Mathematical Modelling and Simulation of Rare Earth Solvent Extraction for the System of (Gd-Tb)Cl_3-HCl-HEHEHP-Shellsol D70

by

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FOREWORD

The Beijing General Research Institute for Non Ferrous Metals (BGRINM) of China and the Australian Nuclear Science and Technology Organisation (ANSTO) are cooperating in a study of Mathematical Modelling / Simulation of Rare Earth Solvent Extraction for the separation of gadolinium and terbium using ethylhexyl phosphinic acid mono-2-ethylhexyl ester (HEH(EHP)) in Shellsol D70.

The collaboration involves exchange of scientists between the two organisations. This technical report is the first part of the joint research project carried out at BGRINM from March 1993 to December 1993. ANSTO scientist, Mr Clifford Quan, took part in task 5 of the project from October 4, 1993 to November 5, 1993. The second part of the project was carried out at ANSTO with a reciprocal visit of a BGRINM scientist.

ABSTRACT

Equations were developed to model equilibrium in the binary rare earth solvent extraction system; (Gd-Tb)Cl_3-HCl-HEHEHP-Shellsol D70. The mathematical relationship described the equilibrium rare earth concentration in the organic phase as a function of the total rare earth concentration, acidity and mole fraction of one rare earth in the aqueous phase. The equations were derived from step-by-step regression analysis of data from 36 equilibrium shake-out tests in which variables were measured over the following feed solution ranges: total rare earth concentration 0.2-1.0 *M*, acidity 0.05-0.80 *M*, mole fraction of Gd 0.005-0.995. All experiments were carried out at an organic/aqueous phase ratio of 1 using 1.5 *M* ethylhexyl phosphinic acid mono-2-ethylhexyl ester (HEH(EHP)) in Shellsol D70. The average difference between the experimental and calculated values was < 4%. These models can be used to study the extraction behaviour, and to simulate multi-stage extraction and separation of the rare earths.

To verify the model, a 14-stage counter-current extraction circuit was experimentally simulated using separating funnels. Excellent agreement was found between the simulation and stage-wise calculations using a computer program written by BGRINM which takes account of changes in acidity that accompanying rare earth extraction and the organic concentration of rare earths as predicted by the mathematical model.

Separation of gadolinium and terbium was also demonstrated in a small mixer-settlers circuit comprising 10 extraction stages and 5 scrubbing stages. The feed solution contained 75% Gd and 25% Tb. The mixer settler circuit was operated for 45 hours to ensure equilibrium was established. The rare earth mass balances agreed within 3%. The product streams comprised a raffinate containing 93.6% Gd and an organic containing 90.4% Tb. Both purities are slightly lower than predicted by the stage-wise calculation and the simulation experiments using separation funnels. The discrepancies were mainly attributed to the fact that stage efficiencies were less than 100%, and/or the fact that a different organic-phase diluent was used in the mixer settler experiment.

The good agreement between the calculated and the experimental results (especially in the separation funnel experiments where the stage efficiency was 100%) indicates that the model accurately describes the equilibrium conditions over the wide range of concentrations and acidities occurring within a counter-current solvent extraction circuit.

CONTENTS

1. Introduction

The separation of pure rare earth elements (REE) is one of the most difficult challenges of inorganic chemistry because of the extreme similarity in the properties of these elements. Solvent extraction is generally used in industry for their separation and the process requires many stages. The laboratory experiments to study the separation of pure REE require considerable resources (both personnel and materials) to simulate in-series extraction conditions to obtain the optimum process parameters. It is desirable, therefore, to adopt computer technology for replacing part of the experimental and simulation procedures. The application of advanced computational techniques requires development of mathematical relationships (models) to describe the inter-relationship of variables in the extraction system. Since 1970, considerable research has been carried out internationally in the area of mathematical models for rare earth extraction [1-12], but no report was found for the system of $(Gd\text{-}Tb)Cl_3\text{-}HCl\text{-}HEHEHP\text{-}Shellsol\ D70$.

The purpose of this investigation was to study the equilibrium of the above system with the primary objective of formulating two empirical mathematical models to describe the equilibrium relationship of Gd or Tb concentration in the organic phase as a function of the total RE concentration, acidity and mole fraction of Gd (or Tb) in the aqueous phase. The following parameters were considered:

- total rare earth concentration 0.2-1.0 *M*,
- acidity 0.05-0.8 *M*,
- mole fraction of Gd 0.005-0.995.

The experimental conditions were determined using the orthogonal design method. A total of 36 shake-out experiments were then carried out for the equilibrium data, from which two mathematical models were derived using step-by-step regression analysis of the data. These models can be used to study the effect of aqueous total RE concentration, acidity and mole fraction of Gd on the distribution coefficient and separation factor of RE in the system. The models can also be applied in the simulation of a multi-stage solvent extraction process for the separation of Gd and Tb.

Two computer programs were written in Basic Language for an IBM compatible PC. The first program was for the establishment of mathematical models (either in polynomial or exponential expression) using step-by step multiple regression analysis. The second program was for the stage-by-stage calculation of material balances.

2. EXPERIMENTAL

2.1 Chemical Reagents and Analyses

Gadolinium oxide (Gd_2O_3) and terbium oxide (Tb_4O_7) having purity greater than 99.9% were supplied by the RE separation group of Jiu-Jiang Non Ferrous Metals Co. in China. Industrial grade organic extractant P507, or 2-ethylhexyl-phosphonic acid mono-2-ethylhexyl ester (HEHEHP) containing >93% monomer of P507 was a product of Jiang Tze Chemical Co. of China. The diluent, Shellsol D70, having specific gravity 0.796 was obtained from Shell Chemicals, Australia. Reagent grade hydrochloric acid and ammonia were supplied from the Beijing Chemicals Co.

Total rare earth concentrations were measured by volumetric titration with EDTA or by gravimetry. RE composition was determined by X-ray fluorescence. Aqueous phase acidity was determined by titration with a standard NaOH solution using a mixed indicator (an alcohol solution of 0.1% methylene blue and 0.1% methyl red). The concentration (purity) of the HEHEHP was also determined by titration with a standard NaOH solution after diluting with ethanol solution.

2.2 Preparation of Solutions

Rare earth feed solution:

The rare earth solutions were prepared by dissolving the individual oxides of gadolinium and terbium in concentrated HCl and by evaporating the excess acid carefully in a hot plate until pH 3-4. The final solution was filtered through a fine filter paper to remove any precipitates of impurities. The rare earth concentration was analysed and the solution stored for later use. The two RE mixed solution was prepared by combining the two single RE solutions in the required proportions.

Organic solvent:

The P507 organic extractant was mixed with Shellsol D70 diluent to form a 1.5 *M* of P507 on a monomeric basis.

Scrub solution:

The scrub solution was prepared by diluting a concentrated HCl solution to the required acidity of 1.3 *M* with deionised water.

Strip solution:

The strip solution was prepared by diluting a concentrated HCl solution to 6 *M* with deionised water.

2.3 Experimental Procedures

2.3.1 Single Stage Experiment

A known volume of aqueous feed solution (having known concentration and acidity) was equilibrated with an equal volume of the organic solvent in a separating funnel by shaking the two phases vigorously on a shaking table for 10 min, allowing the phases to separate for 10 min, and then repeating the shaking and separation procedures twice more. The phases were then separated and filtered. The aqueous phase total RE concentration and acidity were determined from samples of the aqueous filtrates. The extracted RE was also recovered from the organic phase by back-extracting four times using 6 *M* of HCl at an organic solvent to acid volume ratio of 5:1. All the stripped solutions were combined in a volumetric flask and made up to volume with deionised water for RE analysis.

2.3.2 Multi-Stage Solvent Extraction Simulation

A fourteen stage, counter-current liquid-liquid extraction circuit was simulated in the laboratory using separating funnels. The procedure is illustrated in **Figure 1**. A series of separating funnels were numbered and arranged to represent the total number of stages. Each separating funnel represented one theoretical stage: S1 to S5 referred to the scrubbing section and S6 to S14 corresponded to the extraction section in which S6 was the feed stage. The test began from the feed stage funnel where solutions of the RE feed, organic solvent and scrub acid were placed into the funnel in proportion to the desired phases ratio. After shaking for 10 min and standing, the two phases were separated and transferred to the respective adjacent funnels in opposite directions. The aqueous phase, A6, was transferred to S7 and the organic phase, O6, to S5. According to the required phase ratio, known volumes of both scrub solution and organic solvent were then put in S5 and S7. After shaking and standing, the aqueous phases of S5 and S7 were transferred to S6 and S8 respectively, and their organic phases were transferred to S4 and S6, respectively. The procedure continued by adding scrub solution and organic solvent to both S4 and S8, and feed solution to S6.

In the next separation, the aqueous phases of S4, S6 and S8 were transferred to S5, S7 and S9, respectively, and the organic phases were transferred to S3, S5 and S7, respectively, and so on. After a series of separation, the aqueous phase of S14 and the organic phase of S1 exited out of the circuit. They were collected or discarded as appropriate. The row count began when the transfer of phases had been completed for the total number of stages (see **Figure 1**). The shaking and separation procedures continued until the extraction system reached equilibrium.

