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Extraction Separation of Tervalent Americium and Lanthanides in the Presence of Some Soft and Hard Donors and Dicarbollide

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ABSTRACT

Some combinations of extractants involving dicarbollide as one component for the separation of Am/Ln were studied. Extraction by TOPO is not influenced to a great extent by the presence of dicarbollide, and TPTZ in the presence of dicarbollide is ineffective for the extraction from 0.1 M HNO_3. General aspects of the selectivity of lanthanides and of Am/Ln separation in the presence of various reagents are discussed with emphasis on the difficulties of the separation of Am from light lanthanides. A new extraction procedure by dicarbollide in the presence of an excess of *o*-phenanthroline over the mineral acid is proposed. This led to the highest separation factors D_{Am}/D_{Eu} (20–34) from 0.1 M HNO_3. The behavior of other lanthanides is similar to that of Eu, with a maximum distribution ratio for Nd ($D_{Nd}/D_{Eu} = 2$).

INTRODUCTION

Successful completion of programs in which the transplutonides are transmuted and, consequently, safe disposal is needed, requires development of very selective separation methods. The separation of Am (Cm) from lanthanides is generally a difficult task due to the high weight excess of lanthanides in spent nuclear fuel and due to the chemical similarity of both groups. Extraction methods are usually preferred in technological applications.

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In extraction separations, usually two methods based on different sequences of bond strengths of the complexes formed for the two groups are used. Use of hard donors of mainly the oxygen type usually leads to a rather high Eu/Am separation factor [Eu is better extracted; D_{Eu}/D_{Am} as high as 23 is reported for dibutyl phosphoric acid (1)]. Extraction of macroamounts of lanthanides is technologically not too expedient and, moreover, these systems show more serious drawbacks as a rule. Since the stability of a complex of hard oxygen donors is primarily determined by ionic interaction, the separation of the pair Nd^{3+}/Am^{3+} (with, for example, TBP), is hardly possible, and Ce^{3+} is less extracted than is Am^{3+} (2). Hence, the separation of the groups is not possible for lighter lanthanides, but these are mainly present in irradiated nuclear fuel. This drawback can be circumvented only by using some other complexant in the aqueous phase, as in the formerly used TALSPEAK process, with concomitant problems such as a high concentration of salts in the product.

On the other hand, soft donors linked to tervalent cations mainly by coordination bonds, invariably complex (and extract) Am^{3+} and Cm^{3+} better than any other lanthanide cation and are, therefore, ideally suited for technological purposes. Soft Cl^- donors have been used in the TRAMEX process (which is inconvenient due to corrosion properties and other problems connected with the high Cl^- concentrations needed), but more sophisticated soft donors were proposed and later studied by Musikas et al.

These were sulfur donor atom extractants, usually di(2-ethylhexyl)dithiophosphoric acid. The extractant in a mixture with TBP in dodecane leads to effective separation of Am and Eu from 0.05 M HNO_3 in countercurrent conditions (3, 4). However, this method was abandoned due to its insufficient chemical stability (5).

From *N*-heterocyclic donors, mainly *o*-phenanthroline was studied (2, 6, 7). Rather high separation factors ($D_{Am}/D_{Eu} \cong$ 16–19) were obtained for 0.25 M *o*-phenanthroline + 0.25 M nonanoic acid in nitrobenzene; however, the acidity of HNO_3 had to be lower than 0.01 M. Very high separation factors were obtained for a mixture of 4,7-diphenyl-1,10-phenanthroline and 4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-thione from pH 3.75 and 0.2 M $NaClO_4$, i.e., D_{Am}/D_{Eu} = 190 (8). The high pH of the aqueous phase needed with these extractions is prohibitive for their use in technological conditions.

Hence, other *N* donors that permit extraction of Am from 0.125 M HNO_3, viz., tris-2-pyridyl-1,3,5-triazine (TPTZ), were studied extensively (5, 9–11). The final choice of the authors for countercurrent experiments was 0.03 M TPTZ + 0.05 M dinonylnaphthalenesulfonic acid (HDNNS) in CCl_4 for which the separation factor is $D_{Am}/D_{Eu} \cong$ 10 for 0.125 M

HNO_3. Due to the losses of TPTZ into the raffinate (D_{TPTZ} under the above conditions is about 10), the TPTZ at a 0.003 M concentration was added to the feed and scrub. According to the authors, this drawback could be solved by recuperating TPTZ from the raffinate after neutralization. However, the poor hydrodynamic behavior of the system seems to be more serious. HDNNS, in fact, is an anionic detergent, and the authors proposed that it should be substituted for by an anion of another strong acid.

This suggestion initiated the present study in which we tried to use the strongly hydrophobic and acidic dicarbollide anion instead of $DNNS^-$. Its convenient properties for radiochemical technology have been proved in a number of papers. The dicarbollide process, originally invented in the Czech Republic (12), was studied in cooperation with Russian scientists and ultimately used in Russia for the separation of $^{134,137}Cs$, ^{90}Sr, and transplutonides on a plant scale (13).

The aim of this work is to show rather completely the behavior of Am^{3+} and of Eu^{3+} (Nd^{3+}) in some systems containing dicarbollides and potentially applicable extractants for group separation. The most details are given for the system with *o*-phenanthroline. Systems with dicarbollides and crown ethers have been reported by others: Am/Eu separation (14), lanthanide separation (15, 16).

EXPERIMENTAL

Reagents

Chlorinated dicarbollide, H^+ form hydrate, mean composition hexachloroderivative ($H^+BCl_6^-$), was prepared by Katchem, Czech Republic. The Zr number, defined as the distribution ratio of $^{95}Zr + {}^{95}Nb$ between 3 M HNO_3 and 0.06 M reagent in nitrobenzene after 30 minutes of shaking, was 0.003. All other reagents and solvents were of reagent grade purity and were not further purified before use.

