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Synergetic Extraction in Systems with Dicarbollide and Bidentate Phosphonate

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ABSTRACT

A process for the extraction of tervalent metal cations from 3 M HNO_3 highly radioactive waste based on synergetic mixtures of dicarbollide with neutral organophosphonate (dibutyl diethylcarbamoylmethylene phosphonate) is proposed. Due to the great hydrophobicity of dicarbollide anion, the species $ML_n^{3+} \cdot 3BCl^-$ is extracted and the extraction in this TRUDIC process decreases with aqueous acidity, contrary to TRUEX process. HL^+BCl^- is the main particle in the organic phase. The extraction of Cs^+, Sr^{2+}, Ba^{2+}, and Ru is low, and the extraction of Zr can be suppressed by citric acid. Possible advantages of the system are discussed.

INTRODUCTION

The extraction of tervalent actinides (Am^{3+}, Cm^{3+}) is a crucial point in the further development of projects in which highly radioactive waste (HLW) would be transmuted and problems of the long-term disposal of wastes could be relieved (e.g., the OMEGA project in Japan).

The acidity of HLW after reprocessing is about 3 M HNO_3. A new class of extractants (bidentate phosphonates, phosphine oxides, and malonamides) for the extraction of tervalent lanthanides and actinides from acidic media has been intensively studied (e.g., Refs. 1 and 2). A process using octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethyl phosphine oxide

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(CMPO) and called TRUEX will apparently be used in the United States (1), whereas *N*,*N*-tetraalkyl alkyl propane diamides $(RR'NCO)_2CHR''$ (DIAM) have been proposed in France (3).

Whereas organophosphorus extractants under hydrolysis and radiolysis form acidic extractants which deteriorate the backextraction of M^{3+} at low acidities, no change in the distribution ratio of Am^{3+} in the system 1 mol/L DMDB 3,6 ODPDA [(3,6-dioxadodecyl) malonic acid *sym*-dibutyldimethyldiamide] in *t*-butylbenzene occurred after γ-irradiation to the total dose (710 kGy) when the organic solution was in contact with 0.5 M HNO_3 ($D_{Am} < 0.2$, conditions suitable for backextraction) (3). Although this result is encouraging, the DIAM process is not completely free of difficulties. Am^{3+} was not stripped as effectively as expected in countercurrent experiments because of the presence of TcO_4^- which retains Am^{3+} in the organic phase at low acidities (3). On the other hand, no problems with stripping the tervalent metals from the organic phase occurred during countercurrent tests of the TRUEX process with real HLW raffinate according to a recent paper from the reprocessing facility PNC in Japan (4).

The dicarbollide process was proposed at NRI and Institute of Inorganic Chemistry, Czechoslovakian Academy of Science (5). It was initially aimed at the separation of ^{137}Cs and ^{90}Sr directly from 3 M HNO_3 Purex waste, but after showing good properties for this, the extraction of tervalent metal cations was also attempted (6). Although objections to the toxicity of the solvent (nitrobenzene) are sometimes raised (2, 7, 8), the usefulness of the process was documented in Russia (9) where 40 m^3 of the Purex raffinate was reprocessed and 240 g of ^{241}Am was obtained. The advantages of the halogenated dicarbollide reagents [bis(8,9,12-halogen$_3$-dicarbollide)-cobalt(III)ate (10)] are their high chemical and radiation stabilities, their extremely high lipophilicity (11), and the wide documentation on their use in radiochemical technology (12). However, for extraction of the tervalent elements, the original HLW feed must be deacidified to the 0.3–0.5 M HNO_3 range.

In previous work we found that in the presence of neutral ligands able to selectively bind Sr^{2+} ions–polyethylene glycols (PEGs), the extraction of the latter increases by several orders of magnitude in systems with dicarbollide (13, 14). This is so even when nonsubstituted hydrophilic PEGs are used (15). The generic name of the process with PEGs is PEGDIC, and this process has been tested on a plant scale in Russia.

