MASTER

IS-332

EQUILIBRIUM DISTRIBUTION STUDIES OF DYSPROSIUM NITRATE-ERBIUM NITRATE-NITRIC ACID-TRIBUTYL PHOSPHATE SYSTEMS

By
Michael Robert Dinnin, Jr.
Morton Smutz

November 1960

Ames Laboratory
Iowa State University
Ames, Iowa

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CHEMISTRY

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NOMENCLATURE

m_T - total molality of either phase; equivalents of total nitrate per 1000 grams of solvent

m_{HNO_3} - molality of nitric acid in either phase

m_{Dy} - molality of dysprosium nitrate in either phase given in terms of nitrate ion

m_{Er} - molality of erbium nitrate in either phase given in terms of nitrate ion

K - distribution coefficient of any solute; concentration of solute in organic phase divided by concentration of same solute in aqueous phase

K_{HNO_3} - distribution coefficient of nitric acid; m_{HNO_3}(org.)/m_{HNO_3}(aq.)

K_{Dy} - distribution coefficient of dysprosium nitrate; m_{Dy}(org.)/m_{Dy}(aq.)

K_{Er} - distribution coefficient of erbium nitrate; m_{Er}(org.)/m_{Er}(aq.)

K_T distribution coefficient based on the total molality of each phase; m_T(org.)/m_T(aq.)

β_{A-B} - separation factor between A and B; K_A/K_B

β_{Er-Dy} - separation factor between erbium nitrate and dysprosium nitrate; K_{Er}/K_{Dy}

X_{RE} - rare-earth nitrate composition; equivalents of rare-earth nitrate per total equivalents of nitrate (aqueous phase)

X_{Dy} - dysprosium nitrate composition; equivalents of dysprosium nitrate per total equivalents of nitrate (aqueous phase)

X_{Er} - erbium nitrate composition; equivalents of erbium nitrate per total equivalents of nitrate (aqueous phase)

x_{Dy} - equivalents of dysprosium nitrate per total equivalents of rare-earth nitrate (aqueous phase)

x_{Er} - equivalents of erbium nitrate per total equivalents of rare-earth nitrate (aqueous phase)

org. - abbreviation of organic phase

aq. - abbreviation of aqueous phase

EQUILIBRIUM DISTRIBUTION STUDIES OF DYSPROSIUM NITRATE-ERBIUM NITRATE-NITRIC ACID-TRIBUYTL PHOSPHATE SYSTEMS*

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by

Michael Robert Dinnin, Jr., and Morton Smutz

ABSTRACT

The equilibrium distribution of dysprosium nitrate, erbium nitrate, and nitric acid between water and tributyl phosphate was studied in this research. Separate equilibrium data were obtained for the distribution of dysprosium nitrate-nitric acid, erbium nitrate-nitric acid, and dysprosium nitrate-erbium nitrate-nitric acid mixtures. The equilibrium data were obtained by making single stage extractions from aqueous feed solutions using commercial grade tributyl phosphate. Equilibrium distribution of solutes was determined by analysis of each phase from the single stage extractions.

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Equilibrium data for the dysprosium nitrate-nitric acid and erbium nitrate-nitric acid mixtures were correlated in such a manner that the total distribution of solutes and the distribution of nitric acid could be found for dysprosium nitrate-erbium nitrate-nitric acid mixtures. The separation factor between dysprosium nitrate and erbium nitrate for dysprosium nitrate-erbium nitrate-nitric acid mixtures was shown as a function of the total molality of the aqueous phase. Equilibrium distribution curves were presented for pure dysprosium nitrate and pure erbium nitrate.

A method was presented for predicting the concentrations of dysprosium nitrate, erbium nitrate, and nitric acid in an organic phase of tributyl phosphate when the concentrations of these same three solutes in the aqueous phase were known, and the two phases were in equilibrium. This method was demonstrated by means of a sample

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*This report is based on an M. S. thesis by Michael Robert Dinnin, Jr., submitted November, 1960, to Iowa State University, Ames, Iowa. This work was done under contract with the Atomic Energy Commission.

calculation. Also, a comparison between predicted concentrations and actual concentrations obtained from ten extractions with dysprosium nitrate-erbium nitrate-nitric acid mixtures was presented.

INTRODUCTION

The fifteen elements of atomic number 57 through 71 are commonly referred to as the rare-earth metals. Industrial uses for these metals are relatively small at the present time, although considerable research with the rare earths is now in progress and it is possible that there may be an increased demand for them in the near future. The term rare is somewhat of a misnomer because the raw materials from which these elements can be produced are quite plentiful. However, the rare earths always occur as mixtures in nature, and separating them from one another is difficult due to their chemical similarity.

Commercial production of the rare earths is now carried out by the separation process of ion exchange. The ion exchange method is advantageous in that it gives very good separations, but there are drawbacks such as low flow rates and semi-continuous operation which could be improved by using the separation technique of solvent extraction. For some time it has been known that the rare earths could also be separated by solvent extraction, and considerable research has been directed towards the development of a solvent extraction process for producing the rare earths.

The solvent most commonly used for extracting the rare earths is tributyl phosphate (TBP). The rare earths are first digested from the ores using sulfuric acid. Next they are separated from impurities and converted to the nitrate form. The rare-earth nitrates and nitric acid in aqueous solution are then brought in contact with the tributyl phosphate. In order to design a multistage solvent extraction process for separating the rare earths, which utilizes this principle, it is necessary to be able to predict the equilibrium conditions throughout the process. This prediction of equilibrium must take into account the equilibrium distribution of nitric acid and the rare-earth nitrates which are present. Schoenherr (8) was the first to develop a method of prediction where nitric acid was considered as one of the solutes. He used a samarium nitrate-neodymium nitrate-nitric acid-TBP-water system. However, before Schoenherr's method of equilibrium prediction could be applied to the entire rare-earth series, further investigation of other rare-earth nitrate-nitric acid-TBP-water systems was needed to determine if their behavior would be the same.

The equilibrium distribution of the dysprosium nitrate-erbium nitrate-nitric acid-TBP-water system was studied in this research in order to develop a method of predicting equilibrium distribution for two of the heavier elements in the rare-earth series. The method for predicting equilibrium distribution could then be used for finding stagewise conditions for this system when designing a solvent extraction process. Concurrent with this research, the equilibrium distribution of the lanthanum nitrate-praeseodymium nitrate-nitric acid-TBP-water system was being studied by Sharp.[1] It is expected that the prediction technique will lead to a method for predicting equilibria for any rare-earth nitrate-nitric acid-TBP-water system.

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[1] B. M. Sharp, Ames, Iowa. Equilibrium distribution of the lanthanum nitrate-praeseodymium nitrate-nitric acid-TBP-water system. Private communication. 1960.

Dysprosium and erbium were chosen for the study because they were two of the heavier rare earths sufficiently plentiful from a cost standpoint, and also, the concentration of dysprosium and erbium could be found by infra-red spectrophotometric analysis for the extractions in which the two were present together as mixed nitrates.

LITERATURE REVIEW

In 1937, Fischer, et al. (4) made the first study concerned with separating the rare-earth elements by solvent extraction. They found a separation factor of 1.5 between adjacent rare-earth chlorides when extracting with various alcohols and ethers. Their experimental data have not been verified by other investigators.

Peppard, et al. (7) investigated the equilibrium distribution of different rare earth nitrates between tributyl phosphate and water in the presence of nitric acid. All their data were obtained at low rare earth concentrations.

Weaver, et al. (10) produced one kilogram of 95 per cent gadolinium oxide by means of solvent extraction. They started with a feed considerably enriched in gadolinium oxide and kept the nitric acid concentration above 10 normal at all times. Tributyl phosphate was used as the solvent.

Bochinski, et al. (3) reported that the rare-earth nitrates could be separated by extracting with tributyl phosphate without using excess nitric acid or salting-out agents. They found that the separation factors between rare-earth nitrates increased with increasing rare-earth concentration and were independent of the composition of the rare-earth nitrate mixture. It was determined that the distribution of rare earths between the aqueous and organic phase was practically independent of rare earth composition and seemed to depend only on the total concentration of the rare earths present. They presented a calculation method for determining optimum operating conditions in a solvent extraction process for separating the rare earths. This calculation method was substantiated by experimental results obtained from a multistage countercurrent extraction run.

Knapp (6) obtained equilibrium data for the extraction of the monazite rare earths with tributyl phosphate. He studied the effects of nitric acid concentration and salting-out agents on separation factors and distribution coefficients. The extractability of the pure rare earths was found to increase with atomic number up to dysprosium and then decrease with further increase in atomic number. Distribution curves of the pure rare earths were used to predict the effect of rare-earth concentration on separation factors in systems which contained no acids or salting-out agents.

Atwood (1) studied the effect of chelating agents on the separation factors between adjacent rare earths. Salts of ethylenediaminetetra-acetic acid were used as the chelating agents. He found that the addition of these salts increased the separation factor for rare-earth mixtures in which the rare earth which formed the more stable chelate was the less extractable rare earth.

Schoenherr (8) obtained equilibrium data for mixtures of neodymium nitrate-nitric acid, samarium nitrate-nitric acid, and neodymium nitrate-samarium nitrate-nitric acid distributed between water and tributyl phosphate. He presented a method for predicting the equilibrium distribution of mixtures of neodymium nitrate, samarium nitrate, and nitric acid which utilized the equilibrium distribution and separation factor data obtained. A sample calculation was given to illustrate this method of predicting equilibria. He stated that equilibria for other rare-earth nitrate-nitric acid mixtures might also be predicted in a similar manner.

EXPERIMENTAL PROCEDURE

The purpose of this experimental work was to obtain equilibrium distribution data for the following systems: 1) dysprosium nitrate-nitric acid-tributyl phosphate-water, 2) erbium nitrate-nitric acid-tributyl phosphate-water, and 3) dysprosium nitrate-erbium nitrate-nitric acid-tributyl phosphate-water. The equilibrium data obtained for the first two systems were to be used in predicting the equilibrium distribution of solutes in the third system.

These distribution data were obtained by contacting an aqueous feed solution containing the desired solutes with an organic solvent, and performing a single stage extraction. The organic solvent, which was commercial grade tributyl phosphate (TBP), was equilibrated with water before being used in the extractions.

