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Extraction of ^{137}Cs and ^{90}Sr from Alkaline Solutions with High $NaNO_3$ Content with Tetrahexyldicarbollide

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ABSTRACT

The extraction properties of a new extractant, tetrahexyldicarbollylcobaltate, were studied. The reagent is stable in contact with alkaline solutions and permits (with the addition of PEG 400 or Slovafol 909) the extraction of both ^{95}Sr and ^{137}Cs from 1 M NaOH + 4 M $NaNO_3$. The system studied was mainly 0.06 M reagent in isopropylbenzene + 1 vol% PEG 400. The extraction results compare well with the analogous reference system of nonsubstituted dicarbollylcobaltate in nitrobenzene. Possible ways of backextraction are discussed, and the system seems to be a candidate for further study for the separation of elements from high level waste in alkaline form and with a high $NaNO_3$ content. The reagent and its application for the treatment of alkaline nuclear wastes was first proposed at Los Alamos National Laboratory, USA.

INTRODUCTION

Extraction of radioactive ^{137}Cs and ^{90}Sr is an important goal in the treatment of highly radioactive nuclear wastes. There have been many proposals for appropriate technology based mainly on liquid/liquid extraction or ion-exchange processes. From recent accomplishments it may be noted that Diphonix-CS resin for the uptake of ^{137}Cs and ^{90}Sr from highly alkaline solutions has proved radiationally and chemically stable (1). Recent studies in alkane-soluble calix[4]arene-bis-(*t*-octylbenzo-crown-6) reported good extraction and the stripping of ^{137}Cs from real Hanford alkaline high level waste (diluted to 5 M $NaNO_3$) in a process called SRTALK; however, on the acidic

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side the extractant is subject to nitration (2). As reported in Ref. 2, the other variant process (SREX) is not applicable for the removal of cesium. Nevertheless, still another variant based on the use of a crown ether extractant (denoted Crown 17′, based on dibenzo-18-crown-6 ether) is considered to be a "combined CSEX-SREX process" in Ref. 1, i.e., suitable for the extraction of both Cs and Sr. The latter process seems to suffer from chemical decomposition of the crown upon contact with nitric acid, but the authors claim that side-arm branching at the benzylic position has been found to dramatically reduce this drawback (1). A new extraction method for the isolation of ^{137}Cs based on the use of crown ether and a heteropolyacid anion in a polar solvent was recently proposed and tested in China (3).

Of all possible methods, only one is being used industrially at present. This is the "dicarbollide process," based on a Czech invention (4). The chemical part of it was developed at NRI in former Czechoslovakia during long running cooperation with the Russian Radium Institute (5). A plant for the separation of ^{137}Cs and ^{90}Sr from acidic high level waste began operation at the Russian nuclear complex Mayak in 1996 (6).

The success of the process on a plant scale may be generally described by its adherence to a number of factors, of which the most important are believed to be:

(i) Good extraction properties of the proposed extractant (i.e., relatively high distribution coefficients of the nuclides of interest into the organic phase, and basically nonextractability of the other components).
(ii) Finding a method by which the nuclides of interest are stripped back to the aqueous phase in the next step with a possibility of again attaining an extractant with the same characteristics as in (i) (stripping and regeneration).
(iii) Low losses of any valuable material (i.e., reagent and synergist) from the organic phase into the aqueous phase.
(iv) Sufficient chemical and radiation stability of the extractant.
(v) Availability and nontoxicity of the extractants, solvents, and backextracting agents, and the inflammability and nonexplosive properties of any mixture used in the process by itself or when in contact with any other phase.

Some of the items are interconnected, such as the cost of an extractant vs its durability + low losses into the resulting aqueous phase (indirectly proportional). For some, a compromise must be sought [mainly for Item (ii) in the dicarbollide process]. Point (ii) seems to be crucial for the development of a viable technology.