Since the neutral bidentate phosphonates and phosphine oxides form stable positively charged complexes with tervalent metals, it seems to be a logical continuation to use them in systems with dicarbollide. The TRUDIC process should be analogous to PEGDIC but for tervalent metals. Because the organophosphorus compounds have no pronounced affin-

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ity toward Cs^+ cations and are usually hydrophobic (1), it may be supposed that in comparison with classical dicarbollide and PEGDIC processes, the extraction of Cs^+ will be suppressed by competitive reactions. On the other hand, it is believed that in comparison with the TRUEX process, the dependence of $D_{M(III)}$ on acidity may be reversed in the TRUDIC process. If ion pairs of the type $ML_n^{3+}\cdot(NO_3)_3^-$ are extracted into moderately polar and polar solvents, then the presence of dicarbollide anion will lead to the transformation of the above associate into $ML_n^{3+}\cdot(BCl)_3^-$ because the extraction constant of the BCl^- anion is several orders of magnitude higher than that of NO_3^- (nitrobenzene, Ref. 11). Hence, on increasing the nitric acid concentration, no increase of the concentration of counterions should be observed and only the competition of H^+ for Eu^{3+} should be detectable. Because it may also be reasonably supposed that extraction of a phosphorus-containing reagent will be much higher than in the TRUEX process, we used dibutyl diethylcarbamoylmethylene phosphonate (DBDECMP) in this work. It was previously abandoned due to its great losses into the aqueous phase in the TRUEX process.

The TRUDIC process was first announced in 1981 (16) but more detailed information is given only here.

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EXPERIMENTAL

Reagents

Chlorinated dicarbollide, Cs^+ salt, and a mean composition hexachloro derivative (H^+BCl^-) were prepared by Spolana, Neratovice, Czechoslovakia. The Zr number, defined as the distribution ratio of ^{95}Zr + ^{95}Nb between 3 M HNO_3 and the 0.06 M reagent in nitrobenzene after 30 minutes of shaking of the batch used, did not exceed 0.005. DBDECMP was an Alpha-Ventron product; another batch was synthesized and purified at the Technical University, Prague. The two samples showed the same extraction behavior and were not further purified. All other reagents used were of reagent grade purity.

Radioisotopes

The standard radioisotopes ^{137}Cs, ^{85}Sr, ^{133}Ba, $^{153,154}Eu$, ^{106}Ru, ^{241}Am, and ^{95}Zr + ^{95}Nb were used. The latter isotope, supplied in the form of oxalates, was evaporated to dryness at least 10 times with 10 M HNO_3 and H_2O_2 in order to destroy the oxalates.

Preparation of Extractant

The Cs salt of dicarbollide dissolved in nitrobenzene or in a nitrobenzene/carbon tetrachloride mixture was converted into the H-form by shaking the organic solution with fresh portions of 8 M HNO_3 of the same volume eight times and twice with 3 M HNO_3. The organic phase was filtered, and the H^+ content was determined by diluting 1 mL of the organic solution with 15 mL ethanol and titrating with 0.1 M aqueous NaOH solution using bromocresol green as the indicator (red–green).

Extraction of Metal Cations

The phases were shaken in 10 mL stoppered test tubes at 25 ± 1°C for 15 minutes. This time was sufficient to attain equilibrium (Zr: see the text). The samples of two phases were withdrawn, and the γ-activity was measured with a NaI(Tl) well-type scintillator.

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Extraction of DBDECMP

The distribution of DBDECMP was measured by the concentration-dependent distribution method. After making a calibration curve of D_{Eu} vs DBDECMP concentration, the D_{Eu} for the equilibrium aqueous phase from the experiment with the distribution of DBDECMP was determined at standard conditions.

RESULTS AND DISCUSSION

Synergistic Enhancement of the Extraction of Eu^{3+} into Nitrobenzene

Analogously to our previous work concerning the PEGDIC process (13), the influence of the addition of DBDECMP to some reagents used for extractions into nitrobenzene was screened. The pertinent results are given in Table 1.

TABLE 1
Synergistic Enhancement of D_{Eu} upon Addition of DBDECMP to Some Reagents

	Concentration of DBDECMP (mol/L)				
Reagent	0	0.02	0.04	0.1	0.2
Phosphomolybdic acid[a]	0.002	81.2	440	506	256
Polyiodides[b]	0.001	0.003	0.002	0.002	0.003

[a] 40 g HPMo/L in nitrobenzene.

[b] 0.2 M I in nitrobenzene and 0.04 M NaI in the aqueous phase; aqueous phase in both cases 2 M HNO_3.

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It is seen that there is a quite strong influence for the system with phosphomolybdic acid ($S = 2.5 \times 10^5$ at maximum). Also, the distribution ratio of the reagent is greatly increased (the aqueous phase becomes colorless after the first addition of DBDECMP). In contrast to the PEG–polyiodide–Sr^{2+} system (13), no synergy is observed for polyiodides.

