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DISTRIBUTION OF RARE-EARTH NITRATES
BETWEEN TRIBUTYL PHOSPHATE AND NITRIC ACID

A. C. Topp
and
Boyd Weaver

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STABLE ISOTOPE RESEARCH AND PRODUCTION DIVISION
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ABSTRACT

Coefficients have been determined for the distribution of samarium, gadolinium, dysprosium and yttrium nitrates between nitric acid and tributyl phosphate at various acidities and rare-earth concentrations. The dependence of extraction on rare-earth concentration increases with acidity and with atomic number of the rare earths.

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DISTRIBUTION OF RARE-EARTH NITRATES
BETWEEN TRIBUTYL PHOSPHATE AND NITRIC ACID

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INTRODUCTION

The Stable Isotope Research and Production Division of the Oak Ridge National Laboratory has separated rare-earth nitrates by liquid-liquid extraction.¹ The solvents used in all recent separations were nitric acid of various concentrations and undiluted tributyl phosphate.

The present work was undertaken to supply fundamental and operating data for the process. Distribution coefficients for the rare-earth nitrates between tributyl phosphate and nitric acid were determined with nitric acid in the concentration range of 8.5 to 17 normal and for rare-earth nitrate concentrations in the feed in the range of 3 to 80 grams per liter, expressed as oxide.

The materials studied were samarium nitrate (99.5%), gadolinium nitrate (99.3%) and a mixture of nitrates prepared from Lindsay Chemical Company mixed oxides, Code Number 920. This last material was a sample from the feed for the pulse column and was composed of the following oxides: 2% neodymium, 60% samarium, 1.5% europium, 25% gadolinium, 0.6% terbium, 4% dysprosium, 5% yttrium and traces of holium and erbium.

1. Boyd Weaver, F. A. Kappelmann, A. C. Topp, J.A.C.S. 75, 3943, (1953).

EXPERIMENTAL

Stock solutions of the rare-earth nitrates were prepared in nitric acid of various concentrations. The concentration of the rare-earth nitrates in the feed was changed by diluting the stock solution with nitric acid of the same normality as that of the stock solution. Tributyl phosphate was equilibrated with nitric acid having the same concentration as that of the feed solution. In a series of distribution coefficient determinations, at a given normality of nitric acid, the only variable was the concentration of the rare-earth nitrate in the feed.

The extractions were made by shaking 25 ml. portions of feed solution and equilibrated tributyl phosphate in a separatory funnel. The layers were separated and the rare earths precipitated from each with oxalic acid. The precipitates were ignited and weighed as the oxides. The distribution coefficients, i.e., the ratio of the concentration of the solute in the organic phase to that in the aqueous phase, were determined by dividing the weight of oxide from the organic phase by the weight of oxide from the aqueous phase.

The experiments were carried out in an air-conditioned room at a temperature of 24°C. Solutions were allowed to reach temperature equilibrium with the room before use in the extractions. This was deemed sufficient temperature control as previous work had shown that temperature changes of the magnitude encountered had negligible effect on the distribution coefficients.²

2. ORNL-1409, Liquid-Liquid Extraction of Neodymium and Samarium Nitrates, A. C. Topp.

Tributyl phosphate was used as obtained from the manufacturer, with no treatment prior to equilibrating with nitric acid. Previous practice was to wash the organic solvent with 5% sodium carbonate solution² but a preliminary investigation showed no difference in the distribution coefficient when the sodium carbonate wash was omitted.

RESULTS

Distribution Coefficients of Samarium Nitrate

Distribution coefficients for samarium nitrate were determined between tributyl phosphate and various concentrations of nitric acid. At each concentration of nitric acid the concentration of samarium nitrate in the feed was varied. The highest concentration of the salt was limited by its solubility in the nitric acid and the lowest by the small weight of oxide recovered introducing a large error in the distribution coefficient.

The concentrations of the nitric acid were chosen to cover the range used in operation of the pulse column, and further, it developed that within this range change in the distribution coefficients due to changes in the concentration of the feed occurred.

The results are summarized in Table I. Figure 1 shows the change in distribution coefficient with change in concentration of samarium nitrate in the feed solution at a fixed nitric acid concentration in the system.