Stock solutions of dysprosium nitrate and erbium nitrate were prepared by dissolving the oxide of the rare earth in nitric acid. The solution was then brought to a boil in order to drive off the excess nitric acid, leaving the rare-earth nitrate in aqueous solution. These stock solutions were analyzed to determine the rare-earth nitrate content. Feed solutions to be used in the single stage extractions were then prepared by taking aliquots from the rare-earth nitrate stock solutions and adjusting the acid content to the desired level by adding a known amount of reagent grade nitric acid. These feed solutions of known composition and concentration were shaken together with the water equilibrated tributyl phosphate in sixty milliliter separatory funnels. Constant shaking for sixty seconds allowed a close approach to equilibrium, and the extractions were carried out at room temperature which was approximately 76° F. By varying the amounts of the different solutes in the feed solutions, it was possible to get equilibrium data which covered a range of compositions and concentrations for the three systems.

Once equilibrium was attained, the phases were separated and samples were taken from each phase in order to determine the equilibrium distribution of solutes. Two methods were used to analyze for the rare earths. The first method was a gravimetric determination in which the rare-earth nitrate was precipitated from solution using saturated oxalic acid. The rare-earth oxalate was then filtered and burned to the oxide at 900° C. The second method used to determine the rare-earth concentration was a chelometric titration using arsenazo as the indicator. Nitric acid content was determined by complexing the rare-earth nitrate with potassium ferrocyanide and then titrating for the remaining acid with sodium hydroxide. Before analyzing the organic phase samples, it was necessary to strip the solutes from the tributyl phosphate using water.

EXPERIMENTAL RESULTS

Equilibrium data obtained for the dysprosium nitrate-nitric acid-TBP-water system and the erbium nitrate-nitric acid-TBP-water system are presented in Table 1 and Table 2. The rare-earth nitrate molalities and nitric acid molalities referred to throughout this report are given in terms of the common nitrate ion concentration. In other words, a solution of one molal rare-earth nitrate concentration would be three molal in nitrate ion concentration. In this manner, the concentration of all solutes could be expressed on the same basis. The nomenclature section should be consulted for an explanation of the symbols which are used.

Using the equilibrium data from Table 1 and Table 2, two types of plots were constructed. In both types, total molality of the aqueous phase was used as a parameter. The first type was a plot of the total distribution coefficient versus the rare-earth nitrate composition. These plots are presented in Figure 1 for the dysprosium nitrate-nitric acid-TBP-water system, and in Figure 2 for the erbium nitrate-nitric acid-TBP-water system. The second type was a plot of the nitric acid distribution coefficient versus the rare-earth nitrate composition. These plots are presented in Figure 3 through Figure 9 for both sets of equilibrium data given in Table 1 and Table 2.

Equilibrium data obtained by Schoenherr (9) for the distribution of pure nitric acid between water-equilibrated TBP and water were plotted in Figure 10. Also presented in Figure 10 are curves of pure dysprosium nitrate distribution and pure erbium nitrate distribution.

The equilibrium data obtained from the extractions with the dysprosium nitrate-erbium nitrate-nitric acid-TBP-water system are given in Table 3. From these data, a plot of the separation factor between erbium and dysprosium versus the total molality of the aqueous phase was constructed as shown in Figure 11. The position of the straight line through these points was determined by a least squares analysis of the data.

The method of predicting equilibria for a dysprosium nitrate-erbium nitrate-nitric acid-TBP-water system used in this report enables the composition of an organic phase to be predicted which would be in equilibrium with an aqueous phase of known composition. Using this method for predicting equilibria, the composition of the organic phase was calculated for each of the ten extractions made with the dysprosium nitrate-erbium nitrate-nitric acid-TBP-water system. The results of these predictions, along with the per cent errors from the actual values given in Table 3, are presented in Table 4.

Table 1. Equilibrium distribution data for the dysprosium nitrate-nitric acid-tributyl phosphate-water system

Run number	Aqueous phase concentrations in molalities			Organic phase concentrations in molalities			Distribution coefficients	
	m_{Dy}	m_{HNO_3}	m_T	m_{Dy}	m_{HNO_3}	m_T	K_T	K_{HNO_3}
1	1.829	1.961	3.790	0.870	1.530	2.400	0.633	0.780
2	3.535	1.718	5.253	1.756	1.238	2.994	0.570	0.721
3	0.342	2.297	2.639	0.109	1.696	1.805	0.684	0.738
4	0.814	1.836	2.650	0.293	1.476	1.769	0.668	0.804
5	1.527	1.087	2.614	0.684	1.101	1.785	0.683	1.013
6	2.184	0.523	2.707	1.213	0.633	1.846	0.682	1.210
7	2.590	0.198	2.788	1.633	0.269	1.902	0.682	1.359
8	0.424	3.068	3.492	0.184	2.023	2.207	0.632	0.659
9	1.025	2.416	3.441	0.457	1.725	2.132	0.634	0.714
10	2.029	1.370	3.399	0.992	1.203	2.195	0.646	0.878
11	2.792	0.444	3.236	1.730	0.521	2.251	0.696	1.173
12	3.236	0.228	3.464	2.219	0.249	2.458	0.712	1.092
13	0.545	6.222	6.767	0.305	2.849	3.154	0.466	0.458
14	1.348	3.971	5.319	0.673	2.193	2.866	0.539	0.552
15	2.774	2.544	5.318	1.301	1.656	2.957	0.556	0.651

Table 1 (continued)

Run number	Aqueous phase concentrations in molalities			Organic phase concentrations in molalities			Distribution coefficients	
	m_{Dy}	m_{HNO_3}	m_T	m_{Dy}	m_{HNO_3}	m_T	K_T	K_{HNO_3}
16	0.685	7.200	7.885	0.395	2.942	3.337	0.423	0.409
17	1.936	5.835	7.771	0.889	2.660	3.549	0.457	0.456
18	4.187	3.733	7.920	1.576	1.994	3.570	0.451	0.534
19	6.531	1.385	7.916	2.369	0.930	3.299	0.417	0.671
20	7.685	0.539	8.224	2.924	0.390	3.314	0.403	0.724
21	0.958	10.016	10.974	0.612	3.378	3.990	0.364	0.337
22	2.880	8.121	11.001	1.140	2.906	4.046	0.368	0.358
23	5.491	7.431	12.922	1.676	2.776	4.452	0.345	0.374
24	4.218	1.063	5.281	2.073	0.863	2.936	0.556	0.812
25	4.829	0.457	5.286	2.650	0.355	3.005	0.568	0.777
26	8.818	2.211	11.029	2.460	1.401	3.861	0.350	0.634
27	10.581	0.887	11.468	3.032	0.686	3.718	0.324	0.773
28	1.127	14.340	15.467	0.935	3.791	4.726	0.306	0.264
29	3.715	11.507	15.222	1.520	3.312	4.832	0.317	0.288

Table 1 (continued)

Run number	Aqueous phase concentrations in molalities			Organic phase concentrations in molalities			Distribution coefficients	
	m_{Dy}	m_{HNO_3}	m_T	m_{Dy}	m_{HNO_3}	m_T	K_T	K_{HNO_3}
30	8.355	7.357	15.712	2.029	2.775	4.804	0.306	0.377
31	11.411	3.269	14.680	2.504	2.019	4.523	0.308	0.618
32	12.649	1.308	13.957	3.014	1.074	4.088	0.293	0.821
33	0.867	11.298	12.165	0.896	3.766	4.662	0.383	0.333
34	3.412	11.024	14.436	1.470	3.341	4.811	0.333	0.303
35	1.204	16.627	17.831	1.178	3.730	4.908	0.275	0.224
36	4.139	13.686	17.825	1.750	3.638	5.388	0.302	0.266
37	2.699	21.039	23.738	1.899	4.510	6.409	0.270	0.214

Table 2. Equilibrium distribution data for the erbium nitrate-nitric acid-tributyl phosphate-water system

Run number	Aqueous phase concentrations in molalities			Organic phase concentrations in molalities			Distribution coefficients	
	m_{Dy}	m_{HNO_3}	m_T	m_{Dy}	m_{HNO_3}	m_T	K_T	K_{HNO_3}
1	0.391	1.418	1.809	0.0669	1.249	1.316	0.727	0.881
2	1.035	1.691	2.726	0.303	1.527	1.830	0.671	0.903
3	1.661	1.100	2.761	0.558	1.199	1.757	0.636	1.090
4	2.133	0.352	2.485	1.044	0.541	1.585	0.638	1.537
5	2.489	0.108	2.597	1.599	0.195	1.794	0.691	1.806
6	0.488	1.993	2.481	0.119	1.588	1.707	0.688	0.797
7	1.393	1.403	2.796	0.456	1.295	1.751	0.626	0.923
8	2.106	1.613	3.719	0.902	1.456	2.358	0.634	0.903
9	2.865	0.864	3.729	1.389	0.984	2.373	0.636	1.139
10	3.363	0.319	3.682	2.107	0.426	2.533	0.688	1.335
11	0.554	4.719	5.273	0.261	2.538	2.799	0.531	0.538
12	1.668	3.476	5.144	0.703	2.127	2.830	0.550	0.612
13	2.886	2.869	5.755	1.171	1.844	3.015	0.524	0.643
14	4.094	1.255	5.349	1.837	1.124	2.961	0.554	0.896
15	4.823	0.447	5.270	2.490	0.428	2.918	0.554	0.957

Table 2 (continued)

Run number	Aqueous phase concentrations in molalities			Organic phase concentrations in molalities			Distribution coefficients	
	m_{Dy}	m_{HNO_3}	m_T	m_{Dy}	m_{HNO_3}	m_T	K_T	K_{HNO_3}
16	0.689	6.991	7.680	0.441	3.011	3.452	0.449	0.431
17	2.339	5.335	7.674	1.015	2.465	3.480	0.453	0.462
18	4.084	3.655	7.739	1.493	1.977	3.470	0.448	0.541
19	5.900	1.984	7.884	2.053	1.388	3.441	0.436	0.700
20	7.460	0.658	8.118	2.854	0.514	3.368	0.415	0.781
21	1.046	14.318	15.364	1.030	3.786	4.816	0.313	0.264
22	4.563	10.623	15.186	1.981	2.956	4.937	0.325	0.278
23	8.255	7.254	15.509	2.011	2.914	4.925	0.318	0.402
24	11.789	4.310	16.099	2.417	1.989	4.406	0.274	0.461
25	13.923	1.288	15.211	3.000	1.119	4.119	0.271	0.869
26	0.980	10.439	11.419	0.608	3.568	4.176	0.366	0.342
27	3.316	7.517	10.833	1.261	2.808	4.069	0.376	0.374
28	5.892	5.143	11.035	1.726	2.317	4.043	0.366	0.451
29	8.395	2.680	11.075	2.249	1.734	3.983	0.360	0.647
30	10.634	0.842	11.476	2.997	0.756	3.753	0.327	0.898