The backextraction and regeneration step has proven to be the most difficult to solve, and many variants were studied before a viable variant was chosen (7). This consists in backextraction of Cs by rather concentrated nitric acid (9–11 M). Thus, in spite of the other drawbacks of using so strong an acid, the backextractant is essentially of the "no salt" type and the Cs product is easily isolated from the raffinate. It was found that protonized hydrazine in the form of a bivalent cation competes successfully with Sr^{2+} and Ba^{2+} cations, and hence solutions of hydrazine in nitric acid (0.5 M hydrazine in 2 M HNO_3 for Sr, 2 M hydrazine in 4 M HNO_3 for Ba) were used for the backextraction of those elements. Regeneration of the organic phase in both Cs and Sr backextractions is simple by washing with 3 M HNO_3 (7).

Some questions to be solved are of a general and technical character: fast kinetics, clear interface during the process, no formation of foams, possible influence of reagents added during a previous process on the performance of the current process, hydromechanical properties, ease of obtaining a concentrated product from the backextract, ultimate fate of the reagents, etc. The typical route of development, as it was in the dicarbollide technology case, is: laboratory test-tube batch experiments (a true basis of the process) → proposal of possible flow sheet and modeling of it → countercurrent experiments with a nonactive mixture with the same chemical composition found in the real HLW (simulant) → hot cell experiments with the same mixture spiked with real HLW → long-term experiment in a real plant with real HLW (7).

Chlorinated dicarbollylcobaltate $[(C_2B_9H_{(11-n)}Cl_n)_2Co]^-$ anion ($n = 5$–7) is extremely stable, even when boiled with concentrated nitric acid, and is therefore particularly suited for isolation of the two above nuclides from acidic Purex HLW. However, the anion quickly decomposes in contact with 1 M NaOH in water. Still, large amounts of HLW in the world are present in the form of alkaline solutions.

According to published data on a new type of alkylated dicarbollides prepared at Los Alamos National Laboratory (LANL), those compounds may be stable in alkaline solutions. Alkylated dicarbollides may also be an elegant way to solve the long felt problem of the toxic nitrobenzene originally used in the dicarbollide process (8). Due to their hydrophobicity, they dissolve in nonnitrated aromatic solvents like mesitylene or diethylbenzene (8, 9).

For these reasons we decided to study one representative of the group, namely tetrahexyldicarbollide, as a possible candidate for a technological process. We limited ourselves in this study to describe partially the Points (i)–(iii) enumerated above. Instead of giving the account of the best obtainable results, we concentrate here on points of a more general character, mainly how from general ideas on the mechanism and physical chemistry of ion solvation, the results may be to a considerable extent predicted and the search process thus shortened. During the completion of this paper we read a new paper from LANL (10) which in several instances mutually backs up the data found in our two laboratories. The coincidences will be noted throughout our paper. Also, when appropriate, references to the original chlorinated dicarbollide process will be given (7).

EXPERIMENTAL

Reagents and Radioisotopes

The reagents used were of A.R. grade and not further purified with the exception of isopropylbenzene (cumene) (Fluka, pure, >98%). Slovafol 909 is *p*-nonylphenol nonaethylene glycol from Nováky, Slovakia. Radioisotopes ^{137}Cs, ^{85}Sr, ^{152,154}Eu, and ^{133}Ba of standard radionuclide purity were used.

Preparation of Cs^+ $4HexDic^-$

The reagent was prepared according to a procedure (11) modified with the slightly changed conditions of a method published recently (10). Ethylene glycol dimethyl ether was used as solvent in cobaltacarbaborane synthesis, and the isolation and purification of the product were modified (89.4% yield of the sandwich). The overall yield, based on starting from *o*-carborane, was 71%. The compound was characterized by high field ^{1}H and ^{11}B NMR spectroscopy (500 and 160 MHz), and exhibited the identical spectra as those recorded previously (11). The purity of the compound (>95%) was checked by a modified reverse-phase ion pair HPLC method with diode array detection, similar to that described in the literature (12). The main impurities detected in the sample were dihexyl cobalta-dicarbollide and unreacted starting $[(C_6H_{13})_2C_2B_9H_{10}]^-$ anion. These impurities should not substantially affect the overall behavior of the reagent.

