Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Sreelatha, S. , Sai, P. S. T. , Rao, T. Prasada , Narayanan, C. S. and Damodaran, A. D.(1991) 'Thermodynamic Modeling of Chemical Equilibria in Liquid-Liquid Extraction of Lutetium', Separation Science and Technology, 26: 12, 1531 — 1547

To link to this Article: DOI: 10.1080/01496399108050549

URL: http://dx.doi.org/10.1080/01496399108050549

SEPARATION SCIENCE AND TECHNOLOGY, 26(12), pp. 1531–1547, 1991

Thermodynamic Modeling of Chemical Equilibria in Liquid–Liquid Extraction of Lutetium

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Abstract

The extraction equilibrium data of lutetium from sodium succinate solution with Aliquat 336 in benzene is systematically investigated. The aqueous phase metal complexation and polymerization in the organic phase are taken into account in obtaining extraction coefficients, stability constants, hydrolysis constants, solubility product, and extraction constants. A thermodynamic model of the above equilibrium extraction data is developed for use in computer simulation of the extraction process. The correlations are based on chemical mass action principles in which the metal complexation in the aqueous phase, polymerization in the organic phase, precipitation in the aqueous phase, and aqueous phase activity coefficients are considered. Extraction behavior of other lanthanides from a succinate medium is also discussed.

INTRODUCTION

Liquid–liquid extraction methods for the separation of lanthanides essentially deal with the extraction of metal inorganic complexes such as chloride, nitrate, sulfate, and thiocyanate (*1–4*). Moore (*5*) was the first to advocate the use of carboxylic acids for the extraction of lanthanides because they can form strong anionic complexes which can be extracted with amine extractants and thus offer wide scope. In spite of this, little work has been done on liquid–liquid extraction studies of lanthanides from carboxylic acid media. Recently, sodium succinate (*6–8*) and sodium malonate (*9*, *10*) solutions were used for inter- and intragroup separation of several *p*-block and transition metals with amine extractants. A possible separation of neodymium and samarium from sodium succinate solutions was reported by extraction with tri-*n*-octylamine (*6*). These reports essentially deal with analytical separations. A detailed study on the equilibrium extraction behavior of lanthanides from carboxylic acid media has not been reported.

Empirical and semiempirical models (*11–13*) are most often described for computer simulation of metal extraction processes in hydrometallurgy. These approaches are not reliable for conditions outside the experimental database used to validate the model. A recent trend has been the development of thermodynamic models for process design work on liquid–liquid extraction, e.g., lanthanides (*14*), iron (*15*), and americium (*16*).

EXPERIMENTAL

Apparatus

A Hitachi 220 double beam microprocessor-controlled molecular absorption spectrophotometer was used for measuring absorbances. An Elico digital pH meter was used for pH measurements. All the programs were written in FORTRAN IV and executed on a 32-bit minicomputer (HCL, Horizon III).

Reagents

Aliquat 336 was procured from Fluka, Switzerland, and was used without further purification. A 5% (v/v) solution in benzene was prepared by diluting 25 mL Aliquat 336 (chloride form) with benzene to 500 mL. This Aliquat 336 solution was converted into succinate form by equilibrating twice with 500 mL of 0.1 *M* sodium succinate (pH 7.2).

Stock solutions of the lanthanides were prepared from their oxides (Rare Earth Products, Cheshire, UK, 99.99%) by dissolving in 2 mL of 1:1 hydrochloric acid and diluting to 100 mL. Sodium succinate solution was prepared by dissolving succinic acid (BDH, GPR) in a minimum amount of sodium hydroxide and adjusting to the required pH by using dilute sodium hydroxide.

Arsenazo I (Fluka, Switzerland) was prepared by dissolving 25 mg of this reagent in 250 mL conductivity water.

Ammonium acetate buffer (pH 7.5) was prepared by dissolving 19.25 g in 250 mL water and adjusting the pH with HCl/NaOH.

All other chemicals were of analytical reagent grade and were used without further purification.

Extraction Equilibrium Procedure

Extraction coefficients were determined by shaking equal volumes of the aqueous and organic phases (10 mL) for 5 min in a 60-mL separating funnel at room temperature. The pH value of the aqueous phase measured after phase separation was taken as the equilibrium pH value. A 5-mL aliquot of the aqueous phase was pipetted into a 25-mL beaker, and 1 mL ammonium acetate buffer and 5 mL Arsenazo I were added. After adjusting the pH to 7.5 ± 0.1, the solution was transferred to a 25-mL volumetric flask and made up to the mark.

