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Extraction Behavior and Simulation of Rare Earths in Phosphonic Acid Systems

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ABSTRACT

In this work, equilibrium data in the (Sm-Gd)Cl_3–HCl–H_2O–1 M saponified and nonsaponified HEHEHP–isoparaffin system were determined. The total and individual effects of rare earth (RE) concentrations on the separation factor were obtained. Based on the equilibrium data, five mathematical models describing the extraction of Sm and Gd under equilibrium conditions were developed. The models cover wide ranges of various parameters such as the total RE concentration in equilibrated aqueous phase from 0.045 to 0.6 M; acidity in equilibrated aqueous phase from 0.09 to 0.65 M; and mole fraction of Sm from 0.008 to 0.991 with small average relative errors ($<$3.5%). These models describe the extraction behavior of Sm and Gd, including the distribution of rare-earth concentrations in both the aqueous and the organic phases, the effects of acidity, RE concentration, and the mole fraction of Sm in aqueous phase and the RE concentration in the organic phase. A solvent extraction simulation and experiment were performed for the (Sm-Gd)Cl_3–H_2O–1 M HEHEHP–isoparaffin system. The simulation output result was used to design experimental solvent extraction circuits in laboratory. The purity of the products obtained, samarium as well as gadolinium, was higher than 98%.

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Key Words. Solvent extraction; Rare earth; Phosphonic acid; simulation

INTRODUCTION

The chemical and physical properties of rare-earth elements are so similar that their separation from each other is, as a general rule, a difficult problem. Ion-exchange methods and solvent extraction are techniques currently employed for mutual separation or purification of rare earths. Solvent extraction is generally accepted as the most appropriate commercial technology, since it is suitable for the treatment of large volumes by continuous processes. The separation of rare-earth elements by the solvent extraction technique is a subject of great current interest (1–15).

Several organophosphorus extractants (14–33), such as di-2-ethylhexyl phosphoric acid (HDEHP), tributylphosphate (TBP), and most recently 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEHEHP), have became more and more important in the rare-earth separation industry. Compared with others, the disadvantage of HDEHP is the high acidity which is required for backextraction. This is a consequence of the very stable complex with RE. Consequently, large amounts of reagents are employed for neutralizing the stripping solution after the rare-earth elements have been collected as hydroxides or as oxalates, resulting in a higher operation cost. This weak point is partially overcome by using HEHEHP instead of HDEHP. In addition, HEHEHP allows the extraction to be operated under higher concentrations of rare earths, because it can be more heavily loaded with RE than HDEHP before the onset of saturation effects. This results in an increase of the extraction efficiency. Therefore, HEHEHP was selected as the extractant in the present investigation.

The equilibrium mathematical model is a powerful tool in the research of the behavior of extraction systems, as well as for the static simulation of fractional extraction. The extraction equilibrium of Sm and Gd has been studied at low and common concentrations (less than 0.1 M). However, available equilibrium models at concentrations suitable for the commercial solvent extraction processes are scarce. There is one lacunae of knowledge about cross-correlation between the variables: $[RE]_a$, $[RE]_o$, aqueous phase acidity, and the mol fractions of the components.

The RE concentration in the equilibrated aqueous phase is lower than the RE concentration of the initial solution. Comparing the initial and equilibrium data with nonammoniated extractant, the following relation between initial acidity $[H^+]_i$, aqueous phase acidity $[H^+]_e$, and RE equilibrium concentration in the organic phase $[RE]_o$ is obtained:

$$[RE]_o * 3 + [H^+]_i = [H^+]_e$$

This relation indicates the acidity at equilibrium. It is one of the important requirements to simulate countercurrent extraction. This equation of acidity verifies the proposed ion-exchange mechanism for the extraction of lanthanides with an acidic organophosphorous extractant, i.e., 1 mole of RE^{3+} may replace 3 moles of H^+ from the extractant to the aqueous phase:

$$2RE^{3+} + 3(HA)_2 = RE_2A_3 + 6H^+$$

Obviously, since the extraction happened between both phases, the aqueous phase acidity and RE concentration are different from the initial solution. Generally, the aqueous phase acidity is higher than the initial one.

In a countercurrent extraction, ammonium cations enter into the circuit with the extractant. In general, ammonium cations only exist in the stage at which the extractant enters into the system. It goes out of the process in the raffinate. At this stage the ammonium in the organic phase is easily replaced by the rare earth of the aqueous phase and transferred to the latter phase, finally flowing out with the raffinate. Obviously, at this stage the reaction and medium have differing conditions than in other stages, so that the rare-earth distribution equilibrium is different from other stages as well. Therefore, it is necessary to have a special model to describe the equilibrium at this stage.

Except for the stage at which the extractant enters the system, the acidity of the aqueous phase may be lower and no ammonium exists in either phase of other stages of the extraction section. In order to model these latter stages, the equilibrium data at lower aqueous phase acidity must be obtained. Using ammoniated solvent, even though the aqueous phase acidity may be controlled at low pH, the equilibrium aqueous phase contains ammonium chloride.

It is therefore the aim of this study to: (a) obtain single-stage equilibrium experimental data for the extraction of Sm and Gd from hydrochloric acid solutions with 1 M saponified and the nonsaponified HEHEHP in isoparaffin at the typical concentrations of commercial solvent extraction processes; (b) correlate the data mathematically to obtain equilibrium models; (c) study the behavior of Sm-Gd in the systems mentioned above using the models developed; and (d) simulate mathematically the Sm-Gd fractional extraction separation process and perform the circuit for separation of Sm and Gd on a laboratory scale.

EXPERIMENTAL

Extraction Equilibrium Procedure

The two rare-earth oxides Gd_2O_3 and Sm_2O_3 used in this study were obtained from the Jioujiang Rare Earth Plant of the People's Republic of China and had purities greater than 99.5 and 99%, respectively, with respect to the presence of other rare-earth elements. HEHEHP produced by Albright & Wilson Corp. (USA), was used without further purification. The diluent, isoparaffin, was supplied by the Unipar Quimica Corp. of Brazil. Throughout this study, 1 M HEHEHP in isoparaffin was employed as the organic solvent. The hydrochloric acid and ammonia were of analytical grade. The aqueous RE solutions were obtained from the RE oxide consumed by concentrated HCl. The HEHEHP in the isoparaffin exchanged, i.e., loaded with RE, was prepared by extraction of the rare earth from an aqueous solution at low acidity with ammoniated extractant. The concentration in the organic phase was determined by one backextraction, then the aqueous phase was analyzed.