Table 3. Equilibrium distribution data for the dysprosium nitrate-erbium nitrate-nitric acid-tributyl phosphate-water system

Run number	Aqueous phase concentrations in molalities				Organic phase concentrations in molalities				Distribution coefficients		Separation factor
	m_{Dy}	m_{Er}	m_{HNO_3}	m_T	m_{Dy}	m_{Er}	m_{HNO_3}	m_T	K_T	K_{HNO_3}	β_{Er-Dy}
1	1.939	1.478	1.869	5.286	0.918	0.592	1.411	2.921	0.553	0.755	0.848
2	1.372	1.974	3.027	6.373	0.600	0.775	1.906	3.281	0.515	0.630	0.899
3	2.703	2.122	3.382	8.207	0.915	0.779	1.945	3.639	0.443	0.575	1.083
4	2.908	4.456	3.212	10.576	0.801	1.253	1.828	3.882	0.367	0.569	1.023
5	4.953	4.605	3.162	12.720	1.101	1.202	1.892	4.195	0.330	0.598	1.176
6	1.414	1.992	1.819	5.225	0.683	0.836	1.314	2.833	0.542	0.722	0.870
7	2.008	1.378	2.953	6.339	0.890	0.531	1.741	3.162	0.499	0.590	0.869
8	2.216	2.609	3.355	8.180	0.749	0.876	1.820	3.445	0.421	0.542	0.994
9	4.481	2.889	3.172	10.542	1.217	0.833	1.755	3.805	0.361	0.553	1.059
10	6.254	3.313	3.156	12.723	1.449	0.847	1.821	4.117	0.324	0.577	1.103

Table 4. Predicted equilibrium data for the dysprosium nitrate-erbium nitrate-nitric acid-tributyl phosphate-water system and per cent errors from actual values

Run number	1	2	3	4	5	6	7	8	9	10
K_T	0.555	0.506	0.450	0.382	0.335	0.558	0.510	0.449	0.383	0.334
% error	+0.36	-1.74	+1.58	+4.09	+1.52	+ 2.95	+2.20	+6.65	+6.09	+3.09
m_T (org.)	2.94	3.22	3.69	4.04	4.26	2.92	3.23	3.67	4.04	4.25
% error	+0.68	-1.83	+1.37	+4.12	+1.43	+ 3.18	+2.22	+6.38	+6.04	+3.15
K_{HNO_3}	0.770	0.620	0.580	0.582	0.581	0.799	0.621	0.577	0.575	0.579
% error	+1.99	-1.59	+0.87	+2.28	-2.84	+10.66	+5.25	+6.46	+3.98	+0.35
m_{HNO_3} (org.)	1.91	1.88	1.96	1.87	1.84	1.45	1.83	1.94	1.82	1.83
% error	+2.14	-1.57	+0.51	+2.19	-2.65	+10.69	+5.17	+6.59	+3.41	+0.55
m_{Dy} (org.)	0.901	0.580	0.954	0.838	1.07	0.662	0.861	0.812	1.33	1.52
% error	-1.35	-3.30	+4.26	+4.62	-2.73	- 3.07	-2.92	+8.41	+9.02	+4.83
m_{Er} (org.)	0.599	0.760	0.726	1.33	1.10	0.808	0.536	0.918	0.890	0.900
% error	+1.18	-1.94	-6.80	+6.40	-8.33	- 3.35	+0.94	+4.79	+6.84	+6.25

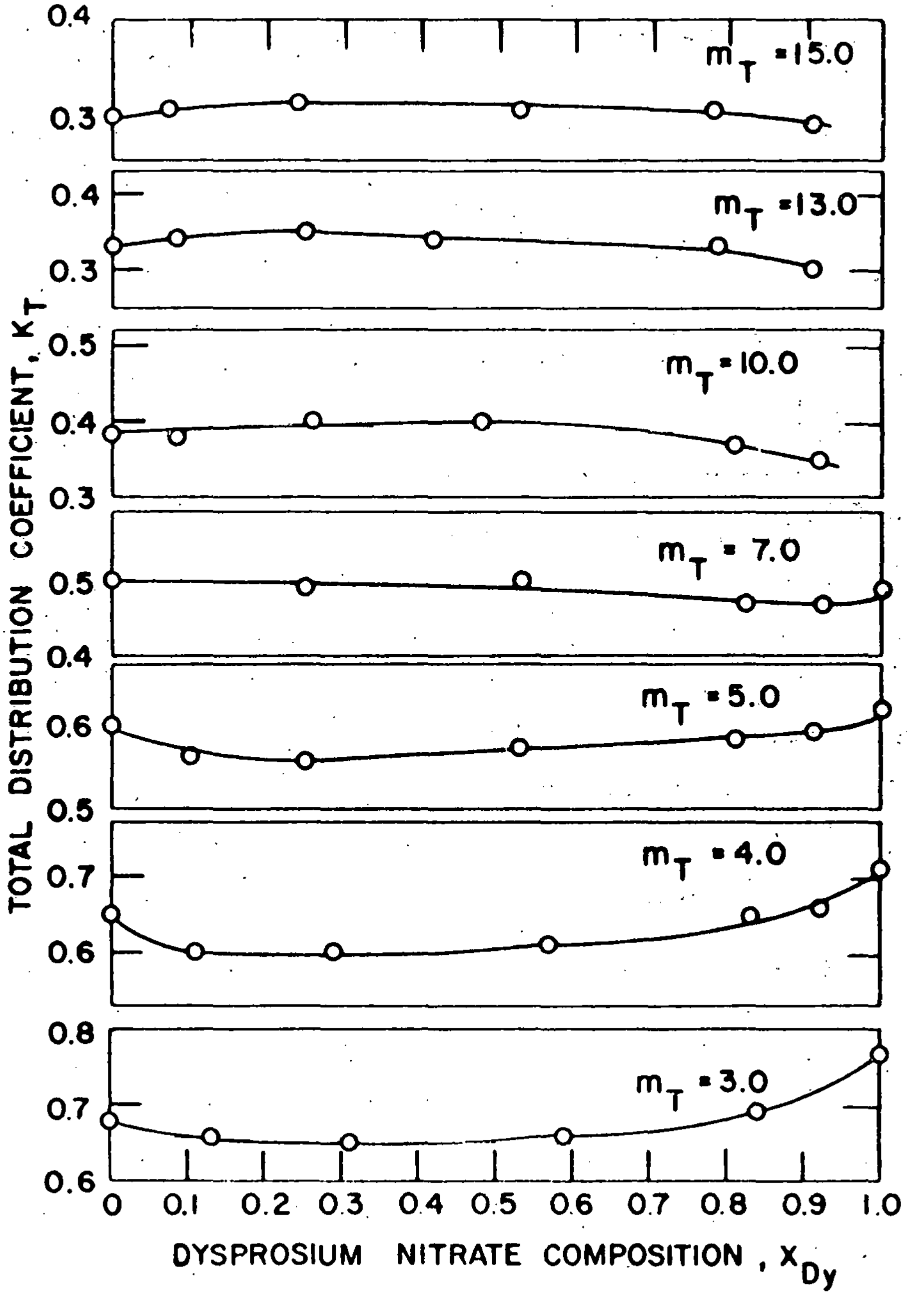


Figure 1. Total distribution coefficient for dysprosium nitrate-nitric acid mixtures as a function of the composition and concentration of the aqueous phase

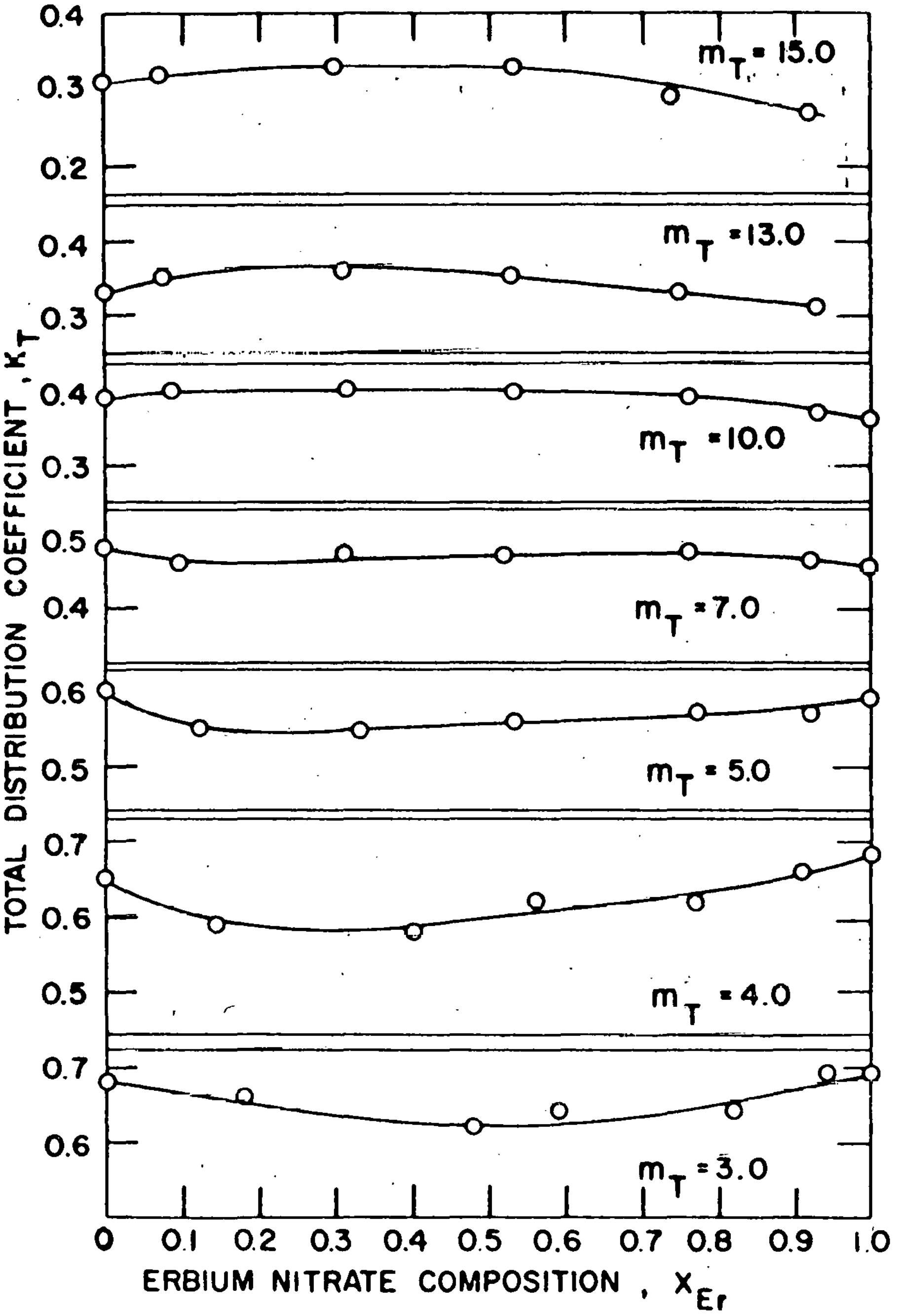


Figure 2. Total distribution coefficient for erbium nitrate-nitric acid mixtures as a function of the composition and concentration of the aqueous phase