Radioisotopes

^{241}Am and ^{155}Eu radioisotopes in a 0.1 M HNO_3 stock solution were used. Whenever the separation factor D_{Am}/D_{Eu} was determined, both isotopes were used in one test tube. The γ activity, obtained by integration of the peaks at 60 keV for Am and at 86 and 105 keV for Eu, was corrected for Am for the interference of ^{155}Eu. With the GeLi detector used, the correction factors were 0.0853 and 0.1204, respectively, and the same correction obtained from the two peaks served as proof of the correctness of the measurement.

Preparation of Extractant

The chlorinated dicarbollide H^+ (10.060 g) was dissolved in 100 mL nitrobenzene. The solution was shaken three times with the same volume of 3 M HNO_3, once with 0.5 M HNO_3, and the organic solution was filtered through paper filter in order to remove any possible aqueous phase present. Then a 1 mL sample was withdrawn, diluted with 15 mL EtOH and titrated with an aqueous 0.1 M KOH solution using bromocresol blue as the indicator. The resulting stock solution was 0.147 M.

To obtain a Na^+ salt solution in nitrobenzene, the above stock solution was shaken five times with new portions of 2 M $NaNO_3$ (resulting pH $\geq$ 5) and the solution was filtered. No transfer of anion into the aqueous phase occurred under these conditions.

Procedures and Measurements

The extractions were performed in stoppered glass tubes with equal volumes of the phases (2 mL). Shaking was carried out for Nd^{3+} for 30 minutes in a thermostated box (25 ± 1°C), but in other cases only 5 minutes of shaking at 24 ± 1°C was used (equilibrium established). In all cases the tubes were centrifuged before the samples were withdrawn.

The concentration of Nd^{3+} (Ce^{3+}) in the aqueous phase was measured spectrophotometrically with Arsenazo III at pH $\cong$ 2.3 and a reagent concentration of 0.002% (λ_{max} = 653 nm, ϵ_{max} = 39,500 cm^{-1}). It was confirmed by independent experiments that any organic solvent dissolved in the aqueous phase does not influence the absorption, but TPTZ in higher concentrations increases the absorption value. (This was not the case here.)

A spectrophotometric method for the determination of TPTZ in the aqueous phase was developed. The TPTZ content was measured in a solution of 0.05 M $CoCl_2$ in 0.25 M HNO_3 (Co–TPTZ complex: λ_{max} = 370 nm, ϵ_{max} = 754.1 cm^{-1}). Nitrobenzene dissolved in water interferes since its absorption starts at 400 nm and increases at lower wavelengths, but an approximative value can be determined at the shoulder of the 370 nm peak (actually, λ = 415 nm was used).

Spectrophotometric measurements were performed by recording with a UV-VIS spectrophotometer Shimadzu 2200 with a cell of 1 cm length. A HM-30V TOA Electronics pH meter coupled with a combined glass-calomel electrode was used.

An ICP mass spectrometer (ICP MS Fisons Instrument VG PQ Ω, England) was used for the determination of the separation factors among lanthanide elements. In a mixture of rare-earth cations, the following isotopes were determined: La-139; Ce-140; Pr-141; Nd-146; Sm-147; Eu-151, 153;

Gd-157, 158; Tb-159; Dy-162; Ho-165; Er-166; Tm-169; Yb-174; and Lu-175. The aqueous solution in the same experiments as with radioactive Eu and Am was spiked with 1–2 vol% of a stock solution containing 1.02 ppm of each lanthanide in 1% HNO_3 solution. The equilibrium concentration in the organic phase was determined after backextraction by 0.5 M HNO_3. In all cases the blank value was subtracted.

RESULTS AND DISCUSSION

Extraction in the Presence of TOPO and Dicarbollide

Trioctylphosphine oxide is a typical hard donor extractant enabling extraction of two groups of tervalent cations from moderate acidic media.

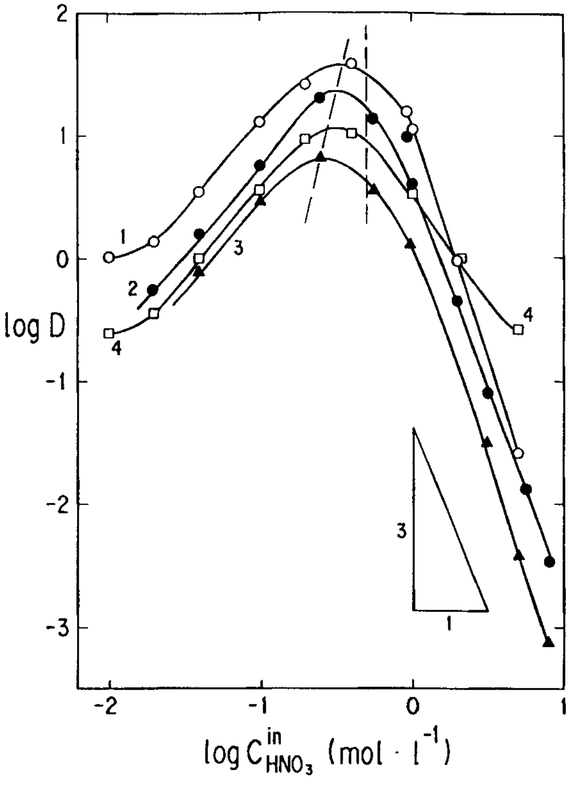

FIG. 1 Extraction of Eu^{3+} and Am^{3+} from nitric acid solutions by TOPO in different solvents. 1: Nitrobenzene; 2: tetrachloroethylene (17); 3: 1,2-dichloroethane (17); 4: 30% TBP in dodecane. Open symbols, Eu^{3+}. Closed symbols, Am^{3+}.