Preparation of Solid H^+ $4HexDic^-$ and Na^+ $4HexDic^-$

The solid compounds were prepared via diethyl ether extraction. Cs^+ $4HexDic^-$ (1–5 g) was dissolved in 50 mL of diethyl ether in a separation funnel. The solution was shaken 3 times with fresh portions of aqueous 3 M HCl or 20% H_2SO_4, and the aqueous phases were discarded. For H^+ $4HexDic^-$, the organic solution was carefully washed with deionized water until the exiting aqueous phase was only slightly acidic. The organic phase was evaporated to constant weight at room temperature. The procedure was similar for Na^+ $4HexDic^-$, but after acid treatment the organic phase was washed with water only once, then twice with 0.5 M NaOH, and again washed by water until the exiting aqueous phase was only slightly alkaline pH (about 5 washings). Contact with anything else but acid must be gentle; if an emulsion forms with vigorous shaking, and disengagement of the phases may take up to a week. According to the weights of the initial material and product, the solid Na^+ $4HexDic^-$ is nearly monohydrate upon drying at room temperature to constant weight. The product is a violet, rather sticky substance, and the crystalline water cannot be removed by drying by heating (melting). No decomposition of the anion occurred during the procedures described at this paragraph.

Extractions and Measurement

As a rule, 1:1 mL of the phases were shaken in closed test tubes for 30 minutes at 25 ± 2°C. The kinetics of extraction was checked independently, and it was found that the equilibrium value was attained after 1 minute of shaking. Quick kinetics was also proved in Ref. 10. After extraction, 0.5 mL aliquots were withdrawn and measured with NaI(Tl) crystal.

RESULTS AND DISCUSSION

Chemical Stability

The chemical stability of 4HexDic$^-$ anion was tested by contact of Cs$^+$ 4HexDic$^-$ solution in toluene with nitric acid and NaOH solutions (see Table 1). It is seen that with nitric acid contact the decomposition is rather quick (about half value of D_{Cs} measured after 1 week contact with 3 M HNO_3). The reagent is practically stable in contact with alkaline solutions (the small increases of D_{Cs} values found after 15 and 21 days of contact were due to some evaporation of toluene from the test tubes). These findings correspond well to the results of Ref. 10 where it was found that the solutions of 4HexDic$^-$ in diethylbenzenes and mesitylene were 98% degraded by contact with 1 M HNO_3 but fully stable with 1 M NaOH (40°C, 50 days of contact, Ref. 10).

However, the stability cannot be fully ascribed to the hydrophobicity of the anion and the small extraction of OH$^-$ ion as proposed in Ref. 10. In fact, chlorinated dicarbollide, even in nitrobenzene solution, very quickly decomposes in contact with 1 M NaOH upon shaking, and some kind of interfacial destruction may take place. It seems that the four hexyl substituents of the

TABLE 1

Chemical Stability of 0.06 M Cs$^+$ 4HexDic$^-$ in Toluene Solution Measured by the Change of the Distribution Ratio of ^{137}Cs, D_{Cs}, upon Contact with HNO_3 and NaOH Aqueous Solutions

	Days				
Aqueous solution	0	2	7	15	21
1 M NaOH	27.3	25.8	22.7	25.7	31.4
2 M NaOH	21.1	20.1	19.8	23.5	25.6
0.5 M HNO_3	12.7	6.8	3.9	3.0	3.1
3.0 M HNO_3	4.1	3.0	1.8	1.1	0.9

$4HexDic^-$ anion by themselves provide rather effective shielding against decomposition of the skeleton by a base.