The absorbances of the solutions were measured at 575 nm, and the lanthanide concentrations were computed from the respective calibration graphs. The lanthanide concentration in the organic phase was obtained by difference. The lanthanide concentration in the organic phase was periodically checked after stripping with 2 × 5 mL perchloric acid. These concentration values were used to obtain the extraction coefficient, D, defined as

$$D = [\overline{\mathrm{Ln}}]/[\mathrm{Ln}]$$

Theory

A method was evolved for distinguishing the monomeric or polymeric species of the extractable ion-association complexes, for example (A^+B^-) and $(A^+B^-)_2$. This is an extension of the method described by Holme et al. (*17*) and subsequently modified by Sanchez et al. (*18*) for distinguishing mononuclear and polynuclear coordination complexes in several aqueous spectrophotometric determinations.

The extraction of lutetium as its succinate complex at pH 7 by Aliquat 336 in benzene can be described as

$$(\mathrm{Lu(succinate)}_2^-)_m + \overline{(\mathrm{R_4N^+})_n} \xrightleftharpoons{K_0} \overline{(\mathrm{LuL_2^-})_m(\mathrm{R_4N^+})_n} \qquad (1)$$

$$K_0 = \frac{\overline{[\mathrm{A}_m\mathrm{B}_n]}}{[\mathrm{A}]^m[\overline{\mathrm{B}}]^n} \qquad (2)$$

where

$$\mathrm{A} = [\mathrm{LuL_2}]^- \text{ and } \mathrm{B} = \overline{\mathrm{R_4N^+}}$$

$$[\mathrm{A}] = a - m[\mathrm{A}_M\mathrm{B}_n] \qquad (3)$$

$$[\mathrm{B}] = b - n[\mathrm{A}_m\mathrm{B}_n] \qquad (4)$$

where a and b are the initial concentrations of A and B respectively.

$$[\mathrm{A}_m\mathrm{B}_n] = \overline{C}/M \qquad (5)$$

where C is the concentration of A_mB_n in g/L and M is the atomic weight of lutetium.

At a constant concentration of reactant A as the concentration of B is increased, C reaches a maximum value of $\bar{C}_0$, i.e.,

$$\lim_{b \to \alpha} [A_mB_n] = a/m \tag{6}$$

then

$$\bar{C}_0/M = a/m \tag{7}$$

Combining Eqs. (5) and (7):

$$[A_mB_n] = \bar{C}a/m\bar{C}_0 \tag{8}$$

By combining Eqs. (2), (3), (4), and (8):

$$K_0 = \frac{(a/m)(\bar{C}/(\bar{C}_0)}{\left(a - a\frac{\bar{C}}{\bar{C}_0}\right)^m \left(b - a\frac{n\bar{C}}{m\bar{C}_0}\right)^n} \tag{9}$$

Equation (9) may be written

$$\frac{1}{[B]^n} = \frac{1}{b - \frac{n}{m}\left(\frac{\bar{C}}{\bar{C}_0}\right)^n} = \frac{K_0a^m\left(1 - \frac{\bar{C}}{\bar{C}_0}\right)^m}{\frac{a\bar{C}}{m\bar{C}_0}} \cdot$$

$$= K_0ma^{(m-1)}\left(1 - \frac{\bar{C}}{\bar{C}_0}\right)^m \frac{\bar{C}_0}{\bar{C}} \tag{10}$$

By taking the mth root of Eq. (10):

$$\frac{1}{[B]^{n/m}} = (K_0ma^{(m-1)})^{1/m}\left(1 - \frac{\bar{C}}{\bar{C}_0}\right)\left(\frac{\bar{C}_0}{\bar{C}}\right)^{1/m} \tag{11}$$

$$= (K_0ma^{(m-1)})^{1/m} - x^{(1/m)-1} \tag{12}$$

where $x = \bar{C}_0/\bar{C}$.

By taking logarithms and multiplying by m/n:

$$\log \frac{1}{[\mathrm{B}]} = \frac{1}{n} \log (K_0 m a^{(m-1)}) + \frac{m}{n} \log (x^{1/m} - x^{(1/m)-1}) \qquad (13)$$

The above equation has the general form

$$Y = C + PX \qquad (14)$$

i.e., a straight line with an ordinate of log 1/[B] and with an independent variable $\log (x^{1/m} - x^{(1/m-1)})$. The independent variable is different for every value of m. If the value of m tested on the independent variable is incorrect, the slope value (i.e., m/n) will deviate from the correct value of m/n. The straight line obtained for complex AB is different from $(\mathrm{AB})_2$ and $(\mathrm{AB})_3$ because the independent variables and ordinates of the origin differ as shown below:

For complex AB,

$$\log \frac{1}{[\mathrm{B}]} = \log K_0 + \log (x - 1) \qquad (15)$$

For complex $(\mathrm{AB})_2$,

$$\log \frac{1}{[\mathrm{B}]} = \frac{1}{2} \log 2aK_0 + \log (x^{1/2} - x^{(1/2-1)}) \qquad (16)$$

For complex $(\mathrm{AB})_3$,

$$\log \frac{1}{[\mathrm{B}]} = \frac{1}{3} \log 3a^2K_0 + \log (x^{1/3} - x^{(1/3-1)}) \qquad (17)$$

The monomeric or correct polymer complex was identified by calculating the slope value obtained by Eqs. (15)–(17) and choosing the one which is closer to an m/n value of 1. The extraction constant was calculated from the intercept value by substitution in the appropriate equation.

