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Mixed-Ligand Chelate Extraction of Lanthanides with 1-Phenyl-3-methyl-4-(trifluoroacetyl)-5-pyrazolone and Some Phosphine Oxide Compounds

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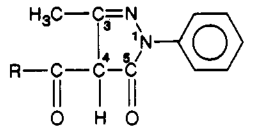
Mixed-ligand chelate extraction of lanthanides (Ln) such as La, Pr, Eu, Ho, and Yb into chloroform with 1-phenyl-3-methyl-4-(trifluoroacetyl)-5-pyrazolone (HPMTFP) and with one of three phosphine oxide compounds is studied. The phosphine oxide compounds employed in the present work are tri-*n*-octylphosphine oxide (TOPO), *n*-octylphenyl(*N*,*N*-diisobutylcarbamoylmethyl)phosphine oxide (CMPO), and methylenebis(diphenylphosphine oxide) (MBDPO). Lanthanide ions are found to be extracted from a 0.1 M sodium perchlorate medium as $\mathrm{Ln(PMTFP)_3(TOPO)_2}$ and $\mathrm{Ln(PMTFP)_3(CMPO)}$, respectively. In the extraction of lanthanides with the mixture of HPMTFP and MBDPO, the extracted species are found to be $\mathrm{Ln(PMTFP)_3(MBDPO)}$ or $\mathrm{Ln(PMTFP)_2(ClO_4)(MBDPO)_2}$ in the absence or presence of sodium perchlorate, respectively. The extraction constants of these systems do not increase monotonically with atomic number but have a maximum at Eu or Ho.

Introduction

The separation of tervalent lanthanides via solvent extraction is still an interesting and formidable problem. The solvent extraction of lanthanides by using a mixture of an acylpyrazolone and an auxiliary reagent has been under investigation.[1-3] Not only improved extraction but also a greater separation could often be obtained by adding an auxiliary reagent to the chelate extraction system. In the present work, a combination of HPMTFP and phosphine oxide compounds has been selected to explore further the adduct formation reaction of the neutral ligands.

1-Phenyl-3-methyl-4-acyl-5-pyrazolones (A) are well-known as powerful extractants, particularly for the "hard" metal ions such as lanthanides and alkaline earth metals.[4-6] Such metal ions are extractable from acidic media because of the strong acidity of the acylpyrazolone. HPMTFP, a 4-trifluoroacetyl-substituted pyrazolone, exhibits an extremely strong acidity (pK_a = 3.12) caused by the strong electron-withdrawing nature of the trifluoromethyl group.[3,4]



A

Nitrogen bases such as alkylamines, pyridine, and 1,10-phenanthroline are not effective adductants for metal chelates extracted in the low pH ranges characteristic of the acylpyrazolone extractants. Instead, the neutral oxygenated phosphorus compounds, which have a low proton affinity, are appropriate auxiliary ligands. TOPO is a monodentate phosphine oxide ligand whose basicity is strong enough to form stable adducts with metal chelates. CMPO belongs to a new class of selective extractants that have been used for actinides, belonging to the neutral bifunctional (carbamoylmethyl)phosphoryl compounds.[7] MBDPO is a bidentate phosphine oxide compound.[8,9] This report is devoted to the study of adduct formation reaction between the series of lanthanide acylpyrazolone chelates and these auxiliary ligands. It is hoped thereby to get a better understanding for the extraction separation of lanthanides.

Table I. Summary of Results on Extraction of Lanthanides with HPMTFP and TOPO or CMPO[a]

neutral ligand	element	slope	$\mathrm{pH}_{1/2}$[c]	no. of points
none	La	2.98 ± 0.06[b]	4.06	6
	Pr	3.20 ± 0.06	3.66	6
	Eu	3.00 ± 0.09	3.26	6
	Ho	2.86 ± 0.11	3.12	6
	Yb	2.74 ± 0.11	3.05	7
TOPO	La	2.89 ± 0.02	2.60	7
	Pr	2.97 ± 0.03	2.27	7
	Eu	3.15 ± 0.07	1.98	7
	Ho	3.05 ± 0.04	1.97	7
	Yb	3.25 ± 0.10	1.88	6
CMPO	La	3.22 ± 0.08	2.51	8
	Pr	2.97 ± 0.08	2.13	5
	Eu	3.13 ± 0.07	1.85	5
	Ho	2.94 ± 0.08	1.82	6
	Yb	3.18 ± 0.10	1.86	7