The total concentration of rare-earth elements was determined by EDTA complexometric titration, while the acidity of the system was determined by neutralization. These analyses were performed three times per sample. The composition of the rare-earth solutions was determined by atomic emission spectroscopy inductive coupled plasma or x-ray fluorescence spectroscopy. Besides these analyses, the samples for analysis of the acidity and rare-earth concentration were conducted by titration as follows: in a sample containing HCl and RE, a few drops of mixed indicator (alcohol solution of 0.1% methylene blue and 0.1% methyl red) were added, and acidity was titrated with a standard NaOH solution with color change from violet to green at the end point. To this titrated solution, 5 drops of 1:10 [HCl] $=$ 1.0 M, 10 mL buffer solution, and 2 to 3 drops of oxylene indicator (0.1% water solution) were added and titrated with a standard EDTA solution to produce a color change from violet-red to yellow-green at the end point. The scrub solution used was 1 M.

Three types of batch contacts were performed: with ammonia-saponified HEHEHP, with untreated HEHEHP, and with RE-loaded HEHEHP. In all experiments the contact time was 5 minutes.

The equilibrium data at lower aqueous phase acidity and no ammonium in the aqueous phase were also obtained. In order to examine the effects of RE extraction in single bath contacts in the absence of ammonium chloride, the concentration of RE in the contact was a summation of RE introduced initially from the aqueous phase and RE present in the organic phase as RE–HEHEHP complex.

Simulation

A countercurrent extraction (fractional extraction) is schematically illustrated in Fig. 1. This process of countercurrent extraction can be simulated and achieved in the laboratory with separatory funnels.

A series of separatory funnels was numbered and arranged to represent the total stages in the test. Assuming the total number of stages to be 10, for example, Stages #1 to #5 represented the scrubbing section, Stage #6 corresponded to the feed stage, and from #7 to #10 corresponded to the extraction

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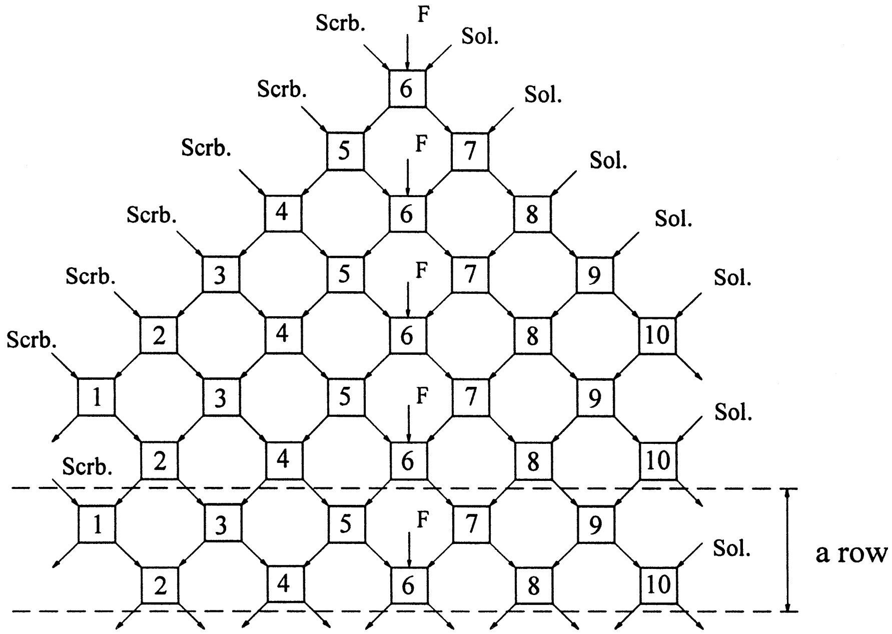

FIG. 1 The schematic flow diagram for a countercurrent extraction system.

section. The test began in the feed stage where the feed solution, the scrub solution, and the solvent were put in contact in the selected proportions. After mixing and standing, the aqueous and organic phases were separated, each one going to the respective adjacent funnels in opposite directions. The aqueous phase was transferred into Stage #7 and the organic phase into #5. Scrub and solvent solutions were added in #5 and #7, respectively. After mixing and standing, the aqueous phases of #5 and #7 were transferred into #6 and #8, respectively; and the organic phases into #4 and #6, respectively. Adding scrub and solvent in #4 and #8, the feed solution was fed into #6. After mixing and standing, the aqueous phases of #4, #6, and #8 were transferred into #5, #7, and #9, while the organic phases of #4, #6, and #8 were transferred into #3, #5, and #7, respectively. Scrub and solvent were added to Stages #3 and #9, respectively. After mixing and standing, the procedure described above was repeated. When the aqueous phase reached Stage #10 and/or the organic phase went back to Stage #1, the aqueous phase was discarded (or collected) from #1 and/or the organic phase was also discarded (or collected) from #10 after the final mixing and standing procedures. The operation is schematically shown in Fig. 2.

After the aqueous phase reached Stage #1 and/or the organic phase reached Stage #10, the number of rows was counted. A row was defined as one eluted portion of the organic phase or the raffinate phase. In our experimental observation, when the number of rows operated was 3 to 4 times the number of

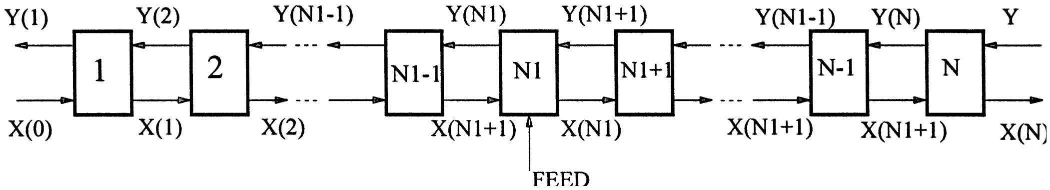

FIG. 2 Schematic representation of a countercurrent extraction with separator funnels.

stages, the equilibrium of the extraction system was considered to have approached steady-state. Samples were taken from the aqueous and organic effluents to analyze the rare-earth components and concentrations. According to the analytical results, the mass balance may be calculated and from the results of such a mass balance it was determined if the system had reached its equilibrium, indicating if the experiment was to be continued or finished.

If it was decided to finish the experiment, samples were taken from the aqueous and organic phases of each stage (or part of the stages) for analysis. The equilibrium data included the rare-earth components and concentrations in both the aqueous and organic phases, as well as the aqueous phase acidity in the aqueous phase. In order to obtain a proper mass balance and to avoid changing the organic:aqueous phase ratios in the countercurrent simulation, it was critical that quantitative transfer of phases to subsequent stages was realized. The scrub solution was prepared with the HCl concentration determined in the simulation. One must bear in mind that this original solution has no RE when used in the first contact. It is also important to consider that the scrub process is intended to remove (backextract) the REs selectively from the loaded solvent. The aqueous effluent stream, the raffinate, must carry all the Sm without any Gd. The extraction approach used to generate all data was backextraction.