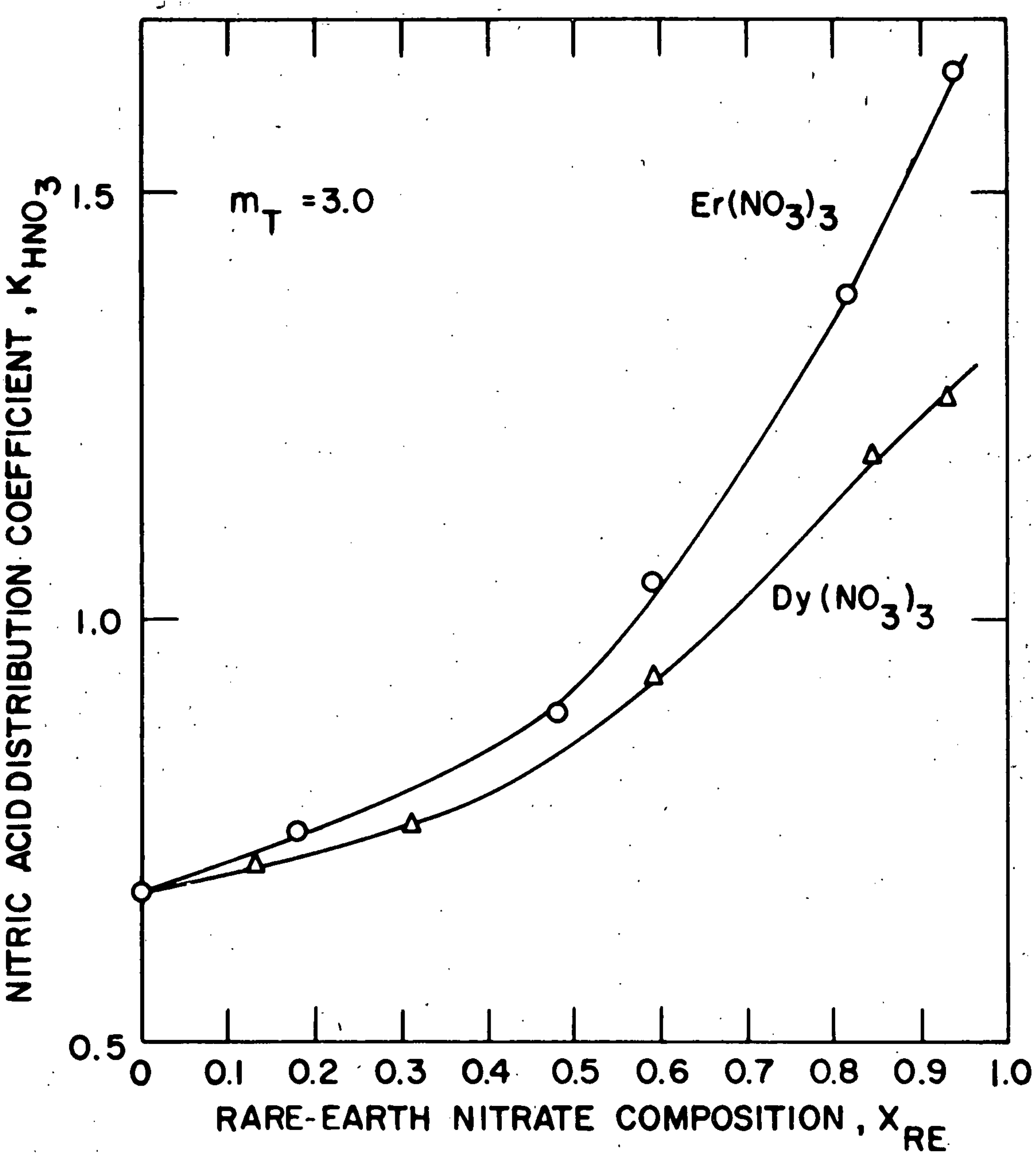


Figure 3. Nitric acid distribution coefficient for dysprosium nitrate-nitric acid and erbium nitrate-nitric acid mixtures as a function of the composition of the aqueous phase at m_T (aq.) equal to 3.0

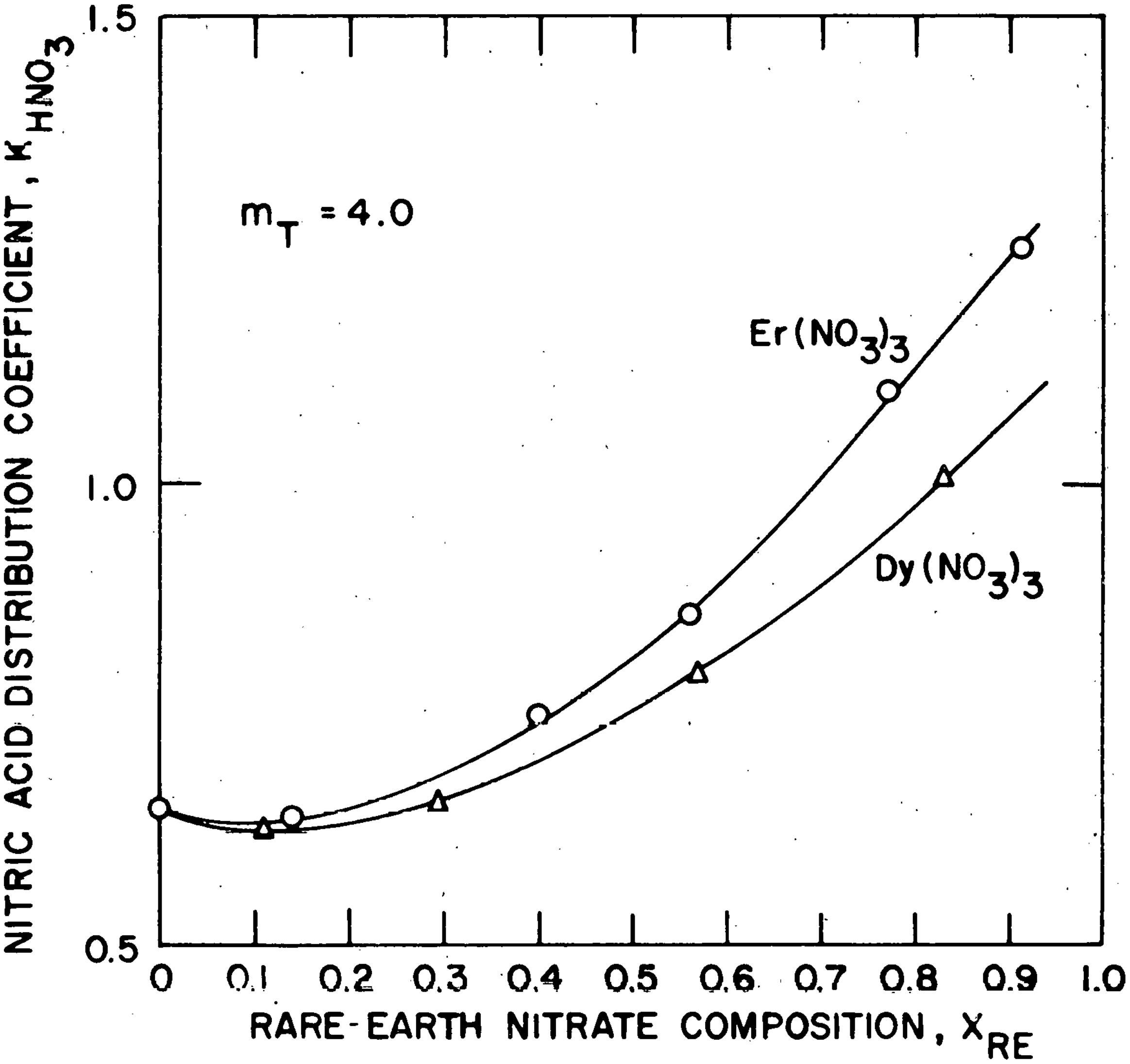


Figure 4. Nitric acid distribution coefficient for dysprosium nitrate-nitric acid and erbium nitrate-nitric acid mixtures as a function of the composition of the aqueous phase at m_T (aq.) equal to 4.0