Table I

DISTRIBUTION COEFFICIENTS OF SAMARIUM NITRATE BETWEEN
TRIBUTYL PHOSPHATE AND NITRIC ACID

Normality HNO_3	Feed: g/l. Sm_2O_3	R (O/A)
10.2	68.0	0.77
10.2	54.6	0.67
10.2	40.7	0.68
10.2	27.3	0.69
10.2	13.6	0.85
10.2	5.4	0.91
12.8	65.6	1.70
12.8	52.2	1.81
12.8	39.5	1.94
12.8	26.1	2.07
12.8	13.1	2.13
12.8	5.2	2.37
14.5	67.2	2.99
14.5	53.5	3.42
14.5	40.0	3.84
14.5	26.7	4.44
14.5	13.4	5.62
14.5	2.7	9.25
17.4	69.1	7.67
17.4	55.4	10.5
17.4	41.5	13.2
17.4	27.7	16.1
17.4	13.8	18.6
17.4	5.5	39.9

FIGURE 1. CHANGE IN DISTRIBUTION COEFFICIENT OF $\text{Sm}(\text{NO}_3)_3$ WITH CHANGE IN CONCENTRATION OF FEED

Values for the distribution coefficients for samarium nitrate at fixed concentrations of the salt in the feed and for different concentrations of nitric acid are obtained from Figure 1. They are given in Table II. The change in distribution coefficient with change in concentration of nitric acid in the system is shown graphically in Figure 2.

TABLE II
DISTRIBUTION COEFFICIENTS OF SAMARIUM
NITRATE FROM FIGURE 1

Feed: g/l Sm_2O_3	Normality HNO_3	R (O/A)
60	10.2	0.7
60	12.8	1.7
60	14.5	3.2
60	17.4	9.8
50	10.2	0.7
50	12.8	1.8
50	14.5	3.6
50	17.4	11.6
40	10.2	0.7
40	12.8	1.9
40	14.5	3.9
40	17.4	13.6
30	10.2	0.7
30	12.8	2.0
30	14.5	4.3
30	17.4	15.6
20	10.2	0.7
20	12.8	2.1
20	14.5	4.9
20	17.4	17.5
10	10.2	0.8
10	12.8	2.2
10	14.5	6.5
10	17.4	19.5

FIGURE 2. CHANGE IN DISTRIBUTION COEFFICIENT OF SAMARIUM NITRATE
WITH CHANGE IN CONCENTRATION OF NITRIC ACID

Distribution Coefficients of Gadolinium Nitrate

Distribution coefficients of gadolinium nitrate between tributyl phosphate and various concentrations of nitric acid were determined with different concentrations of the salt in the feed solutions. The results are given in Table III and are shown graphically in Figure 3, where the curves represent the changes in distribution coefficients with changes in concentration of gadolinium nitrate in the feed at fixed concentrations of nitric acid in the system.

TABLE III

DISTRIBUTION COEFFICIENTS OF GADOLINIUM NITRATE
BETWEEN NITRIC ACID AND TRIBUTYL PHOSPHATE

Normality HNO_3	Feed: g/l Gd_2O_3	R (O/A)
8.5	55.4	0.8
8.5	44.4	0.8
8.5	33.2	0.8
8.5	22.2	0.8
8.5	11.1	0.8
8.5	4.4	0.8
11.0	63.3	1.7
11.0	50.6	1.8
11.0	37.9	1.9
11.0	25.3	2.1
11.0	12.6	2.3
11.0	5.1	2.4
13.1	60.6	4.0
13.1	48.5	4.5
13.1	36.4	5.3
13.1	24.3	6.0
13.1	12.1	6.9
13.1	4.9	9.6
14.7	59.7	8.1
14.7	47.6	11.1
14.7	35.6	12.7
14.7	24.1	14.0
14.7	12.1	20.4
14.7	2.4	73.0
16.9	61.8	18.8
16.9	49.4	23.7
16.9	36.8	32.8
16.9	24.7	40.2

FIGURE 3. CHANGE IN DISTRIBUTION COEFFICIENT OF GADOLINIUM NITRATE WITH CHANGE IN CONCENTRATION OF FEED

The relationship between the distribution coefficients of gadolinium nitrate and concentration of nitric acid at various concentrations of the salt in the feed as obtained from Figure 3 is summarized in Table IV. The values in Table IV are shown in Figure 4, where the curves represent the change in distribution coefficient with change in nitric acid concentration in the system at fixed concentrations of salt in the feed.

TABLE IV
DISTRIBUTION OF COEFFICIENTS OF GADOLINIUM
NITRATE FROM FIGURE 3

Feed: g/l Gd_2O_3	Normality HNO_3	R (O/A)
60	8.5	0.8
60	11.0	1.7
60	13.1	3.9
60	14.7	8.3
60	16.9	19.2
50	8.5	0.8
50	11.0	1.8
50	13.1	4.5
50	14.7	10.0
50	16.9	25.0
40	8.5	0.8
40	11.0	2.0
40	13.1	5.1
40	14.7	11.7
40	16.9	30.8
30	8.5	0.8
30	11.0	2.1
30	13.1	5.7
30	14.7	13.5
30	16.9	36.7
20	8.5	0.8
20	11.0	2.2
20	13.1	6.3
20	14.7	15.4
20	16.9	42.5
10	8.5	0.8
10	11.0	2.3
10	13.1	7.5
10	14.7	20.0
10	16.9	48.4

FIGURE 4. CHANGE IN DISTRIBUTION COEFFICIENT OF GADOLINIUM NITRATE WITH CHANGE IN CONCENTRATION OF NITRIC ACID

Separation Factors of Samarium and Gadolinium Nitrates

The separation factor of two solutes is the ratio of their distribution coefficients between two immiscible solvents. The distribution coefficients for samarium nitrate and gadolinium nitrate are obtained from Figures 2 and 4, respectively, under the same conditions of concentration of the salts and concentration of nitric acid. The values are compiled in Table V together with the separation factors calculated from them.