RESULTS AND DISCUSSION

The extraction behavior of lutetium with Aliquat 336 in benzene from sodium succinate solutions was studied. The stoichiometry and equilibrium constants for the extraction reactions were obtained from the relationship

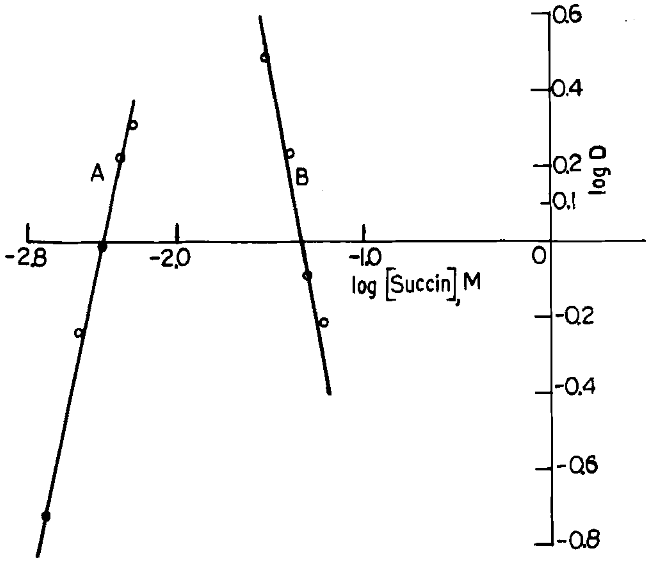

FIG. 1. Plot of log D vs log [L] during extraction of lutetium (5.72×10^{-5} M) with 0.1 M Aliquat 336 in benzene (pH 7.2).

between log D and logarithms of the concentrations of sodium succinate and Aliquat 336. At an equilibrium pH of 7.2, succinic acid is essentially present as succinate^{2-} (~98%) and the slopes of log D plots against log (L^{2-}) and log (R_4N^+) are close to 2 and 1, respectively (cf. Fig. 1 (curve A) and 2). Hence, the extraction equilibrium of lutetium from succinate solutions with Aliquat 336 in benzene can be expressed as (charges are omitted for simplicity)

$$\mathrm{Lu} + 2\mathrm{L} + \mathrm{R_4N} \overset{K_0}{\rightleftharpoons} \overline{(\mathrm{LuL_2})\cdot \mathrm{R_4N}} \tag{18}$$

$$K_0 = \frac{\overline{[\mathrm{LuL_2}]\cdot \mathrm{R_4N}}}{[\mathrm{Lu}][\mathrm{L}]^2[\mathrm{R_4N}]} \tag{19}$$

$$\log K_0 = \log D - 2\log[\mathrm{L}] - \log[\mathrm{R_4N}] \tag{20}$$

The extraction constants calculated from Eq. (20) are 5.764 ± 0.06 (log D vs log [L]) and 5.406 ± 0.08 (log D vs log [R_4N]). The log K_0 obtained by averaging the above two values (each of which was determined with an equal number of points) was calculated to be 5.585 ± 0.10 (the standard

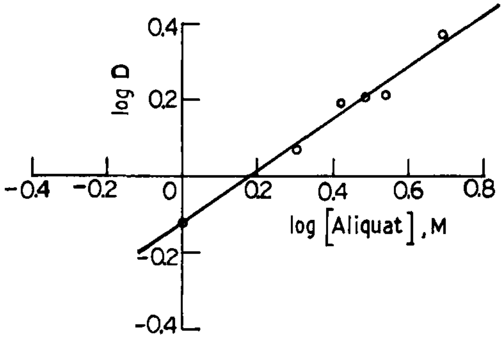

FIG. 2. Plot of log D vs log $[R_3N]$ during extraction of lutetium (5.72×10^{-5} M) in the presence of 0.025 M sodium succinate (pH 7.2) in benzene.

deviation was obtained by taking the quadrature of the individual standard deviation values).

The influence of the initial metal ion concentration on the extraction of lutetium from succinate media with Aliquat 336 in benzene was studied in the range from 5.7×10^{-6} to 1.5×10^{-4} M.