The chemical instability in acid is not caused by HNO_3 oxidation of the reagent, nor is it the only operating factor. Surprisingly enough, it has been found that the solid form of H^+ $4HexDic^-$ is not fully stable. The latter has been prepared under mild conditions via shaking Cs^+ $4HexDic^-$ solution in diethyl ether with 20 vol% H_2SO_4 or 3 M HCl, washing with distilled water, and subsequently evaporating the solvent at room temperature (see the Experimental section). Yet the solid phase, which extracted well at the beginning, turned into an unusable compound after 1 month in a closed flask, although the violet color of the preparation did not change. Perhaps the solid compound contained small amounts of H_2SO_4 which were not washed out and which caused decomposition, or perhaps the proton of the acid may cause this effect. This is corroborated by the fact that solid Na^+ $4HexDic^-$ is fully stable (shown by working with it for over 10 months).

Hence, the chemical stability of tetrahexyldicarbollide and its possible region of use is quite the opposite of chlorinated dicarbollide. The former can be used in an alkaline region while avoiding any contact with an aqueous acid, whereas the latter can be used only in acidic media.

In Reference 10 the cesium salt of Cs^+ $4HexDic^-$ (0.05 M solution in diethylbenzene) was converted into its acid form by shaking it 6 times with 8 N H_2SO_4, but again it has been observed that after 1–2 months of storage the solution sometimes changed into a nonextracting green substance. This strengthens our doubts about the long-term stability of H^+ $4HexDic^-$ as a chemical entity.

Extractions in the Univalent Cations Series

When the salts M^+ $[(C_2B_9H_{11})_2Co]^-$, M^+B^-, are extracted into nitrobenzene, they are almost fully dissociated in the organic phase. The order of extractability of univalent cations, $Li^+ < H^+ < Na^+ < NH_4^+ < K^+ < Rb^+ < Cs^+$, is given by the respective standard Gibbs energies of transfer of the ions between water saturated with nitrobenzene and nitrobenzene saturated with water (13). Experiments conducted to determine the value of $K(Cs^+/M^+) = [Cs^+]_o[M^+]_a/[Cs^+]_a[M^+]_o = D_{Cs}/D_M$ (where $[M^+]$ denotes the equilibrium concentration of M^+ in the aqueous, "a," or organic, "o," phase and D_M is a distribution ratio of M^+, $D_M = [M^+]_o/[M^+]_a$) were based on studying the change of D_{Cs} of Cs^+ $[(C_2B_9H_{11})_2Co]^-$ upon variation of the concentration of $M^+NO_3^-$ in the aqueous phase (13). For the system with $[(C_2B_9H_{11})_2Co]^-$ and water–nitrobenzene, it has been found that for $c(MNO_3) = 0.03$–1.9 M, the dependence of $K(Cs^+/M^+)$ on the aqueous phase ionic strength I can be well expressed as $\log K(Cs^+/M^+) = a + b(I)^{0.5}$ (11). The exchange extraction constant $K(Cs^+/M^+)$ was calculated for each point according to the equation given in Ref. 11:

$$K(\mathrm{Cs}^+/\mathrm{M}^+) = D_{\mathrm{Cs}}[c_{\mathrm{M(aq,\ init)}}(D_{\mathrm{Cs}} + 1)/c_{\mathrm{Cs(org,\ init)}} - 1] \quad (1)$$

where the subscript "init" denotes the initial concentrations in the respective phases, and the volume ratio of the organic to be aqueous phase was 1.

The results of the same experiment with 4HexDic$^-$ instead of B$^-$ are given in Fig. 1. In the experiments, 5×10^{-3} M Cs$^+$ 4HexDic$^-$ was always used in an organic solvent. Varying concentrations of M$^+$ NO_3^- (or HNO_3) were added (0.03–0.4 M) to the aqueous phase. The dependences of log $K(\mathrm{Cs}^+/\mathrm{M}^+)$ on $(I)^{0.5}$ are plotted in Figs. 1 and 2. In Table 2 the values of $K(\mathrm{Cs}^+/\mathrm{M}^+)$ extrapolated to zero ionic strength are summarized, and it can be seen that there is nearly perfect agreement for the sets of values with B$^-$ and 4HexDic$^-$ in nitrobenzene as a solvent. This again proves the underlying physicochemical principle that the cation selectivities ought to be independent of the kind of anion used, provided full dissociation occurs in both the organic and aqueous phases. Further, it indirectly proves the full dissociation of M$^+$ 4HexDic$^-$ salts in nitrobenzene and also that the reagent 4HexDic$^-$ is chem-

