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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
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To cite this Article Hori, T. , Kawashima, M. and Freiser, H.(1980) 'Mixed Ligand Chelate Extraction of Lanthanides: I. 8-Quinolinol Systems', Separation Science and Technology, 15: 4, 861 — 875
To link to this Article: DOI: 10.1080/01496398008076275
URL: http://dx.doi.org/10.1080/01496398008076275

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SEPARATION SCIENCE AND TECHNOLOGY, 15(4), pp. 861-875, 1980

MIXED LIGAND CHELATE EXTRACTION OF LANTHANIDES:
I. 8-QUINOLINOL SYSTEMS

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ABSTRACT

A detailed study of the equilibrium extraction behavior of a series of representative tervalent lanthanide ions, La, Pr, Eu, Ho, and Yb, into chloroform solutions containing either 8-quinolinol (HQ) alone or mixed with 1,10-phenanthroline (phen), was carried out. The results demonstrated that, except for La which extracted as a simple chelate, LaQ_3, the lanthanides extract as self-adduct chelates, $LnQ_3 \cdot 2HQ$, and at higher HQ concentrations, $LnQ_3 \cdot 3HQ$. In the presence of phen, mixed ligand chelates of all the lanthanides but La of the formula $LnQ_3 \cdot 2HQ \cdot phen$ are formed. The use of the experimental parameters, pH, concentration of both HQ and phen to optimize the separation of the lanthanides is discussed. It is concluded that chelate extraction systems in which adduct and mixed ligand complexes are formed enhance separation capability.

INTRODUCTION

Although not quite rivalling isotopes in difficulty, lanthanides represent a formidable separations challenge. Differences in aqueous phase chemical behavior of the individual lanthanides can be expected to be greater with chelating agents than with simple

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inorganic reagents employed for separation. Despite the vast literature dealing with elucidation of molecular structural factors of both reagents and metal ions affecting the stability of metal chelates, very little attention has been devoted to a systematic study of factors affecting differences of stability between pairs of metal ions, or selectivity. One such study, using pattern recognition techniques and covering the polyaminocarboxylic acids, has indicated the relatively small influence of the nature of substituents in a particular reagent family on the selectivity towards the lanthanides (1). Despite this mildly discouraging result, chelating agents offer a realistic hope of successful lanthanide separation on the following bases.

Along with differences in simple chelate stability, one can hope to exploit differences in phase distribution constants associated with separation. Furthermore, since tervalent lanthanide ions have maximum coordination numbers greater than six, they can be expected to form coordinately-unsaturated chelates, represented by the formula $LnL_3 \cdot aHL$, where HL is a monoprotic acid that is a bidentate chelating agent. Hence, differences in the formation constants of such species, termed adducts, as well as those in which one or more molecules of another neutral ligand, B, participate, $LnL_3 \cdot aHL \cdot bB$, termed mixed ligand chelates, may add to selectivity. Finally, with systems involving such a diversity of chemical interactions, careful attention to control of experimental parameters can result in better selectivity than indicated by separation coefficients calculated by the usually employed ratio of equilibrium constants.

8-Quinolinol and 1,10-phenanthroline were chosen for this study because earlier work in this Laboratory demonstrated the advantages of adduct and mixed ligand extractions for zinc, a metal ion whose complexes are frequently coordinatively-unsaturated (2). Use of 8-quinolinol for lanthanide extraction has been reported earlier (3), but without any indication of adduct formation.

EXPERIMENTAL

Reagents

Stock solutions of lanthanum, praseodymium, europium, holmium and ytterbium ion were prepared from the corresponding chloride salt hexahydrates (Alfa Inorganics, Inc.), having a purity of 99.9%. These solutions were standardized by complexometry and the concentrations were determined as 4.00×10^{-3} M (555 μg La/mL), 3.81×10^{-3} M (537 μg Pr/mL), 4.01×10^{-3} M (609 μg Eu/mL), 4.01×10^{-3} M (661 μg Ho/mL) and 3.97×10^{-3} M (687 μg Yb/mL), respectively. These solutions were stored in polyethylene bottles and properly diluted for use.