Reported values of D_{Am} at maximum (0.25 M HNO_3 and 0.5 M TOPO) are 7 for 1,2-dichloroethane and 11 for tetrachloroethylene (17). Among moderately polar or polar solvents, the extraction is highest with nitrobenzene, as seen in Fig. 1. This solvent (as distinct from 30% TBP in *n*-dodecane) would not permit backextraction by dilute acid, a step needed for further Am/Ln separation.

Based on the presence of maxima on the curves of $D_{M(III)}$ vs $c(HNO_3)$, TOPO is similar to other phosphine oxides, phosphinates, and phosphonates (17). Because of the recently reported (18) strong increase of $D_{M^{3+}}$ in extraction by dibutyldiethyl carbamoylmethylene phosphonate (DBDECMP) upon addition of dicarbollide anion, it is of interest to know its influence on TOPO extraction.

Some pertinent results are given in Fig. 2. It is seen from the figure that generally there is only a small influence of dicarbollide on europium

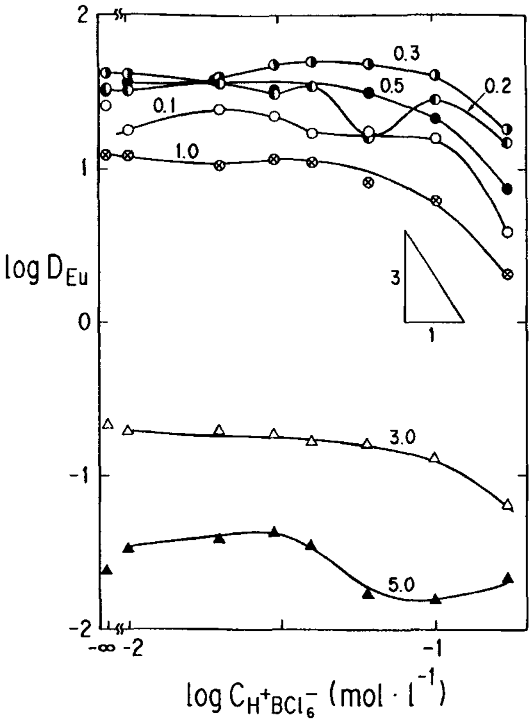

FIG. 2 Extraction of Eu^{3+} by 0.5 M TOPO in nitrobenzene from nitric acid solutions in the presence of dicarbollide. The initial concentrations of HNO_3 are denoted by numbers close to the curves.

extraction except for high concentrations of the reagent. One possible explanation of this difference between TOPO and DBDECMP is that TOPO is hydrophobic enough so that a high concentration of $H^+TOPO{\cdot}NO_3^-$ species (possibly dissociated) is attained, and therefore the exchange of a NO_3^- anion for a dicarbollide anion does not lead to any further increase of reagent concentration in the organic phase. However, for high concentrations of H^+BCl^-, the competitive reaction between H^+ and Eu^{3+} for TOPO becomes important and D_{Eu} decreases. This figure is especially interesting because of the minimum on the curve for 0.2 M HNO_3. We considered it at first as a possible artifact, but Fig. 3 shows the reality of the phenomenon.

It is seen from Fig. 3(a) that the behavior of Am^{3+} and Eu^{3+} is very different in the sense that the minimum for Eu^{3+} does not appear for Am^{3+}. The effect is very sensitive to the aqueous acidity, and at the conditions of Fig. 3(b) it is nonexistent. The reasons for this effect cannot be decided on the basis of the present results, but from practical point of view—as noted in the Introduction—the separation of the Am/Nd pair with this hard donor is hardly possible.

Extraction in the Presence of TPTZ and Dicarbollide

At present, TPTZ is the only reported soft donor that permits efficient separation of Am^{3+}/Ln^{3+}, even from 0.1 M HNO_3 solutions. Although a micellar mechanism of extraction of Am^{3+} with $DNNS^-$ anion has been postulated with the formation of a rather complex structure

$$\{[AmTPTZ(DNNS)_3]_i[Am(DNNS)_3]_k\text{-}[TPTZ(HDNNS)_2]_j[TPTZ(HDNNS)]_l[HDNNS]_q\}$$

existing in the organic phase (9), it is believed that a general physicochemical principle governing the extraction is the formation of the hydrophobic species $H^+L{\cdot}A^-$ (dissociated in polar solvents) which in turn extracts Am^{3+}. If A^- is strongly hydrophobic and a strong acid (in order to avoid competitive formation of nonefficient HA), then the distribution ratio of even the very hydrophilic ligand L can be substantially increased [e.g., more than four orders of magnitude if L is water-soluble polyethylene glycol 400 and A^- is dicarbollide anion (19)].