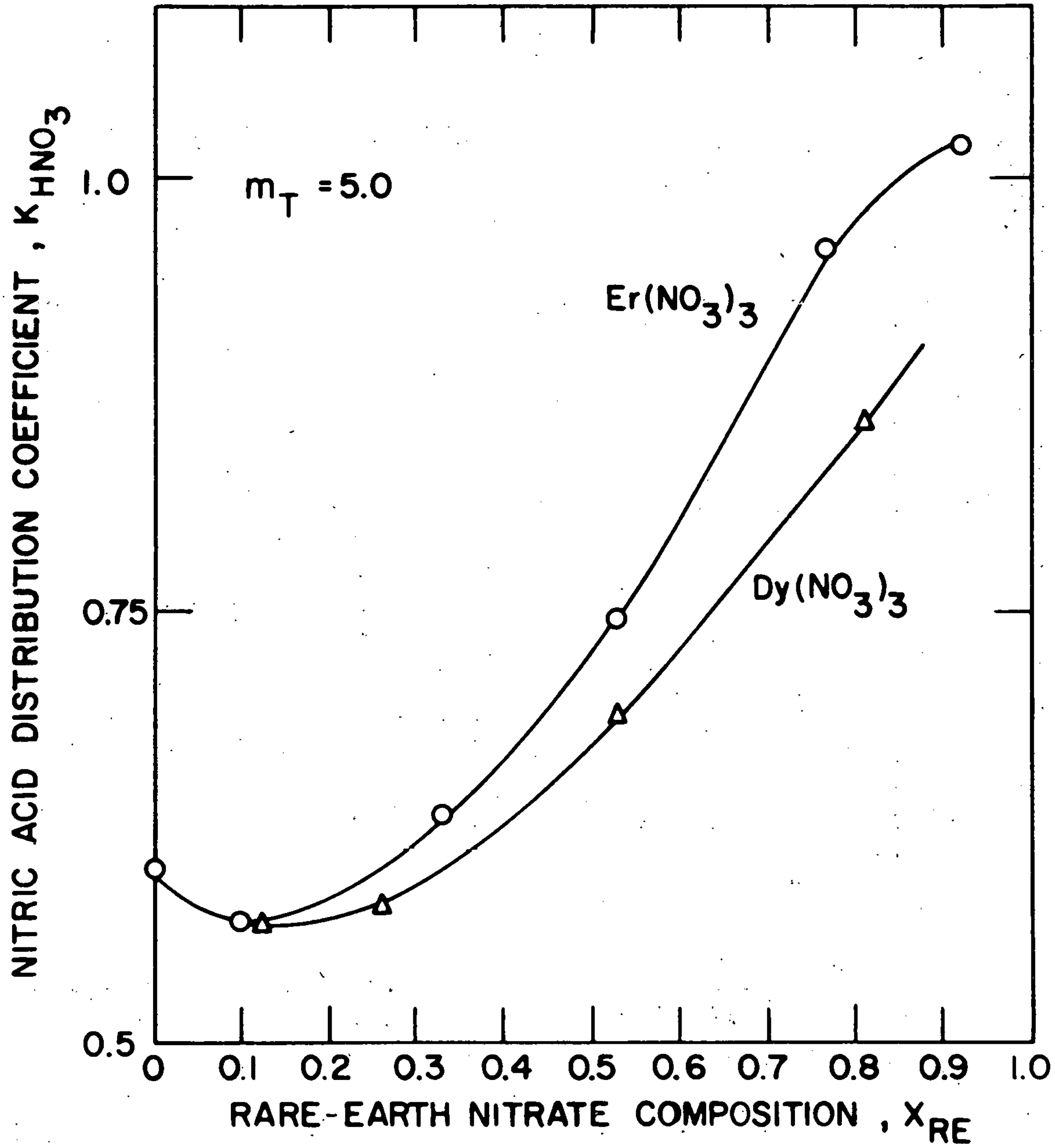


Figure 5. Nitric acid distribution coefficient for dysprosium nitrate-nitric acid and erbium nitrate-nitric acid mixtures as a function of the composition of the aqueous phase at m_T (aq.) equal to 5.0

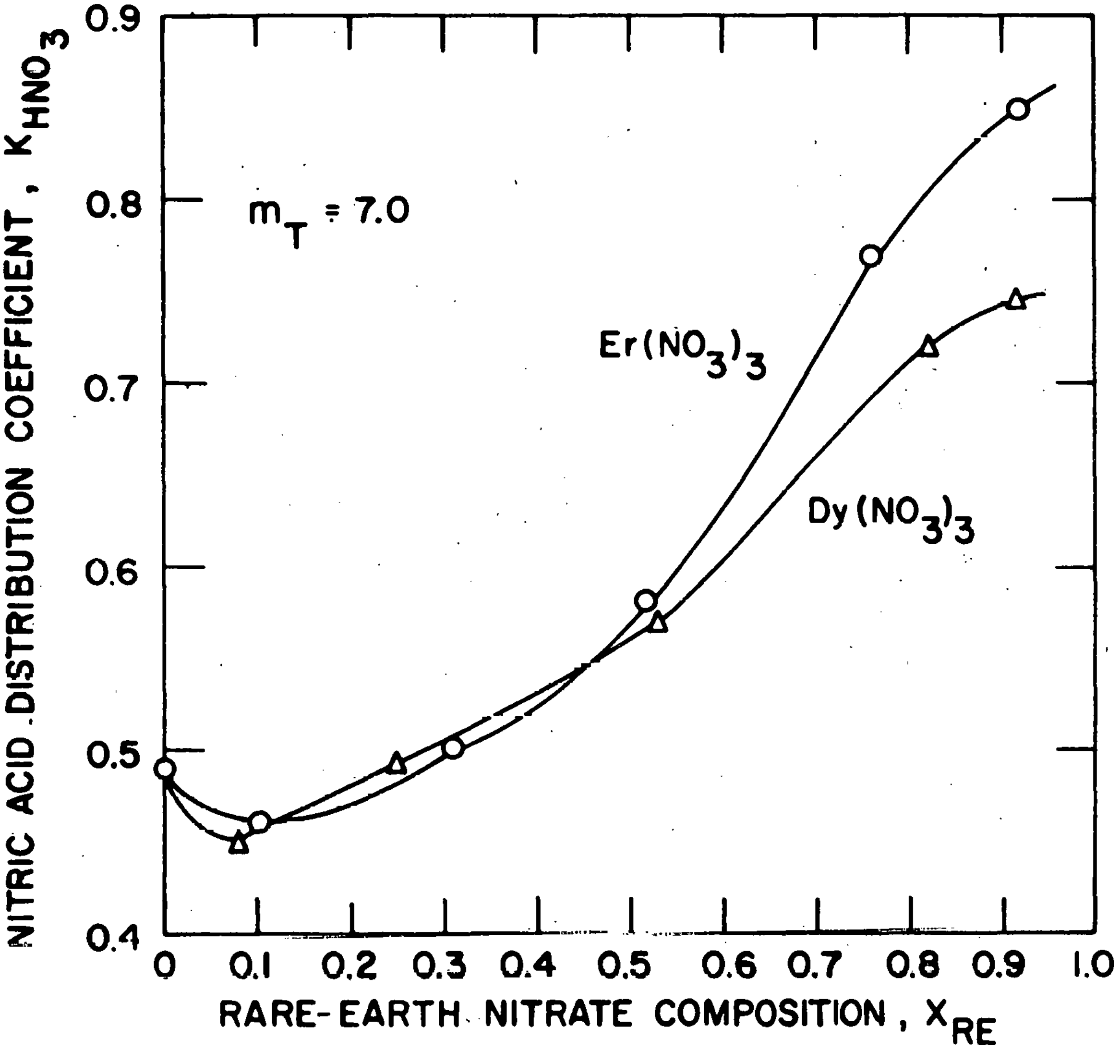
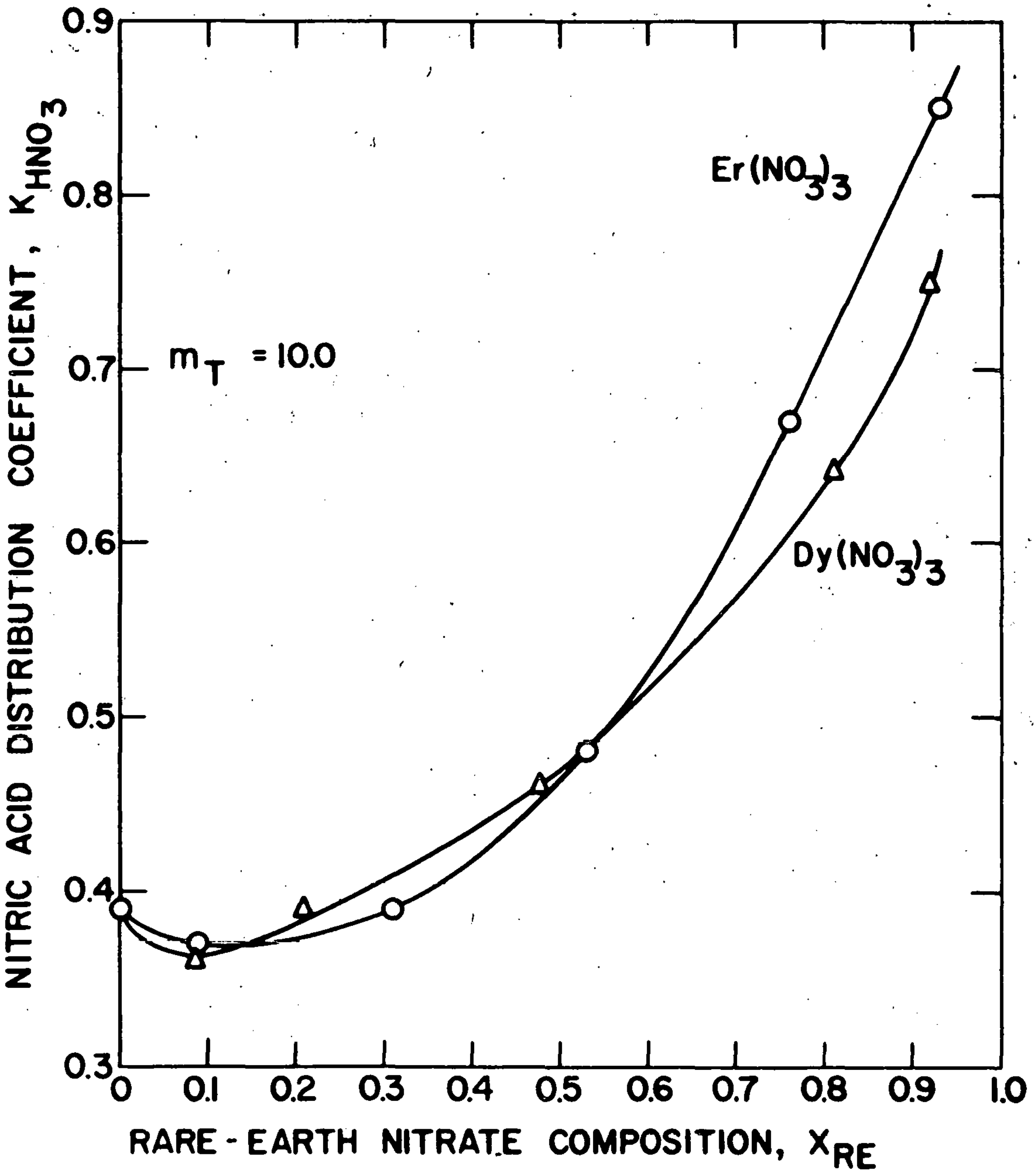


