layed, the elution curves to be spread out and the peak concentration of rare earths to be lowered. This spreading or trailing out of an elution curve for an element tends to be detrimental to the separation obtained when mixtures of two or more elements are involved.

The best separation of the pairs of rare earths tested, using 0.5% citrate solution as eluant, was obtained at a linear flow rate of 0.5 cm./min. and pH value 3.80. It was also found that 0.5 citrate at pH values 4.20 and 4.40 and linear flow rate of 0.5 cm./min. gave fair separations in about one-third the time required for eluant of pH value 3.80.

AMES, IOWA RECEIVED MARCH 14, 1949

[CONTRIBUTION NO. 51 FROM THE INSTITUTE OF ATOMIC RESEARCH AND FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Separation of Rare Earths by Ion Exchange. V. Investigations with One-tenth Per Cent. Citric Acid–Ammonium Citrate Solutions[1]

BY F. H. SPEDDING, E. I. FULMER, J. E. POWELL AND T. A. BUTLER

I. Introduction

Variables concerned with the ion-exchange separation of rare earths, using 5% citrate solution as eluant, have been rather extensively studied[2-9] and preliminary investigations have been made in this Laboratory using 0.5%[10,11] and 0.1%[12] citrate. The elution curves with 0.1% citrate were so different, both qualitatively and quantitatively, as to warrant further investigation. It will become evident that the theories[5,8,13] advanced concerning the separation of rare earth elements by ion exchange do not satisfactorily explain all the phenomena observed with 0.1% citrate solutions. It is the opinion of the authors that a general theory, applicable to a wide range of conditions, awaits the obtaining of many more data.

II. Materials, Apparatus and General Procedure

A complete description of materials, apparatus and general procedure is given in a previous paper[11] of this series. Unless otherwise noted the column beds were of −30 + 40 Amberlite IR-100 resin, 120 cm. long and 22 mm. in diameter; the charges consisted of 0.01 mole total rare earth chlorides adsorbed from a liter of aqueous solution. One-tenth per cent. citrate solution was used as eluant in all the experiments described in this paper.

III. Experimental

A. The Elution of Equimolar Mixtures of Samarium and Neodymium in the pH Range 5.00–6.00.—Columns were loaded with 1.713 g. of an equimolar mixture of Sm_2O_3 and Nd_2O_3. Elution curves for pH values of 5.00, 5.50 and 6.00, using a linear flow rate of 0.5 cm./min., are given in Fig. 1 and the data shown in Table I.

TABLE I

DATA FOR THE ELUTION OF EQUIMOLAR MIXTURES OF SAMARIUM AND NEODYMIUM USING 0.1% CITRATE AT SEVERAL pH VALUES

	Volume in liters		Percentage recovered 99.5% pure	
pH of eluant	Break-through	Total	Sm_2O_3	Nd_2O_3
5.00	38.8	Discontinued at 74.4	99	99
5.50	35.1	47.9	76[a]	83[a]
6.00	29.8	36.4	53[b]	47[b]

[a] The value calculated might have been as much as 10% higher if smaller fractions of eluate had been collected for analysis. [b] The value calculated might have been as much as 20% higher if smaller fractions of eluate had been collected for analysis.

The elution rate increased with increase in pH but the degree of separation decreased. At pH of 5.00 the separation was excellent but the elution rate was too slow for practical purposes. Three separations could be made at a pH of 6.00, or two at 5.50 with the same volume of eluant required to complete one separation at a pH of 5.00. In either case the actual yields of pure rare earths obtained would be greater than those obtained at a pH value of 5.00. The regions of overlap between the Sm and Nd bands were approximately the same width at all pH values investigated. The decrease in separation with increasing pH was due primarily to the increase in concentration of rare earths in this mixed portion of the elution curve.

B. The Elution of Equimolar Mixtures of Neodymium and Praseodymium at pH Values of 5.00 and 5.50.—An equimolar mixture of neodymium and praseodymium, made up from 0.841 g. of Nd_2O_3 and 0.854 g. of Pr_6O_{11} was adsorbed on each column and then eluted at a linear flow rate of 0.5 cm./min. The elution curves are given in Fig. 2. The elution at the lower pH was not carried to completion and the fractions were not analyzed, since the elu-

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(1) This document is based, in part, on work performed under contract W-7405 eng.-82 for the Atomic Energy Commission.

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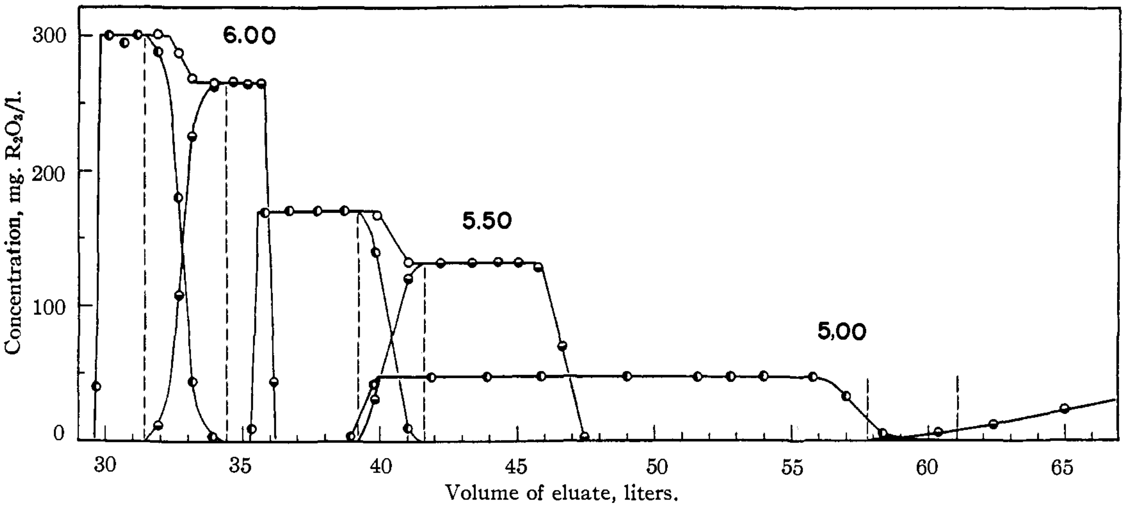