Extraction with DBDECMP Alone

Extraction of M(3+) cations with bidentate extractants into nitrobenzene has not been studied except for a recent publication (17) where the data for three phosphine oxides [DOD(iB)CMPO, OφD(iB)CMPO, and Dφ(iB)CMPO, see Ref. 17 for the full names)] and six solvents are given (D_{Am}).

The dependencies of D_{Eu} on acidity with extractions into various mixtures of nitrobenzene and CCl_4 are given in Fig. 1. The shape of the curves with a maximum typical for TRUEX is apparent. The extraction sharply increases with NB content, and the difference log $D_{\mathrm{Eu}}^{\mathrm{max}}$(NB) − log

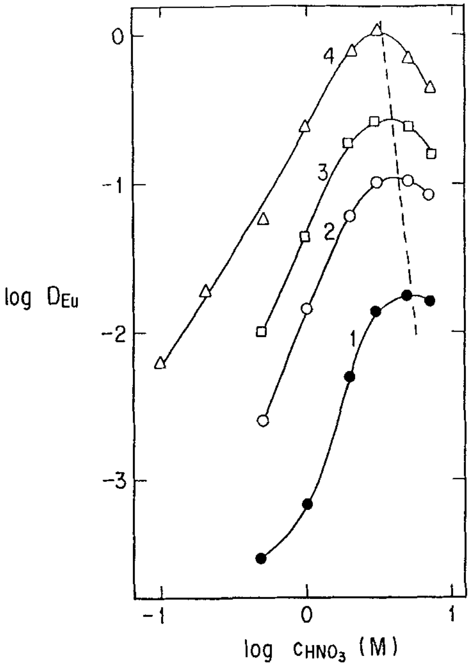

FIG. 1 Dependence of the distribution ratio of Eu^{3+} on the nitric acid concentration during the extraction by 0.1 M DBDECMP into the mixtures of nitrobenzene and CCl_4. (1) 20% by volume of nitrobenzene, (2) 40%, (3) 60%, (4) 100%; the maxima of the curves are connected by the dashed line.

$D_{Eu}^{max}(CCl_4)$ amounts to 2.2 (the maximum for pure CCl_4, not shown in the figure, occurs at ~5 M HNO_3).

In other series the dependence of D_{Eu} on the NB content in the mixture was studied. When log D_{Eu} is plotted against log (vol% NB in mixture) (= f), a perfectly straight line is obtained (Table 2). Since f is proportional to the molar concentration of the nitrobenzene in the mixture, it can be inferred that 2.6 molecules of nitrobenzene are involved in the extracted complex (vide infra).

Also, the dependence of log D_{Eu} on log c_L yields straight lines. The data given in Table 2 are for two mixtures with the highest nitrobenzene content. Substantially lower n values (n = 1.74 for nitrobenzene) than for extraction with bidentate compounds were obtained. However, Horwitz also reports $n = 2$ for the extraction of Am^{3+} into 1,2-dichloroethane, 1,2-dibromoethane, and nitrobenzene with various bidentate phosphonates and phosphine oxides (17).

The significance of the "solvation numbers" obtained here is not large. It must be noted that for various extraction systems involving a nonpolar solvent and nitrobenzene, the slope of log–log analysis usually yields a straight line, but the slopes are nonintegers, sometimes too large (up to 12), and depend on the character of the "inert" nonpolar solvent used. In spite of great effort to establish a reasonable physical model (18), the exact nature of the phenomenon has not been fully elucidated. The same seems to be true for log–log plots in which the number of ligand molecules entering the complex is to be determined. The noninteger values in Table

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TABLE 2

Parameters of Eu^{3+} Extraction by DBDECMP into Pure Nitrobenzene and Nitrobenzene + CCl_4 Mixtures[a]

Solvent	a	b (slope)	(n), r[b]
Nitrobenzene[c]	1.708	1.737	(8), 1.000
Nitrobenzene + CCl_4[d]	1.502	1.972	(10), 0.995
Nitrobenzene + CCl_4[e]	−5.133	2.591	(7), 1.000

[a] 3 M HNO_3 in all cases.

[b] Parameters of linear correlation, n = number of points, r = correlation coefficient.