DISCUSSION

In a binary extraction system with an acidic extractant, the rare earth concentration in the organic phase is a function of some variables in the aqueous phase, like total RE concentration ($X1$), acidity ($X2$), and the mole fraction of either of the RE elements ($X3$). In order to find the relationship among these variables with the minimum number of experiments, the crossover design method was employed to determine the necessary experiments.

In the system studied here, 1 M HEHEHP saponified with ammonia (30% mol/mol) was used as the extractant to decrease the extraction acidity as well as to enhance the extraction capacity of the extractant, i.e., the lower the acidity of the aqueous phase, the higher will be the extraction of the RE.

It must be pointed that until now no kinetics studies have been performed that would indicate exactly how saponification could affect the exchange process, but our experience has demonstrated this is very helpful to the solvent extraction of RE.

In a fractional extraction, ammonia enters into the system with the extractant. In general, ammonium only exists in the stage at which the extractant enters the system. In this stage the ammonium in the organic phase is easily replaced by the rare earth in the aqueous phase and is thus transferred to the aqueous phase, finally flowing out with the raffinate. Obviously, at this stage the reaction and medium have different conditions from other stages, so the distribution equilibrium is also different from other stages. The extraction in the subsequent extraction stages is the result of hydrogen-ion transfer from unsaponified solvent. Therefore, it is necessary to have a special model to describe the equilibrium at this stage. In order to obtain the equilibrium data, the saponified extractant (saponified percentage 30%) should be used in this experiment.

Based on the concentration and composition of the feed to be separated in the industrial Sm and Gd separation process, the experimental parameters were selected in the following regions: initial RE concentration, 0.2—0.45 M; initial acidity, 0.05–0.2 M; and initial mole fraction of Gd 0.01–0.05. Each variable was further divided into four levels.

Using ammoniated solvent, even though the aqueous phase acidity may be kept at a low pH, the equilibrium aqueous phase will contain ammonium chloride. Otherwise, using the solvent without ammonia, even though no ammonium chloride would be present in the equilibrium aqueous phase, the aqueous phase acidity would increase because hydrogen ions would be transferred into the aqueous phase while rare earth is being extracted. The lower the initial solution acidity, the more the acidity increases. It would be impossible to get the desired data (lower aqueous phase acidity and no ammonium chloride) in both these ways. Only in this way will the equilibrium data at lower aqueous phase acidity and no ammonium in the aqueous phase be obtained. The procedure to obtain an extractant with rare earth is to extract the rare earth at low acidity with ammoniated extractant. Based on the concentration and composition of the feed to be separated in the industrial Sm and Gd separation process, the experimental parameters were selected in the following regions: initial RE concentration, 0.1–0.4 M; initial acidity, 0.01–0.3 M; and initial mole fraction of Gd, 0.02–0.45.

There are usually higher acidities in the scrubbing section and in several stages of the extraction section. In order to obtain equilibrium data of the latter stages, the experiments must be done using the extractant without rare earth or ammonium cations. According to the concentration and composition of the feed to be separated and the acidity in the scrubbing section, the experimental conditions were chosen as follows: initial RE concentration, 0.1–0.6 M; initial acidity, 0.01–0.6 M; and initial mole fraction of Gd, 0.02–0.99.

Figure 3 illustrates that in a binary mixture the RE concentration in the organic phase varies in a nonlinear fashion with respect to the total RE concentration in the aqueous phase in the range from 0.05 to 0.55 M and at a constant acidity. For convenience of representation, the mole fraction of Sm was fixed, in this case to 0.65. It is clearly seen that when the RE concentration in the aqueous phase increases from 0.2 to 0.55 M, the RE concentration in the organic phase increases at the higher acidity. At lower acidity the RE concentration in the organic phase first increases and then decreases, and this figure shows that the maximum extraction occurs when the RE aqueous concentration is in the range from 0.30 to 0.35 M.

From Figure 4 it can be understood that the total RE distribution coefficient *D*, defined as the ratio between the concentration of the RE elements in the organic phase, $[\mathrm{RE}]_o$, and the one in the aqueous phase, $[\mathrm{RE}]_a$, $D = ([\mathrm{RE}]_o/[\mathrm{RE}]_a)$, varies inversely with the increase of the RE concentration from 0.05 to 0.55 M as well as the increase in acidity from 0.2 to 0.6 M in the aqueous phase. The higher *D* is obtained at acidities lower than 0.3 M and at RE aqueous concentrations lower than 0.25 M. The parameter *D* changes greatly when the RE aqueous concentration decreases from 0.2 to 0.05 M with the acidity varying from 0.3 to 0.2 M.

It can be seen from Fig. 5 that the distribution coefficient of total rare earth *D* decreases with increasing acidity from 0.2 to 0.55 M, while RE concentra-

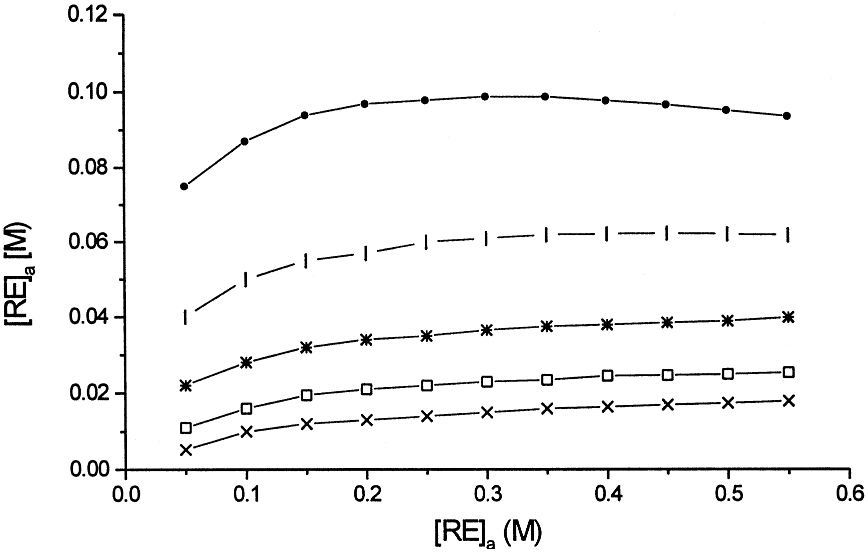

FIG. 3 The equilibrium curves (RE concentration in the aqueous and organic phases; constant mole fraction of Sm = 0.65). The HCl concentrations (in M) from the top down are 0.2, 0.3, 0.4, 0.5, and 0.6.