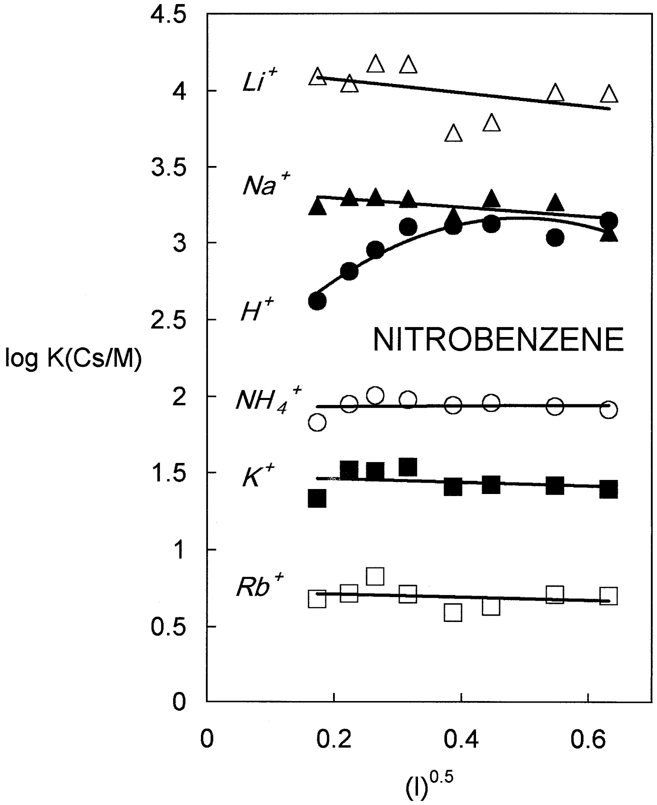

FIG. 1 Influence of $M^+NO_3^-$ and HNO_3 concentration on Cs extraction by 0.06 M Cs$^+$ 4HexDic$^-$ in nitrobenzene. See text for definition of $K(\mathrm{Cs}^+/\mathrm{M}^+)$ and Table 2 for regression lines.

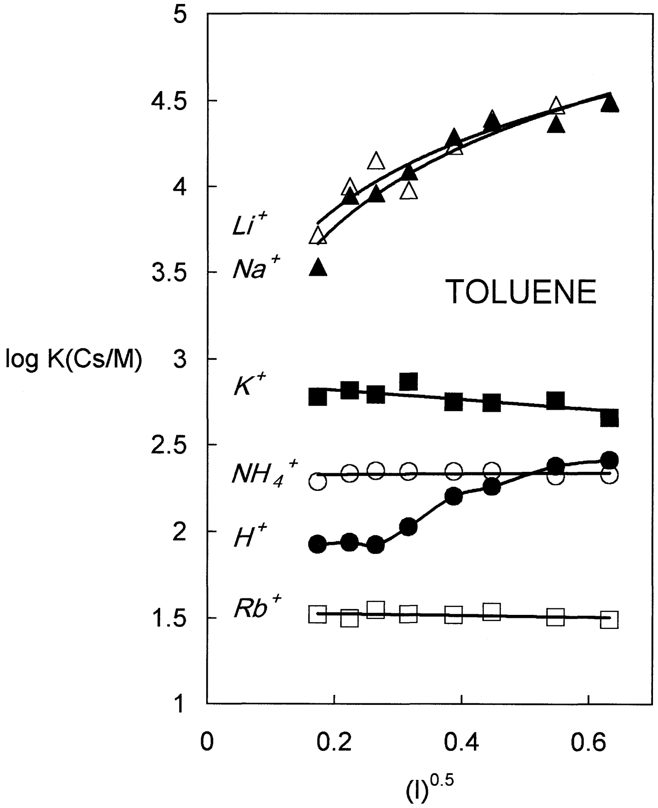

FIG. 2 Influence of $M^+NO_3^-$ and HNO_3 concentration on Cs extraction by 0.005 M Cs^+ 4HexDic$^-$ in toluene. See text for definition of $K(Cs^+/M^+)$ and Table 2 for regression lines.