[c] Log $D_{Eu} = a + b \log c_{DBDECMP}$; $\log c_{DBDECMP} = -1.71$ to -0.47 ($\log D_{Eu} = -1.27$ to 0.88).

[d] Log $D_{Eu} = a + b \log c_{DBDECMP}$; mixture of 60 vol% nitrobenzene + 40% CCl_4, $\log c_{DBDECMP} = -1.70$ to -0.535 ($\log D_{Eu} = -1.91$ to 0.43).

[e] 0.1 M DBDECMP, various amounts of CCl_4 (f = 20, 40, 60, 70, 80, 90, 100 vol%), $\log D_{Eu} = a + b \log f$.

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2 are suspect, and further complications occur when dicarbollide is added to the system.

The distribution ratio of DBDECMP between water and solvent as determined by the concentration-dependent method is 54 ± 5 and 60 ± 7 for nitrobenzene and 60 vol% of NB + 40% CCl_4, respectively, at 25°C.

Reversal of the Acid Dependencies after Introducing Dicarbollide

Whereas the curves in the presence of DBDECMP alone are quite typical, a complete change occurs after the addition of dicarbollide (Fig. 2).

It is seen that the stepwise addition of dicarbollide leads to an increase of the distribution ratios of Eu^{3+} in the region of low acidities. The result of this effect is that for higher concentrations of dicarbollide, a decrease of D_{Eu} with increasing acidity is observed. The presence of S-like depen-

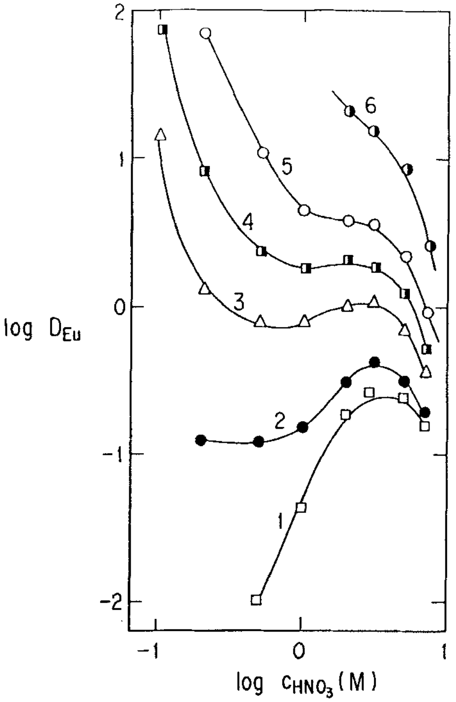

FIG. 2 Effect of the addition of the dicarbollide anion on the extraction of Eu^{3+} by DBDECMP into the 60 vol% nitrobenzene–40 vol% CCl_4 mixture. 0.1 M DBDECMP; H^+BCl^- mol/L: (1) 0, (2) 0.001, (3) 0.005, (4) 0.01, (5) 0.02, (6) 0.04.

dencies (Curves 2,3,4) as well as of plateaus (Curve 5) indicates that two extraction mechanisms apply. The first one is the extraction of Eu^{3+} by the HL^+BCl^- extractant at low acidities, and the second one is the "classical" extraction by $HL^+NO_3^-$. This is corroborated by the results given in Fig. 3 where the extraction was conducted from different mineral acid media in the presence of dicarbollide anion. The extraction increases on the right-hand side exactly in the order of anion extractability into nitrobenzene: Cl^-, $SO_4^{2-} < NO_3^- < ClO_4^-$. On the left-hand side the extraction should be the same because the above anions cannot compete with BCl^- anion at low concentrations. The higher distribution ratios in the presence of perchloric acid are apparently the consequence of the complex formation of Eu^{3+} with the remaining anions, the complex not being extracted. In the absence of DBDECMP, Podzimek et al. found an analogous behavior for the Ce^{3+} cation, i.e., the cation was extracted 1.40 times more in H_2SO_4 and 1.75 times more in $HClO_4$ than in nitric acid (for a reported $\mu = 0.1–0.3$), whereas here the corresponding figures are 1.2 and 3.2, respectively. Recalculating back for the K_1 of $EuNO_3^{2+}$ formation (concentration constant, using the concentrations instead of the activities), the value at $\mu = 2$ used here would be 1.1, which agrees rather well with