Figure 3 shows the log–log plot of equilibrium organic phase lutetium (III) concentration against the equilibrium aqueous phase lutetium (III) concentration. The plot is linear with a slope equal to 1, indicating that

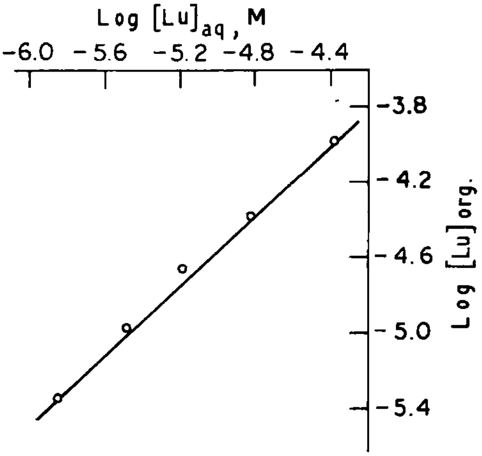

FIG. 3. Effect of metal concentration on the extraction of lutetium from sodium succinate solution (pH 7.2) by 0.1 M Aliquat 336 in benzene.

only monomeric species are extracted into the organic phase. The percent extraction and extraction coefficients of lutetium decrease drastically when the initial aqueous phase concentration of lutetium is greater than 1.5×10^{-4} *M*. Possibly due to competition from 1) formation of nonextractable species such as LuL^+ and $Lu(OH)_n^{(3-n)+}$ or 2) formation of nonextractable polynuclear species in aqueous phase.

The possible polymerization of extracted species in the organic phase was next considered when the initial lutetium concentration was maintained at 5.72×10^{-5} *M*. The plots obtained from Eq. (15), (16), and (17) are shown in Fig. 4. The slope m/n values obtained from these plots are 1.109, 1.026, and 1.072 for $m = 1, 2$, and 3, respectively, i.e., the more probable form of extracted species is $(AB)_2$. Further, the extraction constants calculated from the intercept are 65.77, 4.58×10^7, and 6.19×10^{13} for $m = 1, 2$, and 3, respectively.

The extraction constant obtained with $m = 2$, i.e., dimerization of extracted species, is of same order as was obtained from Eq. (20). Hence the extracted ternary ion-association complex $(\overline{LuL_2R_4N})$ exists as a dimer in the benzene layer in $\overline{(LuL_2 \cdot R_4N)_2}$.

At higher succinic acid concentrations the extraction of lutetium decreases and the slope of log *D* vs log L is −3 (cf. Fig. 1 curve B), indicating the formation of the LuL_3^{3-} species.

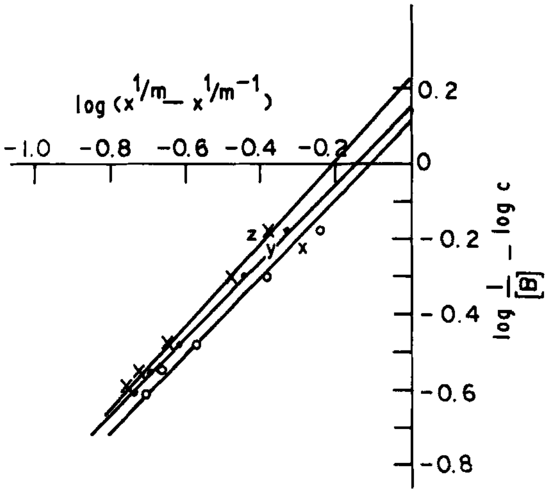

FIG. 4. Experimental lines obtained for the lutetium–succinate–Aliquat 336 system. Curves *x*, *y* and *z* were calculated from Equations 15, 16 and 17 respectively.

Development of Chemical Equilibria-Based Thermodynamic Model of Lutetium–Succinate–Aliquat 336 System

The extraction of lutetium from sodium succinate solutions with Aliquat 336 in benzene at an equilibrium pH of 7.20 in simple form can be described by Eq. (19). The extraction coefficient D in this equation is defined as $D = \overline{(\text{Lu total})}/(\text{Lu total})$. However, by taking the aqueous phase complexation, viz., the presence of lutetium as $(\text{LuL})^+$ alone or as the $(\text{LuL}_2)^-$ and $(\text{LuL}_3)^{2-}$ species, and assuming the activity coefficient of all aqueous lutetium species ($<10^{-4}$ M) to be constant, Eq. (19) can be rewritten as

$$D = \frac{K_0\overline{[\text{R}_4\text{N}]}[\text{L}]^2}{1 + \beta_1[\text{L}]} \tag{21}$$

$$= \frac{K_0\overline{[\text{R}_4\text{N}]}[\text{L}]^2}{1 + \beta_1[\text{L}] + \beta_3[\text{L}]^3} \tag{22}$$

Equations (21) and (22) can be rearranged in the form of a polynomial to give

$$\frac{\overline{[\text{R}_4\text{N}]}[\text{L}]^2}{D} = \frac{1}{K_0} + \frac{\beta_1}{K_0}[\text{L}] \tag{23}$$

$$= \frac{1}{K_0} + \frac{\beta_1}{K_0}[\text{L}] + \frac{\beta_3}{K_0}[\text{L}]^3 \tag{24}$$