Fig. 1.—The elution of 0.01 mole equimolar mixtures of Sm and Nd from —30 + 40 Amberlite IR-100 beds, 22 mm. in diameter and 120 cm. long, using 0.1% citrate solutions at *p*H values of 5.00, 5.50 and 6.00 and a linear flow rate of 0.5 cm./min.: ○, total R_2O_3; ◐, Sm_2O_3; ⊖, Nd_2O_3; vertical broken lines indicate amount of overlap between Sm and Nd bands.

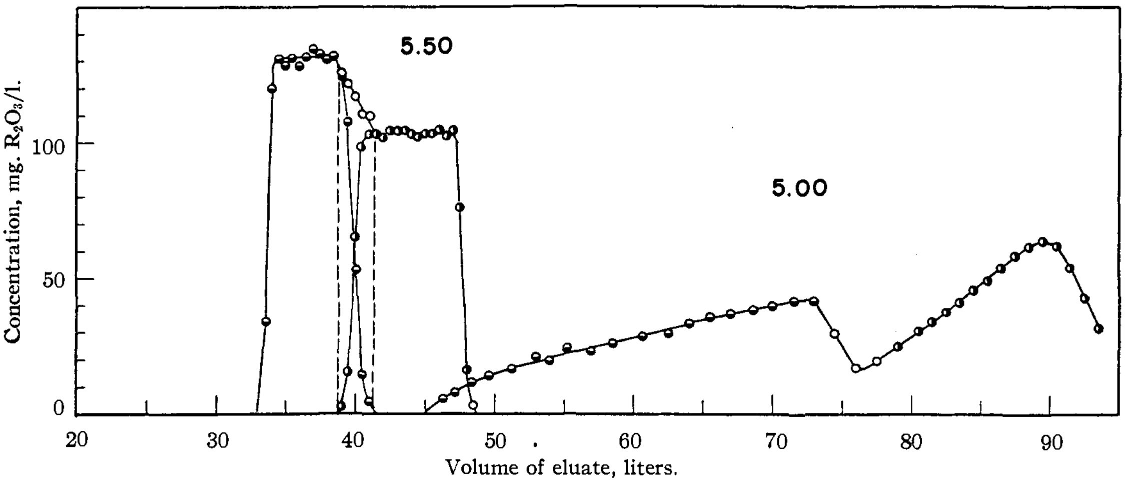

Fig. 2.—The elution of 0.01 mole equimolar mixtures of Nd and Pr from —30 + 40 Amberlite IR-100 beds, 22 mm. in diameter and 120 cm. long, using 0.1% citrate solutions at *p*H values of 5.00 and 5.50 at a linear flow rate of 0.5 cm./min.: ○, total R_2O_3; ⊖, Nd_2O_3; ◑, Pr_6O_{11}; vertical broken lines indicate amount of overlap between Nd and Pr bands.

tion rate was so low that it would serve no practical purpose. However, from the dip in the elution curve and the color of the oxide fractions recovered, it was evident that a very good separation was obtained; as little as 0.5% of Pr_6O_{11} in the ordinarily pale blue Nd_2O_3 produces a distinct discoloration.

Figures 1 and 2 show that the shapes of the elution curves for neodymium in the separation of Sm–Nd and Nd–Pr mixtures are different at a *p*H value of 5.00 than at 5.50. At the lower *p*H the neodymium curve has a gradually sloping form, but at a *p*H of 5.50 it has a vertical front and a flat top. It is quite likely that the complexes involved in the separation at the two *p*H values are different.[12] At a *p*H of 5.50, 82% of the available Nd_2O_3 and 83% of the Pr_6O_{11} were obtained with a purity greater than 99.5%, *i. e.*, no individual fraction of the eluted rare earth containing more than 0.5% of an impurity was included.

C. The Effect of Particle Size of the Resin and the Flow Rate on the Separation of Equimolar Mixtures of Neodymium and Praseodymium at a *p*H of 5.50.—A column having a bed of —60 + 80 Amberlite IR-100 resin, 118.5 cm. long and 22 mm. in diameter, was loaded with an equimolar mixture of neodymium and praseodymium. The sample was eluted at a linear flow rate of 0.5 cm./min. The elution curve for this experiment is compared in Figure 3 to the elution curve with —30 + 40 resin under otherwise identical conditions.

The improved separation with the finer (—60 + 80) resin indicates a more nearly complete equilibrium between the rare earths in solution and the rare earths on the resin. In addition to an approximate four-fold increase in resin surface, there is a shorter diffusion path for those rare earth ions which exchange in the interior of the resin particles. With the shorter diffusion path, less time is required for diffusion of ions into and out of the resin and better equilibrium is maintained between the solution in the resin pores and that which is flowing over the surface of the particles at a constant rate. This argument leads to the conclusion that increasing or decreasing the flow rate would have much the same effect as increasing or decreasing the particle size. These effects have been previously