Figure 6. Nitric acid distribution coefficient for dysprosium nitrate-nitric acid and erbium nitrate-nitric acid mixtures as a function of the composition of the aqueous phase at m_T (aq.) equal to 7.0

Figure 7. Nitric acid distribution coefficient for dysprosium nitrate-nitric acid and erbium nitrate-nitric acid mixtures as a function of the composition of the aqueous phase at m_T (aq.) equal to 10.0



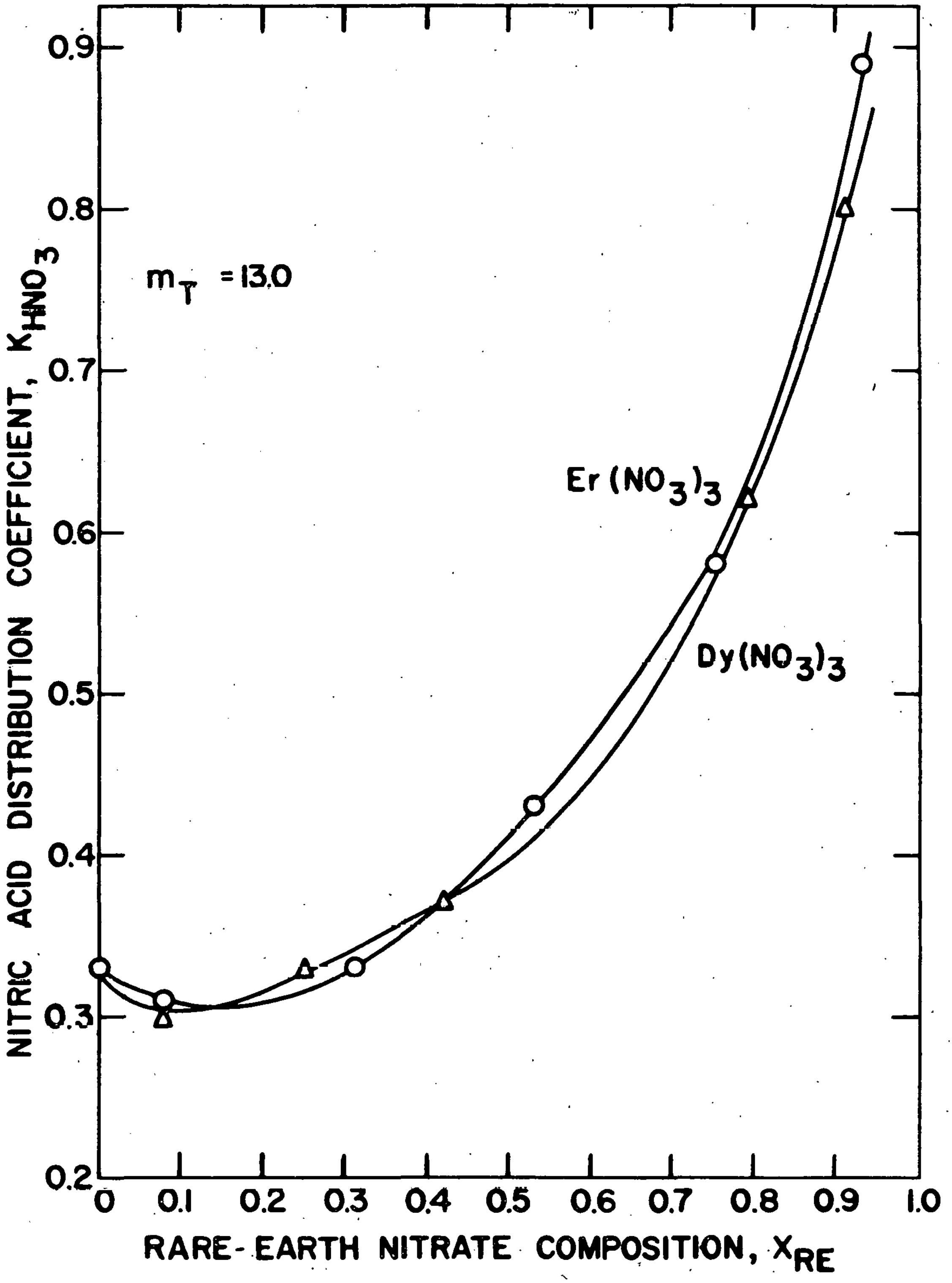


Figure 8. Nitric acid distribution coefficient for dysprosium nitrate-nitric acid and erbium nitrate-nitric acid mixtures as a function of the composition of the aqueous phase m_T (aq.) equal to 13.0

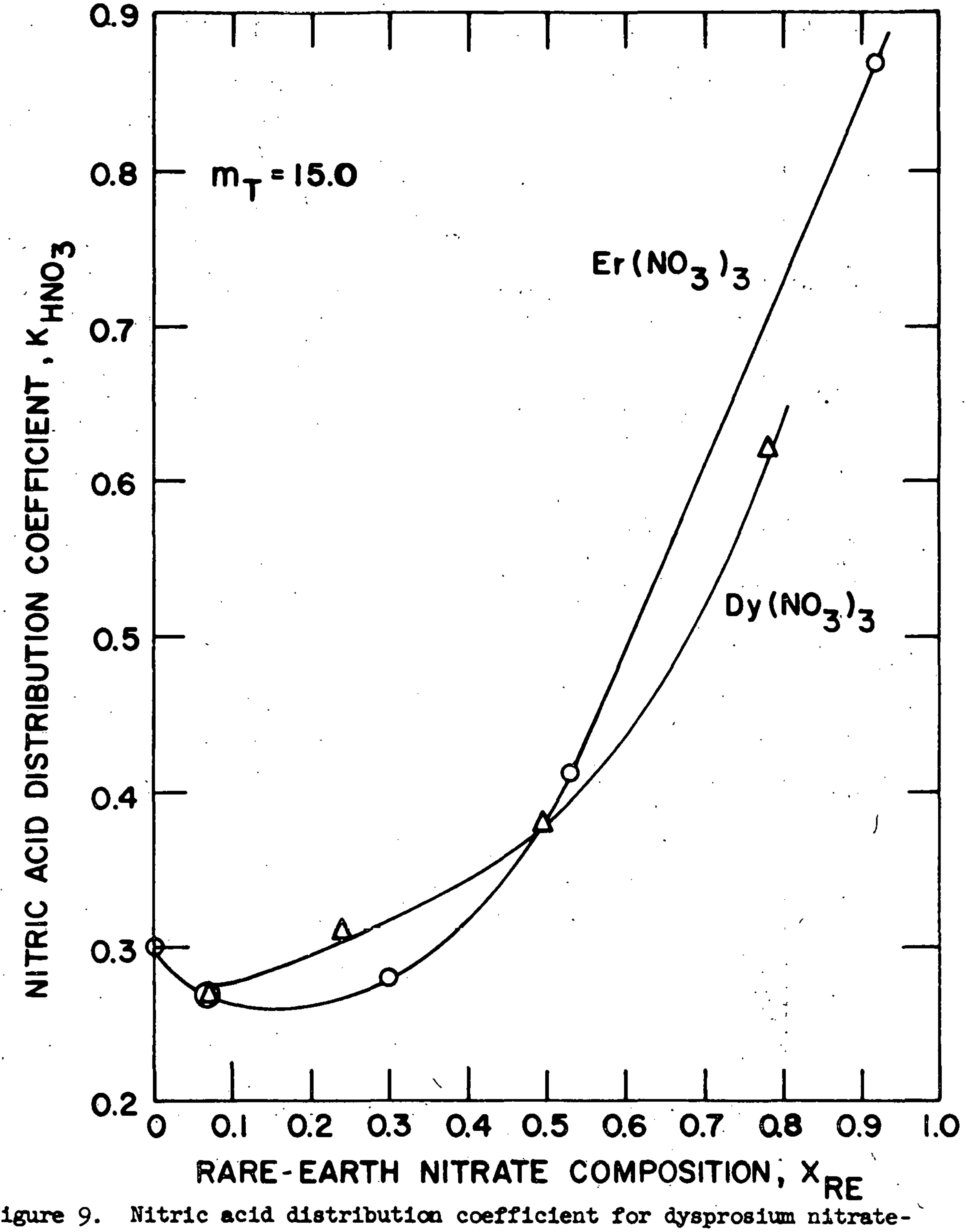


Figure 9. Nitric acid distribution coefficient for dysprosium nitrate-nitric acid and erbium nitrate-nitric acid mixtures as a function of the composition of the aqueous phase at m_T (aq.) equal to 15.0