The extraction and complexation constants obtained by a least-squares fit of the extraction equilibrium data obtained at sodium succinate concentrations of ≤ 0.01 M in Eqs. (23) and (24) are shown in Table 1. The

TABLE 1
Extraction and Complexation Constants of Lutetium–Sodium Succinate–Aliquat 336 System

Extraction/ complexation constant	Equations			
	(23)	(24)	(26)	(31)
K_0	1.38×10^6	3.62×10^5	5.03×10^5	2.24×10^7
K_1	—	—	-7.61×10^7	-9.0×10^{10}
β_1	4.04×10^2	1.31×10^2	71.9	30.86
β_2	—	—	2×10^4	4.98×10^9
β_3	—	1.87×10^6	1.59×10^6	1.93×10^6

computer simulation of extraction coefficients as a function of sodium succinate concentrations based on Eqs. (23) and (24) are shown by Curves A and B in Fig. 5, along with experimentally obtained points. The model based on Eq. (24) is more realistic and has the identical features of the experimental points. Even in this case, the fit is not good at sodium succinate concentrations > 0.01 *M*. The possibility of $(LuL_3)^{2-}$ being extracted with Aliquat 336 cannot be ruled out, and Eq. (24) has to be modified to incorporate this phenomenon. The extraction equilibria of $(LuL_3)^{3-}$ species with Aliquat 336 are written in similar fashion to that of Eq. (19):

$$Lu^{3+} + 3L + 3\overline{[R_4N]} \overset{K_1}{\rightleftharpoons} \overline{LuL_3[R_4N]_3} \tag{25}$$

By incorporating this equilibrium into Eq. (19), the expression for *D* becomes

$$D = \frac{K_0\overline{[R_4N]}[L]^2}{1 + \beta_1[L] + \beta_3[L]^3} + \frac{K_1\overline{[R_4N]}^3[L]^3}{1 + \beta_1[L] + \beta_2[L]^2} \tag{26}$$

The extraction and complexation constants arrived at by solving Eq. (26) by the Newton–Raphson method are presented in Table 1. As can be seen from Curve C of Fig. 5, the addition of the second term improves the

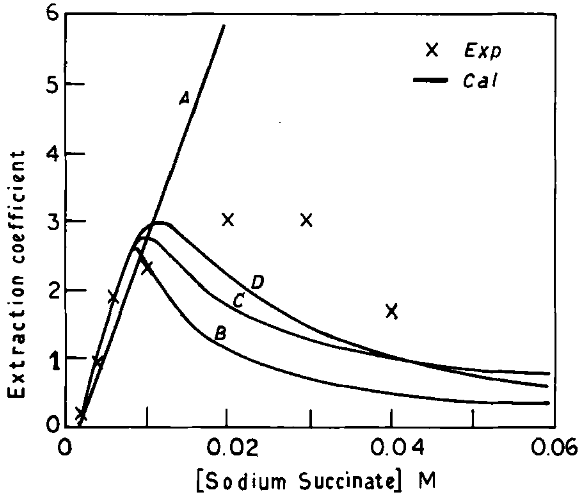

FIG. 5. Measured and calculated lutetium extraction by 0.1 *M* Aliquat 336 in benzene. Curves A, B, C, and D were calculated from Eqs. (23), (24), (26), and (31), respectively.

prediction of extraction coefficients compared to earlier equations. In the model so far considered, the polymerization of the extractant and that of the extracted complex in the benzene phase were not considered. The extracted ion-association complex was found to occur as a dimer (see earlier discussion). Further gel permeation chromatographic experiments revealed that the succinate form of Aliquat 336 in benzene occurs as a trimer. Hence, the extraction equilibria represented in Eq. (19) is rewritten as

$$\mathrm{Lu}^{3+} + \frac{1}{p}\overline{[\mathrm{R_4N}]_p} + 2\mathrm{L} \overset{K_2}{\rightleftharpoons} \frac{1}{x}\overline{(\mathrm{LuL_2 \cdot R_4N})_x} \tag{27}$$

$$K_2 = \frac{(\overline{C})^{1/x}}{[\mathrm{Lu}]\overline{[(\mathrm{R_4N})_p]}^{1/p}[\mathrm{L}]^2} \tag{28}$$

Since the total concentration of metal in the organic phase is x times the concentration of the complex C,

$$K_2 = \frac{x^{-1/x}[\mathrm{Lu}]^{1/x}}{[\mathrm{Lu}]\overline{[(\mathrm{R_4N})_p]}^{1/p}[\mathrm{L}]^2} \tag{29}$$

$$D' = \frac{[\overline{\mathrm{Lu}}]^{1/x}}{[\mathrm{Lu}]} = \frac{K_2\,\overline{[(\mathrm{R_4N})_p]}^{1/p}[\mathrm{L}]^2}{x^{-1/x}(1 + \beta_1[\mathrm{L}] + \beta_3[\mathrm{L}]^3)} \tag{30}$$