The two phases flowed counter-currently. The aqueous phase flowed from S1 to S14, and the organic phase flowed from S14 to S1. During the experiment, samples were taking from both the exit aqueous and exit organic phases for RE concentration analyses. Material balances were carried out from these analytical results to determine the approach to steady-state equilibrium. From experience, the extraction system approaches steady-state when the number of

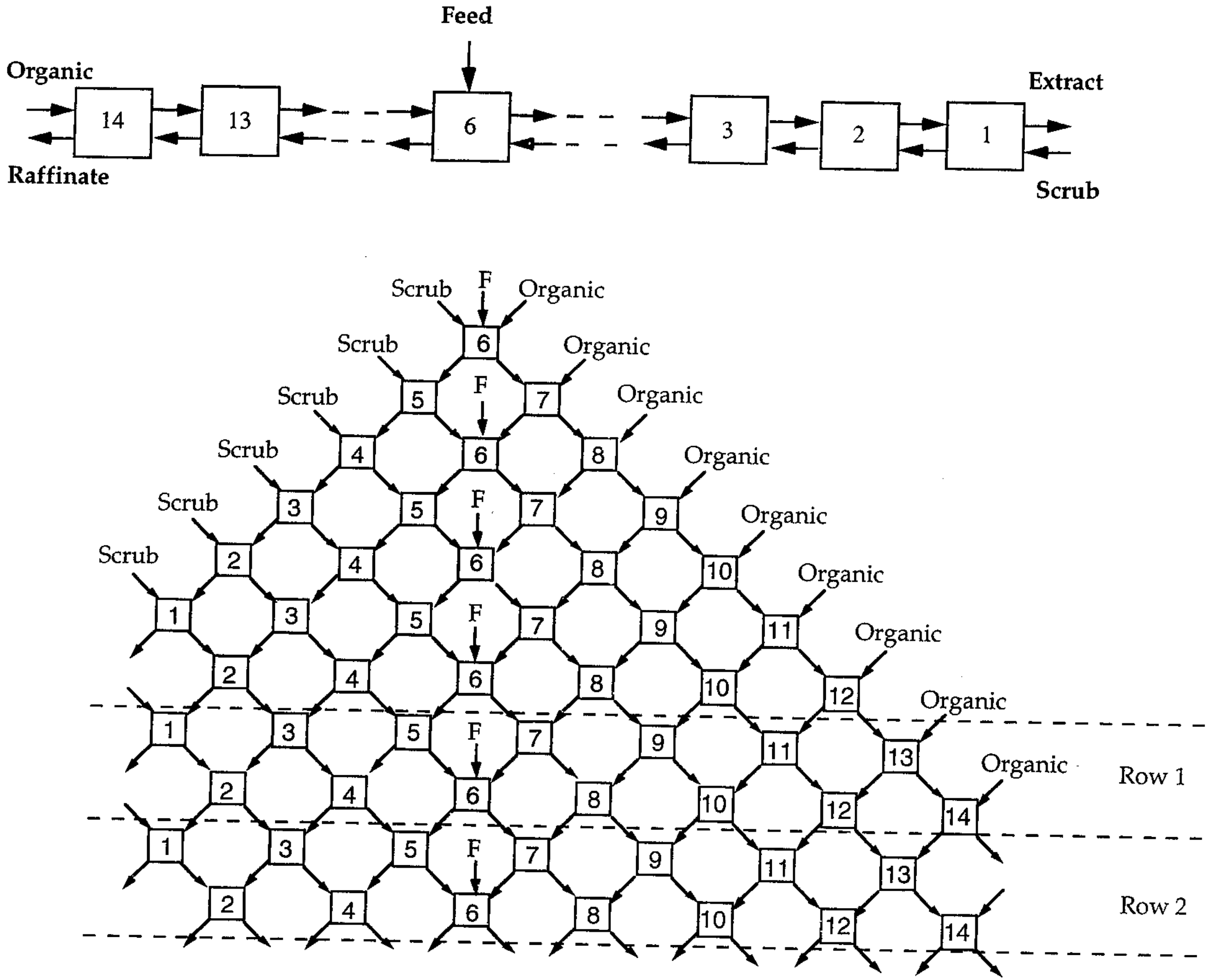

Figure 1: Schematic Diagram of a 14-Stage Counter Current SX Simulation with Separating Funnels

rows in operation is 3 to 4 times the total number of stages. At equilibrium, samples of the two phases were taken at each stage. The organic phase samples were stripped four times with 6 *M* HCl. The equilibrium RE concentration of the aqueous phases and the organic back-extract was then analysed, and the aqueous phase equilibrium acidity was determined by titration.

It was evident that the laboratory simulation experiment was both time consuming and labour intensive involving tedious operating procedures. In the above experiment, a total of 41 shake-outs and transfers was required to reach a first row of the simulation experiment. Subsequently 14 shake-out tests were required for each second, third, fourth *etc.* rows of the experiment. At steady-state, a total of 50 rows of experiment consisting 727 phase transfers were carried out. As the number of stage in the extraction circuit increases, the number of shake-out experiments become larger and the experiment can take weeks to complete. Therefore this laboratory simulation technique is seldomly used for a multi-stage extraction process.

2.4 Design of Experimental Points

An orthogonal design was adopted for the number of shake-out tests to be carried out to obtain equilibrium data. As shown in **Table 1**, a total of 36 shake-out experiments were carried out to cover the following ranges of RE feed: total rare earth concentration 0.2-1.0 *M*, acidity 0.05-0.80 *M*, mole fraction (M.F.) of Gd 0.005-0.995.

TABLE 1
The Orthogonal Collocation Design of Equilibrium Data

Expt. No	[TRE] mole/L	Acidity mole/L	M.F. of Gd	Expt. No	[TRE] mole/L	Acidity mole/L	M. F. of Gd
1	0.20	0.300	0.005	19	0.65	0.800	0.050
2	0.20	0.450	0.100	20	0.65	0.050	0.100
3	0.20	0.600	0.250	21	0.65	0.150	0.250
4	0.20	0.800	0.500	22	0.65	0.300	0.500
5	0.20	0.050	0.750	23	0.65	0.450	0.750
6	0.20	0.150	0.995	24	0.65	0.600	0.995
7	0.35	0.450	0.005	25	0.80	0.050	0.005
8	0.35	0.600	0.100	26	0.80	0.150	0.100
9	0.35	0.800	0.250	27	0.80	0.300	0.250
10	0.35	0.050	0.500	28	0.80	0.450	0.500
11	0.35	0.150	0.750	29	0.80	0.600	0.750
12	0.35	0.300	0.995	30	0.80	0.800	0.995
13	0.50	0.600	0.005	31	1.00	0.150	0.050
14	0.50	0.800	0.100	32	1.00	0.300	0.100
15	0.50	0.050	0.250	33	1.00	0.450	0.250
16	0.50	0.150	0.500	34	1.00	0.600	0.500
17	0.50	0.300	0.750	35	1.00	0.800	0.750
18	0.50	0.450	0.995	36	1.00	0.050	0.995

2.5 Mathematical Modelling

In the (Gd-Tb)Cl_3-HCl-1.5 *M* HEHEHP/Shellsol D70 extraction system, the organic RE concentration (Y_{Gd} or Y_{Tb}) at equilibrium was described as a function of:

(i) total RE concentration in the aqueous phase;
(ii) the aqueous phase acidity; and
(iii) mole fraction of Gd.

The step-by-step regression technique was used to correlate the relationship of these variables. These empirical regression models describe a mathematical relationship between dependent and independent variables but do not imply any physical meaning. In this study the mathematical models were developed using the computer language Basic to perform the stepwise regression calculations.

2.6 Mathematical Simulation and Calculation of a Multi-Stage Solvent Extraction Process

A stage-by-stage calculation procedure was used for the simulation of multi-stage counter-current extraction process. This numerical procedure is generally applicable whenever distribution coefficients are defined (for example by a mathematical relationship) and the phases leaving an extraction stage are in equilibrium. A second Basic language computer program was written for the calculation of steady-state equilibria and mass balance of RE and acidity for individual stages. The calculation was based on the initial RE feed concentration, acidity, percent content of one RE in the feed, flow ratios, total number of stages, and the number of stages in the scrub section. Using the mathematical models, the organic phase composition can be determined if the aqueous phase composition is specified. This type of calculation, combined with material balances of RE and acidity at steady-state, permits stage-to-stage calculations from one end to the other end of the counter-current cascade.

3. RESULTS AND DISCUSSION

3.1 Equilibrium Data

The experimental results of the equilibrium data are summarised in **Table 2**. They show that in the following experimental range:

- equilibrium aqueous RE concentration 0.10-0.96 *M*;
- equilibrium aqueous acidity 0.32-0.90 *M*;
- mole fraction of Gd 0.006-0.996,

the separation factor, β, between Gd and Tb varies slightly and is within the range of 4.77-5.83. The average separation factor is 5.55.

Table 2
Experimental Results of Equilibrium Data
(Extractant: 1.5 M P507 in Shellsol D70, Phase Ratio: O/A = 1)