It was shown that the distribution coefficients of neodymium and samarium nitrates differed when determined separately and when determined in a mixture of the two salts.² The separation factors given in Table V do not take into account the possible mutual effect the salts may have on the individual distribution coefficients or the effect the presence of other rare earth nitrates may have in the extraction of a mixture.

Distribution Coefficients of Mixed Rare-Earth Nitrates

Sample 920

Distribution coefficients were determined for the rare-earth nitrates made from the mixture of oxides used in preparing the feed for the pulse column. The mixed oxides were supplied by Lindsay Chemical Company under code number 920. The analysis of the mixture is given on page 4 of this report.

Feed solutions were 9.9, 12.5 and 15.0 normal with respect to nitric acid, and the corresponding tributyl phosphate portions were equilibrated with nitric acid of the same concentrations. The concentration of rare-

TABLE V

SEPARATION FACTORS OF GADOLINIUM
AND SAMARIUM NITRATES

Normality HNO_3	Feed: g/l oxide	R (O/A) _{Gd}	R (O/A) _{Sm}	R. Gd/R _{Sm}
13	60	3.8	1.8	2.1
13	50	4.2	1.9	2.2
13	40	4.8	2.1	2.3
13	30	5.3	2.2	2.4
13	20	6.0	2.4	2.5
13	10	7.1	2.6	2.7
14	60	5.9	2.6	2.3
14	50	6.9	2.9	2.4
14	40	8.2	3.1	2.6
14	30	9.3	3.4	2.7
14	20	10.5	3.9	2.7
14	10	13.2	4.7	2.8
15	60	9.4	4.0	2.4
15	50	11.4	4.6	2.5
15	40	13.4	4.9	2.7
15	30	15.6	5.5	2.8
15	20	17.4	6.3	2.8
15	10	23.0	8.5	2.7
16	60	14.1	6.1	2.3
16	50	17.4	7.0	2.5
16	40	20.4	7.6	2.7
16	30	23.8	8.5	2.8
16	20	27.4	10.0	2.7
16	10	34.0	12.5	2.7

earth nitrates in the feed were varied by dilution with nitric acid of the above concentrations.

The weights of recovered mixed rare ~~earth~~ oxides from the organic and aqueous fractions were used to calculate the distribution coefficients for the mixture as a whole. The values are given in Table VI in the column headed "Total". These results are plotted in Figure 5 to show the effect of concentration of rare-earth nitrates and concentration of nitric acid on the distribution coefficients of the mixture.

The recovered oxides from the fractions were analyzed spectrographically. The distribution coefficients of samarium, europium, gadolinium, terbium, dysprosium and yttrium were calculated from the weights of recovered oxides and the analyses. With the exceptions of samarium and gadolinium, the weights of the individual rare-earth oxides in the recovered oxides were small. The values of the distribution coefficients, therefore, can be considered only approximations.

The distribution coefficients of the rare-earth nitrates in the mixture are included in Table VI to show the general effect of increasing the values of the distribution coefficients with (a) increasing concentration of nitric acid and (b) decreasing concentration of rare-earth nitrates.

The amounts of samarium and gadolinium nitrates in the feed were calculated from the weight of mixed nitrates. The distribution coefficients, compared on the basis of similar feed and nitric acid concentrations, gave agreement with the distribution coefficients obtained when pure samarium and gadolinium nitrate feed solutions were used.

