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Lanthanides Extraction by 8-Quinolinol and by a Mixture of Quinolinol and Trioctylphosphine Oxide

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ABSTRACT

The solvent extraction of Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+}, Ho^{3+}, and Er^{3+} from a 0.1 M ionic strength medium (CH_3COONa), pH 5.9 (CH_3COOH) by 8-quinolinol (HOx) and by a mixture of HOx and trioctylphosphine oxide (TOPO) in CCl_4, $CHCl_3$, C_6H_6, C_6H_5—NO_2, C_6H_5—CH_3, C_6H_5—Cl and C_6H_5—Br is studied using titrimetric methods. A synergistic factor of over 10,000 is obtained. The atomic number and diluent effects are evident in the calculated formation constants and the lanthanide separation factors. A combination of the data obtained and that of Th^{4+} indicates that an excellent separation of thorium from the lanthanides can be obtained with this extraction system.

INTRODUCTION

Freiser et al. (1–3) studied the synergistic extraction of several lanthanides (La, Pr, Eu, Ho, and Yb) into chloroform solutions by a mixture of oxine and 1,10-phenanthroline (Phen). The synergistic species formed with all the lanthanides (except La, where no synergism is observed) is $Ln(Ox)_3 \cdot 2HOx$-Phen. The formation constant for the Phen adducts, i.e., the addition of Phen to $Ln(Ox)_3 \cdot 2HOx$, in these lanthanides follows the order Pr < Eu < Ho < Yb. It has been suggested that such a system can

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be used for the optimum separation of lanthanides from each other. A mixture of oxine and 6-amino-4,4′-(5-nonyl)-2,2′-bipyridine (ADNBP) was used to extract Yb, Pr, and La (4). It was observed that HOx does not form self-adducts in these systems, and that the extractability is dramatically enhanced by ADNBP. HOx and 4,4′-di(5-nonyl)-2,2′-bipyridine (DNBP) were also studied for extracting Yb, Ho, Eu, and Pr (5). The extraction of thorium by HOx was also investigated (6). Such investigations could be used in the separation of fission products from thorium used as a fuel in breeder reactors. In the present investigation the extraction of several lanthanide ions in a 0.1 M ionic strength aqueous phase by HOx in various diluents and by a mixture of HOx and TOPO in the same diluents was undertaken. A comparison of the data obtained with that on the extraction of thorium is expected to aid in the calculation of the separation factors of lanthanides and thorium. Studying the diluent effect in the extraction and determining the lanthanide–lanthanide separation factor were the objectives of this study.

EXPERIMENTAL

$Ln(ClO_4)_3$ was prepared from the oxide and was standardized with EDTA titration. The extraction procedure was to shake 10 mL of the 0.1 M ionic strength, pH 5.9, aqueous phase with an equal volume of an organic phase made of HOx or HOx + TOPO in one of the seven diluents studied. Shaking was done in a thermostated water bath for a time that ranged between 2 to 5 hours depending on the diluent used.

The initial Ln^{3+} concentration was 10^{-3} M. After equilibration, the lanthanide ion concentration in the aqueous phase was measured by titration with 0.01 M EDTA.

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 examination of the variation of the distribution ratio, *D*, of the metal ion in the organic and aqueous phases with the relevant experimental variables. A log-log plot of extraction in the form of *D* vs a concentration variable indicates the stoichiometry of the formation of the extracted complex and thus leads to the derivation of a suitable equilibrium expression and then to the calculation of equilibrium constants. From such a slope analysis, log *D* vs pH (Fig. 1), log *D* vs log[HOx] (Fig. 2) is a representative example for the extraction of Nd^{3+} by HOx in benzene, nitrobenzene, and toluene. The slope in Figs. 1 and 2 is 3, indicating that

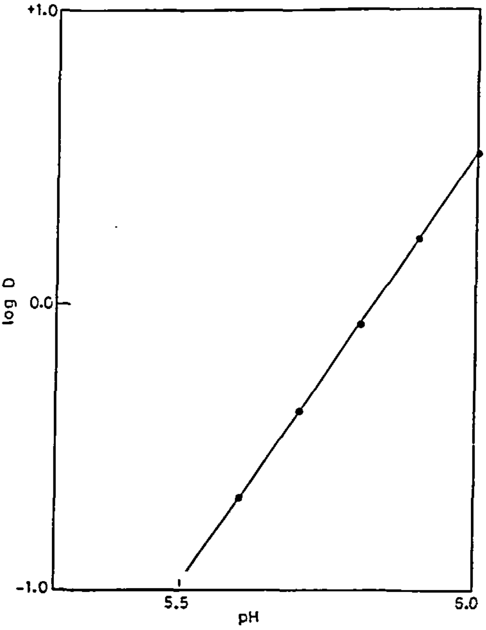

FIG. 1 Effect of hydrogen ion concentration on the extraction of lanthanum.