Expt. No	Initial State (Feed Solution)					Aqueous Phase							Organic Phase					Total D	D	D	Sep'n factor
	Acidity M	Total RE (Gd+Tb), M	Gd M	Tb M	MF (Gd)	Acidity X(2), M	Total RE X(1), M	Total RE g/L	Gd M	Tb M	MF (Gd) X(3)	MF (Tb)	Total RE (Gd+Tb), M	Total RE g/L	Gd Y, M	Tb M	MF (Gd)	D (Gd+Tb)	Gd	Tb	ß (Tb/Gd)
1	0.3019	0.2022	0.0010	0.2012	0.005	0.5486	0.1149	18.33	0.0011	0.1138	0.009172	0.990828	0.0849	13.51	0.0002	0.0847	0.0019	0.7387	0.1494	0.7442	4.98
2	0.4521	0.2008	0.0201	0.1807	0.100	0.6429	0.1392	21.92	0.0196	0.1196	0.140739	0.859261	0.0639	10.19	0.0018	0.0621	0.0282	0.4591	0.0921	0.5192	5.64
3	0.5996	0.2041	0.0510	0.1531	0.250	0.7198	0.1556	24.86	0.0481	0.1075	0.309058	0.690942	0.0458	7.19	0.0034	0.0424	0.0735	0.2944	0.0701	0.3948	5.63
4	0.7980	0.2001	0.1001	0.1001	0.500	0.8683	0.1795	28.23	0.0974	0.0821	0.542360	0.457640	0.0221	3.87	0.0038	0.0183	0.1738	0.1231	0.0394	0.2222	5.63
5	0.0552	0.2032	0.1524	0.0508	0.750	0.3258	0.1040	16.63	0.0925	0.0115	0.889037	0.110963	0.0973	15.28	0.0577	0.0396	0.5928	0.9358	0.6239	3.4343	5.50
6	0.1523	0.2041	0.2031	0.0010	0.995	0.3569	0.1285	20.54	0.1282	0.0003	0.997769	0.002231	0.0746	11.44	0.0736	0.0009	0.9875	0.5803	0.5743	3.2561	5.67
7	0.4598	0.3516	0.0018	0.3498	0.005	0.6778	0.2788	44.10	0.0023	0.2765	0.008142	0.991858	0.0759	12.04	0.0001	0.0758	0.0014	0.2722	0.0482	0.2740	5.68
8	0.6010	0.3558	0.0356	0.3202	0.100	0.7533	0.2947	47.06	0.0340	0.2607	0.115369	0.884631	0.0571	9.11	0.0013	0.0558	0.0236	0.1938	0.0396	0.2139	5.40
9	0.8008	0.3553	0.0888	0.2665	0.250	0.9022	0.3196	50.75	0.0852	0.2344	0.266707	0.733293	0.0327	5.76	0.0022	0.0305	0.0666	0.1023	0.0255	0.1303	5.10
10	0.0514	0.3589	0.1795	0.1795	0.500	0.3805	0.2366	37.66	0.1484	0.0882	0.627240	0.372760	0.1196	18.99	0.0271	0.0925	0.2270	0.5055	0.1829	1.0483	5.73
11	0.1502	0.3553	0.2665	0.0888	0.750	0.4112	0.2607	41.83	0.2196	0.0411	0.842479	0.157521	0.0928	14.53	0.0450	0.0478	0.4846	0.3558	0.2047	1.1643	5.69
12	0.3061	0.3617	0.3599	0.0018	0.995	0.4734	0.3069	48.24	0.3059	0.0010	0.996605	0.003395	0.0572	8.87	0.0562	0.0010	0.9823	0.1863	0.1836	0.9694	5.28
													0.0000								
13	0.6042	0.5092	0.0025	0.5067	0.005	0.7736	0.4427	70.27	0.0026	0.4401	0.005978	0.994022	0.0629	9.95	0.0001	0.0628	0.0010	0.1421	0.0245	0.1428	5.83
14	0.7778	0.4906	0.0491	0.4415	0.100	0.8955	0.4431	70.84	0.0486	0.3945	0.109634	0.890366	0.0441	7.07	0.0009	0.0432	0.0209	0.0996	0.0190	0.1095	5.76
15	0.0514	0.5047	0.1262	0.3785	0.250	0.411	0.3760	59.82	0.1185	0.2575	0.315027	0.684973	0.1321	20.92	0.0098	0.1223	0.0744	0.3513	0.0829	0.4748	5.72
16	0.1544	0.5105	0.2553	0.2553	0.500	0.4556	0.4037	63.51	0.2334	0.1703	0.578037	0.421963	0.1059	16.9	0.0210	0.0849	0.1979	0.2623	0.0898	0.4987	5.55
17	0.3040	0.5051	0.3788	0.1263	0.750	0.5101	0.4309	68.37	0.3462	0.0847	0.803448	0.196552	0.0740	9.4	0.0307	0.0434	0.4143	0.1718	0.0886	0.5119	5.78
18	0.4612	0.5247	0.5221	0.0026	0.995	0.5716	0.4803	74.78	0.4775	0.0028	0.994179	0.005821	0.0399	6.15	0.0386	0.0013	0.9682	0.0831	0.0809	0.4544	5.62
19	0.8050	0.6468	0.0032	0.6436	0.005	0.9109	0.6026	95.10	0.0035	0.5991	0.005875	0.994125	0.0406	7.12	0.0001	0.0406	0.0012	0.0674	0.0142	0.0678	4.77
20	0.0531	0.6497	0.0650	0.5847	0.100	0.4298	0.5208	82.97	0.0632	0.4576	0.121305	0.878695	0.1352	21.29	0.0033	0.1319	0.0242	0.2596	0.0518	0.2883	5.56
21	0.1530	0.6541	0.1635	0.4906	0.250	0.4731	0.5434	86.35	0.1578	0.3856	0.290429	0.709571	0.1145	18.21	0.0079	0.1066	0.0692	0.2107	0.0502	0.2764	5.50
22	0.3075	0.6577	0.3289	0.3289	0.500	0.5451	0.5798	90.67	0.3171	0.2627	0.546948	0.453052	0.0839	13.31	0.0147	0.0693	0.1748	0.1448	0.0463	0.2637	5.70
23	0.4591	0.6614	0.4961	0.1654	0.750	0.6146	0.6145	97.13	0.4777	0.1368	0.777310	0.222690	0.0532	8.38	0.0208	0.0324	0.3909	0.0865	0.0435	0.2367	5.44
24	0.6031	0.6587	0.6554	0.0033	0.995	0.6729	0.6331	98.46	0.6298	0.0033	0.994858	0.005142	0.0258	3.98	0.0252	0.0007	0.9738	0.0408	0.0400	0.2081	5.21
25	0.0524	0.8139	0.0041	0.8098	0.005	0.4294	0.6745	106.76	0.0040	0.6705	0.005978	0.994022	0.1364	21.65	0.0002	0.1362	0.0011	0.2022	0.0384	0.2032	5.30
26	0.1530	0.8013	0.0801	0.7212	0.100	0.4846	0.6910	110.05	0.0799	0.6111	0.115676	0.884324	0.1170	18.76	0.0026	0.1144	0.0226	0.1693	0.0330	0.1871	5.67
27	0.3089	0.8144	0.2036	0.6108	0.250	0.5688	0.7221	114.54	0.1952	0.5269	0.270359	0.729641	0.0915	14.51	0.0058	0.0857	0.0636	0.1267	0.0298	0.1627	5.46
28	0.4647	0.8104	0.4052	0.4052	0.500	0.6394	0.7561	119.73	0.4003	0.3558	0.529385	0.470615	0.0628	9.99	0.0104	0.0524	0.1660	0.0831	0.0261	0.1473	5.65
29	0.6059	0.813	0.6098	0.2033	0.750	0.711	0.7672	120.19	0.5877	0.1795	0.765997	0.234003	0.0383	6.01	0.0139	0.0243	0.3642	0.0499	0.0237	0.1355	5.71
30	0.7980	0.7989	0.7949	0.0040	0.995	0.824	0.7832	122.97	0.7786	0.0046	0.994179	0.005821	0.0129	2.22	0.0125	0.0004	0.9672	0.0165	0.0161	0.0932	5.80
31	0.1548	1.0094	0.0050	1.0044	0.005	0.4832	0.8910	141.74	0.0051	0.8859	0.005669	0.994331	0.1151	18.3	0.0001	0.1150	0.0010	0.1292	0.0235	0.1298	5.52
32	0.3110	1.003	0.1003	0.9027	0.100	0.5695	0.9104	145.41	0.1015	0.8089	0.111478	0.888522	0.0921	14.68	0.0020	0.0902	0.0212	0.1012	0.0193	0.1115	5.79
33	0.4493	1.0057	0.2514	0.7543	0.250	0.6499	0.9347	149.83	0.2479	0.6868	0.265185	0.734815	0.0691	8.83	0.0042	0.0649	0.0604	0.0739	0.0168	0.0945	5.61
34	0.6031	1.0031	0.5016	0.5016	0.500	0.7295	0.9518	151.73	0.4843	0.4675	0.508804	0.491196	0.0457	7.2	0.0073	0.0384	0.1591	0.0480	0.0150	0.0822	5.47
35	0.7980	0.9905	0.7429	0.2476	0.750	0.8497	0.9697	153.96	0.7330	0.2367	0.755857	0.244143	0.0207	3.64	0.0074	0.0133	0.3594	0.0213	0.0101	0.0560	5.52
36	0.0531	1.0349	1.0297	0.0052	0.995	0.3232	0.9228	-	0.9191	0.0037	0.996022	0.003978	0.0959	14.9	0.0937	0.0023	0.9764	0.1039	0.1019	0.6164	6.05

3.2 Mathematical Models

On the basis of the above 36 sets of equilibrium data, two mathematical models for Gd and Tb respectively were derived and represented as:

$$Y_{Gd} = \mathrm{Exp}\,(a_1 + a_2X_1\mathrm{Ln}X_1 + a_3X_2\sqrt{X_3} + a_4X_2\mathrm{Ln}X_1 + a_5X_3X_3 + a_6\sqrt{X_2}\,\mathrm{Ln}X_3 + a_7\sqrt{X_3}\mathrm{Ln}X_2 + a_8\mathrm{Ln}X_2\mathrm{Ln}X_2)$$

$$Y_{Tb} = \mathrm{Exp}\,(a_1 + a_2X_1\sqrt{X_2} + a_3X_2X_3 + a_4X_2\sqrt{X_3} + a_5X_3\sqrt{X_3} + a_6\sqrt{X_1}\,\sqrt{X_2} + a_7\sqrt{X_2}\mathrm{Ln}X_3 + a_8\mathrm{Ln}X_2\mathrm{Ln}X_3)$$

In these exponential expressions Y_{Gd} and Y_{Tb} are the concentrations of Gd and Tb in the organic phases; X_1, X_2 and X_3 are the total aqueous phase RE concentration, acidity and mole fraction of Gd respectively; a_1 to a_8 are coefficients of the models which are different for Gd and Tb. The values for the coefficients are given in **Table 3**. The experimental and calculated results (from the models) are presented in **Tables 4** and **5**. The average relative errors are <4% and the correlation coefficient is 0.9997.