Indeed, the distribution ratio of TPTZ is much higher in systems with dicarbollide than in those with $DNNS^-$ ($D_{TPTZ} \geq 260$ for initially 0.07 M TPTZ and 0.147 M $H^+BCl_6^-$ in nitrobenzene and 0.25 M HNO_3). Also, the distribution ratio of Ce^{3+} and Nd^{3+} at conditions similar to those used by Musikas decreased similarly with an increasing concentration of TPTZ. However, in dramatic contrast, there is no separation of the Am/Eu pair

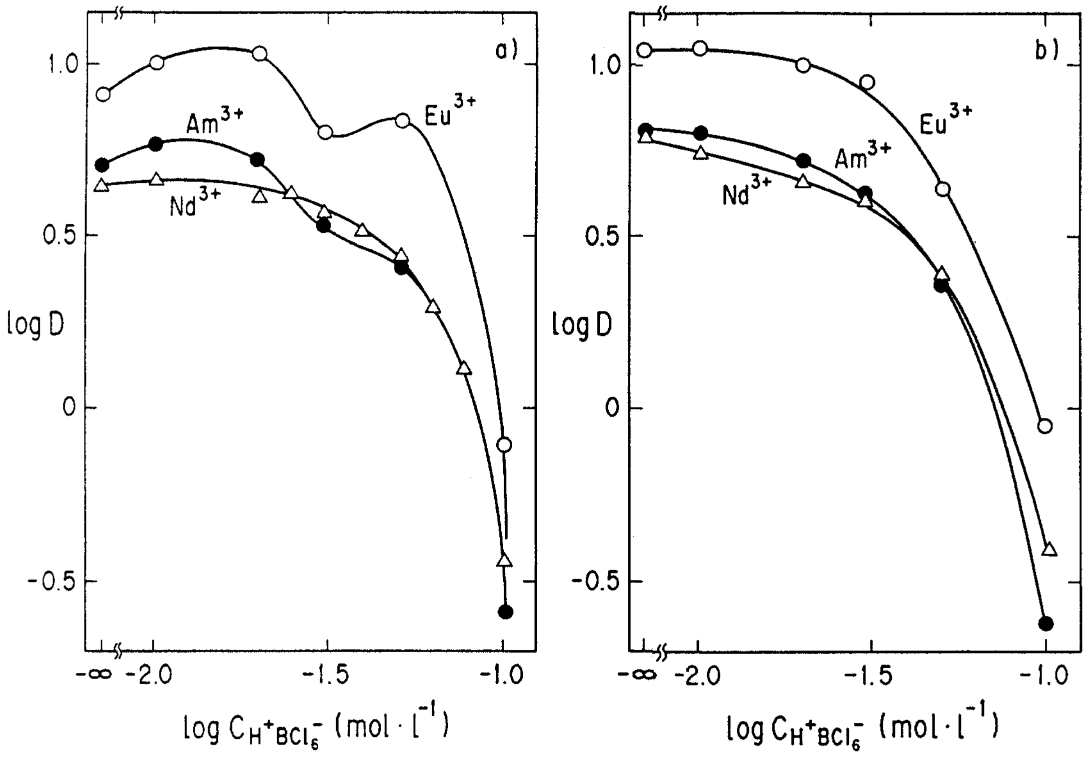

FIG. 3 Extraction of Am^{3+}, Eu^{3+}, and Nd^{3+} from dilute nitric acid by 0.25 M TOPO and dicarbollide in nitrobenzene. Microamounts of Eu and Am. Nd initial concentration: 2.93×10^{-3} M (a) and 5.18×10^{-3} M (b). HNO_3 initial concentration: 0.132 M (a) and 0.234 M (b).

in systems with nitrobenzene and dicarbollide, as shown in Fig. 4. This is so even if a more dilute nitric acid is used and if polyethylene glycol 1000 as a synergetic agent for increasing the distribution ratios of tervalent cations is used.

The explanation involving both observed effects (i.e., no Am/Eu separation and a decrease of *D* with TPTZ concentration) is based on the supposed existence of TPTZ in its protonized form at the conditions given above. Hence, no complexation of Eu^{3+} and Am^{3+} does occur, and both cations are nearly equally expelled from the organic phase by protonized TPTZ.

For a full prediction of the extractability of Am^{3+}, knowledge of at least four constants is required (this applies for any cation and ligand extracted into a polar solvent where dissociation of the species is possible). These are the protonation constants of the ligand in water and in the organic solvent, and the stability constants of the Am complex in water and in the solvent. These are not independent, and a concept of individual extraction constants developed before (20) seems to be useful.

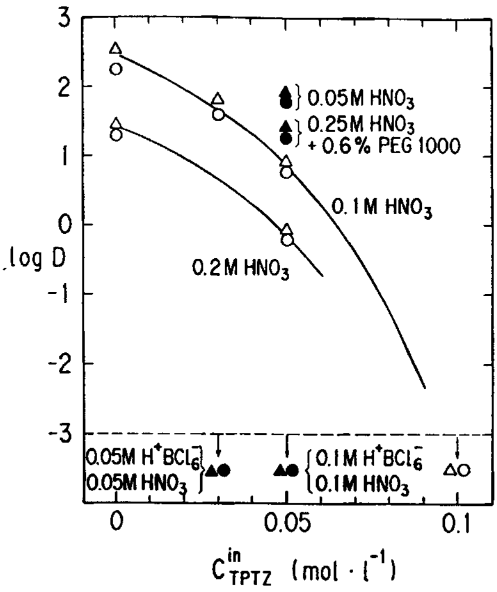

FIG. 4 Extraction of Am^{3+} and Eu^{3+} by a nitrobenzene solution of dicarbollide and TPTZ. Triangles denote Am^{3+}, circles Eu^{3+}, closed symbols are points not belonging to the series. The concentration of dicarbollide was, if not indicated otherwise, 0.204 M. The dashed line denotes the limit under which measurement was not reliable.