Again, as earlier, by taking into consideration the extraction of the $(\mathrm{LuL_3})^{3-}$ species,

$$D = \frac{\overline{[\mathrm{Lu}]}^{1/x}}{[\mathrm{Lu}]} = \frac{K_2\overline{[(\mathrm{R_4N})_p]}^{1/p}[\mathrm{L}]^2}{x^{-1/x}(1 + \beta_1[\mathrm{L}] + \beta_3[\mathrm{L}]^3)} + \frac{K_3\overline{[(\mathrm{R_4N})_p]}^{3/p}[\mathrm{L}]^3}{x^{-1/x}(1 + \beta_1[\mathrm{L}] + \beta_2[\mathrm{L}]^2)} \tag{31}$$

The extraction constants and complexation constants obtained by solving Eq. (31) are shown in Table 1. As can be seen from Curve D in Fig. 5, the incorporation of polymerization of extractant and the extracted complex in the benzene layer resulted in improvement of the model. The slight deviation at higher sodium succinate concentration is probably due to the fact that 1) the activities of succinate are not used in calculation of D and 2) the assumption that the presence of hydroxyl complexes of lutetium and the possible distribution of succinate in other forms are negligible at pH 7.2. All these phenomena will have a significant role in predicting the extraction coefficient as a function of pH and hence should be incorporated in the model. Thus, by taking into account the presence of various hydrolyzed forms of metal, Eq. (31) is modified as

$$D' = \frac{K_2\overline{[(\mathrm{R_4N})_p]}^{1/p}[\mathrm{L}_T]^2}{x^{-1/x}(1 + \beta_1\mathrm{L}_T + \beta_3[\mathrm{L}_T]^3 + \beta_4[\mathrm{OH}] + \beta_5[\mathrm{OH}^-]^2)}$$

$$+ \frac{K_3\overline{[(\mathrm{R_4N})_p]}^{3/p}[\mathrm{L}_T]^3}{x^{-1/x}(1 + \beta_1[\mathrm{L}_T] + \beta_2[\mathrm{L}_T]^2 + \beta_4[\mathrm{OH}] + \beta_5[\mathrm{OH}]^2)} \qquad (32)$$

Further, by considering the presence of different species of succinic acid, i.e., L^{2-}, HL, and $\mathrm{H_2L}$, and representing the concentration of various species in activities:

$$[\mathrm{L}^{2-}] = \frac{ka_1ka_2[\mathrm{L}_T]}{p\left(\dfrac{ka_1ka_2}{\gamma_2} + \dfrac{ka_1[\mathrm{H}]}{\gamma_1} + [\mathrm{H}]^2\right)\left(1 + \dfrac{1}{p}\right)} \qquad (33)$$

The mean stoichiometric activity coefficients were calculated by using Bromley's method (*19*):

$$\log \gamma_\pm = \frac{-Az_+z_-I^{1/2}}{1 + PI^{1/2}} + \frac{(0.06 + 0.6B)z_+z_-I}{\left(1 + \dfrac{1.5}{z_+z_-}I\right)^2} + BI$$

$$\{\mathrm{HL}^-\} = \frac{[\mathrm{L}_T][\mathrm{H}]}{ka_2}$$

$$\{\mathrm{H_2L}\} = \frac{[\mathrm{L}_T][\mathrm{H}]^2}{ka_1ka_2}$$

Since Aliquat 336 in benzene is preequilibrated with succinate solutions to convert it into the succinate form, Eq. (33) can be simplified by neglecting the partition coefficient term. Further, in the pH range under investigation, $a_{\mathrm{H_2L}}$ has a negligible influence on the extraction coefficient values.

The extraction coefficients calculated by using Eq. (32) match the experimental points in the pH range, as seen in Fig. 6.

The above model is then applied to predict the extraction isotherm of lutetium at different concentrations of sodium succinate and Aliquat 336.

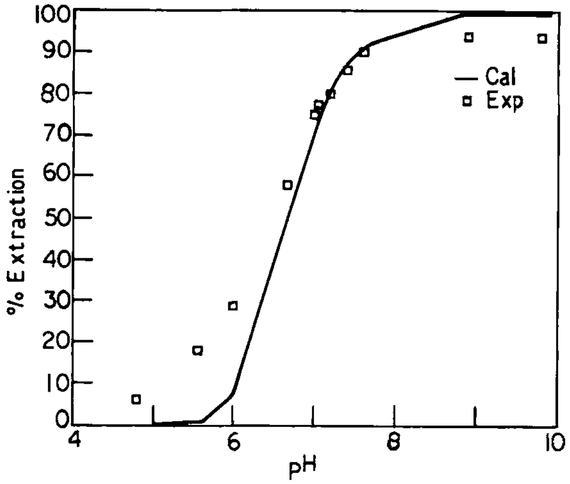

FIG. 6. Plot of calculated and measured extraction coefficients as a function of pH during the extraction of 5.72×10^{-5} *M* lutetium with 0.1 *M* Aliquat 336 in benzene from 0.025 *M* sodium succinate solutions.