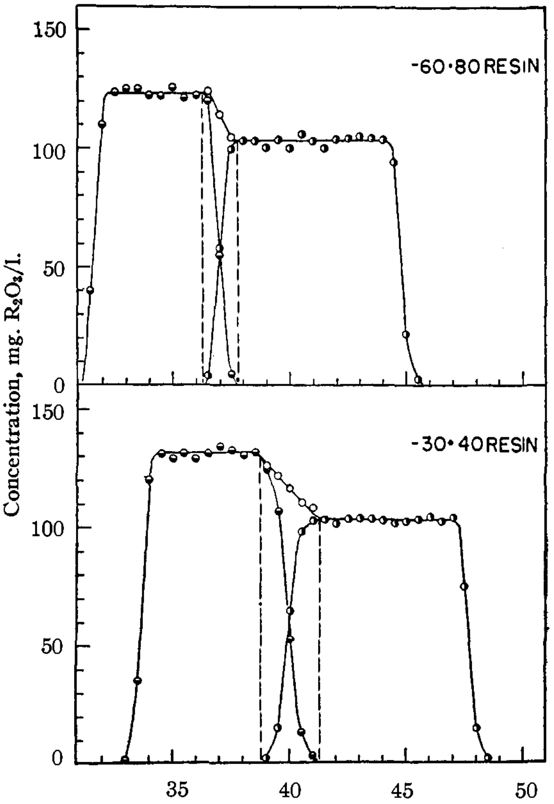

Fig. 3.—The effect of particle size of the resin on the separation of equimolar mixtures of Nd and Pr using 0.1% citrate at a *p*H of 5.50 and a linear flow rate of 0.5 cm. per min.: O, total R_2O_3; ◒, Nd_2O_3; ◑, Pr_6O_{11}; vertical broken lines indicate amount of overlap between Nd and Pr bands.

noted by Mayer and Tompkins.[8] This conclusion is substantiated by the data in Table II which were obtained by eluting 0.01 mole of an equimolar mixture of neodymium and praseodymium from a series of resin beds at a *p*H of 5.50.

TABLE II

THE EFFECT OF FLOW RATE ON THE SEPARATION OF EQUIMOLAR MIXTURES OF NEODYMIUM AND PRASEODYMIUM

	(1)	(2)	(3)
Linear flow rate, cm./min.	0.5	1.0	2.0
Volume of eluate in mixed region, l.	2.5	5.5	8.5
% Nd_2O_3 obtainable pure	82	69	55
% Pr_6O_{11} obtainable pure	83	55	35

The overlap or mixed portion of the elution curve increased with flow rate and the separation decreased as was predicted. The time required for diffusion of ions into and out of the resin pores is not the only factor involved in the overlap of elution bands. It has been observed in experiments with Amberlite XE-45 and Nalcite HCR, which change color slightly in different cycles, that channeling in the resin bed is actually responsible for a large part of the overlap. Flow rate is a contributing factor in the amount of channeling which occurs—in general the faster the flow rate the greater the channeling observed.

D. The Effect of Column Length on the Separation of Equimolar Mixtures of Samarium and Neodymium at *p*H Values of 5.30, 5.50 and 6.00.—Columns 30, 60, 90, 120 cm. long were loaded with an equimolar mixture of samarium and neodymium. The rare earths were eluted at a *p*H of 5.30 and a linear flow rate of 0.5 cm./min. Elution curves for this series of experiments are shown in Fig. 4 and pertinent data are given in Table III.

TABLE III

THE EFFECT OF COLUMN LENGTH AT A *p*H OF 5.30

Bed height, cm.	30	60	90	120
Total vol. of eluant required, l.	18.3	36.5	49.0	57.0
% Sm_2O_3 obtainable pure	37.5	90.4	86.9	83.4
% Nd_2O_3 obtainable pure	32.4	94.5	88.3	90.3

Columns 30, 60, 120 and 240 cm. long were loaded with an equimolar mixture of samarium and neodymium as before. The samples were eluted at a *p*H of 5.50 using a linear flow rate of 0.5 cm./min. The elution curves are plotted along with their *p*H curves in Fig. 5 and pertinent data from these experiments are compared in Table IV.

TABLE IV

THE EFFECT OF COLUMN LENGTH AT A *p*H OF 5.50

Bed height, cm.	30	60	120	240
Total vol. of eluant required, l.	16.0	28.5	47.0	83.0
% Sm_2O_3 obtainable pure	47.4	85.0	80.7	80.6
% Nd_2O_3 obtainable pure	21.0	81.5	77.5	85.4

Columns 30, 60, 90 and 120 cm. long were loaded with an equimolar mixture of samarium and neodymium. The samples were eluted at a *p*H of 6.00 and a linear flow rate of 0.25 cm./min. The *p*H of the eluate was not followed in this experiment. However, from another investigation at the same *p*H it was found that the *p*H value associated with the plateau of the samarium elution curve was 5.10 ± 0.02 and that of the neodymium elution curve was 5.20 ± 0.02. Data for the above series of four column lengths are plotted in Fig. 6 and pertinent data from these experiments are given in Table V.

TABLE V

THE EFFECT OF COLUMN LENGTH AT A *p*H OF 6.00

Bed height, cm.	30	60	90	120
Total vol. of eluant required, l.	12.6	20.6	28.2	38.1
% Sm_2O_3 obtainable pure	68.5	84.9	76.4	72.5
% Nd_2O_3 obtainable pure	71.6	90.3	80.4	79.0

The following conclusions may be drawn from data obtained in the column length experiments just described.

For a particular set of conditions, there was essentially no change in the shape of the elution curve as the column length was increased beyond a certain minimum length required for the initial development of the elution bands. For a *p*H of 6.00 the minimum bed length was just a little more than 30 cm., at 5.50 it was much greater than 30 but less than 60 cm.; at a *p*H of 5.30 the minimum length was between 60 and 90 cm.