Since TPTZ forms at pH < 2 for the doubly protonized species H_2L^{2+}, in the presence of the same particle in the nitrobenzene phase we can write

$$K_1^oK_2^o = [H_2L^{2+}]_o/[H^+]_o^2[L]_o = K_1K_2K_i(H_2L^{2+})/K_i(H^+)^2K_i(L) \quad (1)$$

where sub- and superscripts o denote the organic phase, and $K_i(X)$ is the individual extraction constant of X (in the case of a neutral particle, L is equal to its distribution ratio) (19). Log $K_i(H^+) = -5.7$, and log $K(L) \cong 1.9$ [the D_L value for the water–1-decanol system is 82, and the ratio of solubilities of TPTZ in nitrobenzene and decanol is 1.042 (9)]. If we suppose conservatively that $K_i(H_2L^{2+})$ is about two orders of magnitude lower than $K_i(L)$ due to the hydrophilicity increase upon protonization [for comparison, the difference of log $K_i(P)$ − log $K_i(HP^+)$, where P is *o*-phenanthroline or one from the other three substituted phenanthrolines in the extraction system water–1,2-dichloroethane amounts to 0.91 ± 0.2 (21)], the resulting $K_1^oK_2^o$ in nitrobenzene would be log $K_1^oK_2^o \cong$ log $K_1K_2 + 9.4$. This result means that at any low concentration of H^+ ions in the nitrobenzene phase (which is inevitable if we want to conduct the extraction from acidic aqueous media), TPTZ will practically always be present as protonized H_2TPTZ^{2+}. Physically, this result simply means that in nitrobenzene, which is considerably less basic than water, the competition of solvent molecules for protons is too weak to assure its effective split from the H_2TPTZ^{2+} cation. Even so, the extraction of Am could occur only if the stability constant of the $AmTPTZ^{3+}$ complex in nitrobenzene were sufficiently high. A relationship analogous to Eq. (1) can be easily derived for the stability constant $\beta^o_{Am,TPTZ}$ corresponding to the reaction $Am^{3+} + TPTZ_o = AmTPTZ_o^{3+}$. Again, the stability constants of various complexes of metal cations with electroneutral ligands are usually several orders of magnitude higher in nitrobenzene than in water (e.g., Ref. 22). The obvious reason for this increase is the same as in the case of protons, i.e., the more basic water molecules compete more strongly than nitrobenzene for the cation. Since these two effects operate in opposite directions, it is a priori difficult to make a prediction of the extractability of a given ion and experimental screening tests are needed.

One possible way to increase extraction is to change the solvent. Nitrobenzene was replaced by 1-octanol (with a basicity comparable to that of water) in the hope of decreasing the protonation constant. However, in a 0.1 M solution of $H^+BCl_6^-$, the solubility of TPTZ was only 0.01 M. With this extractant, the distribution ratios of both Am^{3+} and Eu^{3+} were lower than 10^{-3} for 0.1 M HNO_3.

Finally, we explored the possibility that some ternary complex AmTPTZ·L has formed. The results depicted in Fig. 5 show that the addi-

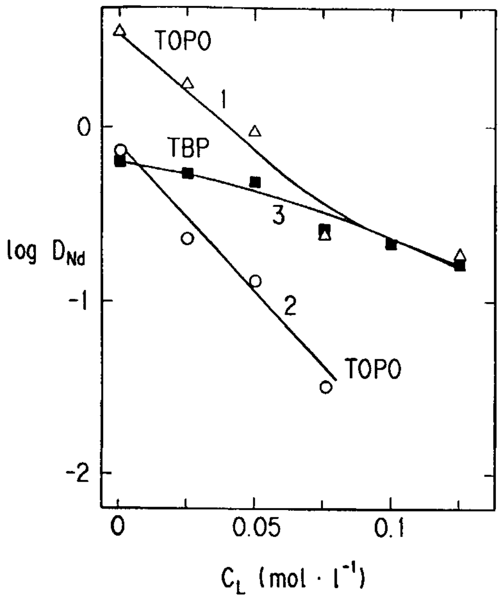

FIG. 5 Extraction of Nd^{3+} by three-component mixtures of extractants in nitrobenzene. 0.153 M $H^+BCl_6^-$ + 0.025 M TPTZ + L; L = TOPO for Curves 1 and 2, TBP for Curve 3. 1: c_{Nd}^{in} = 0.0055 M, $c_{HNO_3}^{in}$ = 0.092 M; 2 and 3: c_{Nd}^{in} = 0.011 M, $c_{HNO_3}^{in}$ = 0.25 M.

tion of either tributylphosphate or tri-*n*-octylphosphine oxide leads to a decrease in the distribution ratio of Nd^{3+}, apparently due to the competition of the protonized forms of these reagents rather than to any ternary complex formation.

In conclusion, TPTZ in combination with even a very hydrophobic anion in polar solvents does not seem suitable for the separation of Am/Eu from acidic media. The main reason seems to be excessive protonization of the reactant. It is supposed that in micellar systems with $DNNS^-$ this protonization is suppressed, but the observed decrease of D_{Am} with TPTZ concentration still remains unexplained.

Separation of Am/Ln by *o*-Phenanthroline and Dicarbollide

Le Marois and Musikas report (6) data on the extraction of Am^{3+} and Eu^{3+} into 0.5 M *o*-phenanthroline in nitrobenzene in the presence of dibutylphosphoric acid (DBPA) from 0.1 M HNO_3. For c_{DBPA} = 0.001 M and 0.1 M, log D_{Am} was −1.17 and 3.14, respectively, and the respective separation factors D_{Am}/D_{Eu} were 4.90 and 1.55. The most important result of the present work is lowering the acidity of the aqueous phase by more than three orders of magnitude, since the equilibrium pHs of the aqueous phase reported in Reference 6 were 4.16 and 4.04, respectively. This is caused by protonation of *o*-phenanthroline which serves here as a complexant both for H^+ and M^{3+} ions.