TABLE 3
Coefficients for the Models

Model	Coefficients							
	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_8
Y_{Gd}	-4.333270	-0.732220	-1.132279	+0.2818873	+0.2916799	+1.167995	-2.910207	-1.068527
Y_{Tb}	-0.426715	-2.275521	+5.842902	-8.942314	-1.018605	+3.36458	+1.65254	-0.0463482

3.3 Study of the Extraction Behaviour of Rare Earths using the Equilibrium Models

The derived mathematical models can be used to study the extraction behaviour of Gd and Tb in [illegible] system of (Gd-Tb)Cl_3-HCl-1.5 *M* HEH(EHP)/Shellsol D70. In this study, the equilibrium [illegible]bution relationship of rare earths in the two phases, the effect of aqueous phase total RE [illegible]tration, acidity and mole fraction of Gd on the distribution coefficients and separation [illegible] are presented and described. The results are graphically shown in **Figures 2** to **6**.

[illegible]ant aqueous acidity (0.3, 0.45, 0.6, 0.75 and 0.9 *M* HCl), and 0.65 mole fraction of [illegible]stribution of RE in the two phases is shown in **Figure 2**. The results obtained were a [illegible]st parallel curves. In the aqueous RE concentration range, $[RE]_{aq}$ = 0.1-0.9 *M*, at [illegible] the RE concentration in the organic phase, $[RE]_o$, increased with increasing aqueous [illegible]tion apparent reaching a maximum at 0.5 *M* aqueous RE concentration. Further [illegible] aqueous RE concentration had very little effect on the organic RE concentration.

For the same aqueous RE concentration, the organic RE concentration decreased as the aqueous acidity increased.

The effect of aqueous RE concentration on the distribution coefficient, D, is shown in **Figure 3**. At constant aqueous acidity, the distribution coefficient of RE increased with decreasing aqueous RE concentration. The trend was more obvious when the aqueous RE concentration was less than 0.4 *M* and at low aqueous acidity.

The effect of changing aqueous RE concentration on the distribution coefficients and the separation factor, β, between Tb and Gd is shown in **Figures 4(a)** and **4(b)**. The graphs represent the result at 0.5 *M* HCl, 0.65 mole fraction of Gd and the aqueous RE concentration varying from 0.1 to 0.9 *M*. The separation factor was almost constant and appeared as a near parallel straight line to the abscissa. The result demonstrated that the RE concentration in the range studied had little effect on the separation factor of the two RE. The trends of total and single distribution coefficients of the RE (D_{Gd+Tb}, and D_{Gd} or D_{Tb}) were similar to the results shown in **Figure 3**.

The effect of aqueous phase acidity on the distribution coefficient is shown in **Figures 5(a)** and **5(b)**. In the organo-phosphorus acidic extractant system, the acidity plays an important role for RE extraction. Under the following conditions: aqueous RE concentration 0.4 *M*, Gd mole fraction 0.65, aqueous acidity 0.3-0.9 *M*, the distribution coefficients of Gd, Tb and both increased rapidly as the aqueous phase acidity decreased. The change was very significant in the acidity range less than 0.6 *M* HCl. The separation factor between Tb and Gd varied slightly in the range of 5.4-6.2.

The effect of Gd mole fraction on the distribution coefficient of the RE is shown in **Figures 6(a)** and **6(b)**. At a aqueous RE concentration of 0.4 *M* and acidity of 0.5 *M*, the distribution coefficient of Gd and Tb increased with increasing mole fraction of Gd, however, the total distribution coefficient decreased. The effect was attributed to the increasing quantity of the less extracted component of Gd in the system so that its extraction became more dominant. Also because the distribution of D_{Gd} is smaller than D_{Tb} the total distribution coefficient of D_{Gd+Tb} decreased with increase Gd concentration. The separation factor between Tb and Gd varied slightly in the range of 5.4-6.0 for Gd mole fraction ranging 0.1-0.99.

TABLE 4
Comparison Results for the Empirical Mathematical Model of Gd

Experimental No	Experimental Value, Y	Calculated Value, Y cal.	Absolute Error	% Error
1	1.5745E-04	1.4747E-04	9.9781E-06	6.34
2	1.8037E-03	1.8008E-03	2.8752E-06	0.16
3	3.3691E-03	3.4438E-03	-7.4625E-05	-2.21
4	3.8398E-03	3.8847E-03	-4.4908E-05	-1.17
5	5.7688E-02	5.8951E-02	-1.2633E-03	-2.19
6	7.3637E-02	7.4222E-02	-5.8527E-04	-0.79
7	1.0949E-04	1.1492E-04	-5.4293E-06	-4.96
8	1.3473E-03	1.3470E-03	3.2422E-07	0.02
9	2.1773E-03	2.0579E-03	1.1946E-04	5.49
10	2.7148E-02	2.8121E-02	-9.7296E-04	-3.58
11	4.4956E-02	4.7301E-02	-2.3451E-03	-5.21
12	5.6170E-02	5.5103E-02	1.0667E-03	1.9
13	6.4840E-05	6.8639E-05	-3.7995E-06	-5.86
14	9.2293E-04	9.5206E-04	-2.9121E-05	-3.16
15	9.8239E-03	9.4015E-03	4.2237E-04	4.30
16	2.0956E-02	2.1721E-02	-7.6537E-04	-3.65
17	3.0664E-02	3.2422E-02	-1.7587E-03	-5.74
18	3.8620E-02	3.8121E-02	4.9899E-04	1.29
19	5.0272E-05	4.3887E-05	6.3842E-06	12.70
20	3.2729E-03	2.8799E-03	3.9307E-04	12.01
21	7.9274E-03	7.7969E-03	1.3055E-04	1.65
22	1.4675E-02	1.5567E-02	-8.9214E-04	-6.08
23	2.0789E-02	2.0843E-02	-5.4317E-05	-0.26
24	2.5172E-02	2.4673E-02	4.9904E-04	1.98
25	1.5468E-04	1.6396E-04	-9.2837E-06	-6.00
26	2.6396E-03	2.5365E-03	1.0314E-04	3.91
27	5.8195E-03	5.7104E-03	1.0909E-04	1.87
28	1.0428E-02	1.0730E-02	-3.0264E-04	-2.90
29	1.3935E-02	1.3718E-02	2.1700E-04	1.56
30	1.2515E-02	1.2571E-02	-5.5488E-05	-0.44
31	1.1867E-04	1.3362E-04	-1.4949E-05	-12.60
32	1.9555E-03	1.9835E-03	-2.8055E-05	-1.43
33	4.1745E-03	4.2524E-03	-7.7877E-05	-1.87
34	7.2690E-03	7.0953E-03	1.7362E-04	2.39
35	7.4390E-03	7.4005E-03	3.8557E-05	0.52
36	9.3657E-02	8.6511E-02	7.1458E-03	7.63

Average Relative Error = 3.78%, and Correlation Coefficient = 0.9997

TABLE 5
Comparison Results for the Empirical Mathematical Model of Tb

Experimental No	Experimental Value, Y	Calculated Value, Y cal.	Absolute Error	% Error
1	8.4723E-02	8.2123E-02	2.5996E-03	3.07
2	6.2106E-02	6.0951E-02	1.1549E-03	1.86
3	4.2441E-02	4.2143E-02	2.9781E-04	0.70
4	1.8250E-02	1.9349E-02	-1.0989E-03	-6.02
5	3.9632E-02	4.1836E-02	-2.2036E-03	-5.56
6	9.3347E-04	9.3490E-04	-1.4292E-06	-0.15
7	7.5771E-02	7.3352E-02	2.4189E-03	3.19
8	5.5763E-02	5.5355E-02	4.0770E-04	0.73
9	3.0533E-02	3.0651E-02	-1.1792E-04	-0.39
10	9.2452E-02	9.2990E-02	-5.3865E-04	-0.58
11	4.7814E-02	4.7406E-02	4.0836E-04	0.85
12	1.0100E-03	9.5970E-04	5.0329E-05	4.98
13	6.2825E-02	6.2901E-02	-7.5604E-05	-0.12
14	4.3207E-02	4.0837E-02	2.3696E-03	5.48
15	1.2228E-01	1.2531E-01	-3.0295E-03	-2.48
16	8.4944E-02	8.4759E-02	1.8525E-04	0.22
17	4.3356E-02	4.2630E-02	7.2605E-04	1.67
18	1.2705E-03	1.2162E-03	5.4290E-05	4.27
19	4.0590E-02	4.5400E-02	-4.8102E-03	-11.85
20	1.3193E-01	1.3493E-01	-3.0018E-03	-2.28
21	1.0657E-01	1.0971E-01	-3.1380E-03	-2.95
22	6.9273E-02	6.7595E-02	1.6775E-03	2.42
23	3.2391E-02	3.3075E-02	-6.8384E-04	-2.11
24	6.7758E-04	6.9334E-04	-1.5760E-05	-2.33
25	1.3625E-01	1.3906E-01	-2.8135E-03	-2.07
26	1.1436E-01	1.1683E-01	-2.4712E-03	-2.16
27	8.5701E-02	8.3475E-02	2.2253E-03	2.60
28	5.2402E-02	4.9714E-02	2.6881E-03	5.13
29	2.4325E-02	2.4018E-02	3.0706E-04	1.26
30	4.2470E-04	4.3427E-04	-9.5661E-06	-2.25
31	1.1498E-01	1.1685E-01	-1.8671E-03	-1.62
32	9.0185E-02	8.8790E-02	1.3948E-03	1.55
33	6.4935E-02	6.1912E-02	3.0239E-03	4.66
34	3.8411E-02	3.5502E-02	2.9086E-03	7.57
35	1.3261E-02	1.4218E-02	-9.5719E-04	-7.22
36	2.2627E-03	2.3248E-03	-6.2106E-05	-2.75