TABLE 2

Selectivity of Extraction in the Series of Univalent Ions for B^- and 4HexDic$^-$ in Nitrobenzene and 4HexDic$^-$ in Toluene Log(K(Cs/M)) at Zero Ionic Strength of Aqueous Phase

System	Cs/Li	Cs/Na	Cs/H	Cs/NH_4	Cs/K	Cs/Rb
B^-, NB[a]	4.10	3.35	3.20	2.02	1.44	0.70
4HexDic$^-$, NB[b]	4.16	3.35	—[c]	1.93	1.48	0.73
4HexDic$^-$, T[d]	—[e]	—[e]	(?)[f]	2.32	2.87	1.54

[a] Log $K(Cs^+/M^+)$ for system $[(C_2B_9H_{11})_2Co]^-$ water–nitrobenzene, data from Ref. 11. For log $K(Cs^+/Rb^+)$, from Ref. 7.

[b] Log $K(Cs^+/M^+)$ for system 4HexDic$^-$ water–nitrobenzene, this work. The regression straight lines in Fig. 1 for $\log K(Cs^+/M^+) = a + b(I)^{0.5}$ are as follows: (Cs^+/Li^+), $a = 4.165$, $b = -0.446$; (Cs^+/Na^+), $a = 3.355$, $b = -0.307$; (Cs^+/NH_4^+), $a = 1.927$, $b = 0.0255$, (Cs^+/K^+), $a = 1.485$, $b = -0.116$; (Cs^+/Rb^+), $a = 0.733$, $b = -0.0988$.

[c] Not available, see Fig. 1.

[d] Log K(Cs/M) for system 4HexDic$^-$ water–toluene, this work. The regression straight lines in Fig. 2 for $\log K(Cs/M) = a + b(I)^{0.5}$ are as follows: (Cs/K), $a = 2.873$, $b = -0.278$; (Cs/NH_4), $a = 2.324$, $b = 0.023$; (Cs/Rb), $a = 1.535$, $b = -0.0485$.

[e] Not available. In Fig. 2 the full line was drawn as $\log K(Cs/M) = a \ln(I)^{0.5} + b$.

[f] Not available, or ~ 1.9 at low I, or ~2.5 at high I, see Fig. 2.

ically pure, i.e., it does not contain any compounds able to specifically bind any of the involved cations or to have a competitive effect on extraction.

The character of dependences of extractions into toluene is different from that of nitrobenzene (Fig. 2). In fact, straight lines can only be drawn for Cs exchange for K, NH_4, and Rb. The rather dramatic decrease of $K(\mathrm{Cs/Li})$ and $K(\mathrm{Cs/Na})$ with decreasing salt content in the aqueous phase can not now be explained. It is supposed that all salts in essentially nonpolar toluene are associated there. Hence, the respective exchange constants correspond to the reaction $\mathrm{Cs4HexDic_o} + \mathrm{M_a^+} = \mathrm{M4HexDic_o} + \mathrm{Cs_a^+}$ rather than to the exchange of free ions. It is interesting to note that the selectivities are higher than for the water–nitrobenzene system. The increases of log $K(\mathrm{Cs/M})$ are 0.39 for NH_4, 1.39 for K, and 0.81 for Rb, which show the much higher discriminating power of the water–toluene than of the water–nitrobenzene system. The enhancement of selectivity for the Cs/Rb pair may be important for any possible technology since nonactive Rb in HLW is a major disturbing species in obtaining a pure Cs product (7).