For a given flow rate, the overlapping portion of the elution curves remained practically constant for all *p*H values and all column lengths greater than the minimum required for development of the bands. That is, there was no tendency for the samarium and neodymium bands to move independently once they were developed and, hence, no further separation took place as the column length was increased. This is contrary to the predictions of both the plate[8] and mass transfer[13] theories. The best separation was obtained with the 60-cm. column in all the above investigations. This column length was sufficient at *p*H values of 6.00 and 5.50, and almost long enough at a *p*H of 5.30, for the attainment of fully developed bands. In every case, the separation decreased slightly as the column length was increased beyond this point; this effect was

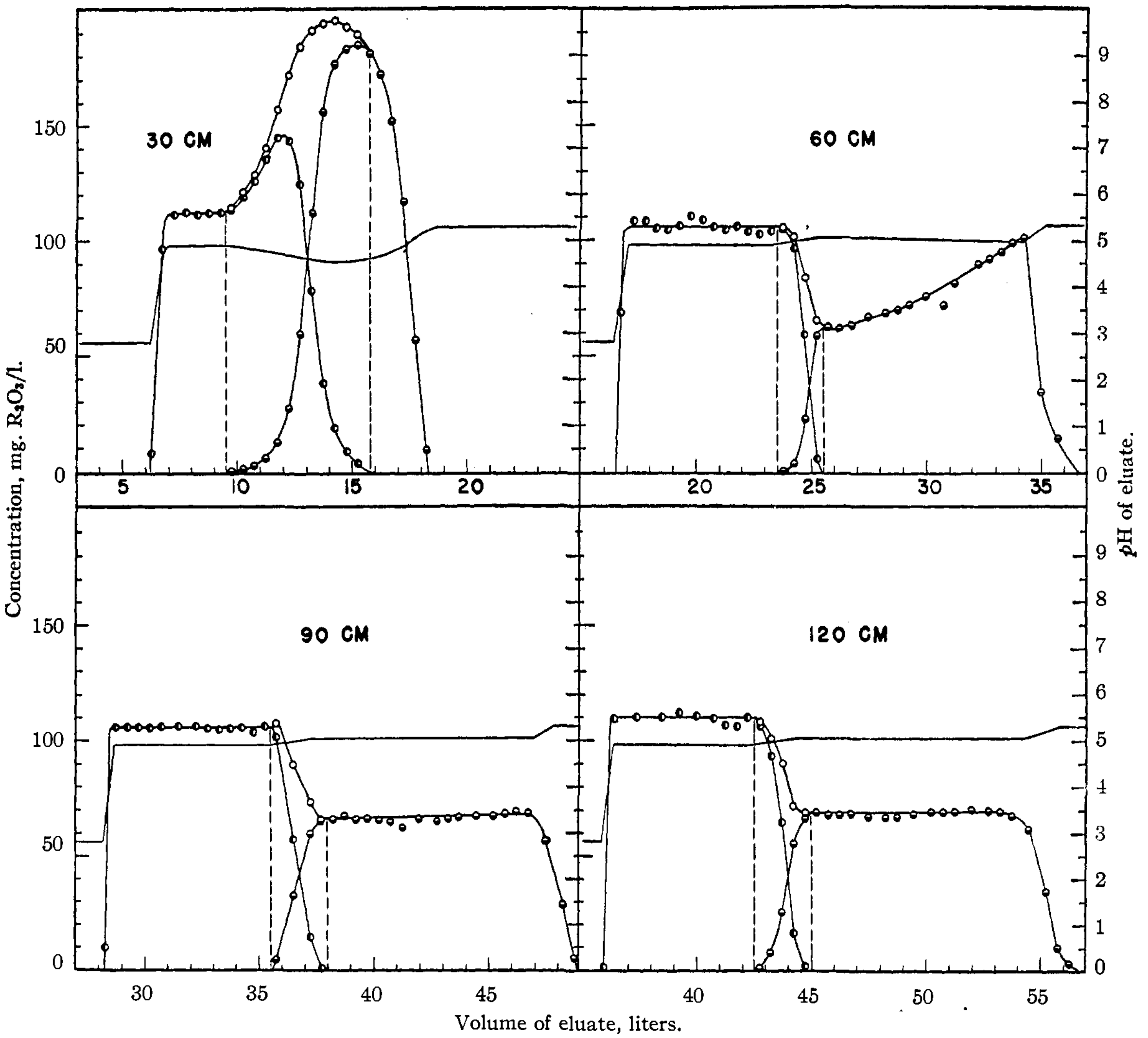

Fig. 4.—The elution of 0.01 mole equimolar mixtures of Sm and Nd from −30 + 40 Amberlite IR-100 resin beds, 22 mm. in diameter and 30, 60, 90 and 120 cm. long, respectively, using 0.1% citrate solution at a pH of 5 30 and a linear flow rate of 0.5 cm./min.: O, total R_2O_3; ◐, Sm_2O_3; ◒, Nd_2O_3; vertical broken lines indicate the amount of overlap between Sm and Nd bands; solid line across figures gives the pH of the eluate, reading on the right hand scale.

undoubtedly due to the increased opportunity for channeling in the greater column lengths.

At the low citrate concentration employed, the replacement of ammonium ion by rare earth and of one rare earth by another in the eluate produced pH changes great enough to allow the separation to be followed by a pH meter of average sensitivity. The difference between the pH values at the samarium and neodymium plateaus was in the order of 0.10 to 0.15 pH unit. The pH of the eluate observed at the samarium and neodymium plateaus of the elution curve increased as the pH of the eluant was increased.

The nearly constant amount of overlap between bands led to the conclusion that the degree of separation could be improved substantially by merely increasing the column load proportionately to the column length. That is, if one could obtain a 50% separation with a column load of 0.01 mole of an equimolar mixture of two rare earths on a column just long enough for complete development of the bands, then one would expect a 75% separation by eluting 0.02 mole of the mixture from a column twice as long and a separation of 87.5% by eluting 0.04 mole of the mixture from a column four times as long. That this conclusion is correct, as long as channeling in the resin bed is kept to a minimum, will be seen in a subsequent experiment.