Average Relative Error = 2.98%, and Correlation Coefficient = 0.9997

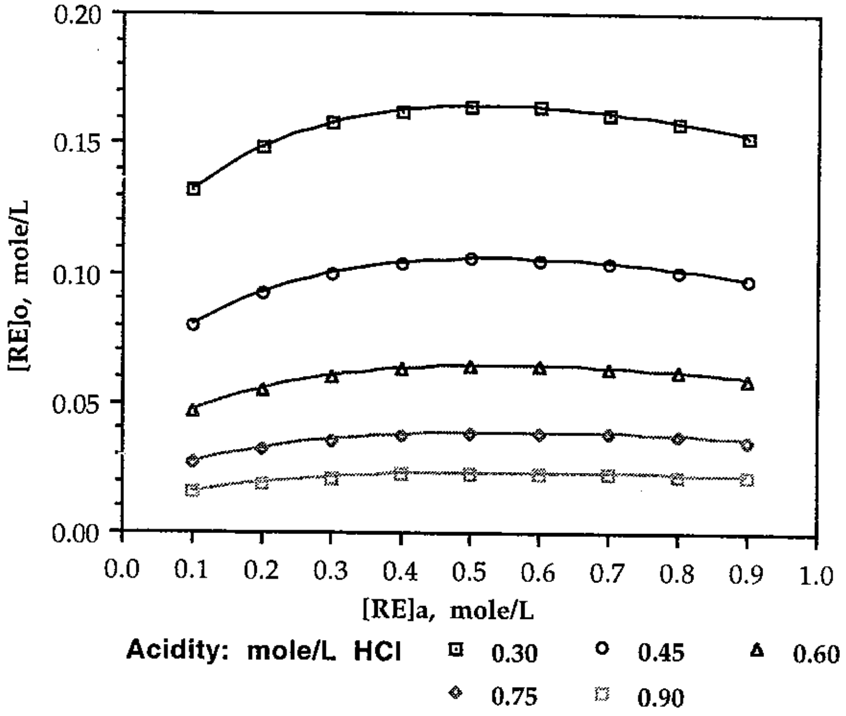

Figure 2 Equilibrium Curves (mole fraction of Gd = 0.65) for Total RE as a Function of Acidity

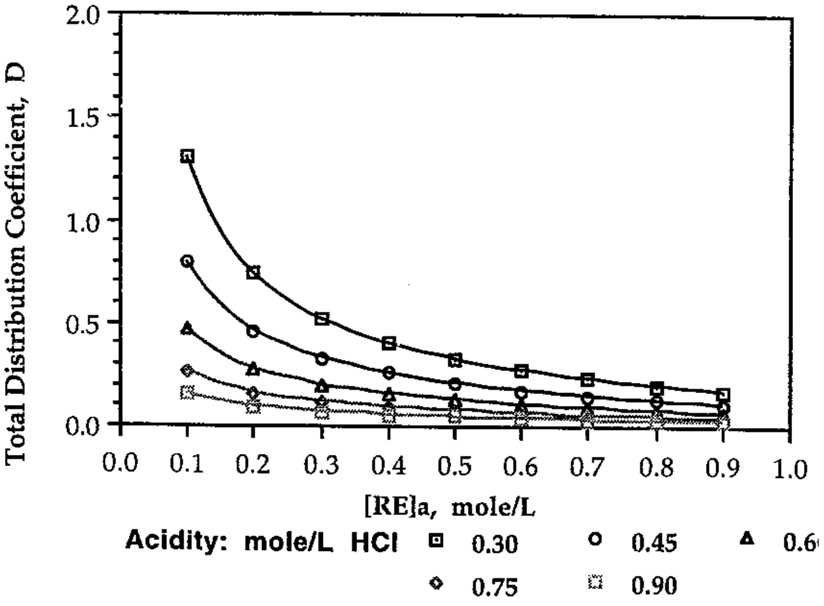

Figure 3 Distribution Coefficient as a Function of Total RE in the Aqueous Phase at Equilibrium

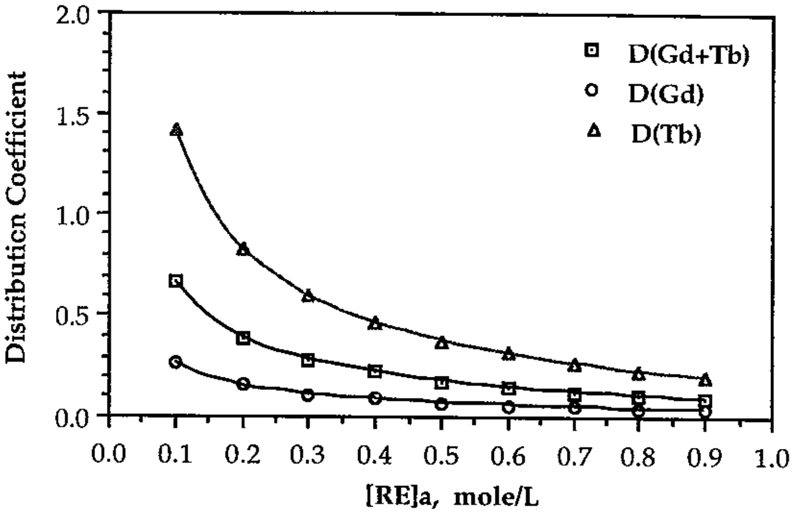

Figure 4(a) Effect of Total RE in the Aqueous Phase on Distribution Coefficient ([HCl]a = 0.5 mole/L, M.F. of Gd = 0.65)

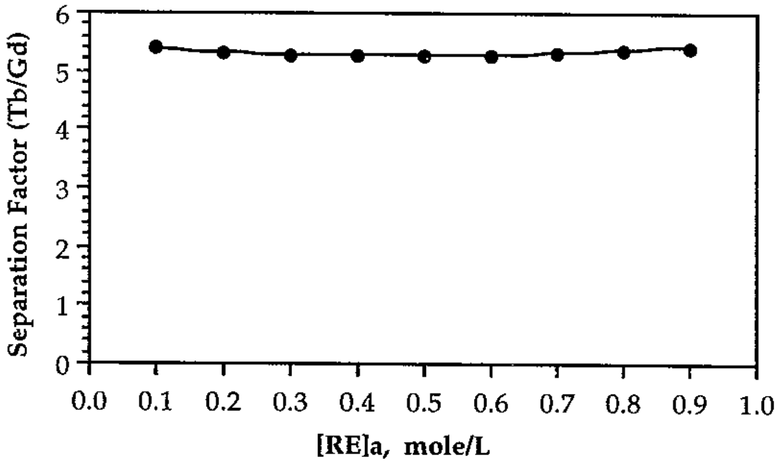

Figure 4(b) Effect of Total RE in the Aqueous Phase on Separation Factor ([HCl]a = 0.5 mole/L, M.F. of Gd = 0.65)

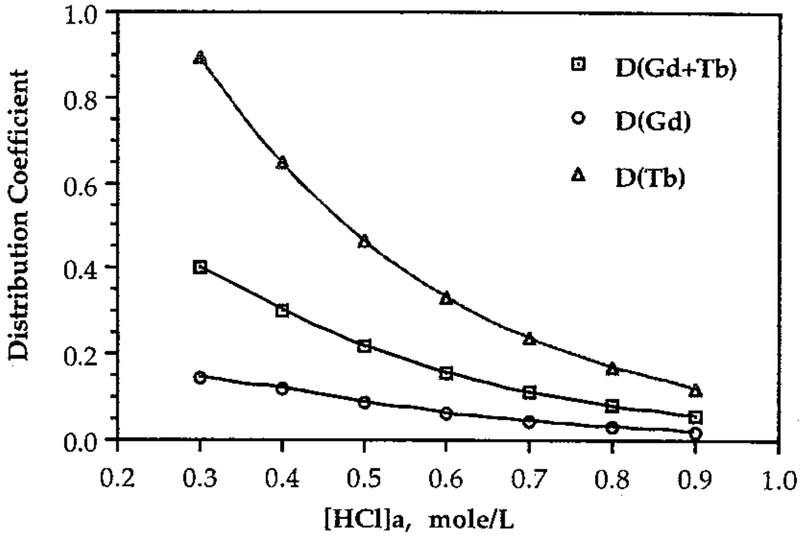

Figure 5(a) Effect of Aqueous Acidity on Distribution Coefficient ([RE]a = 0.4 mole/L, M.F. of Gd = 0.65)

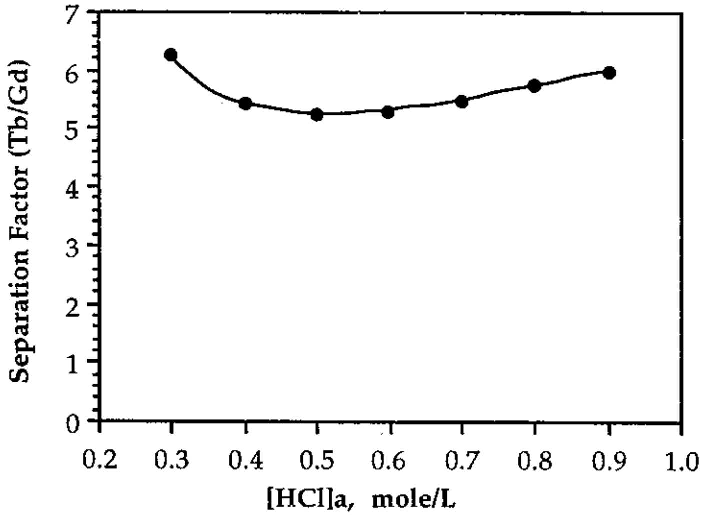

Figure 5(b) Effect of Aqueous Acidity on Separation Factor of Tb/Gd ([RE]a = 0.4 mole/L, M.F. of Gd = 0.65)