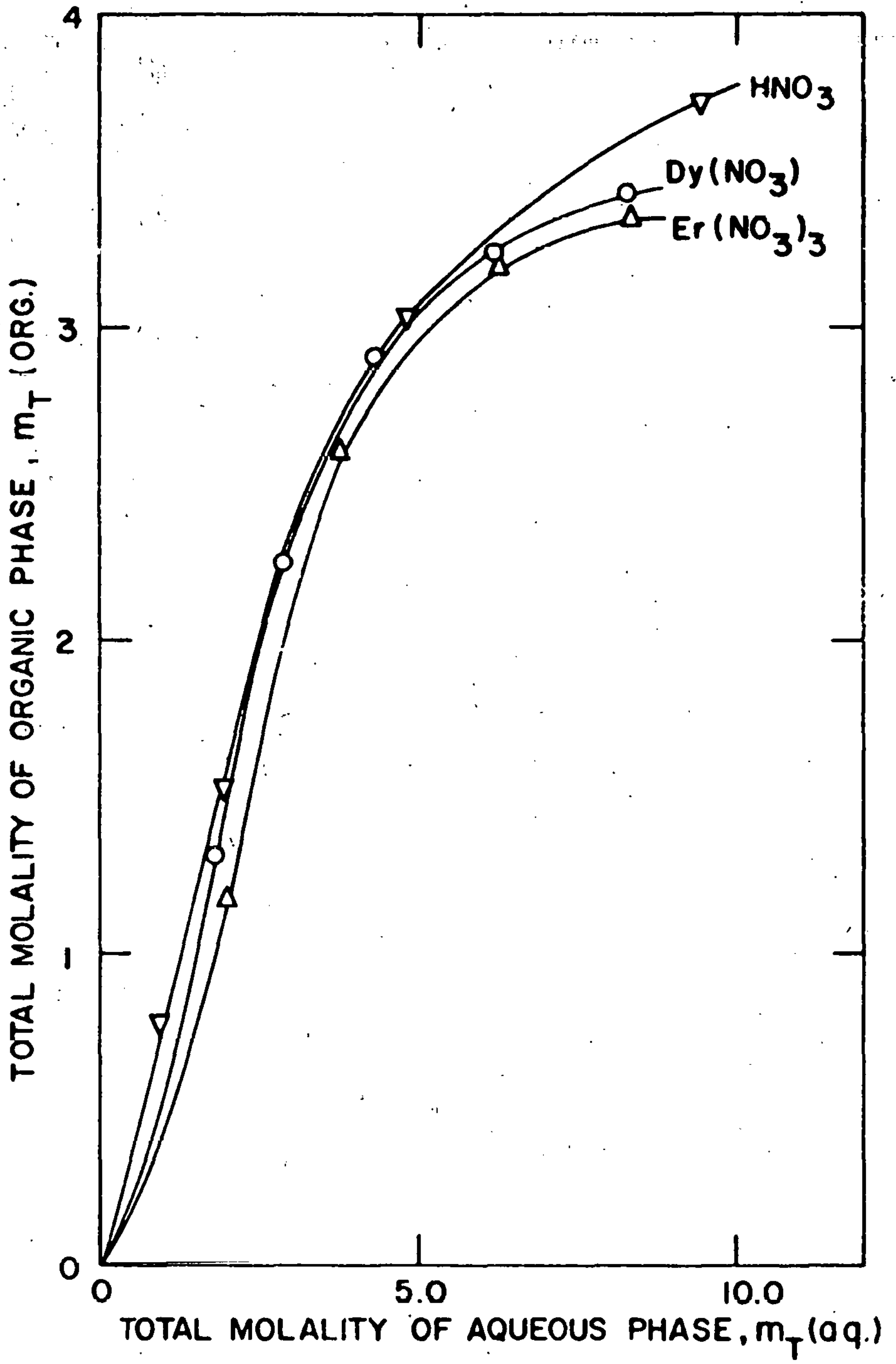


Figure 10. Equilibrium distribution curves for pure nitric acid, pure dysprosium nitrate, and pure erbium nitrate

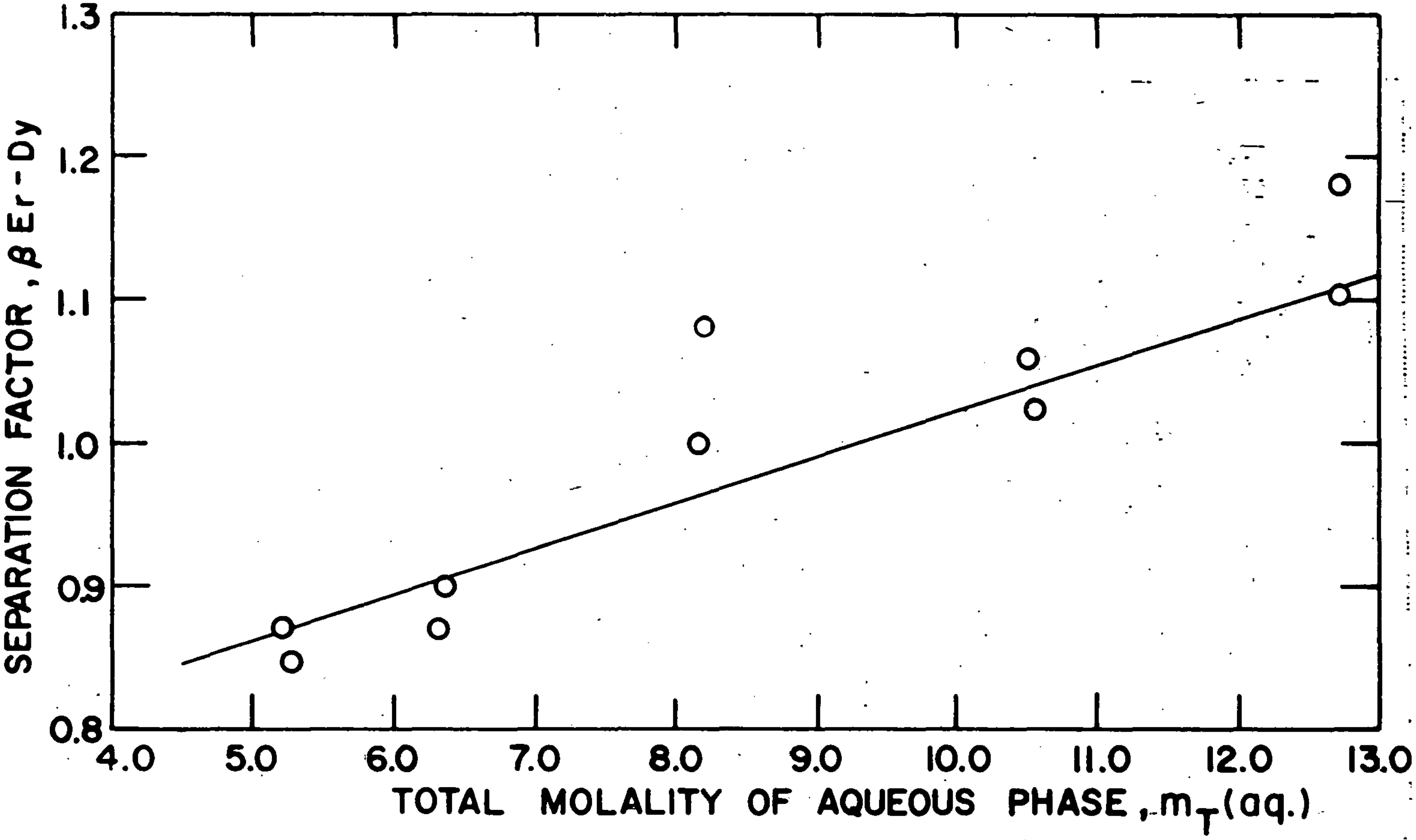


Figure 11. Separation factor between erbium nitrate and dysprosium nitrate for the dysprosium nitrate-erbium nitrate-nitric acid-TBP-water system as a function of the total concentration of the aqueous phase

DISCUSSION OF RESULTS

Equilibrium Data

The equilibrium data presented in Tables 1, 2, and 3 were obtained from a total of seventy-eight single stage extractions made with the dysprosium nitrate-nitric acid-TBP-water system, the erbium nitrate-nitric acid-TBP-water system, and the dysprosium nitrate-erbium nitrate-nitric acid-TBP-water system. For each of these extractions the distribution data were achieved by making a triplicate analysis to determine the concentration of each solute in both phases. In this manner the precision for all analyses was checked, and since the total feed of solutes to each single stage extraction was known, it was possible to check the accuracy of the distribution data for each extraction by making material balances over both phases for each solute present. Material balances for the rare-earth nitrates present usually gave less than two per cent error. The material balances for the nitric acid present usually gave less than four per cent error. The greater error in the nitric acid material balances was due to the analysis for nitric acid which was not quite as precise nor accurate as the rare-earth determination. By checking the distribution data from all extractions, it was possible to discard the data from any extractions which gave unreasonable results.

Correlation of Equilibrium Data

A distribution coefficient is defined as the concentration of a solute in the organic phase divided by the concentration of the same solute in the aqueous phase. It follows that the total distribution coefficient would be the total concentration of the organic phase divided by the total concentration of the aqueous phase.

The relationships of total distribution coefficient versus rare-earth nitrate composition shown in Figure 1 and Figure 2 were obtained by linearly interpolating between equilibrium data of approximately the same composition, X_{RE}, and concentration, m_T (aq.). A hypothetical example of this linear interpolation between equilibrium data for two extractions is given below.

	Extraction 1	Interpolated values	Extraction 2
m_T (aq.)	2.80	3.00	3.20
X_{Dy}	0.09	0.10	0.11
K_T	0.65	0.66	0.67
K_{HNO_3}	0.35	0.40	0.45

Using this method of interpolation it was possible to obtain curves having as a parameter the total molality of the aqueous phase. Correlations of this type enabled the total distribution coefficient to be predicted for mixtures of rare-earth nitrates and nitric acid, if the concentrations of solutes in the aqueous phase were known.

As the rare-earth nitrate compositions approach zero in Figure 1 and Figure 2, the total distribution coefficient becomes the distribution of pure nitric acid at the same total molality of the aqueous phase. This nitric acid distribution coefficient was calculated from the pure nitric acid distribution curve shown in Figure 10. In a similar manner, as the rare-earth nitrate compositions approach one, the total distribution coefficient becomes that of the pure rare-earth nitrate. The distribution coefficients for pure dysprosium nitrate and erbium nitrate at any total molality of the aqueous phase were also calculated by use of Figure 10.

The relationships of nitric acid distribution coefficient versus rare-earth nitrate composition as shown in Figure 3 through Figure 9 were obtained in an identical manner to that described above for Figure 1 and Figure 2. These correlations were used to predict the nitric acid distribution coefficient in mixtures of rare-earth nitrates and nitric acid, when the concentrations of all solutes in the aqueous phase were known.

The separation factor between two solutes is the distribution coefficient of one solute divided by the distribution coefficient of the other solute. It was found by Schoenherr (8) that the separation factor for neodymium with respect to samarium, called the metal separation factor, for the neodymium nitrate-samarium nitrate-nitric acid-TBP-water system was primarily independent of composition and seemed to depend only on the total molality. This would indicate that a straight line relation would be obtained by plotting the metal separation factor versus total molality of the aqueous phase. A plot of this type is shown in Figure 11 for the dysprosium nitrate-erbium nitrate-nitric acid-TBP-water system. Although there was a good deal of scatter present, justification for drawing a straight line through these points seemed reasonable due to the fact that metal separation factors taken from Figure 11 gave satisfactory results when used for predicting equilibria. It should also be noted that the scatter has been somewhat magnified due to the enlargement of the ordinate scale.

Prediction of Equilibria

Although the equilibrium data obtained for the dysprosium nitrate, nitric acid distribution and the erbium nitrate, nitric acid distribution could have been correlated in such a manner as to be able to predict the equilibria that would be attained when a certain aqueous feed solution containing dysprosium nitrate, erbium nitrate, and nitric acid was brought in contact with a solute free amount of TBP, it was thought that a more useful form of predicting equilibria would be one which enabled the composition of an organic phase to be predicted which would be in equilibrium with an aqueous phase of known composition. The prediction method, which is described here, seemed more appropriate in this form since it would facilitate the making of stagewise calculations in solvent extraction theory.