The model fits well when the initial metal concentration is $\leq 1.5 \times 10^{-4}$ *M*. Above this value, the lutetium precipitates as $Lu(OH)_3$, and thus removal from the extraction equilibrium cannot be neglected.

$$\text{Lu as Lu(OH)}_3\text{(solid)} = K_s/[\text{OH}]^3$$

$$M'_T = M_T - M(\text{OH})_3$$

where M_T = initial ion concentration
M'_T = initial metal ion concentration in equilibrium with Aliquat 336

$[\overline{\text{Lu}_T}]$ and [Lu] were calculated with Eq. (32), and $[\text{Lu}]_T$ was arrived at by incorporating the contribution due to $Lu(OH)_3$ which is removed from the extraction equilibrium. The K'_s value was calculated to be 7.59×10^{-25}. Modification of the above thermodynamic model after considering the separation of lutetium as $Lu(OH)_3$ from the extraction equilibrium when $[M^{3+}][OH^-]^3$ exceeds K'_s value was effected.

The fit between calculated and experimental extraction isotherms is quite good, as seen in Fig. 7. Figure 8 shows the various chemical reaction equilibria involved in the lutetium–succinate–Aliquat 336 system.

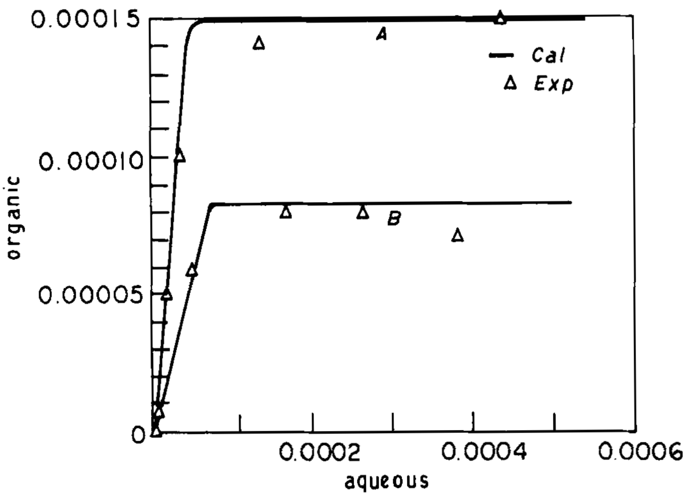

FIG. 7. Measured and calculated lutetium extraction isotherms for 0.01 and 0.025 *M* sodium succinate solutions (Curves A and B).

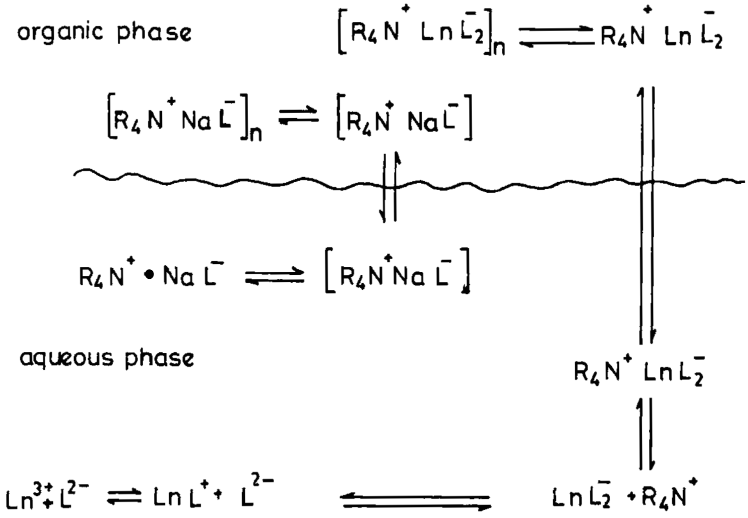

FIG. 8. Chemical reaction equilibria of lutetium–succinate–Aliquat 336 system.