A comparison of the elution curves shown in Figs. 4, 5 and 6 for the 30-cm. columns at different pH values showed that the individual bands were not yet developed due to too great a load of rare earths for the length of bed, but that the development was more nearly complete at a pH of 6.00 than at the lower values. In fact, the 30-cm. column at a pH of 6.00 appeared to be overloaded to about the same extent as the 60-cm. column at a pH of 5.30. This was interpreted to mean that twice as large a sample could be used on a column of fixed length at a pH of 6.00 as at a pH of 5.30. This factor should be considered when increasing column efficiency by increasing column length and column load proportionately. In order to investigate the possibility of using a still higher pH an additional 30-cm. column was eluted under comparable conditions at a pH of 6.30. The elution curve for this pH is compared to the curves at pH values of 5.30, 5.50 and 6.00 in Fig. 7; for the sake of simplicity the analytical curves for the individual components are not included. It can be seen

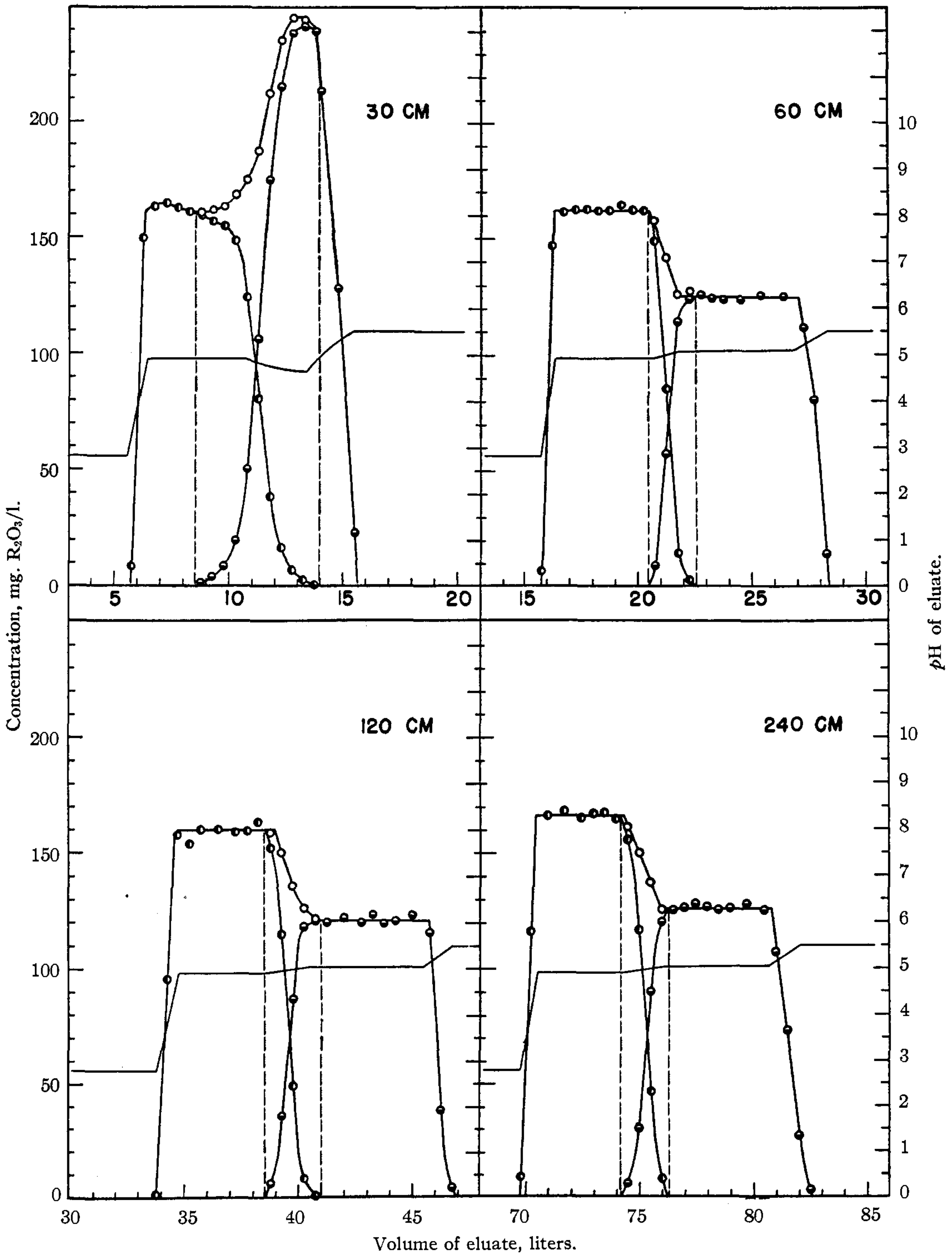

Fig. 5.—The elution of 0.01 mole equimolar mixtures of Sm and Nd from −30 + 40 Amberlite IR-100 resin beds, 22 mm. in diameter and 30, 60, 120 and 240 cm. long, respectively, using 0.1% citrate solution at a *p*H of 5.50 and a linear flow rate of 0.5 cm./min.: ○, total R_2O_3; ◐, Sm_2O_3; ◒, Nd_2O_3; vertical broken lines indicate amount of overlap between Sm and Nd bands; solid line across figures gives the *p*H of the eluate, reading on the right-hand scale.

that there is little advantage in going to a *p*H higher than 6.00 since there is little improvement in the shape of the elution curve.

