare earth complexes is now being made. A few compounds, capable of forming chelates with the rare earths, have already been studied. The comparison of the ratios of the values of  $K_d$  for two rare earths, when solutions of these compounds are used, may be seen in Table XI. This preliminary study indicates that complexing agents considerably better than citrate may be found.

TABLE XI

COMPARISON OF COMPLEXING AGENTS\*

Solution: 10 ml.,  $5 \times 10^{-6}$  M in Eu,  $<10^{-6}$  M in 61, 50 g. of the complexing compound per liter,  $\text{NH}_4^+$  as required to adjust to pH; resin, Dowex 50, ammonium form, 40-60 0 4572 g.

Complexing compound	pH at which $K_d$ of Eu = 21.9	$K_d$ 61/ $K_d$ Eu
Citric acid	3.05	1.45
Tartaric acid	2.85	1.94
Lactic acid	3.40	1.71
Sulfosalicylic acid	5.4	1.49
Ethyl acetoacetate	7.4	1.33
Acetylacetone	7.2	1.91
Oxalic acid	1.7	1.32
Citric acid in 50% EtOH	3.0	1.31

\* Phthalic acid, malonic acid, dihydroxytartaric acid and pyrogallol form precipitates with Eu and 61. Iodide ion has a weak complexing action on these rare earths. Fluoride ion precipitates these rare earths but the difference in the ratio of Eu to 61 remaining in the supernatant is noteworthy.

**Discussion.**—On the basis of the results of this study, it is possible to draw some conclusions as to the relative importance of a number of variables on the column separation. Since  $K_d$  does not change as the resin weight to solution volume is varied, the equilibrium values may be readily applied to column operation. The results of the studies on the effects of pH, citrate concentration, ammonium ion and rare earth concentrations on the relative  $K_d$ 's, give a reliable basis for choosing optimum conditions for column separations insofar as these factors are concerned.

As was mentioned above, the complexing agent has two functions in the column separation: (1) to form rare earth complexes whose dissociation constants vary as widely as possible, and (2) to re-

duce the rare earth ion concentration of the solution to such a degree that Henry's law is obeyed. It is obvious that the smaller the dissociation constant of a rare earth complex the larger the quantity of material, per unit volume of column bed, that can be processed efficiently. However, in searching for complexing agents which will form tighter complexes, the degree of divergence between the strengths of the complexes of different rare earths must not be overlooked. At higher  $pH$ 's, citrate forms rare earth complexes whose dissociation constants are much smaller than those for the complex formed with the  $H_2Cit^-$  ion. However, there seems to be little difference between the dissociation constants of the various rare earth complexes with the  $HCit^{-2}$  and  $Cit^{-3}$  ions, according to the results of this study and the earlier observation that much poorer separations were obtained at higher  $pH$ 's. Thus, in searching for new complexing agents, it is advisable to determine the ratios of the distribution coefficients of two rare earths. The stronger the rare earth complexes with a chelating agent and the more widely their  $K_2$ 's diverge, the larger will be the quantity of rare earths which can be processed per unit volume of the column bed and the more efficient will be their separation.

When citrate is being used, it is better to operate the column at a  $pH$  not in excess of 3.2 at room temperature. If a more rapid rate of removal of the rare earths is desired, it may be obtained either by increasing the total citrate concentration or by increasing the ionic strength by the addition of some salt such as ammonium chloride. However, the ionic strength of the solution should not be increased to the point where the rare earth ion concentration in the solution exceeds the values beyond which Henry's law is obeyed.

In choosing a resin for the column bed, it is desirable to get an exchanger of high combining capacity which shows some divergence in the dissociation constants of its various rare earth compounds. Since the strength of the rare earth-resin bond may be dependent upon the hydrated ionic radius while the strengths of the chelates probably depend more nearly on the non-hydrated ionic radius, the separation effects of resin and the complexing agent supplement rather than oppose each other. The importance of using an exchanger having a high combining capacity when large quantities of rare earths are being separated is obvious.

By studying other elements in a manner similar to that described above, it is possible to choose satisfactory conditions for their separation. A

knowledge of the relative dissociation constants of their resin compounds indicates the degree of separation which is possible by straight ion replacement elution. From the additional knowledge of the dissociation constants of some of the complexes of the elements whose separation is being studied, the ratios of the distribution coefficients, when each of a number of complexing agents is employed for elution, can be calculated. In this manner, it is possible, by means of a few simple experiments, to evaluate the relative merits of a number of conditions in a relatively short time and choose reagents and conditions which will result in a satisfactory separation of the cation mixture.

### Summary

Equilibrium studies of the distribution of rare earths between synthetic ion exchange resins and solutions of varying composition have been made. It was shown that for any given composition of solution the distribution coefficient of a rare earth between the two phases did not change as the ratio of the weight of Dowex 50 resin to the solution volume was varied. The exchange reaction between a rare earth ion and the ammonium resin compound was shown to follow the relationship predicted by the mass law. The exchange constants for several rare earths, equilibrated with the ammonium compound of Dowex 50 resin, vary. This shows that some separation of rare earths is possible without the use of complexing agents when this resin is employed. A study of the citrate complexes showed that the one in which three  $H_2Cit^-$  ions are combined with a rare earth ion is responsible for the relatively large separation factors between these elements. A preliminary, comparative study of the effectiveness of several exchangers and complexing agents was made.

Since the ammonium ion concentration, the total rare earth concentration, the citrate concentration and the  $pH$  are interdependent variables, it should be possible, from the results of these equilibrium studies, to choose a number of sets of "optimum conditions" for a column separation. When Dowex 50 is used in the column, the concentration of the rare earth ions in the solution may not exceed  $3 \times 10^{-4} M$  without adversely affecting the separation. With Amberlite IR-1, this concentration must be below  $10^{-6} M$ . The  $pH$  of the citrate solution should not be greater than 3.2 since appreciable concentrations of the citrate ions  $HCit^{-2}$  and  $Cit^{-3}$  interfere with the separation.

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