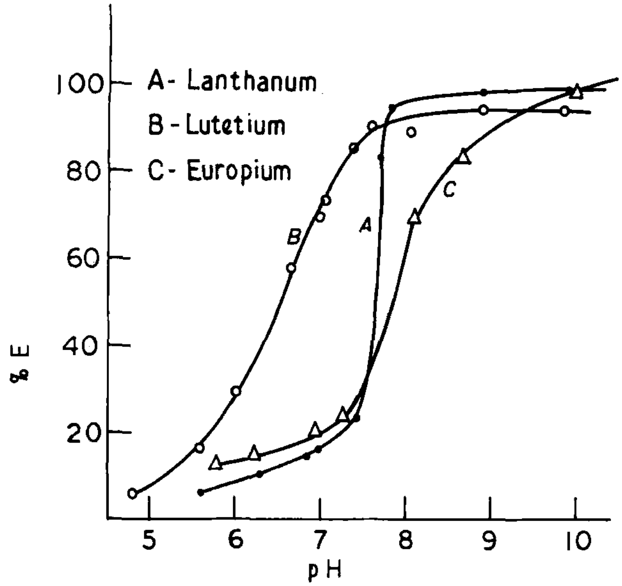

FIG. 9. Effect of pH on the extraction of lanthanum, europium, and lutetium (~5 × 10^{-5} *M*) from 0.025 *M* sodium succinate solution into 0.1 *M* Aliquat 336 in benzene.

Extraction Behavior of Other Lanthanides

Figure 9 shows the extraction behavior of lanthanum, europium, and lutetium as light, middle, and heavy lanthanides, respectively, as a function of pH. In these studies the equilibrium studies were carried out with 5.7 × 10^{-5} *M* individual lanthanide ions from 0.25 *M* sodium succinate solution with Aliquat 336 in benzene. The extraction coefficients of lanthanides at pH 6.25, 6.75, and 7.50 are listed in Table 2. The separation of lutetium from other lanthanides is maximum at pH ~7.00, and Table 3

TABLE 2
Extraction Coefficients of Lanthanides as a Function of Equilibrium pH

	Extraction coefficients of lanthanides, *D*Ln								
pH	La	Pr	Sm	Eu	Gd	Ho	Yb	Lu	Y
6.25	0.111	0.083	0.158	0.168	0.168	0.250	0.519	0.613	0.159
6.75	0.168	0.062	0.200	0.219	0.179	0.277	1.308	1.553	0.250
7.50	5.0	0.449	0.610	0.389	0.282	2.529	4.455	6.06	1.018

TABLE 3
Separation Factor Values of Lanthanide Metals Obtained with Lanthanide–Sodium Succinate–Aliquat 336 System

	Separation factors of lanthanides, pH 7.0, 0.025 *M* succinic acid								
	La	Pr	Sm	Eu	Gd	Ho	Yb	Lu	Y
La	—	0.73	1.11	1.35	1.23	1.98	10.09	11.73	1.46
Pr	1.36	—	1.51	1.84	1.67	2.70	13.76	16.0	1.99
Sm	0.91	0.66	—	1.22	1.11	1.80	9.13	10.62	1.32
Eu	0.74	0.55	0.82	—	0.91	1.48	7.50	8.72	1.09
Gd	0.82	0.60	0.90	1.10	—	1.62	8.24	9.57	1.19
Ho	0.50	0.37	0.56	0.68	0.62	—	5.08	5.91	0.74
Yb	0.10	0.07	0.11	0.13	0.12	0.20	—	1.16	0.15
Lu	0.09	0.06	0.09	0.12	0.11	0.17	0.86	—	0.13
Y	0.68	0.50	0.76	0.92	0.84	1.36	6.91	8.03	—

presents the typical separation factors of lanthanides in lanthanide–sodium succinate–Aliquat 336 liquid–liquid extraction systems.

SYMBOLS

D	extraction coefficient
[Ln]	concentration of lanthanide element in the aqueous phase
Ln	concentration of lanthanide element in the organic phase
K_0	extraction constant of elementary reaction expressed by Eq. (19)
K_1	extraction constant of elementary reaction expressed by Eq. (25)
a	initial concentration of $[LuL_2^-]$
β_1	complexation or equilibrium constant for the formation of $[LuL^+]$
β_2	complexation or equilibrium constant for the formation of $[LuL_2^-]$
β_3	complexation or equilibrium constant for the formation of $[LuL_3^{3-}]$
β_4	complexation or equilibrium constant for the formation of $[Lu(OH)^{2+}]$
β_5	complexation or equilibrium constant for the formation of $[Lu(OH)_2^+]$
L	succinate ion
H_2L	succinic acid
HL	monoprotonated succinate ion
ka_1	first acid dissociation constant of succinic acid
ka_2	second acid dissociation constant of succinic acid

a_2	activity of succinate ion
L_T	total concentration of succinic acid
$\gamma_\pm$	mean activity coefficient, molal concentration scale
A	Debye–Huckel constant
	absolute value of ionic charge
B	a constant per salt; B_+ for cation, B_- for anion
I	ionic strength = $0.5\Sigma m_i z_i^2$
m	molality (g mol/kg solvent)
z	charge number on ion (only absolute values are used)
K_s'	solubility product of $Lu[OH]_3$ in sodium succinate solutions
K_s	solubility product of $Lu[OH]_3$ in water
[]	concentration of particular species
{}	activities of particular species

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Received by editor July 6, 1990