Buffer solutions including 0.0425 M sodium tartrate and 0.012 M succinic acid and/or tris-(hydroxyamino)-methane (THAM) were prepared to cover the pH range of 6.0 to 7.0 and 7.0 to 10.6, respectively.

Arsenazo III solution was prepared by dissolving 50 mg of the reagent (Aldrich Chemical - containing 1 to 5% Ca) with 100 ml of water. This solution was freshly prepared each week.

A 0.1 M sodium formate-formic acid buffer at pH 4.05 (6.8 g of HCO_2Na - 2.5 mL of HCO_2H/liter) was also prepared for back extractions of rare earth metal ions from the chloroform extracts.

8-Quinolinol (oxine) was purified by sublimation and dissolved in chloroform just prior to use.

A 0.1 M phenanthroline solution was prepared by dissolving 1.9823 g of Analytical Grade 1,10-phenanthroline monohydrate (Aldrich Chemical Company, Ind.) in chloroform and diluting it to 100 mL with the same solvent.

To prepare a series of extracting solutions including phenanthroline and oxine, calculated amounts of 0.1 M phenanthroline solution and 1 M oxine solution were taken and mixed in volumetric flasks and the mixtures were diluted to the mark with pure chloroform.

Apparatus

The absorbances were measured in quartz cuvettes of 1 cm pathlength by using a Gilford Model 2400 Spectrophotometer. Measurements of pH were performed by using an Orion Model 701 Digital pH meter, equipped with a glass indicating electrode and a calomel reference electrode (Thomas, Swiss products). The extraction apparatus has been previously described (2).

Extraction Procedure

The buffered lanthanide solution (in which the maximum initial concentration was 1×10^{-5} $\underline{M}$ Ln^{3+}, in order to eliminate any precipitate formation at the interface) and an equal volume of the reagent solution were equilibrated by vigorous shaking. The shaking time was 30 min for all the extractions, a time found to be adequate for equilibration. The mixture was then allowed to stand for about 1 hr for phase separation. The pH value of the aqueous phase after extraction was taken as the equilibrium pH value. After phase separation, an aliquot of the organic phase was pipetted out and used for the determination of the concentration of lanthanide.

Analysis of Lanthanide and Determination of Distribution Ratio

The lanthanide concentration was determined according to the Arsenazo III method (4): the lanthanide in the organic extract was back-extracted in 4 mL of pH 4.05 formate buffer solution by shaking for 5 min. The aqueous phase thus obtained was transferred to a separatory funnel and washed once with 5 mL of pure chloroform to remove the free ligand completely, leaving the lanthanide ion entirely in the buffer solution. One milliliter of the Arsenazo III solution and 0.1 mL of formic acid were added to the aqueous solution, and then the pH was adjusted within 2.6 ± 0.1 with 0.5 $\underline{M}$ HCl. The solution was transferred into a 10-mL volumetric flask and made up to the mark with water. The absorbance was measured at 650 nm. The distribution ratio, D, was calculated from the known total concentration of lanthanide ion and from the equilibrium concentration in the organic phase.

Although the distribution ratio could also be obtained by the measurement of absorbance at 400 nm arising from the metal oxinate in chloroform ($\varepsilon \simeq 6500$), the results obtained by the Arsenazo III method were more accurate and reliable than the oxinate method.

RESULTS AND DISCUSSION

A traditional and effective means of obtaining both stoichiometric and equilibrium constant information about extraction processes, called "slope analysis," is based on a formulation of variation of D, the distribution ratio, with relevant experimental variables. A log-log plot of the extraction data in the form of D vs a concentration variable indicates the stoichiometry of the formation of the extractable complex, and thus leads to the derivation of a suitable equilibrium expression and then to the calculation of equilibrium constants.