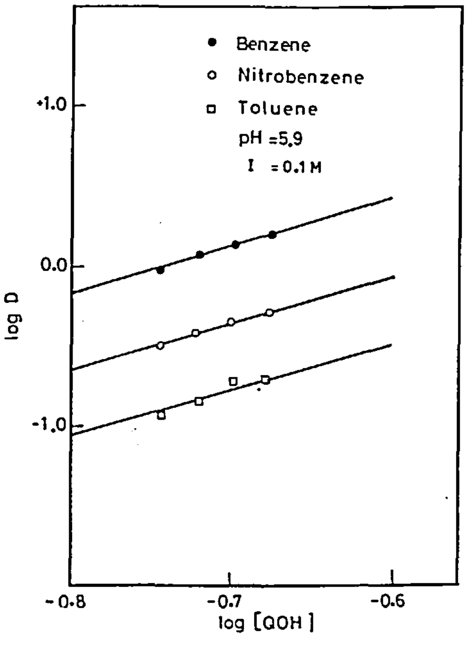

FIG. 2 Effect of QOH concentration on the extraction of Nd^{3+} at 25°C.

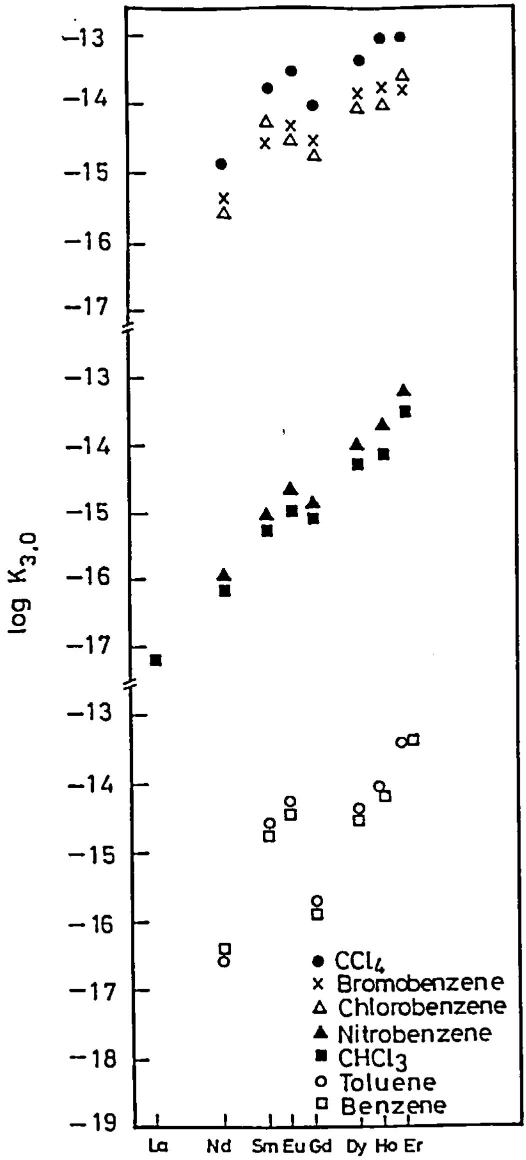

FIG. 3 The relationship between log $K_{3.0}$ and atomic number of the Ln $(QO)_3$ system.