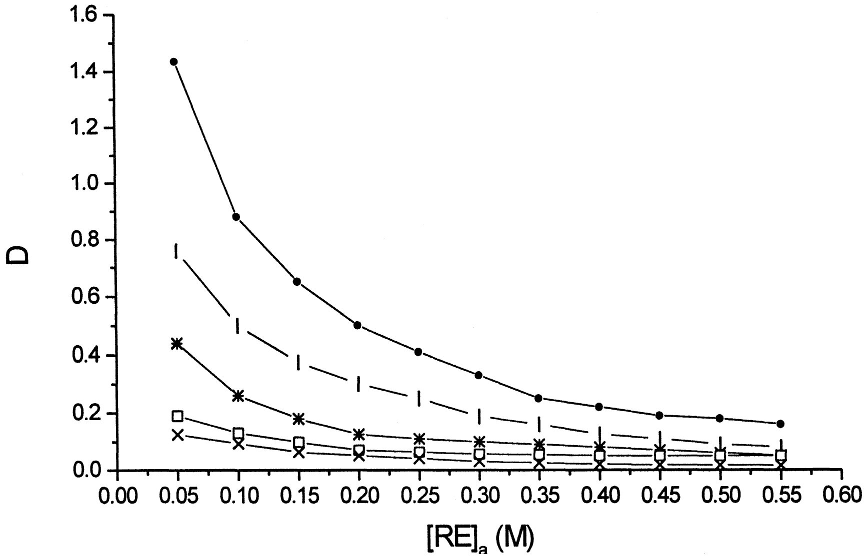

FIG. 4 The relation between the total rare earth distribution coefficient (*D*) and [RE] of the aqueous phase in equilibrium (mole fraction of Sm = 0.65). The HCl concentrations (in M) from the top down are 0.2, 0.3, 0.4, 0.5, and 0.6.

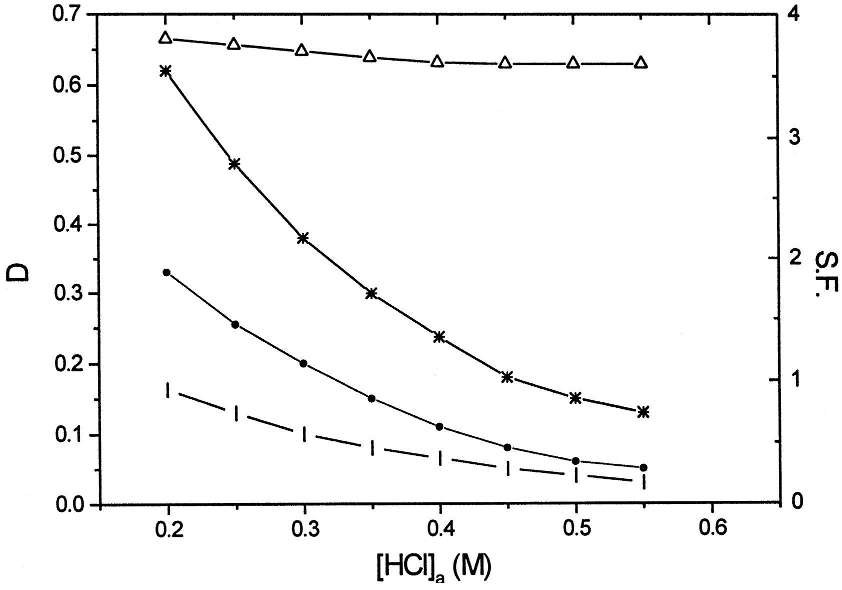

FIG. 5 The effect of acidity on the total rare earth distribution coefficient (*D*) and on the separation factor (S.F.) ($[Re]_a = 0.3$ M, mole fraction of Sm = 0.65). (●) *D*: Sm + Gd; (|) *D*: Sm; (∗) *D*: Gd; (△) S.F.: Sm/Gd.

tion is maintained at 0.3 M and mole fraction of Sm is 0.65. The separation factor (SF) changes slightly from 3.8 to 3.5, which means that at low acidity more rare earth is extracted and Gd can be separated from Sm a little more easily.

In the case where the mole fraction of Sm was maintained at 0.65 and kept constant at an acidity corresponding to 0.3 M, Fig. 6 demonstrates that the distribution coefficient decreases with increasing RE concentration in the aqueous phase. On the other hand, in the range from 0.05 to 0.55 M of the $[RE]_a$, the separation factor does not vary too much.

It is clearly seen from Fig. 7 that the distribution coefficient of total rare earth decreases with increasing mole fraction of Sm, because D_{Sm} is less than D_{Gd}, but both D_{Sm} and D_{Gd} increase with increasing mole fraction of Sm. The separation factor is somewhat different in value but does not change too much. It can also be seen that the equilibrium curves of D_{Sm} and D_{Gd} are almost parallel when the mole fraction of Sm varies from 0.02 to 0.98. This means that the separation factor of Sm with respect to Gd is approximately a constant, and changes only slightly from 3.8 to 3.5 with variations in the mole fraction of Sm.

As mentioned above, in a binary extraction system with acidic extractant, rare-earth concentration in the organic phase is a function of a series of variables in the aqueous phase, i.e., the total rare earth concentration *X1*, the acidity *X2*, and the mole fraction of one of the rare-earth elements *X3*. In order to find the relationship among them, multiple regression is a powerful statistical

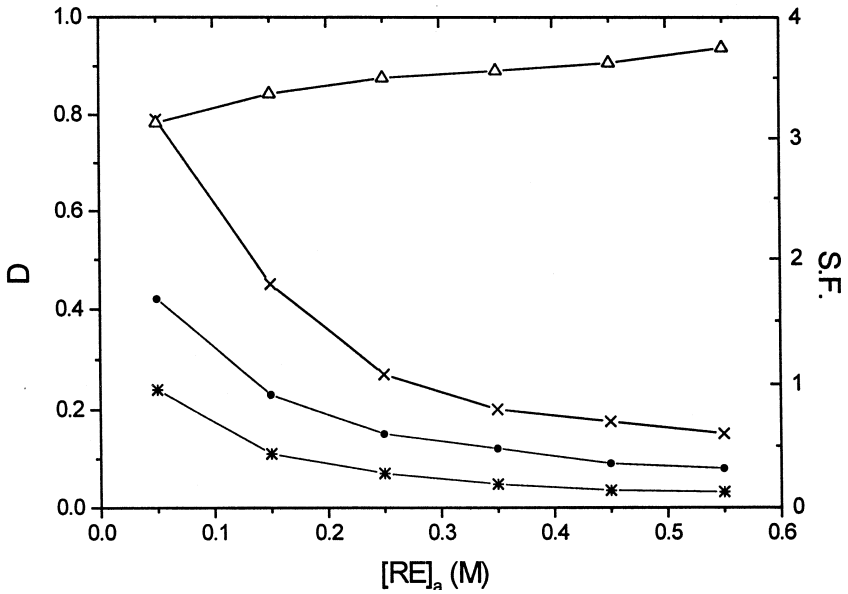

FIG. 6 The effects of [RE] in the aqueous phase on *D* and on the separation factor (S.F.) ([HCl] = 0.3 M, mole fraction of Sm = 0.65). (●) *D*: Sm + Gd; (×) *D*: Sm; (∗) *D*: Gd; (△) S.F.