Considering that the combination of DBPA with *o*-phenanthroline is not convenient because the two have opposite selectivities versus the Am/Eu pair (see the Introduction and more detailed data in Ref. 6), and because the DBP anion may not be exceedingly hydrophobic and a strong

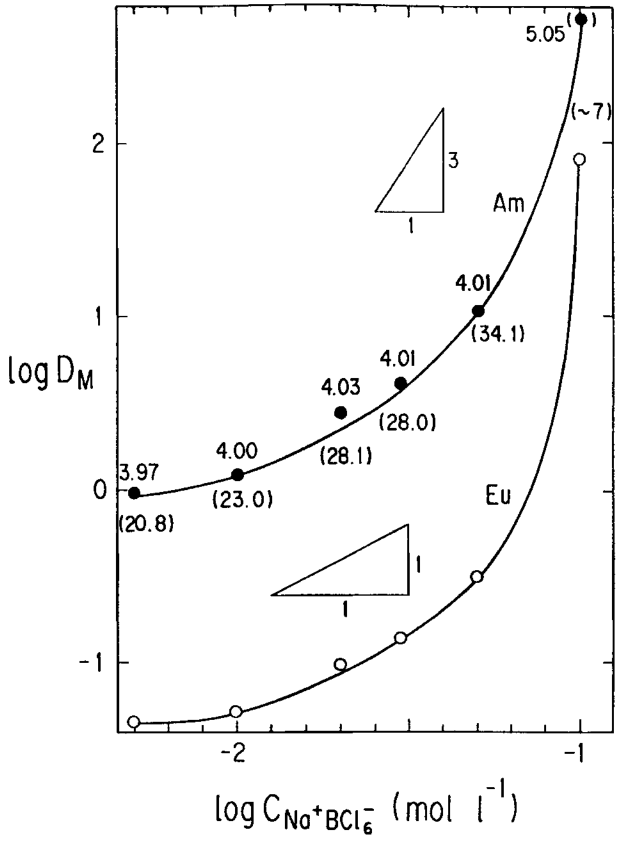

FIG. 6 Extraction of Am^{3+} and Eu^{3+} by 0.25 M *o*-phenanthroline in nitrobenzene in dependence on $Na^+BCl_6^-$ concentration. Initially, 0.1 M HNO_3; (●) Am, (○) Eu. Numbers above the top curve indicate the equilibrium pH of the aqueous phase; numbers in parenthesis are separation factors for the Am/Eu pair.

acid, we used sodium dicarbollide instead of DBPA. In this work we primarily used 0.25 M *o*-phenanthroline solution in nitrobenzene.

Pertinent results on the dependence of distribution and Am/Eu separation on the dicarbollide extractant concentration and on the aqueous initial acidity are given in Figs. 6 and 7, respectively, together with the equilibrium pHs of the aqueous phases.

It is seen from the Fig. 6 that a sufficiently high D_{Am} can be reached from 0.1 M HNO_3 solution by 0.05 M $Na^+BCl_6^-$ + 0.25 M *o*-phenanthroline in nitrobenzene (D_{Am} = 10.8) at high separation from Eu^{3+} (D_{Eu} = 0.316, D_{Am}/D_{Eu} = 34.1). These are the most promising values reported up to now for an initially acidic region. Also, backextraction of both elements may be easily performed by increasing the acidity of the aqueous phase [Fig. 7: for $c(HNO_3) > 0.3$ M, the distribution ratios were lower than 10^{-3} and not reliably measurable]. For these reasons the system is suitable for nuclear technology purposes (23) and deserves further study.

The basic properties of the system can be predicted on the basis of the concept of individual extraction constants; however, more precise values are needed. For a convenient cyclic process, all extractant should be contained in the organic phase or cheap and harmless reagents may be

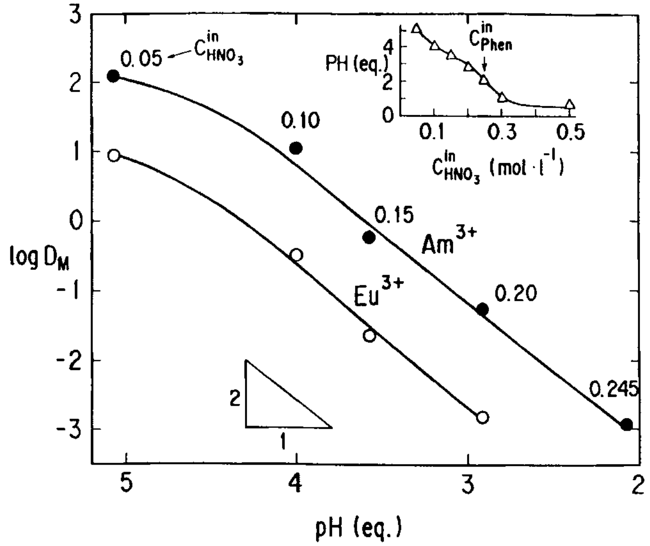

FIG. 7 Extraction of Am^{3+} and Eu^{3+} from nitric acid solutions by 0.25 M *o*-phenanthroline + 0.05 M $Na^+BCl_6^-$ in nitrobenzene. Numbers above the top curve indicate the initial nitric acid concentration. The relationship between $c^{in}_{HNO_3}$ and equilibrium pH is given in the upper figure insert.

consumed. The first condition is assured for the dicarbollide anion because no losses of dicarbollide anion to the aqueous phase were observed for the conditions given in Figs. 6 and 7. The distribution ratio of nonprotonized *o*-phenanthroline between water and nitrobenzene is $D_L = 56 \pm 1$ (2) or 95.5 ± 1 (22). The individual extraction constant of $HPhen^+$ for the water–1,2-dichloroethane system is $\log K_i = 0.63$ according to Yoshida and Freiser (21). Suppose for the moment that the water–nitrobenzene system has the same value, then the $HPhen^+$ ion would be rather hydrophobic, comparable to the tetraethylammonium cation (20). Therefore, $HPhen^+$ would not be extracted in the form of nitrate [this was experimentally confirmed by Le Marois (2)], but almost completely in the form of its dicarbollide salt. Extraction of $HPhen^+$ dicarbollide is apparently the reason for the increase of pH at the last point of Fig. 6. Control of the pH of the equilibrium aqueous phase is automatically attained (which is one of the advantages of the system) by reaction of nitric acid with an excess of *o*-phenanthroline, but in an excess of $Na^+BCl_6^-$ the $HPhen^+$ formed will be mainly extracted. The exact conditions are still to be studied. As seen from Fig. 7, the selectivity of the system seems to be fairly constant in the pH 3–5 region.