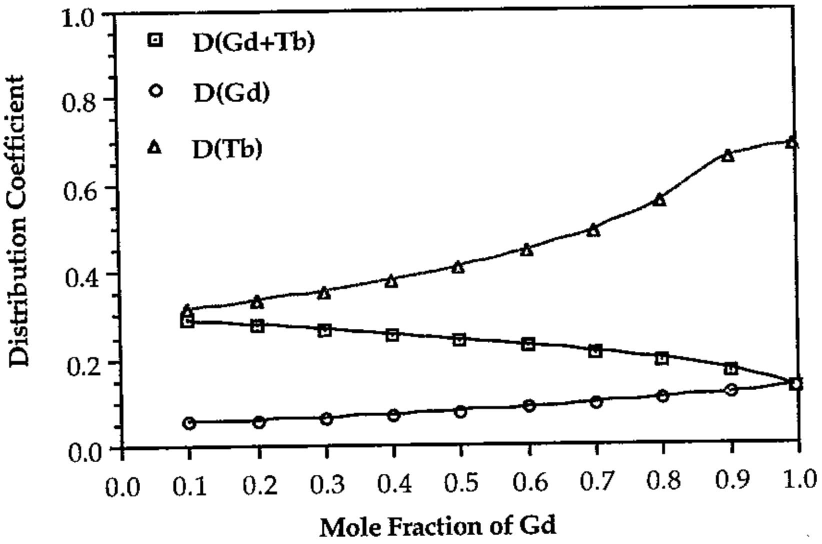

Figure 6(a) Effect of Mole Fraction of Gd on the Distribution Coefficient ([RE]a = 0.4 mole/L, [HCl]a = 0.5 mole/L)

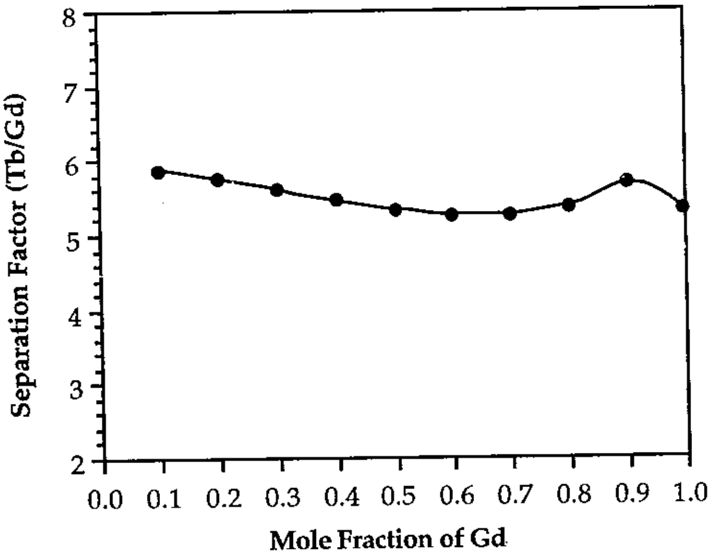

Figure 6(b) Effect of Mole Fraction of Gd on the Separation Factor ([RE]a = 0.4 mole/L, [HCl]a = 0.5 mole/L)

3.4 Multi-stage Extraction, Prediction and Experimental Results

The separation of Gd-Tb was simulated using stagewise calculations on a PC for a 14- and 16-stage circuit. The following process conditions were used:

Feed solution:	$[RE^{3+}] = 0.5051$ *M*, acidity $[H^+] = 0.04905$ *M*, composition 74.6% Gd-25.4% Tb;
Organic phase:	HEHEHP-Shellsol D70, and HEHEHP = 1.5129 *M*;
Flow ratios:	organic: feed: scrub = 2 : 1 : 0.5.
No. of stages:	total 14 stages, 9 stages for extraction section and 5 stages for scrub section. total 16 stages, 10 stages for extraction section and 6 stages for scrub section.

The results of the calculations are summarised in **Tables 6** and 7. The calculated scrub solution acidities were 1.3157 and 1.3083 *M*, respectively for the circuit of 14 and 16 stages.

Calculated results of the aqueous phase (X) and the organic phase (Y) are given in both summary tables. The distribution coefficient, D, the separation factor $\beta_{Tb/Gd}$, and the extraction factor E are also shown for each stage at equilibrium. The extraction factor E is defined as the ratio of the total mass of a RE in the organic phase to that in the aqueous phase. In both tables the extraction factor of Gd is always less than 1. The average extraction factor for Gd is 0.484 and 0.492 for the 14 and the 16 stage circuit, respectively. On the other hand the extraction factor of Tb is greater than 1 in most of the stages with the exception of the last 3 or 4 stages. The average extraction factor for Tb in the circuit is 2.784 and 2.863 respectively. The result illustrates that the separation is quite efficient. After going through 14 or 16 stages of extraction and separation, the yield of Gd product of 97.83% or 98.37% purity in the aqueous phase is 99.52%. The yields of Tb product are 93.88% and 95.68% respectively for the 14 and 16-stage circuit, and the purity obtained are 98.83% and 99.71% respectively. As expected, the separation efficiency is increased by increasing the number of stages, and both the purity and yield of the product are also higher.

On the basis of the calculated results, a 14-stage counter-current solvent extraction experiment was simulated in the laboratory using separating funnels. The experiment was carried out under similar conditions to those used in the calculations. The acidity of the actual prepared scrub solution was 1.322 *M* instead of 1.316 *M* as used in the calculations. The experimental procedure was quite labour intensive and time consuming (as described in **Section 2.3.2**). The experimental results from analyses of both the aqueous and organic phases are shown in **Table 8**. The comparison of the experimental and calculated results for the purity and yield of RE is shown in **Table 9** and graphically presented in **Figures 7, 8** and **9**.

Table 6

Stagewise Calculation for the Extraction Separation of Gd-Tb (14-stage circuit)

Feed Concentration, mol/L, F (3)= 0.5051
Gd Concentration, mol/L, F(1)= 0.3768
Tb Concentration, mol/L, F(2)= 0.1283
Gd %= 74.6 Tb%= 25.4
Feed Flow, L= 1.0
Scrub Flow, L1= 0.5
Solvent Flow, V= 2.0
Total Stages, N= 14.0 Feed Stage, N1= 6.0

R(1)= -0.000768 R(2)= 0.000896

N	X-Gd+Tb	X-Gd	X-Tb	X-HCl	X-MF(Gd	Y-Gd+Tb	Y-Gd	Y-Tb	Y-MF(Tb)	D-Gd	D-Tb	Sep. Factor	E-Gd	E-Tb
1	0.20250	0.01225	0.19024	0.70861	0.06052	0.06093	0.00071	0.06022	0.98834	0.05796	0.31655	5.46156	0.23184	1.26619
2	0.27839	0.04991	0.22848	0.48094	0.17927	0.11152	0.00397	0.10756	0.96444	0.07954	0.47076	5.91834	0.31817	1.88305
3	0.30472	0.12336	0.18135	0.40195	0.40485	0.13050	0.01338	0.11712	0.89748	0.10846	0.64582	5.95431	0.43385	2.58329
4	0.32057	0.20273	0.11785	0.35439	0.63239	0.13708	0.03174	0.10534	0.76843	0.15656	0.89385	5.70919	0.62625	3.57539
5	0.33280	0.25522	0.07758	0.31772	0.76690	0.14104	0.05158	0.08946	0.63427	0.20210	1.15313	5.70575	0.80840	4.61253
6	0.39439	0.32566	0.06873	0.29843	0.82572	0.14410	0.06471	0.07939	0.55095	0.19870	1.15510	5.81316	0.26494	1.54013
7	0.36388	0.31514	0.04873	0.38998	0.86607	0.10414	0.05674	0.04740	0.45515	0.18005	0.97271	5.40252	0.24006	1.29694
8	0.34429	0.30730	0.03699	0.44873	0.89255	0.08126	0.04886	0.03240	0.39874	0.15900	0.87591	5.50896	0.21200	1.16788
9	0.33007	0.30112	0.02894	0.49141	0.91231	0.06657	0.04297	0.02359	0.35445	0.14270	0.81513	5.71220	0.19027	1.08685
10	0.31851	0.29572	0.02279	0.52608	0.92846	0.05590	0.03834	0.01756	0.31410	0.12965	0.77051	5.94304	0.17287	1.02735
11	0.30797	0.29027	0.01770	0.55770	0.94254	0.04723	0.03429	0.01294	0.27397	0.11813	0.73107	6.18865	0.15751	0.97476
12	0.29689	0.28362	0.01326	0.59095	0.95533	0.03932	0.03020	0.00912	0.23195	0.10648	0.68778	6.45924	0.14197	0.91704
13	0.28248	0.27321	0.00927	0.63416	0.96718	0.03101	0.02522	0.00580	0.18690	0.09231	0.62567	6.77797	0.12308	0.83423
14	0.25553	0.25000	0.00553	0.71500	0.97834	0.02021	0.01741	0.00280	0.13864	0.06964	0.50633	7.27067	0.09285	0.67511

Tb purity in stage 1 solvent phase = 0.9883
Gd purity in stage N aqueous phase = 0.9783
Tb recovery = 0.9387
Gd recovery = 0.9952
Average E-Tb of scrub section = 2.7841
Average E-Gd of scrub section = 0.4837
Calculated scrub acidity = 1.3157

Table 7

Stagewise Calculation for the Extraction Separation of Gd-Tb (16-stage circuit)

Feed Concentration, mol/L, F (3)= 0.5051
Gd Concentration, mol/L, F(1)= 0.3768
Tb Concentration, mol/L, F(2)= 0.1283
Gd %= 74.6 Tb%= 25.4
Feed Flow, L= 1.0
Scrub Flow, L1= 0.5
Solvent Flow, V= 2.0
Total Stages, N= 16.0 Feed Stage, N1= 7.0