FIGURE 5. CHANGE IN DISTRIBUTION COEFFICIENTS OF RARE EARTH NITRATES, SAMPLE 920, WITH CHANGE IN CONCENTRATION OF FEED

TABLE VI

DISTRIBUTION COEFFICIENTS OF RARE EARTH NITRATES FROM SAMPLE 920
BETWEEN TRIBUTYL PHOSPHATE AND NITRIC ACID

Normality HNO ₃	Feed g/l oxide	- - - - - R (O/A) Gd - - - - -							Total	R _{Gd} /R _{Sm}
		Sm	Eu	Gd	Tb	Dy	Y			
9.9	65.2	0.66	1.2	1.3	1.4	2.4	4.9	0.87	2.0	
9.9	52.2	0.72	1.0	1.5	1.4	2.0	4.4	0.89	1.5	
9.9	39.1	0.72	1.0	1.2	1.6	2.6	4.6	0.94	1.6	
9.9	26.1	0.74	1.1	1.4	1.6	3.0	4.8	0.98	1.9	
9.9	13.0	0.73	1.2	1.4	-	3.3	4.8	1.01	2.0	
9.9	5.2	0.79	1.2	1.4	-	3.2	4.8	1.04	1.8	
12.5	82.6	1.3	1.8	2.7	-	13	1.3	1.72	2.1	
12.5	66.1	1.5	2.6	3.0	-	16	1.5	1.91	2.0	
12.5	49.6	1.4	2.5	3.9	-	19	1.7	2.13	2.8	
12.5	33.0	1.8	2.9	3.4	-	-	-	2.37	1.9	
12.5	16.5	2.0	3.2	4.4	-	-	-	2.65	2.2	
12.5	6.6	-	-	-	-	-	-	2.84		
15.0	80.9	2.5	4.6	7.5	-	22	-	3.83	3.0	
15.0	64.7	3.1	5.8	9.7	-	21	-	4.58	3.1	
15.0	48.5	3.7	12.5	12.5	-	30	-	5.52	3.4	
15.0	32.4	4.8	16.9	17.0	-	32	-	6.42	3.5	

DISCUSSION

Relation of Distribution Coefficients to Equilibrium Conditions

In experiments involving distribution of a solute between two liquid phases, direct control of concentrations can be had only in the original feed solution. However, the actual distribution is directly dependent not on this concentration, but on that in one or both of the solvents at equilibrium. Therefore, the foregoing data have been plotted in Figure 6 as relationships of distribution coefficients to concentrations in the aqueous phase at equilibrium. Unwieldy extension of the curves was avoided by using a log-log scale. Data on dysprosium and yttrium obtained by F. M. Scheitlin and F. A. Kappelman with the meager supply of these elements available have been combined with the data on samarium and gadolinium.

The horizontal nature of the curves for low acidities indicates that distribution coefficients are independent of rare-earth concentration under these conditions. The increase in inclination at higher acidities indicates a considerable dependency upon concentration. This effect is notably greater for dysprosium and yttrium in the range covered.

The data become still more meaningful when logarithms of distribution coefficients are plotted versus acidity as in Figure 7. Here individual curves represent rare-earth concentrations chosen at regularly spaced logarithmic intervals. All values are taken from Figure 6. The result is a family of curves for each element, diverging from a point or single line.

The logarithm of the separation factor between two elements under a

FIGURE 6. EFFECT OF RARE-EARTH NITRATE CONCENTRATION ON DISTRIBUTION

given set of conditions is the difference between their distribution coefficients under the same conditions. In Figure 8 the separation factors for the pairs gadolinium-samarium and yttrium-gadolinium have been graphically illustrated by deriving values from Figure 7. Up to 13N acid the separation between gadolinium and samarium increases but becomes more dependent upon rare-earth concentration. Beyond 14N acid the separation decreases. The separation between yttrium and gadolinium is decreasing even at 11N.

CONCLUSIONS

The most effective separation between a pair of elements by countercurrent liquid-liquid extraction occurs only when the distribution coefficient for each element remains constant throughout the length of the extraction system on each side of the feed point. Under equilibrium conditions of operation there is always a gradient of solute concentration from the feed point to the ends. Therefore optimum results can be obtained only under conditions which do not cause a dependency of distribution coefficients on solute concentration. In the present case the experimental results indicate that constancy throughout an extractor could be attained only at acidities below about 9N for gadolinium and samarium and at still lower acidities for the yttrium earths.

Some confirmation of these conclusions is given by the fact that samarium has been separated from neodymium very readily at high acidities, while separations have become increasingly difficult as progress was made through the series. On the other hand, the separation factors decrease as

FIGURE 8. EFFECT OF CONCENTRATION OF RARE-EARTHS AND NITRIC ACID ON SEPARATION FACTORS

FIGURE 7. EFFECT OF NITRIC ACID CONCENTRATION ON DISTRIBUTION OF RARE - EARTHS

acidity decreases, possibly enough to overcome all advantage. At very low acidities there is even a reversal in the order of distribution coefficients of the elements.

A few laboratory experiments have been performed by F. A. Kappelmann in an attempt to improve the enhancement of a dysprosium rich mixture by countercurrent extraction in the 6N-9N range. Results were far inferior to those obtained in the 10N-13N range. There remains the possibility that the difficulty was caused in part at least by a very unfavorable arrangement of flow rates in the two sections of the extraction apparatus. The optimum relationship can be determined only by a long series of experiments.