We tried to obtain the dependence of D_{Am} (D_{Eu}) on the concentration of *o*-phenanthroline, but for an *o*-phenanthroline concentration higher than 0.3 M and after some 3 minutes of shaking a white precipitate formed in the aqueous phase (0.02 M $H^+BCl_6^-$ in nitrobenzene, 0.1 M HNO_3). The precipitate also formed when 0.5 M *o*-phenanthroline without dicarbollide was shaken with 0.1 M HNO_3 [not noted by Musikas and LeMarois (6, 7)]. However, a big gain in the hydrophobicity of $MPhen^{3+}$ in comparison with M^{3+} is to be expected. From the available data, Homolka and Wendt reported a -33.3 kJ·mol^{-1} increase of $\Delta G^\circ_{tr}(H_2O \rightarrow NB)$ upon formation of $NiPhen^{2+}$ from Ni^{2+} and $Fe(Phen)_3^{2+}$, which is rather hydrophobic [$\Delta G^\circ_{tr}(H_2O \rightarrow NB) = -11.8$ kJ·mol^{-1}] (24). On the other hand, protonized [$c^\circ(Phen) < c^\circ(HNO_3)$ in the system] *o*-phenanthroline behaves as a typical base (see TPTZ above) with a strong decrease of D_{Eu} and D_{Am} and with a loss of selectivity (Fig. 8).

Separation of Am^{3+} from Tervalent Lanthanides

Surprisingly, most work dealing with Am/Ln separation treats Am^{3+}/Eu^{3+} separation. It has been shown in this work that although some separation of Am^{3+}/Eu^{3+} is possible with the hard donor TOPO, this is not true for the Am^{3+}/Nd^{3+} pair. Some cases are briefly discussed in the following text.

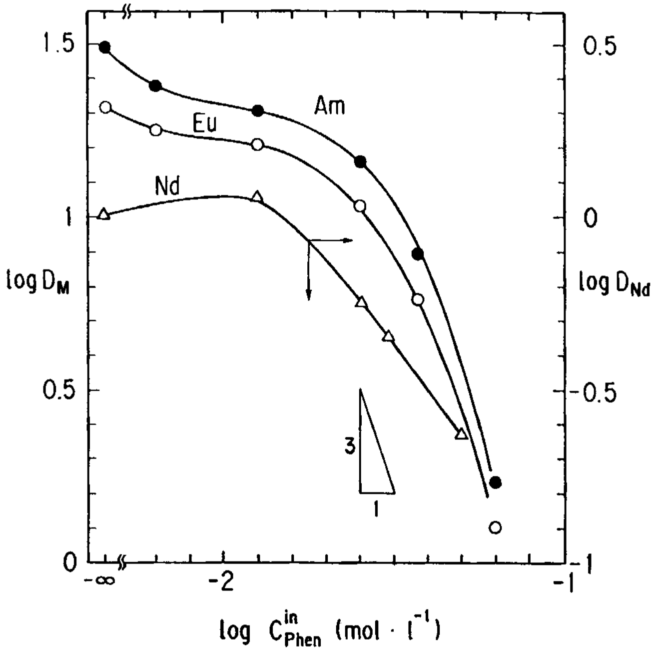

FIG. 8 Extraction of Am^{3+}, Eu^{3+}, and Nd^{3+} from dilute HNO$_3$ by 0.1 M H$^+$BCl$_6^-$ in the presence of *o*-phenanthroline. Curves for Am and Eu: 0.1 M HNO$_3$; Curve for Nd: 0.234 M HNO$_3$, microamounts of Am and Eu, c^{in}_{Nd} = 5.2 × 10^{-3} M.

Hydration-Controlled Systems and Crown Ethers

Lanthanides extracted into nitrobenzene in the presence of dicarbollides are subject to no specific interaction. The simple rule that more hydrated (i.e., with a lower ionic radius) M^{3+} lanthanides are less extracted is quantified if log K^{M}_{3H} constants from the paper of Vaňura (15) are plotted against $-\Delta G^{o}_{hydr}$ of the respective ions (25). A straight-line correlation was proposed by one of us for alkali metal cations (26), which means that only hydration–solvation effects are operative.

18-Crown-6 [another reagent proposed for Am/Ln separation from acidic media (14)], as seen from Fig. 9, behaves quite analogically, only there is a larger selectivity for lighter lanthanides. Hence, any macrocyclic effect (consisting of the fit of a particular ion with the crown) is missing. Low selectivity was reported for the Am/Eu pair (14); however, other lanthanides were not studied. Comparison of the results from References 14 and 15, which differ only in the concentrations used, reveals that the