In the systems under study here, the lanthanide is present largely as its ditartrate complex, LnT_2^-, characterized by the equilibrium

$$\beta_2 = \frac{[LnT_2^-]}{[Ln^{3+}][T^=]^2} \quad . \qquad (1)$$

In the pH range studied which is well above that of $pK_{a2} = 3.94$ (5) of tartaric acid, H_2T, the dianion $T^=$ is the predominant tartrate species, so that Eq. (1) becomes

$$[Ln^{3+}] = C_{Ln}/\beta_2 C_T^2 \ , \qquad (2)$$

where C represents stoichiometric concentration.

The simplest chelate extraction equilibrium expression involving a tervalent lanthanide and 8-quinolinol, HQ, is that for the distribution ratio, D,

$$D \equiv \frac{C_{Ln}(o)}{C_{Ln}} = \frac{\beta_3 K_{DC} K_a^3}{K_{DR}^3 \beta_2 C_T^2} \frac{[HQ]_o^3}{[H^+]^3} \ , \qquad (3)$$

where K_a and K_{DR} are the acid dissociation constant, $10^{-9.9}$, and distribution constant, $10^{2.6}$, of HQ, β_3 and K_{DC} the overall aqueous phase formation constant and the distribution constant of the chelate LnQ_3, and the subscript o refers to concentrations in the organic phase.

The combination of constants and total tartrate concentration can be referred to as the conditional extraction constant, K'_{ex},

$$K'_{ex} \equiv \frac{\beta_3 K_{DC} K_a^3}{K_{DR}^3 \beta_2 C_T^2} . \qquad (4)$$

Examination of Eq. (3) leads to the conclusion that the slope of a log D vs pH plot should be 3, indicating that three hydrogen ions are released in the extraction of the metal ion. As seen in Fig. 1, the behavior of all of the lanthanides conform to this simple formulation.

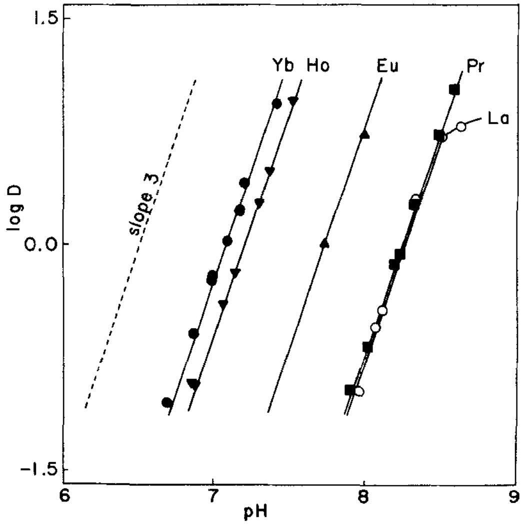

FIGURE 1. Distribution of lanthanides in the presence of 8-quinolinol as a function of pH. $[\text{8-quinolinol}]_o$ = 0.10 M in $CHCl_3$; aqueous phase includes tartrate ion at constant concentration of 0.034 M.

Comparable plots of log D vs log $[HQ]_o$ of the extraction data, while linear, exhibited slopes for all of the ions except La^{3+} that were much higher than the value of three expected for a simple extractable chelate, LnQ_3. Generally, the clarity of interpretation of slope analysis is reduced when the value of the slope is greater than three. Even with reasonably reliable data, experimental error tends to make it difficult to distinguish between values of, say, 5 and 6. In order to overcome this difficulty, an alternate mode of plotting the data was developed and used.

For chelate extractions involving adduct formation, which can be represented by the reaction

$$LnQ_3(o) + mHQ(o) \overset{\beta_{m,o}}{\rightleftarrows} LnQ_3 \cdot mHQ(o),$$