TABLE 1
Log $K_{3.0}$ Values for the Extraction of Lanthanide Elements in Different Diluents at 25°C

	Log $K_{3.0}$ values of diluents						
Element	CCl_4	Bromobenzene	Chlorobenzene	Nitrobenzene	$CHCl_3$	Toluene	Benzene
Nd	−14.820 ± 0.025	−15.370 ± 0.015	−15.490 ± 0.013	−15.970 ± 0.013	−16.100 ± 0.025	−16.550 ± 0.018	−16.560 ± 0.039
Sm	−13.750 ± 0.043	−14.580 ± 0.006	−14.610 ± 0.007	−15.050 ± 0.011	−15.160 ± 0.014	−14.720 ± 0.057	−14.540 ± 0.044
Eu	−13.460 ± 0.020	−14.320 ± 0.023	−14.390 ± 0.032	−14.590 ± 0.007	−14.890 ± 0.009	−14.200 ± 0.051	−14.430 ± 0.038
Gd	−14.000 ± 0.040	−14.560 ± 0.019	−14.670 ± 0.012	−14.890 ± 0.040	−15.000 ± 0.018	−15.710 ± 0.036	−15.860 ± 0.051
Dy	−13.340 ± 0.019	−13.840 ± 0.014	−13.990 ± 0.057	−13.960 ± 0.024	−14.240 ± 0.018	−14.420 ± 0.051	−14.440 ± 0.017
Ho	−12.960 ± 0.037	−13.760 ± 0.032	−13.950 ± 0.039	−13.730 ± 0.066	−14.060 ± 0.044	−14.000 ± 0.074	−14.170 ± 0.080
Er	−13.000 ± 0.052	−13.680 ± 0.173	−13.685 ± 0.046	−13.210 ± 0.039	−13.495 ± 0.078	−13.400 ± 0.017	−13.400 ± 0.071

the extraction reaction can be written as

$$Ln^{3+} + 3HOx_{(O)} \xleftrightarrow{K_{3,0}} Ln(Ox)_{3(O)} + 3H^+ \qquad (1)$$

where (O) represents the organic phase.

Values of $K_{3,0}$ are listed in Table 1 for all the lanthanide ions investigated in the seven different diluents. Figure 3 is a plot of log $K_{3,0}$ vs atomic number Z of the lanthanide ion. It can be seen that $K_{3,0}$ increases gradually as Z increases, with the famililar the Gd^{3+} break (7). A very close agreement of our data with that of Stary (8) is obtained. Stary reported a value of −16.32 ± 0.05 for log $K_{3,0}$ of $Ln(Ox)_3$ using chloroform as a diluent from a 0.1 M ionic strength media.

The effect of the synergistic ligand TOPO, which gives complexes containing only one molecule, is evident in Fig. 4, where a plot of log D vs log[TOPO] has a slope very close to unity. This leads to the extraction

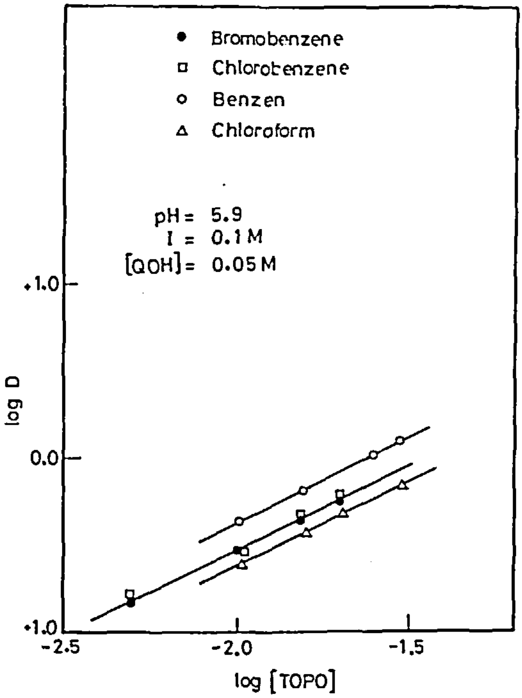

FIG. 4 Effect of TOPO concentration on the extraction of Sm^{3+} at 25°C.