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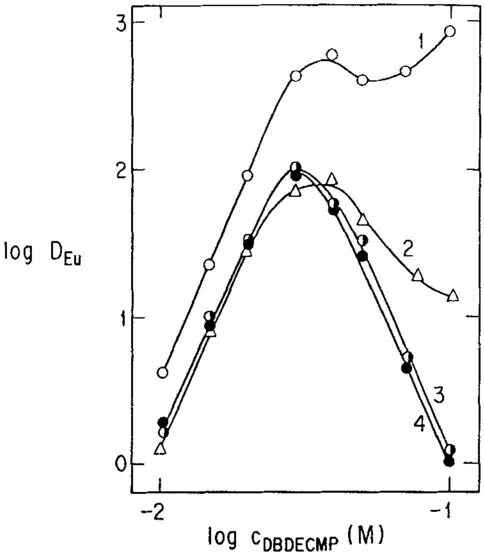

FIG. 3 Extraction of Eu^{3+} from various mineral acids in the presence of dicarbollide and DBDECMP. 0.02 M H^+BCl^- in nitrobenzene: (1) 2 M $HClO_4$, (2) 2 M HNO_3, (3) 2 M HCl, (4) 1 M H_2SO_4.

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Podzimek et al.'s data (19) and Jarvis's recent discussion (20) although the K_2 value cannot be determined here.

It is interesting to note that a rather remarkable increase of the distribution ratios of $D_{Am(Eu)}$ was recently observed for extraction by CMPO compounds from nitric, phosphoric, and sulfuric acid media when ClO_4^- anions were added to the system (21). Also, the reversal of the dependencies of D_{Am} on the concentration of $HClO_4$ for high concentrations of the latter was reported for all the cases studied (21). These effects are quite analogous to the effect of dicarbollide but much lower in magnitude. Although there is no general explanation (20, 21), the qualitative approach based on the order of anion extractibility as outlined here seems to be a first approach which permits anticipation of the experimental results.

Composition of the Complex

If the initial parts of the curves in Fig. 3 are considered as straight line dependencies, rather high solvation numbers of the n ratio (n = DBDECMP/Eu^{3+}) would result from the slope analysis method (n = 4.5–4.8). In another series (Curves 1 and 2 in Fig. 5) the slopes were close to 4 during extraction into a mixture of 60 vol% nitrobenzene + CCl_4.

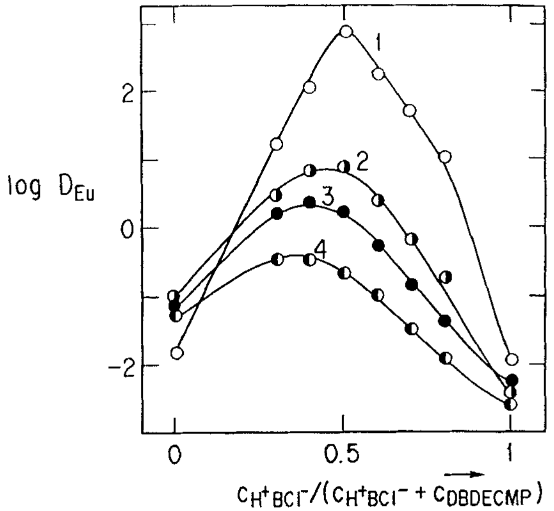

FIG. 4 Isomolar series for the mixtures of H^+BCl^- and DBDECMP. Total concentration: 0.06 mol/L in 60 vol% nitrobenzene + CCl_4. Aqueous acidity: (1) 1 M, (2) 3 M, (3) 5 M, (4) 7 M HNO_3.

However, these number may be artifacts for three reasons: 1) a simple calculation shows that the equilibria in the system need not be described by the mechanism leading to the concept of slope analysis, 2) nitrate extraction even at low concentrations of DBDECMP may lead to an increase of the slope and hence to a higher apparent value of *n*, and 3) it seems that for sterical reasons the value $n = 5$ may not be realistic (but if the particles in the organic phase are dissociated, as is believed to be the case here, there may be more sites available in comparison with extraction into nonpolar solvents).