where $\beta_{m,o}$ is the adduct formation constant, it can be shown that

$$D = K'_{ex} \frac{[HQ]_o^3}{[H]^3} [1 + \beta_{m,o}[HQ]_o^m]. \qquad (5)$$

When $\beta_{m,o}[HQ]_o^m > 1$ in this equation, the effect of adduct formation on the extraction can be effectively isolated by using in place of log D the expression log D - 3pH - 3log $[HQ]_o$ (really, as a limiting value, log K'_{ex}) as the ordinate vs log $[HQ]_o$. Thus the slope of the resulting plot will be, not the possibly unmanageably high 3 + m, but m. As seen in Fig. 2, except for La^{3+}, the lanthanide complexes can be represented by the adducts $LnQ_3 \cdot 2HQ$ or, at higher $[HQ]_o$ values, $LnQ_3 \cdot 3HQ$. Only La^{3+} seems to extract as a simple chelate, LaQ_3, as witnessed by the horizontal linear relationship of (log D - 3pH - 3 log $[HQ]_o$). These findings would lead to the conclusion that it is easier for HQ to replace coordinated water in the higher members of the lanthanide series. In fact, from the linearity of the plots in Fig. 2, there seems to be no range at which the extraction of the simple chelate is predominant. Two clearly distinct linear regions, corresponding to the extraction of $LnQ_3 \cdot 2HQ$ and $LnQ_3 \cdot 3HQ$, are observed. From these data and Eq. (5), it is possible to calculate values of log $K'_{ex}\beta_{2,o}$ and log $K'_{ex}\beta_{3,o}$

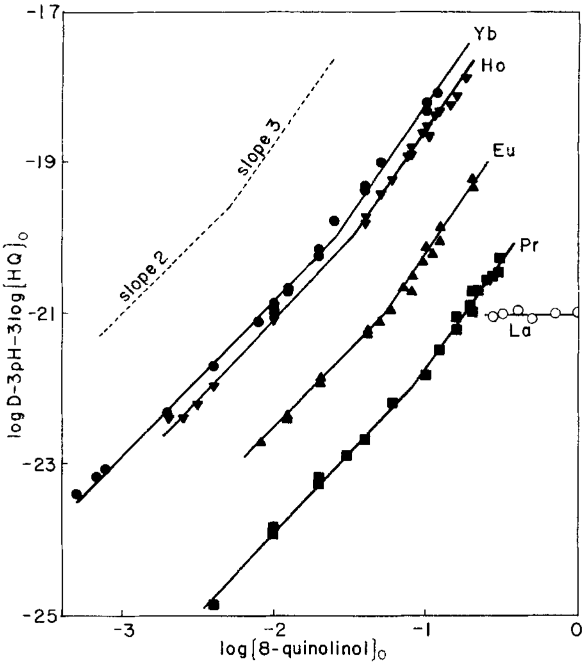

FIGURE 2. Extraction equilibria of lanthanides with 8-quinolinol in $CHCl_3$.

(Table 1). The difference between these two values, designated as Δ in Table 1, corresponds to the equilibrium constant of the addition of the third mole of HQ to $LnQ_3\cdot 2HQ$. The value of Δ also increases with atomic number, although certainly to a much lesser degree than does $\log K'_{ex}\beta_{2,o}$.

It is to be expected that, as the number of ligands coordinated to the Ln^{3+} increase, the "excess Lewis acidity" and therefore the formation constant would decrease. Hence, adding the first two adduct HQ molecules would be characterized by a formation constant greater than or certainly no smaller than twice that for the third, i.e., $\log \beta_{2,o} \geq 2\Delta$. Since the observed relationships are strictly linear down to the lowest values of $[HQ]_o$ studied, this signifies

TABLE 1

Equilibrium Constants in the Lanthanide-8-Quinolinol Systems

	La^{3+}	Pr^{3+}	Eu^{3+}	Ho^{3+}	Yb^{3+}
$\log K'_{ex}\beta_{2,o}$	-	-19.82	-18.48	-17.08	-16.86
$\log K'_{ex}\beta_{3,o}$	-	-18.71	-17.20	-15.60	-15.24
Δ	-	1.1	1.3	1.5	1.6
$\log K'_{ex}$	-21.1	$-25.^{a}$	-	-	$-24.^{a}$
$\log \beta_2{}^{b}$	6.25	6.9	7.4	7.1	7.3
$\log K_{ex}$	-17.8	$-21.^{a}$	-16.6^{a}	-16.0^{a}	$-19.^{a}$
$\log \beta_3 K_{DC}$	19.7	$17.^{a}$	-	-	$22.^{a}$
$\log \beta_3$	17.0	$19.^{a}$	-	-	$22.^{a}$
$\log K_{DC}$	2.7	$-\ 2.^{a}$	-	-	0^{a}
$\log K'_{ex}\beta_{2,1}$	-	-17.30 -16.57^{c}	-15.67	-14.09	-13.68 -13.17^{c}
$\log K_{phen}$	-	2.5 3.3^{c}	2.8	3.0	3.2 3.7^{c}

[a] Maximum values (see text).