R(1)= -0.002894 R(2)= 0.001365

N	X-Gd+Tb	X-Gd	X-Tb	X-HCl	X-MF(Gd)	Y-Gd+Tb	Y-Gd	Y-Tb	Y-MF(Tb)	D-Gd	D-Tb	Sep. Factor	E-Gd	E-Tb
1	0.19646	0.00308	0.19339	0.71429	0.01566	0.06155	0.00018	0.06137	0.99710	0.05844	0.31734	5.43001	0.23377	1.26935
2	0.27044	0.02250	0.24794	0.49236	0.08320	0.11105	0.00167	0.10938	0.98495	0.07422	0.44116	5.94371	0.29689	1.76462
3	0.29454	0.07327	0.22128	0.42005	0.24875	0.12954	0.00653	0.12302	0.94961	0.08912	0.55595	6.23802	0.35649	2.22379
4	0.30859	0.15230	0.15630	0.37790	0.49351	0.13557	0.01922	0.11635	0.85823	0.12620	0.74440	5.89867	0.50479	2.97761
5	0.32100	0.22161	0.09999	0.33888	0.68907	0.13908	0.03898	0.10011	0.71976	0.17589	1.00120	5.69205	0.70358	4.00480
6	0.33190	0.26225	0.06965	0.30798	0.79014	0.14233	0.05630	0.08603	0.60443	0.21468	1.23518	5.75355	0.85872	4.94070
7	0.39449	0.32828	0.06621	0.29399	0.83216	0.14491	0.06646	0.07845	0.54134	0.20245	1.18487	5.85266	0.26993	1.57982
8	0.36430	0.31782	0.04648	0.38456	0.87240	0.10525	0.05871	0.04654	0.44219	0.18473	1.00129	5.42038	0.24630	1.33505
9	0.34521	0.31013	0.03508	0.44182	0.89838	0.08261	0.05086	0.03175	0.38431	0.16400	0.90507	5.51889	0.21866	1.20677
10	0.33169	0.30427	0.02742	0.48239	0.91734	0.06829	0.04510	0.02319	0.33963	0.14822	0.84573	5.70579	0.19763	1.12764
11	0.32111	0.29940	0.02171	0.51414	0.93240	0.05815	0.04070	0.01745	0.30005	0.13594	0.80378	5.91280	0.18125	1.07170
12	0.31200	0.29487	0.01712	0.54148	0.94512	0.05021	0.03705	0.01316	0.26216	0.12565	0.76869	6.11779	0.16753	1.02492
13	0.30326	0.29001	0.01326	0.56767	0.95629	0.04338	0.03366	0.00973	0.22420	0.11606	0.73379	6.32220	0.15475	0.97838
14	0.29359	0.28370	0.00989	0.59669	0.96630	0.03683	0.03001	0.00683	0.18535	0.10578	0.69060	6.52857	0.14104	0.92080
15	0.28029	0.27338	0.00691	0.63659	0.97536	0.02958	0.02527	0.00430	0.14553	0.09244	0.62229	6.73212	0.12325	0.82972
16	0.25415	0.25000	0.00415	0.71500	0.98366	0.01960	0.01754	0.00206	0.10528	0.07016	0.49639	7.07505	0.09355	0.66185

Tb purity in stage 1 solvent phase = 0.9971
Gd purity in stage N aqueous phase = 0.9837
Tb recovery = 0.9567
Gd recovery = 0.9952
Average E-Tb of scrub section = 2.8635
Average E-Gd of scrub section = 0.4924
Calculated scrub acidity = 1.3083

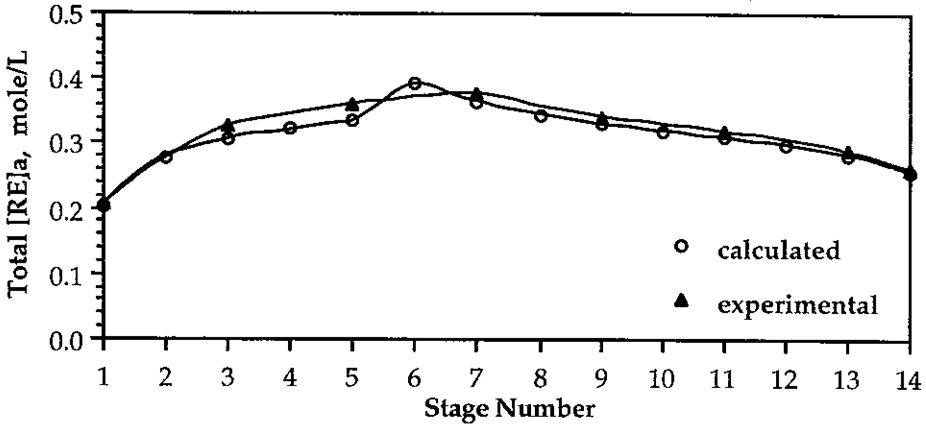

Figure 7 **Equilibrium Aqueous RE Concentration Profile**
(Comparison of Calculated and Experimental Results)

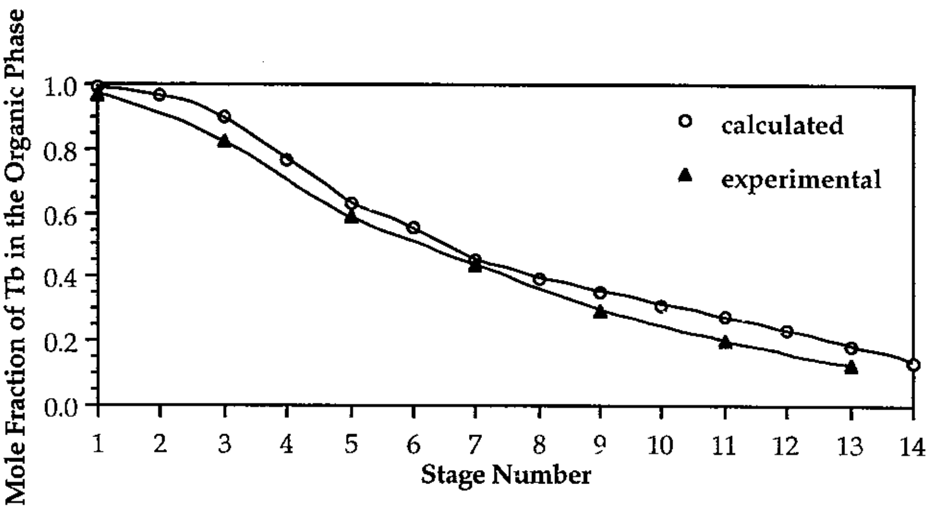

Figure 8 **Mole Fraction Profile of Tb at Equilibrium**
(Comparison of Calculated and Experimental Results)

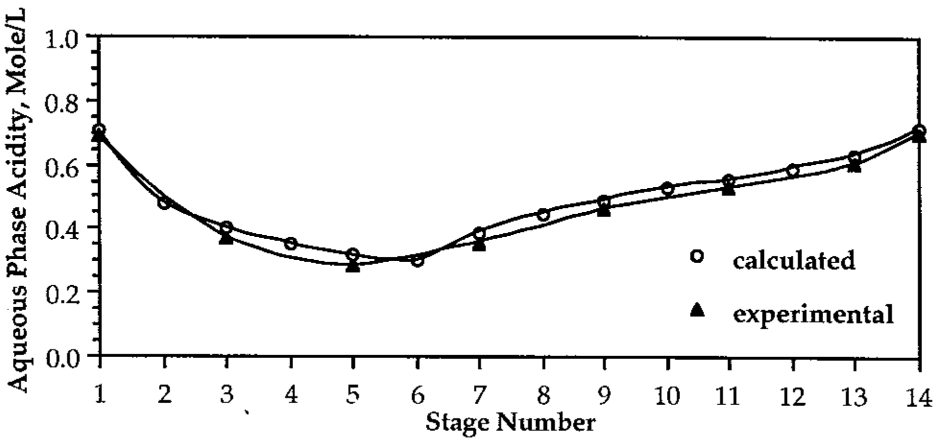

Figure 9 **Equilibrium Aqueous Phase Acidity Profile**
(Comparison of Calculated and Experimental Results)

TABLE 8
Experimental Results of 14-Stage Simulation using Separating Funnels

No. of stages: 14 Feed stage: stage 6
Extraction section: stages 6-14 Scrubbing section: stages 1-5
Acidity of scrub solution: 1.322 *M* HCl
Feed concentration: 0.5051 *M*
Feed acidity: 0.0491 *M* HCl
Feed composition (mole fraction): Gd 74.6%; Tb 25.4%
Organic phase: 1.5 *M* HEH(EHP)-Shellsol D70, and
Phase ratio: organic/feed/scrub = 2/1/0.5

Stage No	RE Conc. mole/L	Acidity mole/L	MF. Gd	MF. Tb	RE Conc. mole/L	MF. Gd	MF. Tb	Separation Factor
1	0.205	0.688	0.144	0.856	0.065	0.030	0.970	5.40
3	0.325	0.374	0.542	0.458	0.134	0.176	0.824	5.54
5	0.359	0.287	0.797	0.203	0.147	0.415	0.585	5.54
7	0.376	0.356	0.876	0.124	0.111	0.564	0.436	5.47
9	0.341	0.460	0.928	0.072	0.071	0.702	0.298	5.45
11	0.319	0.528	0.956	0.044	0.053	0.801	0.200	5.43
13	0.288	0.603	0.975	0.025	0.035	0.875	0.125	5.64
14	0.261	0.699	0.981	0.019	-	-	-	-

TABLE 9
Purity and Yield of Rare Earth Products

	Gadolinium		Terbium	
	Purity, %	Yield, %	Purity, %	Yield, %
Experimental	98.13	99.46	96.98	92.78
Calculated	97.83	98.37	98.83	93.88

The fairly good agreement between the calculated and the experimental results of the aqueous phase RE concentration, acidity, mole fraction of Gd, the organic phase RE concentration, mole fraction of Tb , the yield and purity of Gd and Tb in the products indicates that the steady-state equilibrium mathematical models have accurately described the relationship of variables in the system.

3.5 Multistage Experiment using a Small Mixer-Settler Circuit

A 15-stage small mixer-settler system was set-up and operated to compare the simulation results with actual performance of a continuous multi-stage circuit.