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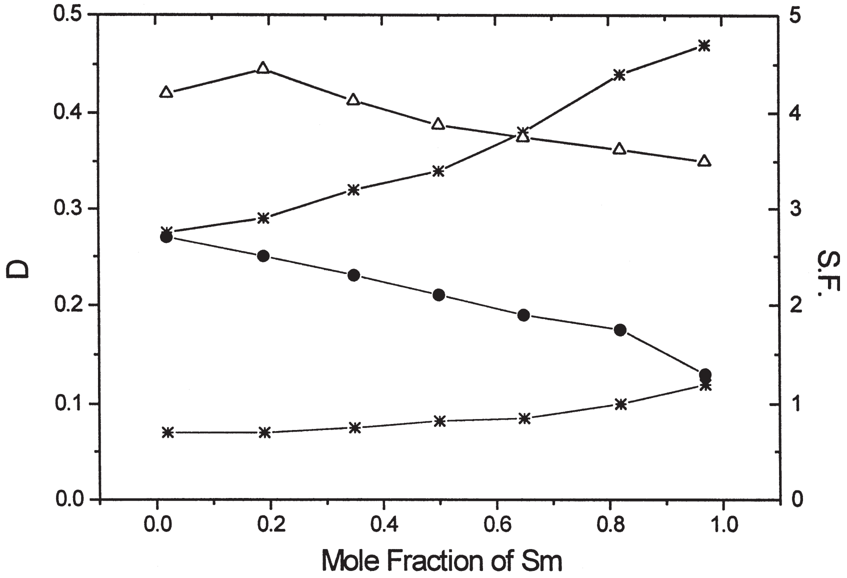

FIG. 7 The effect of the mole fraction of Sm on D and on the separation factor (S.F.) ($[\mathrm{RE}]_a$ = 0.3 M, [HCl] = 0.3 M). (●) D: Sm + Gd; (top ∗ curve) D: Sm; (bottom ∗ curve) D: Gd; (△) S.F.

tool. It can deal with more complex data than other approaches and lead to more quantitative conclusions about the data. In general, the regression model is an empirical model. The model can express which variables are the important ones which affect the independent variables, even though the model only describes a mathematical relationship between dependent and independent variables, and it does not involve any physical consideration. In this work the extraction equilibrium models were developed by a personal computer with a multiple regression program developed in BASIC language.

The models presented below describe how the variables mentioned above, $X1$, $X2$, and $X3$, interact. Each model describes one function $Y_{\mathrm{element}} = f(X1, X2, X3)$. They will be used later in a stagewise calculation of extraction and separation of Sm and Gd.

Using the equilibrium data, which represent the equilibrium of Sm and Gd with ammoniated extractant, Model A and Model B were developed. Both models will be used for the calculation of the solvent inlet stage in fractional extraction.

Model A:

$$Y_{\mathrm{Sm}} = \exp(a1 + \mathrm{sqr}(X1)*(a2*X3 + a4*\log(X3)) + \log(X2)*(a3*X3 + a5*\log(X2)))$$

Average relative error 1.14%, relative factor 0.9964.

Model B:

$$\begin{aligned} Y_{\mathrm{Gd}} = (\exp(&a1 + a2*X2*X2 + \log \\ &\times (X1)*(a3*X3 + a5*\mathrm{sqr}X1)) + \log(X2)*(a4*X3 \\ &+ a6*\mathrm{sqr}(X3)) + a7*\log(X3)*\log(X3))) \end{aligned}$$

Average relative error 2.49%, relative factor 0.9991.

The available parameter ranges of Models A and B are: $X1 = 0.095$–0.36 M; $X2 = 0.09$–0.178 M; $X3 = 0.941$–0.991 M; where Y_{Sm} is the Sm concentration in the organic phase (M), Y_{Gd} is the Gd concentration in the organic phase (M), Y is the total RE concentration in the organic phase (M), $X1$ is the total RE concentration in the aqueous phase (M), $X2$ is the acidity in the aqueous phase (M), and $X3$ is the mole fraction of Sm in the aqueous phase or mole fraction of Gd in aqueous phase (in Model B). $B_{\mathrm{Gd/Sm}}$ is the separation factor between Sm and Gd. The parameters used in Models A and B are listed in Table 1.

Both models are exponential models. The number of parameters is between 5 and 9, the calculation error is between 1.14 and 3.5%. The equilibrium data were predicted with the models and compared with the experimental data. Some of the results are shown in Table 2. It can be seen from them that there are only small differences between the predicted and the experimental data.

Figure 8 shows the comparison of the extraction systems with nonammoniated and with ammoniated extractants. As a matter of fact, it can be recognized that a lower aqueous phase acidity must be maintained in order to promote RE concentration in the organic phase using an ammoniated extractant. An interesting phenomenon was illustrated, that at the same aqueous phase acidity the distribution coefficient with nonammoniated extractant is larger than the distribution coefficient with ammoniated extractant. One part of the chloride ions

TABLE 1
Model Parameters for the Saponified System

Parameter	Model A	Model B
a1	−4.8578	−0.9990
a2	−1.5158	0.4912
a3	0.5760	0.4337
a4	0.0574	7.8813
a5	−0.5745	−10.9919
a6	1.3013	0.5693
a7	−2.2678	0.4117
a8	−0.4816	−0.0336
a9	—	−0.0609

TABLE 2
Comparison between Experimental and Predicted Data by Model A and Model B

No.	$[Sm]_0$ Exp	$[Sm]_0$ Model A	Error (%)	$[Gd]_0$ Exp	$[Gd]_0$ Model B	Error (%)
2	0.10870	0.01790	0.74	0.00350	0.00347	0.76
4	0.09384	0.09546	−1.73	0.01150	0.01140	0.87
6	0.09134	0.09120	0.15	0.00284	0.00285	−0.34
8	0.10040	0.09970	−0.65	0.00324	0.00333	−2.55
10	0.06896	0.06810	1.25	0.00678	0.00687	−1.29
12	0.07525	0.7574	−0.65	0.00324	0.00333	−2.55

is combined with ammonium which increases the $[H^+]$ present in the aqueous phase. This affects the extraction of rare-earth elements in a negative way. The organophosphorous acid extractants form reversed micelles or a water-in-oil microemulsions in *n*-heptane when they are saponified with concentrated alkalies. After equilibrating with water or a solution containing RE, some extractant and diluent in the saponified organic phase transfers into the aqueous phase, and some water solubilized in the water/oil microemulsion returns to the aqueous phase (32, 33).