[b] For formation of LnT_2^- (5).

[c] Corresponds to 4,7-dimethyl-1,10-phenanthroline.

that $\log \beta_{2,o}$ is much larger than 2Δ, higher than 6.5 for Yb and 5.2 for Pr, with the corresponding $\log K'_{ex}$ values being lower, then, than -24 and -25. For purposes of the subsequent discussion, these maximum values have been listed in Table 1. When it is remembered that the $\log K_{DC}$ values for Pr and Yb are maximum rather than true values, the dramatic difference between all of the lanthanide chelates from that of La itself is further emphasized. It is highly probable that the drastic lowering of K_{DC} values calculated for these chelates can be attributed to the presence of coordinated water in the simple chelate.

Finally, by substituting known values of the formation constants of the lanthanide tartrates, LnT_2^- along with the value of C_T used in the experiments, values of K_{ex} can be calculated. These, combined with known values of K_a and K_{DR} of 8-quinolinol, can be used to obtain values of $\beta_3 K_{DC}$, thus unravelling almost all of the component equilibrium constants of the lanthanide oxinate extractions. Of the lanthanide oxinates, the overall stability constant in aqueous medium is known only for La^{3+} (log β_3 = 16.95)(5), but log β_3 values for the others have been potentiometrically determined in 50 v/v% dioxane-water (6). By assuming a constant medium effect (i.e., that the difference in log β_3 obtained in the two solvent media is essentially independent of the metal ion), reasonable values of log β_3 in water can be estimated for the rest. These values are listed in Table 1, along with the log K_{DC} values obtained from the combined values of log $\beta_3 K_{DC}$.

It was anticipated that, in analogy to the previously studied zinc-8-quinolinol extraction system (2), if phenanthroline would affect the extraction, it would act by replacing one or more of the ligand adducts (as well as perhaps some coordinated water). Instead, the phenanthroline <u>added</u> to the biadduct, $LnQ_3 \cdot 2HQ$. In order to take this reaction into account in the overall extraction equilibrium, Eq. (5) can be modified to

$$D = K'_{ex} \frac{[HQ]_o^3}{[H^+]^3} \left(1 + \beta_{m,o}[HQ]_o^m + \beta_{m,n}[HQ]_o^m[\text{phen}]_o^n\right), \qquad (6)$$

where $\beta_{m,o}$ characterizes the formation, in the organic phase, of $LnQ_3 \cdot mHQ \cdot n\text{phen}$ from LnQ_3. Extraction in the presence of phenanthroline was also evaluated by slope analysis. As seen in Fig. 3, the extraction curves of all but La^{3+} shifted to significantly lower pH values, indicative of a phenanthroline complex formation, whose formula still conformed to a component LnQ_3, because the slope of the curve log D vs pH remained 3. In Fig. 4, with $[HQ]_o$ kept constant and both the pH and the $[\text{phen}]_o$ varied in a manner to keep D in a range of optimum reliability (0.1<D<10), the plots of log D $[H^+]^3$ vs log $[\text{phen}]_o$ exhibit, for all of the ions except