[a] $[\mathrm{HPMTFP}]_o = 1 \times 10^{-2}$ M; $[\mathrm{TOPO}]_o = [\mathrm{CMPO}]_o = 1 \times 10^{-3}$ M in chloroform; $[\mathrm{NaClO_4}]$ = 0.1 M. [b] Standard deviation. [c] $\mathrm{pH}_{1/2}$ is the pH value at which D = 1.

Experimental Section

Apparatus and Reagents. The apparatus for the spectrophotometric and pH measurements and materials such as lanthanides, TOPO, Arsenazo III, and buffer solutions have been described previously.[1,10] HPMTFP was synthesized according to the literature.[11a] MBDPO was prepared through the oxidation of bis(diphenylphosphino)methane (Aldrich Chemical Co. Inc.) with a diluted hydrogen peroxide solution and purified by recrystallization from ethanol.[9] A sample of CMPO was kindly obtained from Drs. P. R. Danesi and E. P. Horwitz of the Separations Group of Argonne National Laboratory, and it was used as received.

Procedure. A 10-mL aliquot of an aqueous phase containing 2×10^{-5} M lanthanide ion and 2×10^{-3} M succinic acid as a buffer component was adjusted to a desired pH with a hydrochloric acid or sodium hydroxide solution and was shaken with an equal volume of a chloroform phase containing the required amount of HPMTFP and an adduct-forming reagent for 1 h in a 50-mL glass vial at room temperature. The ionic strength of the aqueous phase was controlled to 0.1 with sodium perchlorate (*Caution*! potential explosion hazard[11b]) when the extraction was made with HPMTFP in the presence of TOPO or CMPO. The concentration of sodium perchlorate was varied when the extractants

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Table II. Summary of Results on HPMTPP Extraction of Lanthanides with MBDPO in the Presence or Absence of Perchlorate Ion

neutral ligand	element	slope	$pH_{1/2}$	no. of points
MBDPO[b]	La	2.96 ± 0.06	2.73	7
	Pr	3.22 ± 0.02	2.37	8
	Eu	3.12 ± 0.05	2.12	5
	Ho	3.19 ± 0.12	2.16	5
	Yb	3.18 ± 0.12	2.22	7
MBDPO[c]	La	1.98 ± 0.05	2.45	10
	Pr	1.81 ± 0.03	2.02	5
	Eu	1.97 ± 0.03	1.82	5
	Ho	~2.5	2.00	7
	Yb	~2.7	2.17	7

[a] $[HPMTFP]_o = [MBDPO]_o = 1 \times 10^{-3}$ M in chloroform. [b] $NaClO_4$ absent. [c] $[NaClO_4] = 0.1$ M.

where HPMTFP and MBDPO. After phase separation, the concentration of lanthanide in the aqueous phase was determined by the Arsenazo III method, as described previously. The concentration of lanthanide in the organic phase was determined in the same manner following back-extraction into hydrochloric acid solution. The pH of the aqueous phase measured after shaking was taken as the equilibrium value.

Results and Discussion

Extraction with HPMTFP Alone. In the absence of adductants, the extraction equilibrium can be expressed as

$$Ln^{3+} + 3HA(o) \rightleftharpoons LnA_3(o) + 3H^+ \qquad (1)$$

where HA stands for HPMTFP and the letter o indicates the species in the organic phase. It should be noted that, in the concentrations employed here, no significant dimerization of the extractant occurs in chloroform. The extraction constant, K_{ex}, is defined as

$$\begin{aligned} K_{ex} &= [LnA_3]_o[H^+]^3/[Ln^{3+}][HA]_o^3 \\ &= D[H^+]^3/[HA]_o^3 \end{aligned} \qquad (2)$$

where D is the lanthanide distribution ratio. As seen in Table I, the plots of log D vs. pH are linear, with slopes very close to 3, in accord with eq 2. The extraction constants were calculated on the basis of eq 2 and summarized in Table III. Generally speaking, in the chelate extraction of lanthanides, the extraction constant increases with atomic number. This general tendency is also observed in the present system.