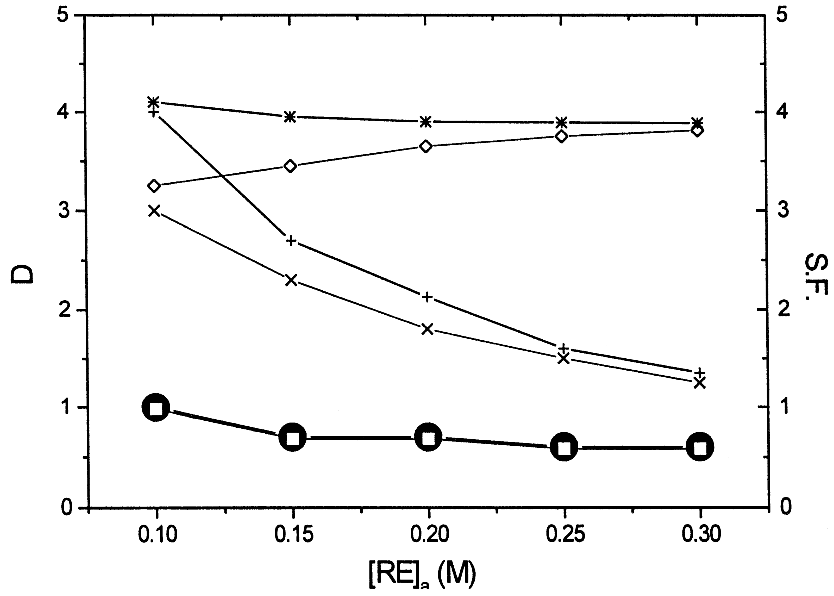

FIG. 8 Comparison of extraction with nonammoniated and ammoniated extractants (mole fraction of Sm = 0.96, [HCl] = 0.12 M). (●) *D*: Sm(nam); (+) *D*: Gd(nam); (∗) E(nam); (□) *D*: Sm(am); (×) *D*: Gd(am); (◊) E(am).

Using the data which represent the equilibrium of Sm and Gd with nonammoniated extractant, Models C and D were obtained. These two models will be used to simulate other stages, except the one of solvent inlet in the fractional extraction.

Model C:

$$\begin{aligned} Y_{\mathrm{Sm}} = \exp(&a1 + a2{\ast}X2{\ast}\mathrm{sqr}(X3) + \log(X1){\ast} \\ &\times (a\,{\ast}X2 + a4{\ast}X3 + a5{\ast}\mathrm{sqr}(X1)) + a6{\ast}\mathrm{sqr} \\ &\times (X2){\ast}\log(X3) + \log(X2){\ast}(a7{\ast}\mathrm{sqr}(X3) + a8{\ast}\log(X2))) \end{aligned}$$

Average relative error 3.5%, relative factor 0.9997.

Model D:

$$\begin{aligned} Y_{\mathrm{Gd}} = \exp((&a1 + \log(X3){\ast}(a2 + a9{\ast}\log(X3)) + (a3{\ast} \\ &X1{\ast}\log(X2) + X2{\ast}(a4{\ast}X2) + a5{\ast}\mathrm{sqr}(X2 + a6{\ast}\log \\ &\times (X1) + a7{\ast}\log(X3)) + a8{\ast}\log(X1){\ast}\log(X1))) \end{aligned}$$

Average relative error 3.28%, relative factor 0.9995.

The ranges for the available parameters used in Models C and D are: $X1 = 0.045\text{–}0.6$ M; $X2 = 0.11\text{–}0.65$ M; $X3 = 0.008\text{–}0.9895$ (Model C), 0.992–0.0105 (Model D).

A further Model E describing the relationship between the total rare-earth concentration in the organic phase and the variables of the aqueous phase was developed. Using this model and Eqs. (1) and (2) below, the concentrations of Sm and Gd in the organic phase were calculated.

$$Y_{\mathrm{Sm}} = Y/((B_{\mathrm{Gd/Sm}}{\ast}(1 - X3)/X3) + 1) \tag{1}$$

$$Y_{\mathrm{Gd}} = Y = Y_{\mathrm{Sm}} \tag{2}$$

Model E:

$$\begin{aligned} Y_{\mathrm{Sm}} = \exp(&a1 + a2{\ast}X2 + a3{\ast}X2{\ast}X3 + a4{\ast} \\ &X2{\ast}\mathrm{sqr}(X3) + \mathrm{sqr}(X1){\ast}(a5{\ast}\log(X1) + a6{\ast}\log(X2)) \\ &+ a7{\ast}\mathrm{sqr}(X2){\ast}\log(X1) + a8{\ast}\log X3){\ast}\log(X3)) \end{aligned}$$

Average relative error 3.32%, relative factor 0.9980.

The parameter ranges allowed in Model E are the same as the ones for Models C and D. In Models C, D, and E, Y_{Sm} is the Sm concentration in the organic phase (M), Y_{Gd} is the Gd concentration in the organic phase (M), Y is the total RE concentration in the organic phase (M), $X1$ is the total RE concentration in the aqueous phase (M), $X2$ is the acidity in the aqueous phase (M), $X3$ is the mole fraction of Sm in the aqueous phase (in Models C, D, A, E), and the mole

TABLE 3
Model Parameters for the Nonsaponified System

Parameter	C	D	E
a1	−5.7506	−2.0473	1.2792
a2	0.2933	−3.5699	−4.8106
a3	−2.5219	6.3781	−5.0843
a4	−4.3067	16.4681	4.3824
a5	−0.4350	−0.6305	−0.4487
a6	—	4.3849	0.2299
a7	—	−0.1390	0.5136
a8	—	—	0.0156
a9	—	—	—

fraction of Gd in the aqueous phase (in Model 2). $B_{\mathrm{Gd/Sm}}$ is the separation factor between Sm and Gd.

The parameters for Models C, D, and E are listed in Table 3. All three of them are exponential models. The number of parameters varies between 5 and 9 and the calculation error is between 1.14 and 3.5%. The equilibrium conditions were predicted with the models and compared with the experimental data; some of the results are shown in Table 4. It can be seen that there are only small differences between the predicted and the experimental data.