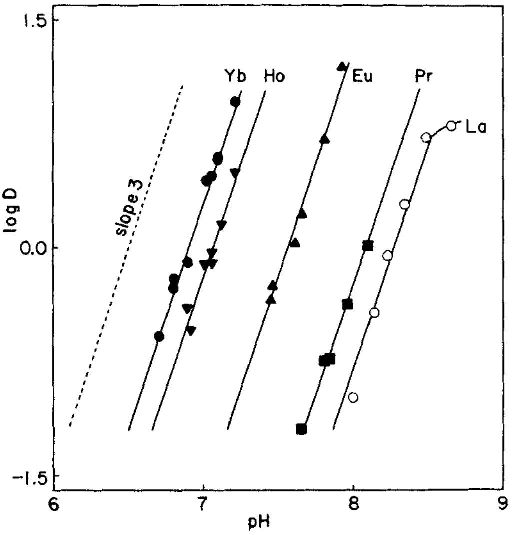

FIGURE 3. Distribution of lanthanides in the presence of 8-quinolinol and 1,10-phenanthroline as a function of pH. $[\text{8-quinolinol}]_o = 0.10\ \underline{M}$ in $CHCl_3$; $[\text{1,10-phenanthroline}]_o = 0.10\ \underline{M}$ in $CHCl_3$; aqueous phase includes tartrate ion at constant concentration of $0.034\ \underline{M}$.

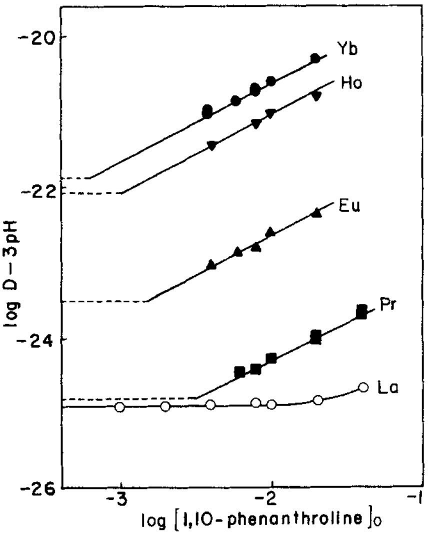

FIGURE 4. Distributions of 1,10-phenanthroline adducts of lanthanide 8-quinolinolates between $CHCl_3$ and water. $[\text{8-quinolinol}]_o = 0.10\ \underline{M}$; dotted lines show values of $\log K'_{ex}\beta_{2,o}\cdot[HQ]_o = 0.10\ \underline{M}$.

La^{3+}, a linear range of unit slope, demonstrating the presence of one phenanthroline in the new complex. At the higher phen concentrations there is some indication that La, too, may form a phen complex, although very weak. Finally, the study of the variation of extraction of lanthanides as a function of 8-quinolinol concentration was evaluated by plotting log $D[H^+]^3[HQ]_o^{-3}[phen]_o^{-1}$ vs log $[HQ]_o$ as suggested by Eq. (6). As seen in Fig. 5, the slopes of these curves are 2 over most of the 8-quinolinol concentration (≥0.01 M) range, signifying that the predominant mixed ligand complex species is LnQ$_3$·2HQ·phen. The constants $K'_{ex}\beta_{2,1}$ were evaluated from the extraction

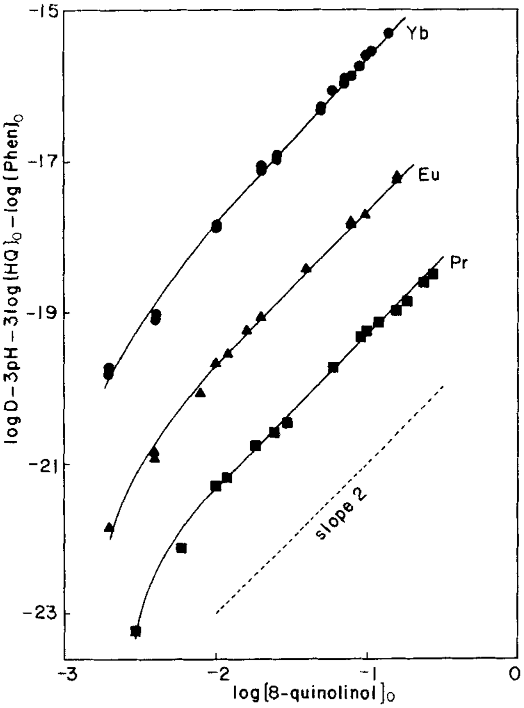

FIGURE 5. Extraction equilibria of lanthanides with 8-quinolinol and 1,10-phenanthroline in CHCl$_3$.