Extraction with a Mixture of HPMTFP and TOPO or CMPO. When an auxiliary reagent, such as TOPO and CMPO (B), is added to the extraction system, enhanced extraction results because of the adduct formation.

The overall extraction equilibrium and the extraction constant, $K_{ex}(B)$, can be expressed as

$$Ln^{3+} + 3HA(o) + nB(o) \rightleftharpoons LnA_3B_n(o) + 3H^+ \qquad (3)$$

$$K_{ex}(B) = [LnA_3B_n][H^+]^3/[Ln^{3+}][HA]_o^3[B]_o^n \qquad (4)$$

where n denotes the number of the auxiliary reagent molecules that attach to the lanthanide chelate. The adduct formation reaction in the organic phase and the stability constant, β_n, are given by

$$LnA_3(o) + nB(o) \rightleftharpoons LnA_3B_n(o) \qquad (5)$$

$$\beta_n = [LnA_3B_n]_o/[LnA_3]_o[B]_o^n \qquad (6)$$

Equation 6 may be expressed by

$$\beta_n = K_{ex}(B)/K_{ex} \qquad (7)$$

From eq 4, the slope of the plot of log D vs. log $[B]_o$ at constant $[HA]_o$ and pH gives n. The results of the extraction of lanthanide using a mixture of HPMTFP and TOPO or CMPO are shown in Table I, where it is seen from the lower $pH_{1/2}$ (pH of 50% extraction) values that highly enhanced extractions are achieved in the presence of as little as 10^{-3} M the auxiliary reagent. While the lanthanide ions are extracted according to the order of atomic number with TOPO as adductant, it is interesting to note that a reversal in selectivity occurs, i.e., that Ho is extracted before Yb, when CMPO is used. In order to clarify the composition of the extracted species, the dependences of D on $[B]_o$ were examined. The plot of log D vs. log $[TOPO]_o$ is linear with a slope of 2 for La and Pr, indicating that two molecules of TOPO are included in the extracted species. In the case of Eu, Ho, and Yb, the corresponding plot is also linear with a slope of 2 at the higher TOPO concentration region but deviates from the straight line at low TOPO concentrations (Figure 1). This deviation can be explained by considering the extraction of MA_3B, which takes place in the lower TOPO concentration range. The extraction constant and the stability constant, β_2, are obtained from the linear portion of the plot of log D vs. log $[TOPO]_o$ by using eq 4 and 7. The stability constant of the 1:1 adduct, β_1, can be evaluated by taking the deviations into consideration by using eq 6. It is interesting that a TOPO monoadduct is observed when the 4-acyl group is aliphatic and a diadduct is formed when the acyl group is aromatic or trifluoroacetyl. This is consistent with the hypothesis that the metal ion in a chelate has more residual Lewis acidity when the primary chelating ligand is weaker.[1-5]

A plot of log D vs. log $[CMPO]_o$ is linear with a slope of unity for all the lanthanide ions examined, indicating that there is one molecule of CMPO in the adduct. The extraction constants and the stability constant, β_1, have been evaluated and summarized in Table III, together with those of the TOPO system.

It may be seen that the log β_1 values of CMPO are larger than log β_1 values for TOPO but much smaller than the log β_2 values of TOPO. Although CMPO has two donor oxygen atoms, the basicity of the oxygen in the carbonyl group is much smaller than that in the phosphoryl group. This is consistent with CMPO's behaving in these complexes as a bidentate ligand. In both systems, the values of adduct formation constants (β_1 and β_2 for TOPO and β_1 for CMPO) decrease monotonically with increasing atomic number. On the other hand, the extraction constants do not increase monotonically, but exhibit maxima at Ho. Generally, in mixed-ligand extraction systems of the lanthanides, the decrease of the adduct formation constant could be explained by a diminution of the coordinating power of the lanthanide ion resulting from a stable chelate formation, with a consequently lower stable adduct formation. In addition, the lanthanide ion, to which three molecules of chelating reagent have already coordinated, allows space for the adduct-forming reagent in proportion to its ionic radius, so that steric hindrance for adduct formation increases with atomic number. Hence, when the equilibrium constant of