The mixer-settler used in this experiment was continuous, horizontal, box-like, and multistage. It was designed and constructed by BGRINM in 10-stage box-type transparent units with adjacent stages having common walls. The mixer dimension is 4.5x4x4.5 cm, and the settler is 11x4x5.5 cm. They are made entirely of Plexiglas and can withstand the HCl-HEHEHP environment. The pump-mixers (impellers) are also made of Plexiglas and driven simultaneously by a pulley system. The interface level is controlled by a screw-type interface adjustment rod. The overall flow through mixer-settler is counter-current while the flow within each stage is co-current. The flows of feed, scrub and organic solution are introduced to the circuit via peristaltic pumps. The following experimental conditions were used:

Feed solution:	[$RECl_3$] 0.4994 *M*; composition 74.62% Gd-25.38% Tb; [H^+] 0.01519 *M*
Organic phase:	HEHEHP-Kerosine, HEHEHP 1.5199 *M*
Scrub solution:	[HCl] 1.3361 *M*
Flow ratio, mL min $^{-1}$:	organic/feed/scrub = 6.4/3.2/1.0
No of stages:	15 stages, 10 stages for extraction and 5 stages for scrubbing

The mixer-settler circuit was operated for 45 h after filling all the stages. The circuit was stopped and both organic and aqueous samples were taken from each stage for analysis. The results are summarised **Table 10**. The aqueous phase mole fraction of Gd in the product (stage 15) is 93.56%, and the organic phase mole fraction of Tb (purity of Tb) in stage 1 is 90.36%. These results and the stage-wise separation factors of Tb with respect to Gd are generally lower than those obtained from the simulation test using separating funnels. The lower separation efficiency (as compared to the model prediction) can be attributed to:

(i) the use of kerosene instead of Shellsol D70 in the mixer-settler experiment, and

(ii) the mixer-settler circuit has a lower stage efficiency than the separating funnel.

A rare earth mass balance was carried out based on samples collected from the last 7 h, and is shown in **Table 11**. The yield of rare earth is only 97.04%. The small discrepancy can be attributed to experimental errors in operation and measurement. Some leakage can also contribute to the error in the RE mass balance.

TABLE 10
Experimental Results of 15 Stages Mixer-Settlers for Gd-Tb Separation

Stage No	Aqueous Phase				Organic Phase			Total D (Gd+Tb)	D Gd	D Tb	Separat'n Factor ß (Tb/Gd)
	Acidity M	Total [RE] M	Total [RE] g/L	MF (Gd)	Total [RE] M	Total RE g/L	MF (Tb)				
1	0.9070	0.1373	25.46	0.2596	0.0505	9.64	0.9036	0.3681	0.371	1.220	3.286
2	0.8422	0.2401	44.80	-	0.0830	15.45	-	0.3457	-	-	-
3	0.7542	0.3048	56.30	0.5000	0.1097	20.50	0.7727	0.3599	0.455	1.545	3.400
4	1.0144	0.3577	65.46	-	0.1194	22.85	-	0.3338	-	-	-
5	0.9635	0.3769	68.68	0.7295	0.1355	25.09	0.5893	0.3595	0.563	2.179	3.870
6	0.8048	0.4160	76.30	0.7800	0.1347	26.33	0.5245	0.3238	0.610	2.384	3.910
7	0.9328	0.3850	70.50	0.8127	0.1081	20.01	0.4907	0.2808	0.627	2.620	4.180
8	0.8658	0.3636	66.20	-	0.0876	16.21	-	0.2409	-	-	-
9	0.9233	0.3494	63.26	0.86	0.0713	13.17	0.4146	0.2042	0.678	3.031	4.470
10	0.8865	0.3351	60.90	-	0.0598	11.06	-	0.1786	-	-	-
11	0.8856	0.3225	58.32	0.89	0.0497	9.23	0.3416	0.1540	0.738	3.180	4.310
12	0.9359	0.3128	56.24	-	0.0424	8.29	-	0.1356	-	-	-
13	0.9159	0.2994	54.04	0.92	0.0349	6.40	0.2846	0.1165	0.781	3.379	4.325
14	0.9131	0.2840	51.30	-	0.0260	4.77	-	0.0915	-	-	-
15	0.9548	0.2618	47.34	0.94	0.0148	2.71	0.2051	0.0567	0.850	3.183	3.746

TABLE 11
Material Balance of Total Rare Earths for the Mixer-Settler Circuit at Equilibrium

INPUT			OUTPUT						YIELD
Feed Solution			Aqueous Phase			Organic Phase			
Conc. mole/L	Volume mL	Total m.mole	Conc. mole/L	Volume mL	Total m.mole	Conc. mole/L	Volume mL	Total m.mole	%
0.4994	1350	674.19	0.2618	1980	518.36	0.0505	2690	132.85	97.0

4. CONCLUSION

The following major conclusions are drawn from the study:

1. For the system of $(Gd\text{-}Tb)Cl_3$-HCl-1.5 mole L^{-1} HEHEHP-Shellsol D70, an orthogonal design was used to obtain 36 sets of equilibrium data. From the results, the distribution coefficients and separation factors of Gd, Tb and total rare earth were calculated. Within the experimental range the variation of separation factor was small and the average separation factor was 5.55.

2. In the following experimental range:

   (i) equilibrium aqueous total RE concentration, $X_1 = 0.1\text{-}0.96\ M$;
   (ii) equilibrium aqueous acidity $X_2 = 0.32\text{-}0.90\ M$; and
   (iii) the mole fraction of Gd, $X_3 = 0.006\text{-}0.996$,

   the step-by-step multiple regression method was used to mathematically correlate the RE concentration in the organic phase as a function of aqueous phase total RE concentration , acidity and the mole fraction of one RE. The empirical mathematical models are:

$$Y_{Gd} = \text{Exp}\,(a_1 + a_2X_1\text{Ln}X_1 + a_3X_2\sqrt{X_3} + a_4X_2\text{Ln}X_1 + a_5X_3X_3 + a_6\sqrt{X_2}\,\text{Ln}X_3 + a_7\sqrt{X_3}\text{Ln}X_2 + a_8\text{Ln}X_2\text{Ln}X_2)$$

$$Y_{Tb} = \text{Exp}\,(a_1 + a_2X_1\sqrt{X_2} + a_3X_2X_3 + a_4X_2\sqrt{X_3} + a_5X_3\sqrt{X_3} + a_6\sqrt{X_1}\,\sqrt{X_2} + a_7\sqrt{X_2}\text{Ln}X_3 + a_8\text{Ln}X_2\text{Ln}X_3)$$

   The average relative error of the models is less than 4% with a correlation coefficient of 0.9996.

3. The derived models were used to study the equilibrium distribution of RE in both phases of the system, and to understand the effect of RE concentration, acidity and mole fraction of Gd on distribution coefficients and separation factors. At constant acidity and RE concentration of 0.1-0.90 *M*, the RE concentration in the organic phase increases with increasing aqueous RE concentration. The increase is more apparent at lower aqueous acidities and reaches a maximum at the aqueous RE concentration of about 0.5 *M*. The organic phase RE concentration is fairly constant with further increasing of aqueous RE concentration.

   At constant aqueous RE concentration, the organic phase RE concentration is lower at higher aqueous acidity. The distribution coefficient of RE increases with decreasing aqueous RE concentration, and decreases with increasing aqueous acidity. The distribution coefficient of Gd and Tb increases with increasing mole fraction of Gd, but the distribution coefficient for total RE decreases. The effect is due to the fact that $D_{Gd} < D_{Tb}$.

4. The stage-by-stage calculation method was used to simulate a counter-current extraction process of 14- and 16- stages for the separation of Gd-Tb. The process conditions were: $RECl_3$ feed solution 0.5051 *M* having a composition of 74.62% Gd - 25.38% Tb; acidity $[H^+]$ 0.04905 mole L^{-1}; organic solvent 1.5129 *M* HEHEHP-Shellsol D70; and flow ratio of organic : feed : scrub = 2 : 1 : 0.5. The separation results for the two respective processes are: 97.83% and 98.37% of Gd with yield of 99.52%; 98.83 and 99.71% of Tb with yield of 93.88% and 95.68% respectively. The calculated HCl scrub acidity should be 1.316 and 1.308 *M* respectively.

5. A 14-stage counter-current extraction simulation using separating funnels was also carried out in the laboratory. The process conditions were the same as those used in the above stage-by-stage calculation. The experimental results with respect to product purity and yields, RE concentration of each stage, aqueous acidity and composition are in good agreement with the calculated results. This means that the derived mathematical models have accurately predicted the relationship between the variables of the system. The practical implication of these models is that they can be used not only for the calculation for Gd-Tb separation, but also for the estimation of Gd-Tb group separation. All elements preceding Gd in the lanthanide series can be represented by Gd, and Tb is used for representing those elements after Tb. The models are purely empirical and their application cannot be extended beyond the experimental range used in this study.

6. Two computer programs were written in Basic language for an IBM compatible PC. The first program was used to determine the mathematical models (either polynominal or exponential) to describe equilibrium in the mixed Gd/Tb system using step-by-step multiple regression procedures, and the second program was for the stage-by-stage calculation of RE and acidity material balances in multi-stage circuits.

7. A continuous, 15-stage counter-current extraction experiment was carried out in a small mixer-settler circuit. In the experiment all other conditions were the same as those used in the separating funnels simulation experiment except that the organic phase Shellsol D70 diluent was replaced with a Chinese kerosene, and an additional stage was added to the extraction section of the circuit. The final products at equilibrium were Gd_2O_3 of 93.56% and Tb_4O_7 of 90.36%. Both purities were lower than the results obtained from the simulation experiment using separating funnels. Some of the distribution coefficients and separation factors for individual stage are also generally lower than the separating funnel experiment. The discrepancies of results can be due to different diluents for the same organic extractant (P507) in the two experiments, and the lower stage efficiency of the mixer-settler as compared to the separating funnels.

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