Suppose that an aqueous phase was given containing the solutes dysprosium nitrate, erbium nitrate and nitric acid, and it was known that this aqueous phase was in equilibrium with an organic phase consisting of the same three solutes dissolved in TBP. The concentration of each solute in the aqueous phase was known, but solute concentrations in the organic phase were unknown.

The first step in predicting equilibria would be to determine the total distribution coefficient, K_T. Assuming that all rare-earth nitrates present in the aqueous phase were dysprosium nitrate, a total distribution coefficient would be calculated from Figure 1 by a linear interpolation between curves of constant aqueous phase molality. Then assuming that all rare-earth nitrates present in the aqueous were erbium nitrate, a second total distribution coefficient would be calculated from Figure 2 in a similar manner. The actual total distribution coefficient for the mixture would then be calculated by a linear interpolation between the above two coefficients according to the fraction (x_{Dy} and x_{Er}) of each rare-earth nitrate present. Knowing the total distribution coefficient, it would be possible to calculate the total molality of the organic phase from the following equation:

$$m_T(\text{org.}) = K_T \times m_T(\text{aq.}) \ . \qquad (1)$$

The nitric acid distribution coefficient would be found in the following manner. Assuming that all rare-earth nitrates present were dysprosium nitrate, a nitric acid distribution coefficient would be calculated using the correlations shown in Figure 3 through Figure 9 by linearly interpolating between appropriate curves at constant aqueous phase molalities. Next assuming that all rare-earth nitrates present were erbium nitrate, the same procedure would be used to get a second nitric acid distribution coefficient. The actual nitric acid distribution coefficient for the mixture would then be calculated by a linear interpolation between these two coefficients according to the fraction (x_{Dy} and x_{Er}) of each rare-earth nitrate present. Using the nitric acid distribution coefficient, the molality of nitric acid in the organic phase would be found from the following equation:

$$m_{HNO_3}(\text{org.}) = K_{HNO_3} \times m_{HNO_3}(\text{aq.}) . \qquad (2)$$

The separation factor between erbium and dysprosium was obtained from Figure 11 at the known total molality of the aqueous phase. Using the equation which defines a separation factor, a relation was derived for the remaining two unknowns, $m_{Dy}(\text{org.})$ and $m_{Er}(\text{org.})$. That is:

$$\beta_{Er\text{-}Dy} \equiv \frac{K_{Er}}{K_{Dy}} = \frac{m_{Er}(\text{org.})}{m_{Er}(\text{aq.})} \div \frac{m_{Dy}(\text{org.})}{m_{Dy}(\text{aq.})} ; \qquad (3)$$

and by rearranging

$$\frac{m_{Er}(\text{org.})}{m_{Dy}(\text{org.})} = \beta_{Er\text{-}Dy} \times \frac{m_{Er}(\text{aq.})}{m_{Dy}(\text{aq.})} . \qquad (4)$$

A second expression relating the two remaining unknowns was the equation for total molality of the organic phase. That is:

$$m_T(\text{org.}) = m_{HNO_3}(\text{org.}) + m_{Dy}(\text{org.}) + m_{Er}(\text{org.}). \qquad (5)$$

Since all values in Equation 4 and Equation 5 would be known except the molalities of erbium nitrate and dysprosium nitrate in the organic phase, it would be possible to solve these two equations simultaneously, thereby completing the prediction for the concentration of all solutes in the organic phase.

Sample Calculation

A sample calculation is now shown to illustrate the equilibrium prediction method described above. Numerical values for this sample calculation were taken from the equilibrium data for extraction number 1 in Table 3.

Suppose an aqueous phase was known which had the following concentrations of solutes:

$$m_{HNO_3} = 1.87 \text{ molal} ;$$
$$m_{Dy} = 1.94 \text{ " } ;$$
$$m_{Er} = 1.48 \text{ " } .$$

From this data x_{Dy}, x_{Er}, and X_{RE} were then calculated. That is:

$$x_{Dy} = \frac{m_{Dy}(aq.)}{m_{Dy}(aq.) + m_{Er}(aq.)} = \frac{1.94}{1.94 + 1.48} - 0.567 ;$$

$$x_{Er} = 1 - x_{Dy} = 1 - 0.567 = 0.433 ;$$

$$X_{RE} = \frac{m_{Dy}(aq.) + m_{Er}(aq.)}{m_T(aq.)} = \frac{1.94 + 1.48}{5.29} = 0.647 .$$

Next the total distribution coefficient was found using the method described earlier in this section. The result obtained was

$$K_T = 0.555 .$$

This value for K_T compared very favorably with the value of 0.553 obtained from actual analysis.

The total molality of the organic phase was calculated by

Equation 1 as

$$m_T(\text{org.}) = 0.55 \times 5.29 ;$$
$$m_T(\text{org.}) = 2.94 \quad .$$

The actual value for total molality of the aqueous phase was equal to 2.92.

The nitric acid distribution coefficient was found using the method described earlier in this section. The result obtained was

$$K_{HNO_3} = 0.770 .$$

The actual value for the nitric acid distribution coefficient was equal to 0.755. The molality of nitric acid in the organic phase was then calculated by Equation 2 as

$$m_{HNO_3}(\text{org.}) = 0.770 \times 1.87 ;$$
$$m_{HNO_3}(\text{org.}) = 1.44 \quad .$$

The actual value for molality of nitric acid in the organic phase was equal to 1.41.

The separation factor between erbium nitrate and dysprosium nitrate at a total molality of the aqueous phase equal to 5.29 was determined from Figure 11 as

$$\beta_{Er-Dy} = 0.872 .$$

This value was then substituted into Equation 4 to obtain

$$\frac{m_{Er}(\text{org.})}{m_{Dy}(\text{org.})} = 0.872 \times \frac{1.48}{1.94} ;$$

$$\frac{m_{Er}(\text{org.})}{m_{Dy}(\text{org.})} = 0.665 \quad . \tag{4a}$$

Also, by substituting into Equation 5 for total molality of the organic phase:

$$m_{Dy}(\text{org.}) + m_{Er}(\text{org.}) = 2.94 - 1.44 \; ;$$

$$m_{Dy}(\text{org.}) + m_{Er}(\text{org.}) = 1.50 \quad . \tag{5a}$$

Equation 4a and Equation 5a were then solved simultaneously to obtain

$$m_{Dy}(\text{org.}) = 0.901$$

and

$$m_{Er}(\text{org.}) = 0.599 \; .$$

These values were very close to the actual values of m_{Dy}(org.) equal to 0.918 and m_{Er}(org.) equal to 0.592 obtained from analysis.

Therefore, the concentration of each solute in the organic phase was predicted from a knowledge of the composition of the aqueous phase that was in equilibrium with this organic phase. The method of predicting equilibria used in this sample calculation is a modification of the method developed by Schoenherr (8) for predicting the equilibria of the neodymium nitrate-samarium nitrate-nitric acid-TBP-water system.

CONCLUSIONS

1. A modification of the method of predicting equilibria developed by Schoenherr (8) for the samarium nitrate-neodymium nitrate-nitric acid-TBP-water system can be used for the dysprosium nitrate-erbium nitrate-nitric acid-TBP-water system. Because these rare earths appear to be similar to all of the other rare earths, except cerium which can exist in aqueous solution in the tetravalent state, the general method should be successful in predicting equilibria for any cerium free rare-earth nitrate-nitric acid-TBP-water system.
2. The separation factor between erbium nitrate and dysprosium nitrate for the dysprosium nitrate-erbium nitrate-nitric acid-TBP-water system was found to be independent of composition and depends on total nitrate concentration only.
3. At low nitric acid concentrations, erbium nitrate is more extractable than dysprosium nitrate, and at high nitric acid concentrations dysprosium nitrate is more extractable than erbium nitrate. To separate the two by solvent extraction it would be necessary to keep the total molality of the aqueous phase well removed from a value of 9.40, because at this point the separation factor is equal to one.
4. The total distribution coefficients and the nitric acid distribution coefficients for dysprosium nitrate-erbium nitrate-nitric acid mixtures can be calculated using the equilibrium data obtained for dysprosium nitrate-nitric acid and erbium nitrate-nitric acid mixtures.

5. The distribution of pure dysprosium nitrate and of pure erbium nitrate closely approximate that of pure nitric acid.
6. The chelometric titration used to determine rare-earth nitrate concentration is considerably faster than the gravimetric rare-earth nitrate analysis, and also, both these methods of analysis give about the same precision and accuracy.

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APPENDIX: ANALYTICAL METHODS

Two methods were used for determining the rare-earth nitrate concentration. In the first method, an aliquot of sample was taken containing at least 0.1 gram of the rare-earth oxide. The sample was then diluted to 300 milliliters with water and brought to a boil on a hot plate. The rare earth was precipitated by adding 100 milliliters of a saturated oxalic acid solution. The precipitate was allowed to settle for 4 hours, and then it was filtered through No. 589 white ribbon paper. The filtrate was washed using a solution containing 20 milliliters of 70% by weight nitric acid solution and 10 grams of oxalic acid per liter of silution. The filtrate was then dried and burned to the oxide at 900° C. in a muffle furnace for 3 hours. The weight of rare-earth oxide present was obtained by difference.

The second method used to find rare-earth nitrate concentration was a chelometric titration developed by Fritz, _et al._ (5). An aliquot of sample was used which contained 0.25 to 1.0 millimole of the rare-earth element. The sample was then diluted to 100 milliliters with water. Ten drops of pyridine were added and the pH was adjusted between 5.5 and 6.5. Two drops of 0.5% by weight arsenazo indicator solution were then added and the solution was titrated with a 0.05 molar solution of EDTA, taking the sharp violet to orange red color change as the end point. This chelometric titration was not discovered until the latter stages of the research problem. It was considerably faster than the gravimetric determination for the rare earths, and it gave comparable accuracy.

For the extractions in which two rare-earth nitrates were present as mixtures, individual rare-earth concentrations were found using the spectrophotometric analysis developed by Banks and Klingman (2).

Nitric acid concentration was determined in the following manner. First an aliquot was taken and diluted to 200 milliliters with water. The rare-earth nitrates in the sample were complexed by adding an excess of saturated potassium ferrocyanide solution. The remaining nitric acid was then titrated with a 0.2 normal solution of sodium hydroxide.

It was necessary to strip the solutes from all organic phase samples before analysis. This was done by contacting the organic phase samples three times with an excess of water before carrying out the analysis.