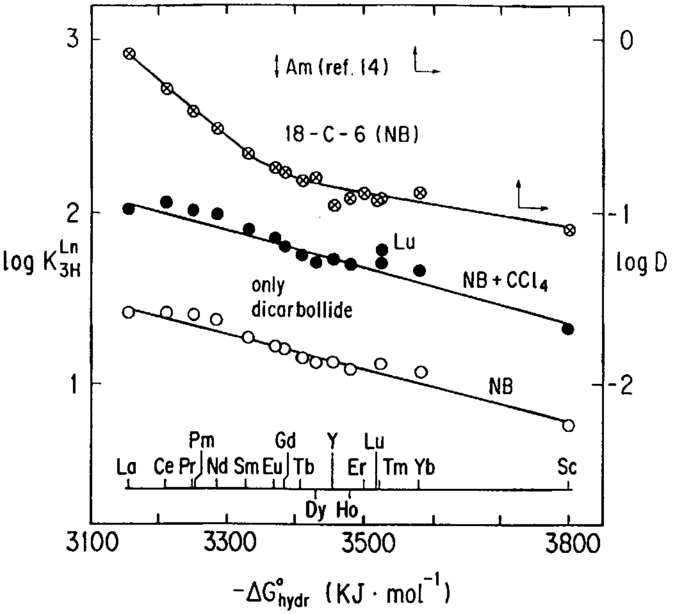

FIG. 9 Extraction of lanthanide M^{3+} cations by dicarbollide in the absence and presence of 18-crown-6. K^{Ln} is the extraction exchange constant of the Ln^{3+}/H^+ exchange. Data for D in the presence of 18-C-6 are for 0.00976 M crown, 0.0312 M $H^+BCl_6^-$, 0.102 M HNO_3, and c_M^{in} = 0.005 M (15). The relative value for Am^{3+} is deduced from the data of Reference 14, at which 0 to 0.2 M crown, 0.3 M $H^+BCl_6^-$, and 1 M HNO_3 were used, and D of microamounts of Am and Eu are reported. ΔG^o_{hydr} values are from Reference 24.

separation of Am^{3+} from lighter lanthanides, such as Ce^{3+}, may not be sufficient (Fig. 9).

Hard Donors

A number of hard donors extract Eu^{3+} better than Am^{3+}. However, separation from lighter lanthanides is not feasible, as discussed in the Introduction. From the physicochemical point of view, the systems can frequently be classified as just opposite of the case treated above. In fact, extraction from the more basic water solution into the less basic nitrobenzene solution may be analogous to the case of the extraction from the more basic TBP solution into the less basic water solution. This explains the opposite dependence of the distribution ratio on ion radius and the reversal of Am/Eu selectivity for systems like TBP (2) as compared with the previous paragraph.

Soft Donors

It is usually argued that the extraction of lanthanides by soft donors is nearly equal, but americium is extracted much better due to the covalent bond formed (11). Data on the stability constants of individual lanthanides with TPTZ and *o*-phenanthroline (2, 9) in aqueous solution was collected, but most distribution data are not available. The sequence of these two sets may not necessarily coincide since other factors are operative, as discussed above for TPTZ.

In this work we studied the extraction of lanthanide cations by *o*-phenanthroline and dicarbollide by ICP MS. The selectivity of Ln/Eu separation is given in Fig. 10. It seems that with *o*-phenanthroline the property which one would otherwise call the "macrocyclic effect" is pronounced. High extraction of Nd^{3+} is easily conceivable if we consider that the ionic radii of Am^{3+} and Nd^{3+} are nearly equal [0.99 and 1.00 Å, respectively (27)]. The high rigidity of the *o*-phenanthroline molecule (2) may create this effect. On the other hand, the heavier lanthanides behave practically identically. One possible explanation is that the supposed decrease of the extraction constant of $LnPhen^{3+}$ with increasing atomic number (radius

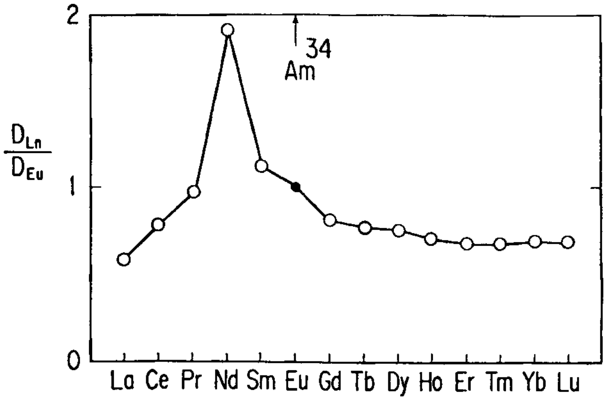

FIG. 10 Separation of individual lanthanides in extraction by 0.25 M *o*-phenanthroline + 0.05 M $Na^+BCl_6^-$ in nitrobenzene from 0.1 M HNO_3 initially. See the Experimental Section for details.

decrease and stronger hydration, see Fig. 9) is compensated for by the increase of the stability constant of the $LnPhen^{3+}$ complex.

CONCLUSIONS

The extraction of Am^{3+} and Ln^{3+} by TOPO is not greatly influenced when using the highly hydrophobic dicarbollide anion. The TPTZ ligand used from aqueous 0.1 M nitric acid is ineffective with dicarbollide at all conditions studied. Its suitability with $DNNS^-$ is probably due to the special conditions of the micellar mechanism of extraction.

The selectivity of extraction of Am^{3+}/Ln^{3+} was studied and evaluated for various systems. Difficulties with the effective separation of Am^{3+} from lighter lanthanides in systems with hard donors and in the 18-crown-6/nitrobenzene system are apparent. It is recommended that instead of reporting only D_{Am}/D_{Eu} data, all lanthanide series be measured by the modern techniques now available.

A system with dicarbollide and *o*-phenanthroline is proposed for further study. D_{Am}/D_{Eu} as high as 34 can be reached from an initial 0.1 M nitric acid solution. The system may be used as a continuation of some process yielding a common transplutonide + lanthanide fraction from Purex wastes such as the TRUEX process.

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