TABLE 2

Log $K_{3,1}$ Values for the Extraction of Lanthanide Elements in Different Diluents at 25°C

Element	Log $K_{3,1}$ values of diluents						
	CCl_4	Nitrobenzene	Toluene	Benzene	Chlorobenzene	Bromobenzene	$CHCl_3$
Nd	−10.320 ± 0.050	−12.190 ± 0.025	−12.440 ± 0.013	−12.440 ± 0.022	−12.460 ± 0.039	−12.480 ± 0.017	−12.470 ± 0.028
Sm	−10.434 ± 0.050	−11.630 ± 0.028	−12.060 ± 0.015	−12.161 ± 0.012	−12.279 ± 0.021	−12.313 ± 0.014	−12.421 ± 0.024
Eu	−10.440 ± 0.038	−11.260 ± 0.041	−12.020 ± 0.016	−12.000 ± 0.017	−11.980 ± 0.031	−12.010 ± 0.025	−12.320 ± 0.039
Gd	−10.360 ± 0.042	−11.520 ± 0.037	−12.400 ± 0.142	−12.510 ± 0.133	−11.950 ± 0.047	−12.060 ± 0.028	−12.380 ± 0.028
Dy	−10.400 ± 0.029	−10.560 ± 0.074	−11.160 ± 0.024	−11.160 ± 0.027	−11.100 ± 0.075	−11.140 ± 0.039	11.270 ± 0.026
Ho	−10.460 ± 0.070	−10.261 ± 0.023	−10.950 ± 0.041	−10.999 ± 0.039	−11.100 ± 0.042	−10.880 ± 0.022	−11.200 ± 0.029
Er	−10.300 ± 0.026	−9.310 ± 0.038	−10.400 ± 0.042	−9.950 ± 0.086	−10.368 ± 0.046	−10.140 ± 0.014	−10.365 ± 0.037

equation

$$Ln^{3+} + 3HOx_{(O)} + TOPO \xleftrightarrow{K_{3.1}} Ln(Ox)_3{\cdot}TOPO_{(O)} + 3H^+ \quad (2)$$

Values of log $K_{3.1}$ for the various lanthanide ions studied are given in Table 2. By subtracting Eq. (1) from Eq. (2), the stability of the adduct in the organic phase can be isolated:

$$Ln(Ox)_{3(O)} + TOPO_{(O)} \xleftrightarrow{\beta} Ln(Ox)_3{\cdot}TOPO_{(O)} \quad (3)$$

The effect of the adduct formation is to increase the extraction equilibrium constant by a factor β. As can be seen from Table 3, enhancement of the extraction may be larger than 10^4 due to increased hydrophobicity of the extracted complex.

For the light lanthanides, log β, decreases as Z increases, as shown in Fig. 5. This is in accordance with the general observation (8) that more stable chelates form less stable adducts.

Values of the separation factor, defined as the difference of the respective extraction constants, are listed in Tables 4 and 5. The data in these tables indicate better separation in the case of lanthanide oxinates than in the case of mixed complexes with TOPO, and that the diluent has a pronounced effect on the separation factors. Diluents that dissolve more water, such as $CHCl_3$, give smaller separation factors, while diluents that dissolve less water give larger separation factors. This is also in agreement with our previous data on trivalent cerium and divalent copper (9, 10). Selectivity in separation is obviously higher in the case of less polar interactions.

TABLE 3

Log β_1 Values for the Extraction of Lanthanide Elements in Different Diluents at 25°C

	Log β_1 values of diluents						
Element	Nitrobenzene	CCl_4	Benzene	Toluene	$CHCl_3$	Chlorobenzene	Bromobenzene
Nd	3.780	4.500	4.120	4.110	3.630	3.030	2.890
Sm	3.420	3.316	2.379	2.660	2.739	2.331	2.267
Eu	3.330	3.020	2.430	2.180	2.570	2.410	2.310
Gd	3.370	3.640	3.350	3.310	2.620	2.720	2.500
Dy	3.400	2.940	3.280	3.260	2.970	2.890	2.700
Ho	3.469	2.500	3.171	3.050	2.860	2.850	2.880
Er	3.900	2.700	3.450	3.000	3.130	3.317	3.540