TABLE 4
Comparison between Experiment and Predicted Data by Models C, D, and E

	$[\mathrm{Sm}]_0$			$[\mathrm{Gd}]_0$			[Sm + Gd]		
No.	Exp	Model C	Error (%)	Exp	Model D	Error (%)	Exp	Model E	Error (%)
4	0.00026	0.00025	3.56	0.08711	0.08721	−0.11	0.08737	0.09013	−3.16
8	0.00395	0.00358	9.26	0.06420	0.06291	2.02	0.06815	0.06588	3.33
12	0.01742	0.01708	1.99	0.04675	0.04727	−1.11	0.06417	0.06357	0.94
16	0.02277	0.02286	−0.41	0.02355	0.02410	−2.33	0.04632	0.04512	2.60
20	0.02393	0.02322	2.96	0.00128	0.00114	10.70	0.02521	0.02568	−1.86
24	0.00190	0.00220	−16.19	0.04296	0.04371	−1.73	0.04486	0.04760	−6.11
28	0.00442	0.00439	0.75	0.02699	0.02652	1.73	0.03141	0.03279	−4.39
32	0.00340	0.00317	6.72	0.00850	0.00793	6.67	0.01190	0.01095	7.95
36	0.00780	0.00821	−5.31	0.00052	0.00051	2.44	0.00832	0.00866	−4.06
40	0.06158	0.06706	−2.89	0.05992	0.05888	1.74	0.12510	0.12858	−2.78
44	0.03093	0.03099	−0.17	0.08217	0.08340	−1.49	0.11310	0.11361	−0.45
48	0.07617	0.07460	2.05	0.00397	0.00395	5.72	0.08014	0.07893	1.52
52	0.04360	0.04445	−1.95	0.02460	0.02339	4.91	0.06820	0.06539	4.12

Simulation

Two approaches are frequently used in the simulation of multistage solvent extraction processes, namely matrix (1) and stagewise (16) calculation. The latter, however, has been preferred due to its better computational speed, higher convergence precision, and smaller memory requirements. Some simulation programs for rare-earth separation processes predict conditions using the analytical form of the McCabe–Thiele diagram, represented by the Kremser equation (17). In this approach no equilibrium data are used. Another kind of program based on the calculation procedure cited above uses the same logical procedure but makes uses of an equilibrium data table. Neither approach deals with acidity balance.

Here a different scheme was used. A large number of equilibrium data was combined with a crossover design, and a mathematical model was developed to fit these data. In this way a tridimensional approach was attained that relates rare-earth contents in an organic phase with pertinent variables such as acidity, total rare earth concentration, and mole fraction. Five mathematical models were developed for (Sm-Gd)Cl_3–H_2O–1 M HEHEHP–isoparaffin.

As indicated above, Models A and B were employed for the simulation at Stage N; Models C and D were employed for other stages. Because it is very difficult to find the quantitative relationship between the initial and the aqueous phase acidities in the extraction system with ammoniated extractant, the inlet acidity of Stage N, X ($N = 1, 5$) cannot be calculated quantitatively. Considering that the acidities in Stage N and the extraction section do not vary too much (using ammoniated extractant), it was presumed in the simulation that the acidities of each stage of the extraction section are almost constant. Obviously, this presumption is not necessary and not suitable in extraction systems with nonammoniated extractant. Considering that the rare-earth concentrations in the organic phase at each stage of the extraction section are around 0.1 M (this data being taken from single-stage experiments), the chosen initial acidity should make the rare-earth concentration in the organic phase to be around 0.1 M. Based on the concentration and composition of the feed solution and the mathematical models, simulation was performed. The results obtained for the system studied here are shown in Table 5.

TABLE 5
Result of the Mathematical Simulation

Feed solution	0.3 M REO, [HCl] = 0.151 M
Feed composition	Sm_2O_3 65%, Gd_2O_3 35%
Solvent	1 M HEHEHP in isoparaffin
Flow ratio: Feed:scrub:solvent	26.4:10.5:4.9
Extraction section	10 stages
Scrub section	5 stages

TABLE 6
Analytical Results of the Product after a Separation Experiment with 17 Stages

	Aqueous phase					Organic phase			
Row	Volume (mL)	Acidity (M)	RE conc (M)	Sm (%)	Gd (%)	Volume (mL)	RE conc (M)	Sm (%)	Gd (%)
68	15.5	0.1530	0.1230	90.07	9.93	25.3	0.0459	0.08	99.92
69	—	0.1520	0.1200	88.59	11.41	25.5	0.0455	6.06	93.94
70	16.0	0.1559	0.1254	88.03	11.97	25.8	0.0470	0.35	99.65
71	16.3	0.1608	0.1316	86.45	13.55	25.0	0.0470	0.13	99.87
Mean	15.9	0.1554	0.1259			25.4	0.0464		

With the simulation of the process conditions of 15 stages, two separation experiments for the binary system were carried out in the laboratory. The first one was a 17-stage test with the following experimental conditions:

Feed solution: 0.3031 M REO, [HCl] = 0.05 M
Feed composition: Sm_2O_3 64.69%, Gd_2O_3 35.31%
Solvent: 1 M HEHEHP in isoparaffin (ammoniated 30%, mol/mol)
Flow ratio: Feed:scrub:solvent = 26.4:10.5:4.9
Scrub solution: 1.1547 M
Extraction section: 10 stages
Scrub section: 7 stages

After performing 60 “rows,” the samples were taken from the organic phase leaving from the first stage, the raffinate leaving from Stage 17, and from both phases in Stages 2, 4, 6, 8, 10, 12, 14, and 16. The analytical results are shown in Tables 6 and 7.

TABLE 7
Results of the Separation Experiment with 17 Stages

	Aqueous phase				Organic phase		
Stage	RE conc (M)	Acidity (M)	Sm (%)	Gd (%)	RE conc (M)	Sm (%)	Gd (%)
2	0.2869	0.3264	0.18	99.82	0.0853	0.31	99.69
4	0.3169	0.2339	1.50	98.50	0.1708	0.36	99.63
6	0.3209	0.2241	10.65	89.35	0.1096	2.73	97.27
8	0.2808	0.1949	48.18	51.82	0.1097	18.44	81.56
10	0.2634	0.2339	51.07	48.93	0.0858	20.04	79.96
12	0.2638	0.2504	52.46	47.54	0.0809	21.15	78.85
14	0.2659	0.2475	57.90	42.10	0.0812	25.54	74.46
16	0.2734	0.2153	75.41	24.59	0.0837	46.22	53.78
17	0.1250	0.1608	86.45	13.55	0.0470	—	—

Mass balance:

Input: amount of RE in feed solution: 0.3031*10.5 = 3.1826 (mmol)
Output: amount of RE in raffinate: 0.1250*15.93 = 1.9913 (mmol)
amount of RE in organic effluent: 0.0464*25.4 = 1.1775 (mM)
total amount of RE 1.9913 + 1.1775 = 3.1688 (mM)
Yield of RE = 3.1688/3.1826 = 99.57%

According to the above conditions through a 17-stage extraction, the purities of Gd and Sm are higher than 99 and 86%, respectively. The yield of total rare earth reaches 99.57%. It can be seen that the experimental results are not very consistent with the simulation results. The Sm (%) in the raffinate was only 86.45%, and a lot of Gd was present. The reasons may be the following:

a) In the simulation the acidity of the extraction section was presumed to be a constant, but the acidity of the extraction section varied in the experiment.
b) In the simulation the RE concentration in the organic phase of extraction section was presumed to be around 0.1 M, but the actual RE concentration was smaller than 0.1 M.
c) In the simulation the volume of scrub solution as well as the volume of solvent were presumed to be constant throughout the extraction system. Actually, the volume of organic effluent is slightly smaller than the volume of the barren solvent due to the ammonium cations transferred from the organic phase into the aqueous phase. Otherwise, the volume of the raffinate is slightly larger than the sum of the volumes of the feed and scrub solution.