In this work, it was the composition of the extracting species we attempted to determine. The isomolar series with microamounts of Eu^{3+} as the indicator is shown in Fig. 4. It is seen that a 1:1 (DBDECMP/H^+BCl^-) complex forms at low acidity of the aqueous phase, with an indication of a possible 1:2 complex. At high acidities it seems that complexes with an amount of H^+BCl^- lower than 1 would form, but this effect can be understood by simply taking into account the above proposed "nitrate mechanism"—i.e., with an excess of nitrate anions, a lower concentration of dicarbollide anion is needed in order to reach maximum extraction. This phenomenon is also apparent if Curves 1 and 2 in Fig. 5 are compared. The shift of the maximum of the extraction of Eu^{3+} to the left for a lower concentration of dicarbollide may be explained by the competitive extraction of the "nitrate" mechanism which starts to apply at lower concentrations of DBDECMP for a lower overall concentration of H^+BCl^-.

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Extraction of Other Elements

In order to understand the selectivity of the process, the extraction of other cations was studied (Figs. 5 and 6).

From Fig. 5 it is apparent that the extraction of Cs^+ ions is largely suppressed in the presence of DBDECMP, which is without doubt a consequence of the large hydrophobicity of the protonized $H.DBDECMP^+$ formed. The small affinity detected of DBDECMP toward Sr^{2+} and Ba^{2+} is interesting. The order of extraction is as for other complex-forming polydentate ligands (e.g., EDTA) and opposite to the case of polyethylene glycols for which Ba^{2+} ions are extracted more than Sr^{2+} ions.

Thus, with dicarbollide alone and with dicarbollide in the presence of various synergetic agents, the selectivities vary considerably. For aqueous 3 M HNO_3, they are as follows:

Dicarbollide process (dicarbollide alone): Only Cs^+ and, to lesser extent, Rb^+ ions are extracted

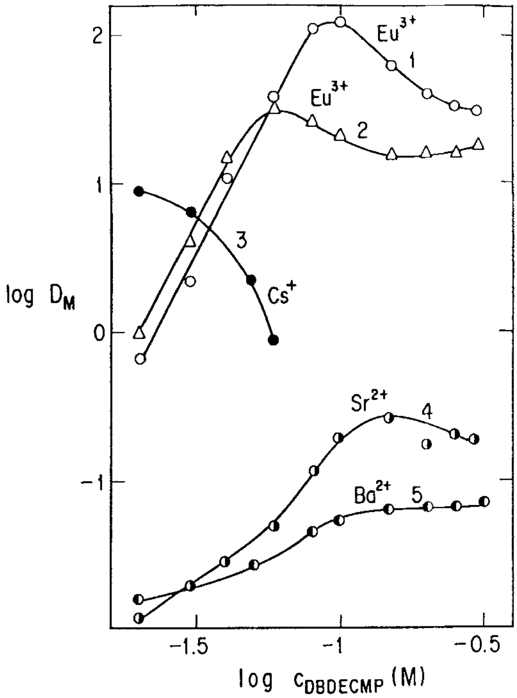

FIG. 5 Extraction of some elements by dicarbollide + DBDECMP, dependence on DBDECMP concentration. 60 vol% nitrobenzene + CCl_4, 3 M HNO_3, concentration of H^+BCl^-: 0.304 M (Curves 2 and 5), 0.06 M (3), 0.065 M (1, 4); (1, 2) Eu^{3+}, (3) Cs^+, (4) Sr^{2+}, (5) Ba^{2+}.

PEGDIC process (dicarbollide + polyethylene glycols): Cs^+, Sr^{2+}, and Ba^{2+} ions are extracted

TRUDIC process (dicarbollide + neutral phosphonate): Eu^{3+} (Am^{3+}) is extracted

The extraction of some metal cations by an equimolar solution of 0.03 M dicarbollide + 0.03 M DBDECMP as it depends on aqueous acidity was studied. The results are given in Fig. 6. It is seen that the extraction of all elements (with the exception of Zr + Nb) falls rapidly with the acidity, especially for Eu (the slopes of the respective straight lines are -3.7 for Eu^{3+}, -2.5 for Ba^{2+}, -2.7_5 for Sr^{2+}, and -2.0 for Cs^+, all, of course, higher than stoichiometric values due to neglect of the activity coefficient correction). The extraction of Zr + Nb is quite appreciable, several orders of magnitude higher than for dicarbollide in the absence of