data summarized in Figs. 3-5 and Eq. (6). These, together with values of $K'_{ex}\beta_{2,o}$ listed in Table 1, can be combined to give values of the equilibrium constant of the formation of the mixed ligand complex from the biadduct, i.e., the constant associated with the addition of one mole of phenanthroline. These values are 10^3 or greater, indicating strongly that phen acts as a bidentate ligand whereas the adducted HQ (the third, at least) has a far smaller constant, 10^{Δ}, characteristic of monodentate coordination. The behavior of the stronger chelating agent, 4,7-dimethyl-1,10-phenanthroline with Yb and Pr was investigated and the results subjected to the same analysis. As seen in Table 1, the expected increase in formation constants was observed.

The chelate extraction systems investigated in this study provide an improved route to the separation of lanthanide ions. The participation of a large number of chemical equilibria in the overall extraction process increases the number of factors that can increase the selectivity of the process. This is readily demonstrated from a comparison of lanthanide distribution ratios calculated from extraction equilibrium data of Table 1. For this purpose a common extraction pH of 7.00 was chosen, and the concentration of 8-quinolinol needed to give 50% extraction of the metal ion (expressed as log $[HQ]_o$, analogous to a $pH_{1/2}$ value) was calculated for the various extracted species, including the hypothetical LnQ_3 (Table 2a). Differences in these log $[HQ]_o$ values between metal ion pairs were then translated into corresponding Δ log D values $\{= (3 + m)\Delta \log [HQ]_o\}$, a measure of the selectivity (Table 2b). For extractions in the presence of phenanthroline, a value of $[phen]_o$ = 0.10 M was assumed.

As clearly seen from Table 2b, there is an almost invaraible improvement in extraction selectivity (Δ log D) as we go from left to right, as the nature of the extracted species becomes more complex, i.e., involving a larger number of chemical reactions. Although the reactions for the lanthanides (except for La) are all alike, differences in equilibrium constant, not too surprisingly, serve

TABLE 2

Selectivity of 8-Quinolinol-1,10-Phenanthroline Extractions

2a. Estimated Values of 8-Quinolinol Concentration Needed for 50% Extraction of Various Lanthanide Complexes from a pH 7.0, 0.034 M Tartrate Medium

	Log $[HQ]_o$ when log D = 0 for the Complex of the Following Structures				
Metal Ion	LnQ_3[a]	LnQ_3[a]	$LnQ_3 \cdot 2HQ$	$LnQ_3 \cdot 3HQ$	$LnQ_3 \cdot 2HQ \cdot phen$
La	-1.07	+0.03	-	-	-
Pr	-1.00	+0.33	-0.24	-0.38	-0.74
Eu	-1.47	-0.03	-0.50	-0.63	-1.07
Ho	-1.67	-0.30	-0.78	-0.88	-1.38
Yb	-1.77	-0.30	-0.83	-0.96	-1.46

2b. Differences in log D Values for Selected Pairs of Lanthanide Ions

Metal Ions Compared					
La-Pr	0.21	0.90	-	-	-
Pr-Eu	1.41	1.08	1.30	1.50	1.65
Eu-Ho	0.60	0.81	1.40	1.50	1.45
Ho-Yb	0.30	0	0.40	0.48	0.40

[a] Both of these are hypothetical complexes, except for La^{3+}. The column on the left corresponds to no tartrate present.

to increase the differences between the neighboring lanthanide metal ions. The separation of La from Pr or any of the other lanthanides can be seen to pose the simplest separation problem because it does not form an extractable adduct or mixed ligand complex. Therefore, its extraction has a greatly different dependence on $[HQ]_o$ and $[phen]_o$ than any of the others.

From these results, which should apply generally to chelate extractants, both those already known as well as to new reagents, it would appear that optimum lanthanide separations can be achieved with the use of adduct and mixed ligand extraction systems.

ACKNOWLEDGMENT

This work was conducted with financial assistance from the U.S. Department of Energy.

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