It was indicated in Table 7 that the purity of Gd is higher that 99%, but Gd is present in the raffinate, so we can suppose that the scrubbed RE amount is sufficient and even above that needed, but the extracted RE amount is not large enough. Therefore, in the second experiment the solvent flow ratio was increased and the acidity of the scrub section was decreased properly. The experimental conditions are as follows:

Feed solution: 0.3031 M REO, [HCl] = 0.05 M
Feed composition: Sm_2O_3 64.69%, Gd_2O_3 35.31%
Solvent: 1 M HEHEHP in isoparaffin (ammoniated 30%, mol/mol)
Scrub solution: 1.002 M
Flow ratio: Feed:scrub:solvent = 29:10:5.8
Extraction section: 10 stages
Scrub section: 11 stages

After performing 70 “rows,” the samples were taken from the organic phase leaving from the first stage, the raffinate leaving from Stage 21, and from both phases in Stages 2, 4, 6, 8, 10, 12, 14, 16, 18, and 20. The results are shown in Tables 8 and 9.

TABLE 8
Analytical Results of the Product after Separation Experiment with 21 Stages

	Aqueous phase					Organic phase			
Row	Volume (mL)	Acidity (M)	RE conc (M)	Sm (%)	Gd (%)	Volume (mL)	RE conc (M)	Sm (%)	Gd (%)
70	15.9	0.1250	0.120	98.87	1.13	27.5	0.03623	0.21	99.79
71	15.6	0.1234	0.121	—	—	27.0	0.03884	—	—
72	16.3	0.125	0.121	98.77	1.23	29.5	0.03623	0.59	99.41
Mean	15.9	0.1245	0.1207	98.5	1.5	28.0	0.03710	—	99.41

Mass balance:

Input: amount of RE in feed solution: 0.3031*10 = 3.031 (mmol)
Output: amount of RE in raffinate: 0.1207*15.9 = 1.9228 (mmol)
amount of RE in organic effluent: 0.0371*28 = 1.3088 (mM)
total amount of RE 1.9288 + 1.3088 = 2.9616 (mM)
Yield of RE = 2.9619/3.031 = 97.71%

According to the above conditions, the purities of Gd and Sm are higher than 99% and 98%, respectively, through a 21-stage extraction. The yield of total rare earth reaches 97.71%.

TABLE 9
Result of the Separation Experiment with 21 Stages

	Aqueous phase				Organic phase		
Stage	RE conc (M)	Acidity (M)	Sm (%)	Gd (%)	RE conc (M)	Sm (%)	Gd (%)
2	0.0266	0.5140	0.27	99.73	0.0562	0.48	99.52
4	0.3335	—	0.40	99.60	0.0973	0.18	99.82
6	0.3490	0.2346	0.84	99.16	0.1046	0.26	99.74
8	0.3511	0.2412	5.34	94.66	0.1058	2.02	97.98
10	0.3450	0.2241	29.15	70.85	0.1059	16.19	83.81
12	0.2778	0.2329	54.74	45.29	0.0908	28.52	71.48
14	0.2773	0.2465	57.33	42.67	0.0833	30.91	69.09
16	0.2833	0.2387	67.35	32.65	0.0820	41.01	58.99
18	0.2979	0.2046	86.98	13.52	0.0866	69.83	30.17
20	0.2901	0.1705	97.50	2.50	0.0928	92.73	7.27

CONCLUSIONS

For a binary mixture when the RE concentration in the aqueous phase increases from 0.2 to 0.55 M, at higher acidity the organic phase RE concentration increases with increasing aqueous phase RE concentration. The total RE concentration in the organic phase decreases with increasing acidity from 0.2 to 0.6 M. The total RE distribution coefficient varies inversely with increasing RE concentration from 0.05 to 0.55 M, acidity from 0.2 to 0.6 M, and mole fraction from 0.02 to 0.98, but the distribution coefficients of Sm and Gd increase with increasing mole fraction of Sm (from 0.02 to 0.98). The separation factor of Gd with respect to Sm is somewhat different in value in the range covered by the experiment, but they do not change significantly. Finally, we can consider the separation factor as having an almost constant value of approximately 3.7. The distribution coefficients of Sm and Gd and the separation factors were obtained from the equilibrium data. The average separation factor between Sm and Gd is 3.7.

On the basis of the equilibrium data, five empirical models were developed. Rare-earth concentration in the organic phase was described in the models as a function of the total rare-earth concentration ($X1$), the acidity ($X2$), and the mole fraction of Sm or Gd ($X3$) in the aqueous phase.

Models A and B represent the equilibrium of Sm and Gd in the system with ammoniated extractant.

Models C and D represent the equilibrium of Sm and Gd in the system with nonammoniated extractant. Model E represents the equilibrium of the total RE concentration in the system with nonammoniated extractant. The published models are valid over wide ranges ($X1 = 0.045$ to 0.6 M, $X2 = 0.09$ to 0.65 M, mole fraction of Sm $X3 = 0.008$ to 0.991) with average errors less than 3.5%. They include 5 to 9 parameters. Good approximation was obtained between the experimental data and the results from the developed models in nonammoniated and ammoniated systems. Mathematical models were used in a stagewise calculation of the extraction and separation of Sm and Gd. the process conditions were provided from the calculation results. An extraction separation circuit of 15 stages was simulated.

According to the calculated process conditions and after some modifications, two separation experiments were performed in a laboratory. From the above conditions, through a 21-stage extraction, the purity of Gd and Sm was higher than 99 and 98%, respectively. The yield of total rare earth reached 97.71%. The conditions found here can be used for the separation of Gd and Sm in a rare-earth multicomponent system where rare-earth elements which are heavier than Gd and lighter than Sm may be considered as Gd and Sm, respectively.

Two programs were written in BASIC language and used for developing the equilibrium models and stagewise calculation. These programs can also be used for any binary metal extraction system.

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