Table III. Extraction Parameters for HPMTFP Systems

neutral ligand		La	Pr	Eu	Ho	Yb
none	log K_{ex}	−6.18	−4.98	−3.78	−3.36	−3.15
TOPO	log K_{ex}(TOPO)	4.20	5.19	6.06	6.08	5.68
	log β_1	...	...	5.88	5.90	6.31
	log β_2	10.38	10.17	9.84	9.44	8.70
CMPO	log K_{ex}(CMPO)	1.47	2.61	3.45	3.54	3.42
	log β_1	7.65	7.59	7.23	6.90	6.57
MBDPO	log K_{ex}(MBDPO)[a]	3.81	4.89	5.64	5.52	5.34
	log β_1	9.99	9.87	9.42	8.88	8.49
	log K^*_{ex}(MBDPO)[b]	8.10	8.96	9.36	8.74	8.15

[a] In the presence of $NaClO_4$. [b] In the absence of $NaClO_4$.

the adduct formation reaction decreases rapidly, the reversal of the extractability, i.e. the extraction constant, takes place.

Extraction with a Mixture of HPMTFP and MBDPO. The extractions of lanthanides with a mixture of HPMTFP and MBDPO were first conducted in the presence of $NaClO_4$ (see below). When perchlorate ion was found to have a significant influence, however, in contrast to the TOPO and CMPO systems, the extractions were conducted in its absence. Lanthanide extraction in the presence of MBDPO is so strongly enhanced that although HPMTFP concentration was reduced from 10^{-2} to 10^{-3} M, extraction occurred in the same pH range used earlier. As before, log D vs. pH plots are linear with a slope of 3 for each of the ions examined, indicating that three hydrogen ions are released in the extraction reaction. The dependence of log D on log $[MBDPO]_o$ was also found to be linear with a unit slope, indicating that the extracted species is LnA_3B. It is interesting that the extractions do not follow the order of the atomic number but show a maximum at Eu. The extraction constants and the adduct formation constant, β_1, are calculated on the basis of eq 4 and 7 and are summarized in Table III. It is clear that the log β_1 values of MBDPO are much larger than those of CMPO and quite similar to the log β_2 values of TOPO. Hence, one can safely conclude that MBDPO acts as a bidentate ligand. The adduct formation constants decrease monotonically with atomic number, so that the extraction constants have a maximum at Eu.

The extraction of lanthanides with a mixture of HPMTFP and MBDPO in the presence of 0.1 M $NaClO_4$ has also been examined. As shown in Table II, La, Pr, and Eu were extractable from more acidic media in this order by adding $NaClO_4$ to the aqueous phase. Here the slope of the log D vs. pH lines is found to be 2. On the other hand, as can be seen in Table II, the enhancement of the extraction of Ho and Yb is not very marked, and the slopes for the straight portion are 2.5 for Ho and 2.7 for Yb. Obviously, lanthanides are extracted by a different mechanism under these conditions, and the perchlorate ion is part of the extracted species. The slope of 2 in Table II indicates that two molecules of HPMTFP are included in the extracted species, and therefore one perchlorate anion must be required to maintain electroneutrality, giving an extracted species that has the formula $LnA_2(ClO_4)B_n$.

With these extractions, the distribution of lanthanides between the organic and aqueous phases can be expressed as

$$D = ([LnA_2(ClO_4)B_n]_o + [LnA_3B]_o)/[Ln^{3+}] \quad (8)$$

The extraction equilibrium and the extraction constant for $LnA_2(ClO_4)B_n$, $K^*_{ex}(MBDPO)$, are given by

$$Ln^{3+} + 2HA_o + ClO_4^+ + nB_o \rightleftharpoons LnA_2(ClO_4)B_{n,o} + 2H^+ \quad (9)$$

$$K^*_{ex}(MBDPO) = [LnA_2(ClO_4)B_n]_o[H^+]^2/[Ln^{3+}][HA]_o^2[ClO_4][B]_o^n \quad (10)$$