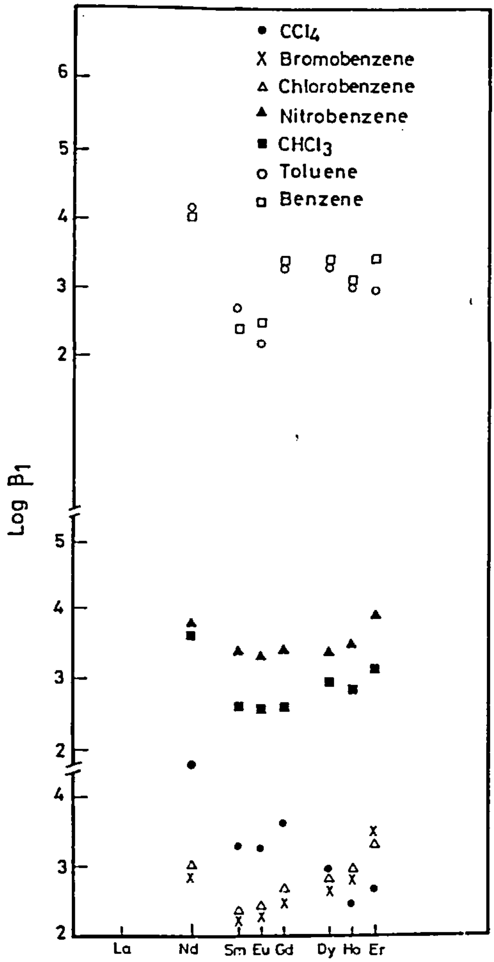

FIG. 5 The relationship between log β_1 and atomic number (organic-phase reaction) of the log $(QO)_3$·TOPO system.

The trend of the separation factor is always large for light lanthanides and very small for the Eu–Gd pair. This pattern in the separation factor vs atomic number can be correlated with the regularities stated by Fidelis and Siekierski (11), who stated that variation in the separation factor with atomic number falls into two subgroups: La–Gd and Gd–Lu, and that

TABLE 4
Separation Factors (S_1) of Lanthanide Elements by the Extraction of $Ln(Ox)_3$, [HOx] = 0.05 M, pH 5.9, at 25°C

	S_1 of diluents						
Element	CCl_4	Bromo-benzene	Chloro-benzene	Nitro-benzene	$CHCl_3$	Toluene	Benzene
Nd–Sm	11.8	6.2	7.6	8.3	8.7	67.6	104.7
Sm–Eu	0.2	1.8	1.7	2.9	1.9	3.3	1.3
Eu–Gd	0.3	0.6	0.5	0.5	0.8	0.03	0.04
Gd–Dy	4.6	5.3	4.8	8.5	5.7	19.5	26.3
Dy–Ho	2.4	1.2	1.1	1.7	1.5	2.6	1.9
Ho–Er	0.9	1.2	1.8	3.3	3.7	4.0	5.9

the changes are similar. It has been proposed that entropy changes upon complexation are responsible for this trend in the separation factors (11).

The calculated distribution ratio of Th^{4+} between 0.02 M HOx in CCl_4 and an aqueous phase of 0.1 M ionic strength (pH 2.9) is 0.059 (6). For Gd^{3+}, the ratio under identical conditions is 4×10^{-11}. This result means there is a Th–Gd separation factor of 1.5×10^9. This factor would increase as the HOx concentration increases. The addition of 0.01 M TOPO as a synergistic base to 0.005 M HOx results in a distribution ratio of 1.2 and 2.7×10^{-11} for Th^{4+} and Gd^{3+}, respectively. This result corresponds to a Th–Gd separation factor of 4.5×10^{11}. In such cases the separation

TABLE 5
Separation Factors (S_2) of Lanthanide Elements by the Extraction of $Ln(Ox)_3 \cdot TOPO$, [HOx] = 0.02 M, [TOPO] = 0.02 M, pH 5.9, at 25°C

	S_1 of diluents						
Element	CCl_4	Bromo-benzene	Chloro-benzene	Nitro-benzene	$CHCl_3$	Toluene	Benzene
Nd–Sm	0.8	1.5	1.5	3.6	1.1	2.4	1.9
Sm–Eu	1.0	2.0	2.0	2.3	1.3	1.1	1.5
Eu–Gd	1.2	0.9	1.0	0.6	0.9	0.4	0.3
Gd–Dy	0.9	8.3	7.0	9.1	12.9	17.4	22.4
Dy–Ho	0.9	1.8	1.0	2.0	1.2	1.6	1.4
Ho–Er	1.4	5.5	5.4	9.1	6.8	3.6	11.2

efficiency, which is more important, has to be determined. This research is under way (12).

It is quite evident that HOx is an excellent agent for separating thorium from lanthanides.

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