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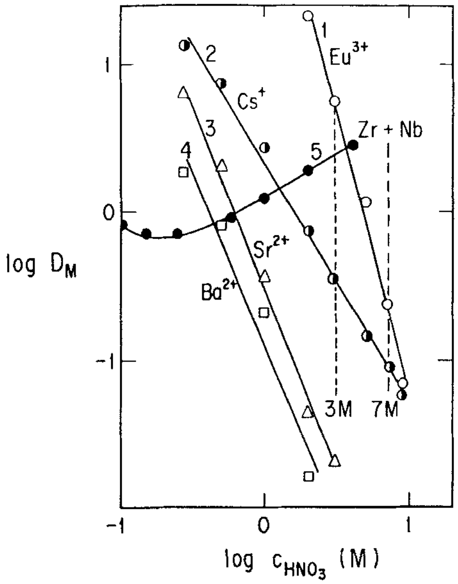

FIG. 6 Extraction of some elements by dicarbollide + DBDECMP, dependence on aqueous acidity. 60 vol% nitrobenzene + CCl_4, 0.03 M H^+BCl^- + 0.03 M DBDECMP: (1) Eu^{3+}, (2) Cs^+, (3) Sr^{2+}, (4) Ba^{2+}, (5) Zr.

DBDECMP. This result indicates that, as expected, the characteristic properties of DBDECMP are not lost in the mixture with dicarbollide. Hence, although the extraction of Pu(IV), U(VI), and Np(IV) was not studied in this work, it is believed that these elements will be coextracted from 3 M HNO_3.

Possible Use of the System

As seen from Fig. 6, Eu^{3+} could be extracted from 3 M HNO_3 by a mixture of 0.03 M dicarbollide + 0.03 M DBDECMP in the nitrobenzene–CCl_4 solvent, whereas stripping could be performed at ~7 M HNO_3.

Ru, which causes some problems in the TRUEX process (4), is not extracted (D_{Ru} from a synthetic HLW of 3 M HNO_3 was only 0.00043 for 0.06 M DBDECMP + 0.04 M dicarbollide). The extraction of Zr was suppressed by using 0.04 M citric acid in the synthetic HLW to values of 0.18 (3 minutes shaking), 0.20 (30 minutes), or 0.26 (120 minutes). Am^{3+} extraction is practically equal to Eu^{3+} (D_{Am}/D_{Eu} = 1.2 for the conditions given above). Losses of both dicarbollide and DBDECMP into the aqueous phase are negligible, and no lowering of the distribution ratio was

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observed after washing of the organic phase with 3 M HNO_3 ten times. Also, the chemical stability of the system seems good, for no signs of decomposition were observed after 1 week of standing with 3–10 M HNO_3.

Because of the high hydrophobicity of $HDBDECMP^+BCl^-$, extraction can be conducted into other less polar solvents than nitrobenzene. Sufficiently high D_{Eu} were obtained for 0.04 M H^+BCl^- + 0.06 M DBDECMP in 1,2-dichloroethane (25.5) and chloroform (9.1) (16). It has been found that Eu^{3+} can be effectively stripped from the above mixture of extractants in nitrobenzene by the 0.2 M sodium salt of DETPA complexone in 1 M lactic acid ($D_{Eu} < 0.1$) (16).

The concentrations of the reagents given in Fig. 6 were chosen to permit extraction and stripping by changing the aqueous acidity. However, much higher, essentially not measurable, D_{Eu} can be obtained for more concentrated extractants (e.g., 0.15 M H^+BCl^- + 0.4 M DBDECMP in 60 vol% nitrobenzene + CCl_4 mixture) from 3 M HNO_3. At these conditions Sr^{2+} and Ba^{2+} are also extracted ($D = 1.4$) whereas Cs^+ remains in the aqueous phase ($D_{Cs} = 0.08$). Thus, this system may also be used for the separation of Sr^{2+} from HLW (22).

The main advantages of the system studied here and the analogous TRUDIC systems are:

Substantial lowering of the losses of neutral phosphonate into the aqueous phase in the presence of highly hydrophobic dicarbollide anion

Reversal of the dependencies of D(III) on the acidity, thus avoiding possible troubles with stripping due to the chemically or radiolytically produced acidic organophosphates in the TRUEX process

The possibility to attaining very high distribution ratios of Eu and Am, even from 3 M HNO_3. This may be desirable in some instances when deep decontamination is needed.

It seems that finding effective stripping agents as well as broadening the study to other neutral organophosphates and solvents would be interesting if the TRUDIC systems are to be applied in practical circumstances. The importance of counteranions (NO_3^-, BCl^-) for extraction by phosphonates was proved here. This will be reflected in a proposal of the mechanism to be published elsewhere.

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