Consequently, eq 8 can be rewritten by using eq 4 and 10, resulting in

$$D = (K^*_{ex}(MBDPO))[HA]_o^2[B]_o^n[ClO_4]/[H^+]_2 + (K_{ex}(MBDPO))[HA]_o^3[B]_o/[H^+]^3 \quad (11)$$

Figure 3 shows a plot of log$(D - (K_{ex}(MDBPO))[HA]_o^3[B]_o/[H^+]^3)$ vs. log $[B]_o$ for Pr as a typical example. According to eq 11, the slope of this straight line yields the number of MBDPO molecules in the extracted species and is found to be very close to 2. Figure 4 is a plot of log $(D - (K_{ex}(MBDPO))[HA]_o^3[B]_o/[H^+]^3)$ vs. log $[ClO_4]$ for Pr. The slope of this plot is almost unity, supporting the previous assumption about the composition of the extracted species. In the case of La, Pr, and Eu, the extraction of $LnA_2(ClO_4)B_2$ is much higher than that of LnA_3B, to the point where extraction of LnA_3B is negligible. On the other hand, in the case of Ho and Yb, the extractions of $LnA_2(ClO_4)B_2$ and LnA_2B both take place in a similar pH region, resulting in such extraction behavior as seen in Figure 2. When these metals are extracted under increasing concentrations of $NaClO_4$ and MBDPO, this results in the elimination of the extraction of LnA_3B; i.e., a slope of 2 could be obtained in a plot of log D vs. pH, when $[MBDPO]_o$ and $[ClO_4]$ were 5×10^{-2} and 0.2 M, respectively.

The extraction constants, $K^*_{ex}(MBDPO)$, were calculated on the basis of eq 10 (Table III). One can observe a similar tendency in the changes in extraction constants in the presence or in the absence of $NaClO_4$. The extraction constant increases as atomic number increases until Eu, and then it starts to decrease. As mentioned previously, a rapid decrease of the stability of adduct formation with MBDPO causes this inversion. This tendency is most remarkable in the HPMTFP–MBDPO–$NaClO_4$ system, where the extraction constant for Yb is very close to that for La.

Values for the separation factor, defined as a difference of the respective extraction constants, are listed in Table IV. While all the systems examined exhibit an excellent extractability, the selectivities are somewhat inferior to those achieved in previous systems. Although addition of an adduct-forming reagent can bring a decrease of the separation factor, it is notable that addition of TOPO or MBDPO improves the separation of the heavier lanthanides by virtue of a surprising increase in the extractability of the lighter metals to a greater extent than those of the heavier ones. Hence, such a system would be of practical value in extracting the lanthanides as a group.

Table IV. Lanthanide Separation Factors for HPMTFP Extractions

neutral ligand	Δ log K^*_{ex}			
	La/Pr	Pr/Eu	Eu/Ho	Ho/Yb
none	1.20	1.20	0.42	0.21
TOPO	0.99	0.87	0.02	−0.40
CMPO	1.14	0.84	0.09	−0.12
MBDPO[a]	1.08	0.75	−0.12	−0.18
MBDPO[b]	0.86	0.40	−0.62	−0.59

[a] In the absence of $NaClO_4$. [b] In the presence of $NaClO_4$.

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Registry No. La, 7439-91-0; Pr, 7440-10-0; Eu, 7440-53-1; Ho, 7440-60-0; Yb, 7440-64-4; HPMTFP, 1691-93-6; TOPO, 78-50-2; CMPO, 83242-95-9; MBDPO, 2071-21-8.

Supplementary Material Available: Figures 1–4, showing the influence of [TOPO] on the extraction of Eu with HPMTFP, plots of the extraction of Ho and Yb with a mixture of HPMTFP and MBDPO in the presence of $NaClO_4$, log $(D - (K_{ex}(MBDPO))[HA]_o^3[B]_o/[H^+]^3)$ vs. log $[B]_o$ for Pr, and log $(D - (K_{ex}(MBDPO))[HA]_o^3[B]_o/[H^+]^3)$ vs. log $[ClO_4]$ for Pr (4 pages). Ordering information is given on any current masthead page.