E. The Effect of Column Length on the Separation of Mixtures of Samarium, Neodymium and Praseodymium at a *p*H of 5.30.—Columns 30, 60 and 120 cm. in length

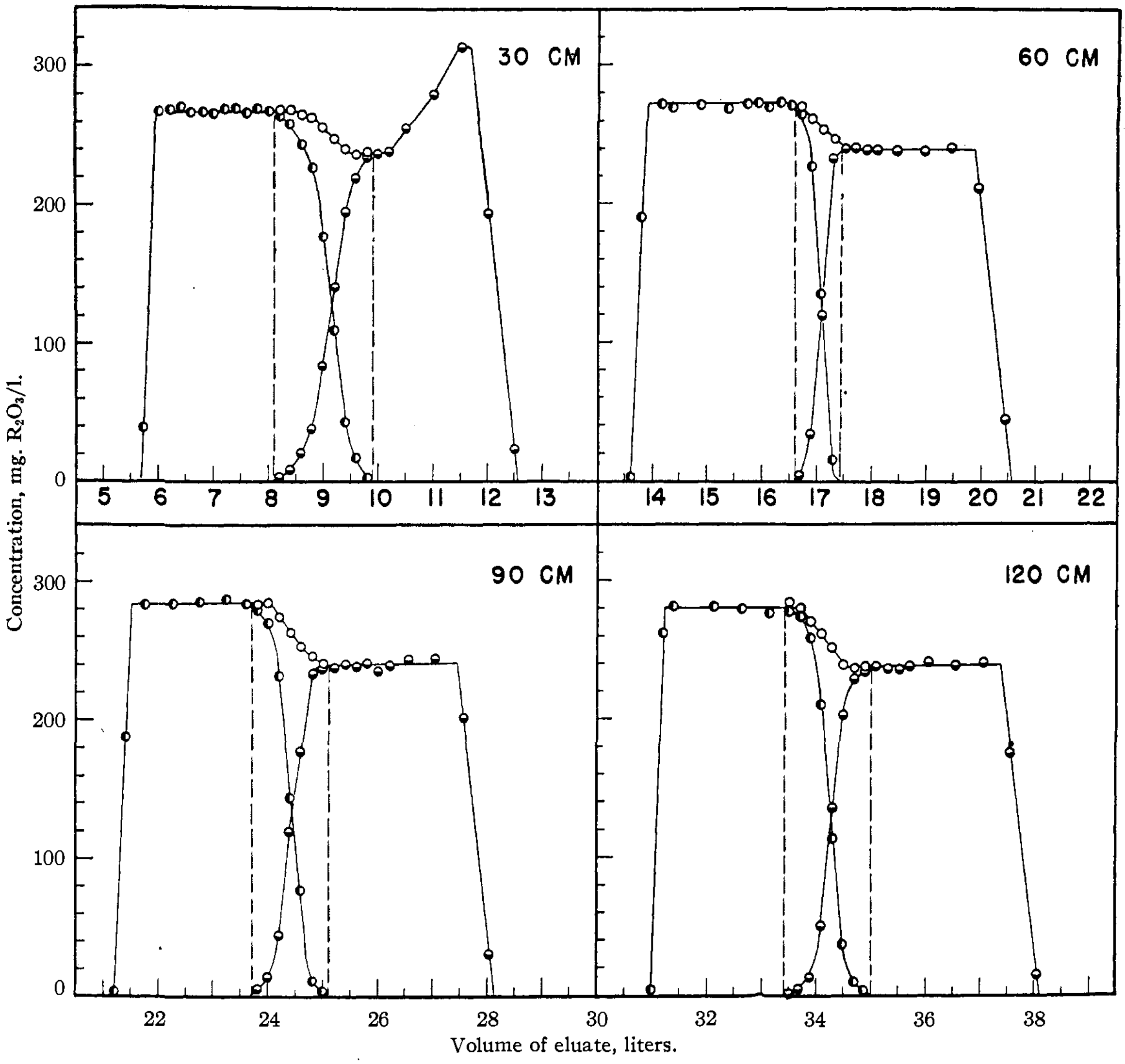

Fig. 6.—The elution of 0.01 mole equimolar mixtures of Sm and Nd from −30 + 40 Amberlite IR-100 resin beds, 22 mm. long and 30, 60, 90 and 120 cm. long, respectively, using 0.1% citrate solution at a pH of 6.00 and a linear flow rate of 0.5 cm./min.: O, total R_2O_5; ◐, Sm_2O_3; ◒, Nd_2O_3; vertical broken lines indicate the amount of overlap between Sm and Nd bands.

were each loaded with a sample consisting of a rare earth oxide mixture weighing 1.71 g. and containing 33.6% Sm_2O_3, 28.8% Nd_2O_3 and 34.7% Pr_6O_{11}. This weight of sample is approximately equivalent to 0.01 mole of mixed rare earth chlorides. The samples were eluted at a linear flow rate of 0.5 cm./min. at a pH of 5.30. The elution curves are given in Fig. 8 and other pertinent data are given in Table VI. It is evident that the shapes of the samarium and neodymium bands are not affected by the presence of praseodymium if the column is not overloaded.

TABLE VI

THE EFFECT OF COLUMN LENGTH USING A THREE-COMPONENT MIXTURE AT A pH OF 5.30

Bed height, cm.	30	60	120
Total vol. of eluant required, l.	20.5	38.9	62.5
% Sm_2O_3 obtainable pure	70.5	71.2	81.5
% Nd_2O_3 obtainable pure	None	44.5	67.3
% Pr_6O_{11} obtainable pure	8.8	67.4	88.0

F. The Effect of Increasing Column Load and Column Length Proportionately at a pH of 6.00.—In Section D it was demonstrated that 1.713 g. of an equimolar mixture of Sm_2O_3 and Nd_2O_3, was somewhat too large for elution from an Amberlite IR-100 resin bed, 22 mm. in diameter and 30 cm. long, with 0.1% citrate at any pH value tested. Consequently, the sample size for the following experiment was based on the smaller load of 1.650 g. of the oxide mixture per 30 cm. of bed height.

Columns 30, 60, 90 and 120 cm. long, were loaded with samples prepared from 1.65, 3.30, 4.95 and 6.60 g. of equimolar Sm_2O_3-Nd_2O_3 mixture, respectively. The samples were eluted at a pH of 6.00 and a flow rate of 0.25 cm./min. Data for the 30, 60 and 90 cm. columns are plotted in Fig. 9 and compiled in Table VII.

It is apparent that column efficiency can be increased by increasing the column length and the sample size proportionately. It is also evident from the data in Table VII that both the break-through volume and the total elution volume are directly proportional to the column length under these conditions. Results are not available for the

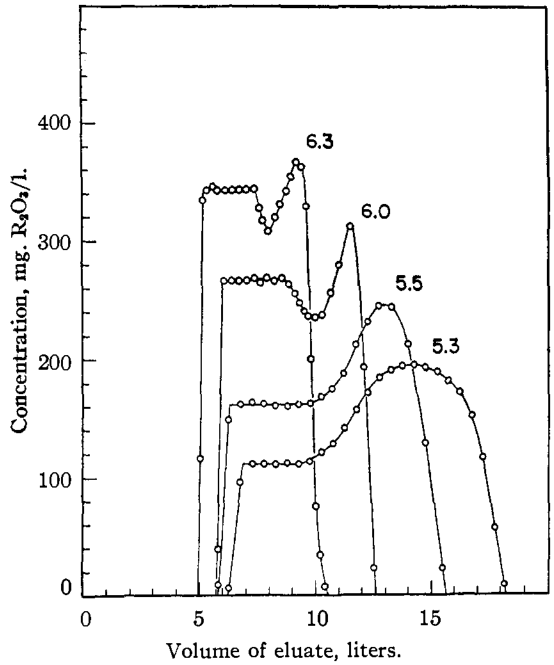

Fig. 7.—The elution of 0.01 mole equimolar mixtures of Sm and Nd from Amberlite IR-100 resin beds, 22 mm. in diameter and 30 cm. long, with 0.1% citrate solution at various *p*H values: the *p*H value is printed beside the curve to which it corresponds.

120-cm. column, since a precipitate formed in the column during the experiment. In subsequent investigations it was found that 6.00 g. of the oxide mixture yielded a precipitate on a 120 cm. column and that 5.00 g. gave a precipitate on a 100-cm. bed. The precipitate in all cases appeared at a point 70–80 cm. from the top of the bed. Since no precipitate occurred in the 90-cm. column of the above series, it appears that the formation of a precipitate was due to excessive sample size rather than to increased column length. Furthermore, since a precipitate was observed with 5.00 g. and not with 4.95 g. of the mixture, it was assumed that 5.00 g. should be set as the upper limit for column load under these conditions. It has been established that an insoluble rare earth complex with the empirical formula $RCit{\cdot}2H_2O$ forms under similar conditions. The details of this work will be published later.

TABLE VII

THE EFFECT OF A PROPORTIONATE INCREASE IN COLUMN LOAD AND COLUMN LENGTH AT A *p*H OF 6.00

Column length, cm.	30	60	90
Sample weight, g. R_2O_3	1.65	3.30	4.95
Break-through volume, l.	5.8	11.5	17.4
Total elution volume, l.	13.0	24.0	36.0
Per cent. Sm_2O_3 obtainable pure	61.7	77.8	90.5
Per cent. Nd_2O_3 obtainable pure	64.0	82.2	88.5

It was apparent from the elution curves in Fig. 9 that the column loads, based on 1.650 g. of equimolar Sm_2O_3–Nd_2O_3 mixture, were somewhat too large for the lengths of column used, since a hump appeared on the neodymium elution band in each curve. Such a hump indicates that the rare earth band has not reached full development on the length of column provided. It was found in a subsequent experiment that decreasing the column load to 1.5 g. of the mixed oxide per 30 cm. of column length was sufficient to eliminate this difficulty.

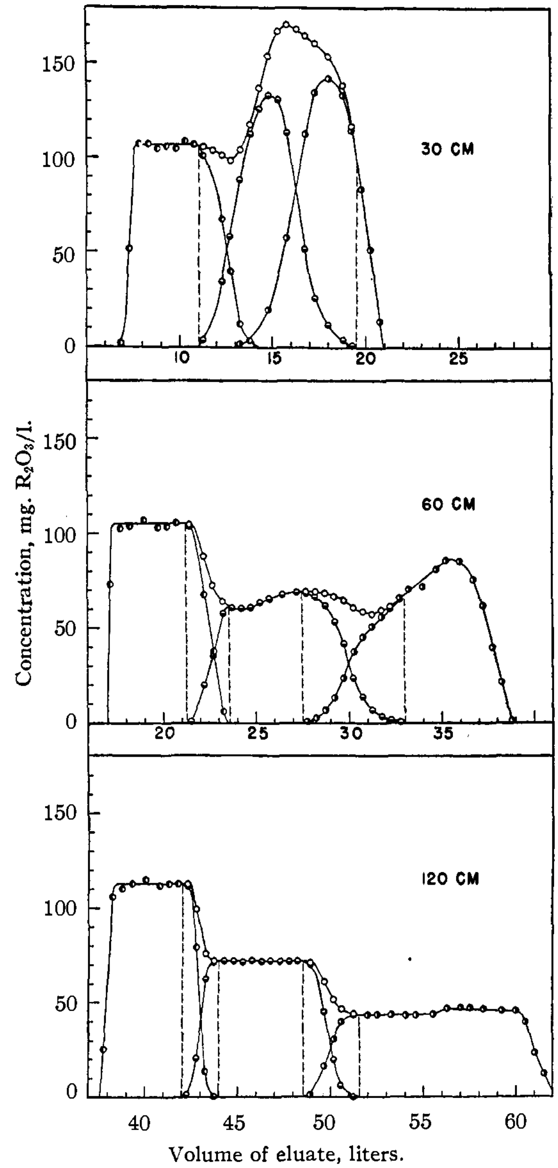

Fig. 8.—The elution of mixtures of Sm, Nd and Pr from −30 + 40 Amberlite IR-100 beds, 22 mm. in diameter and 30, 60 and 120 cm. long, with 0.1% citrate solution at a *p*H of 5.30 and a linear flow rate of 0.5 cm./min.: ○, total R_2O_3; ◐, Sm_2O_3; ⊖, Nd_2O_3; ◑, Pr_6O_{11}; vertical broken lines indicate overlap between bands.

Summary

A number of variables involved in the separation of rare earths with 0.1% citric acid–ammonium citrate solution and Amberlite IR-100 resin beds have been investigated.

Separation of the rare earth pairs studied increased as the *p*H of the eluant decreased, with almost complete separation being obtained at a *p*H value of 5.00. However, since elution time increased greatly with decreasing *p*H, optimum

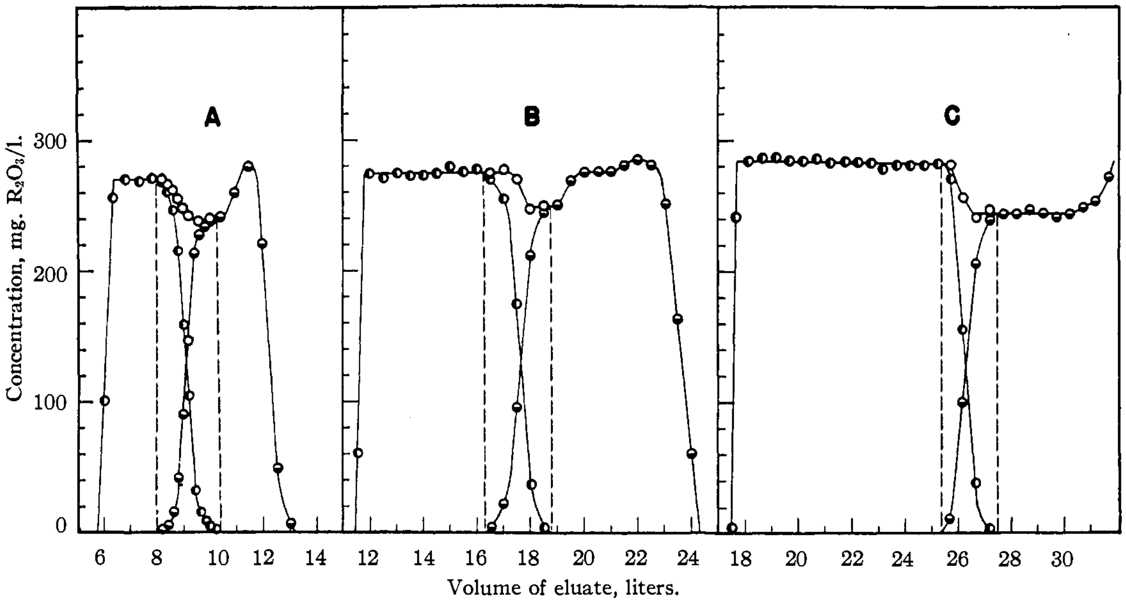

Fig. 9.—The effect of increasing column load and column length proportionately: (A) 1.65 g. equimolar Sm_2O_3–Nd_2O_3 mixture on a 22 mm. × 30 cm. Amberlite IR-100 bed, (B) 3.30 g. on a 22 mm. × 60 cm. bed and (C) 4.95 g. on a 22 mm. × 90 cm. bed; ○, total R_2O_3; ◐, Sm_2O_3; ⊖, Nd_2O_3; broken vertical lines indicate amount of overlap between bands.

yields of pure rare earths for a given operating time were obtained at a higher *p*H.

The slower the flow rate the less was the observed band overlap and the better the separation. Channeling was another effect which was greatly reduced when flow rates were reduced.

With smaller size resin particles less band overlap was observed showing that reduction of particle size affected the separation in a manner similar to reduced flow rate, but with less increase in operating time.

For a fixed charge of rare earth, separation was independent of column length beyond a certain minimum length and in fact became poorer at the longer lengths due to greater opportunity for channeling.

Increasing column length and column load in the same ratio increased the separation. An upper limit on these increases was met in the separations due to a slow-forming rare earth–citrate precipitate.

AMES, IOWA RECEIVED MARCH 14, 1949

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WISCONSIN]

Moving Boundary Systems Formed by Weak Electrolytes. Theory of Simple Systems Formed by Weak Acids and Bases

BY ROBERT A. ALBERTY

Introduction.—When an electric current is passed across an initially sharp junction between two different electrolyte solutions, new concentration gradients form and move away from the initial boundary position. In the case of strong electrolytes such moving boundaries have afforded the most precise method for the determination of transference numbers.[1] In the case of solutions of proteins and other colloidal electrolytes the moving boundary method has made possible an important method for the analysis of complex mixtures such as plasma and for the separation of small amounts of material difficult to isolate by other methods.[2]

The theory of moving boundary systems formed by strong electrolytes has been developed extensively,[3] and Dole[4] has obtained the general solution of the system of moving boundary equations for the case that the relative ion mobilities are constant throughout the system. The theory of moving boundary systems formed by weak electrolytes has not been studied in such detail[5]

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