Extraction at Acid Side

In contrast to classical dicarbollide technology with chlorinated dicarbollide, the cesium salt of the tetrahexyl derivative is well soluble in a number of aromatic solvents. For an initial value of 0.06 M $\mathrm{Cs^+}$ $\mathrm{4HexDic^-}$ in solvent, the distribution ratios for cesium were as follows from 0.5 M HNO_3: xylene 6.74, toluene 8.73, benzene 10.75, ethylbenzene 8.75, cumene 9.87, diethylbenzene 4.70, nitrobenzene 9.10, other nitrosolvents 5–6.

Although the reagent is not stable in contact with nitric acid, the first experiments were made from these media in order to have a rough comparison with the nitrobenzene–chlorinated dicarbollide system. Pertinent results as compared with dicarbollide technology are given in Table 3. These refer to the

TABLE 3
Extraction of ^{137}Cs and ^{85}Sr by 0.052 M $\mathrm{H^+}$ $\mathrm{4HexDic^-}$ in Toluene from Nitric Acid Solutions

	Extractant	
$c(HNO_3)$(M)	D_{Cs}, 0 Slovafol 909	D_{Sr}, 1% Slovafol 909
1	40.1	50.1
2	22.8	11.6
3	10.9	3.22
4	5.97	2.07
5	2.63	0.0055[a]

[a] Green organic phase and precipitate, total destruction of reagent after 30 minutes of contact.

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extraction of ^{137}Cs with 0.06 M H^+ 4HexDic$^-$ into toluene and extraction of ^{85}Sr into the same solution + 1% Slovafol 909 (in dicarbollide technology the extraction is performed into 0.06 M H^+ $[(C_2B_9H_{(11-n)}Cl_n)_2Co]^-$ in nitrobenzene (7)). From the table it is apparent that the extractability of both Cs and Sr from 3 M HNO_3 is nearly the same as in the dicarbollide process, i.e., technologically reasonable values are attained (7). H^+ 4HexDic$^-$ is also an efficient extractant for Eu^{3+} from nitric acid media, even slightly better than chlorinated dicarbollide (7) (see Table 4). However, using 5 M HNO_3 (system with Slovafol 909), after 30 minutes of shaking the reagent has totally decomposed to a green substance (also mentioned in Ref. 10). Since stripping of ^{137}Cs is accomplished by the use of concentrated acid in the original dicarbollide process (7), we still looked at the behavior at high concentrations of HCl and H_2SO_4 (Fig. 3). Although no decomposition occurred during the experiment, the D_{Cs} obtained even with 6 M H_2SO_4 ($D_{Cs} = 1.16$) is still too high and does not permit effective stripping. Moreover, due to the observed instability of even solid H^+ 4HexDic$^-$, the process is certainly not a good choice for the treatment of acidic wastes.

Extractions from NaOH Solutions

Extraction of Cs^+ in the Absence of Synergist

The original information of interest is how Cs^+ ion extracts directly from NaOH solutions into a solution of Na^+ 4HexDic$^-$ in an aromatic diluent. The results are given for toluene as the diluent and 0.06 M Na^+ 4HexDic$^-$ in Fig. 4. It is seen that the rather irregular distribution ratio of Cs does not decrease too much with increasing NaOH concentration, and even some increase is observed for $c(\mathrm{NaOH}) > 1.8$ M. Generally, D_{Cs} values did not drop below 92, which shows very powerful extraction from NaOH. Similar signs of an increase of D_{Cs} values for $c(\mathrm{NaOH}) > 2$ M are reported in Ref. 10 (for 0.05 M H^+ 4HexDic$^-$ in diethylbenzene). However, the overall values of D_{Cs} reported in Ref. 10 are of about one order lower than those found here, which

TABLE 4

Extraction of ^{152,154}Eu by 0.06 M and 0.2 M Na^+ 4HexDic$^-$ (R) into Isopropylbenzene from Nitric Acid

	$c(HNO_3)$ (M)					
	0.05	0.08	0.1	0.3	0.5	1
0.06 M R, D_{Eu}	1270	696	65.2	17.6	3.9	—
0.2 M R, D_{Eu}	2040	2190	131	55.1	11.0	1.60

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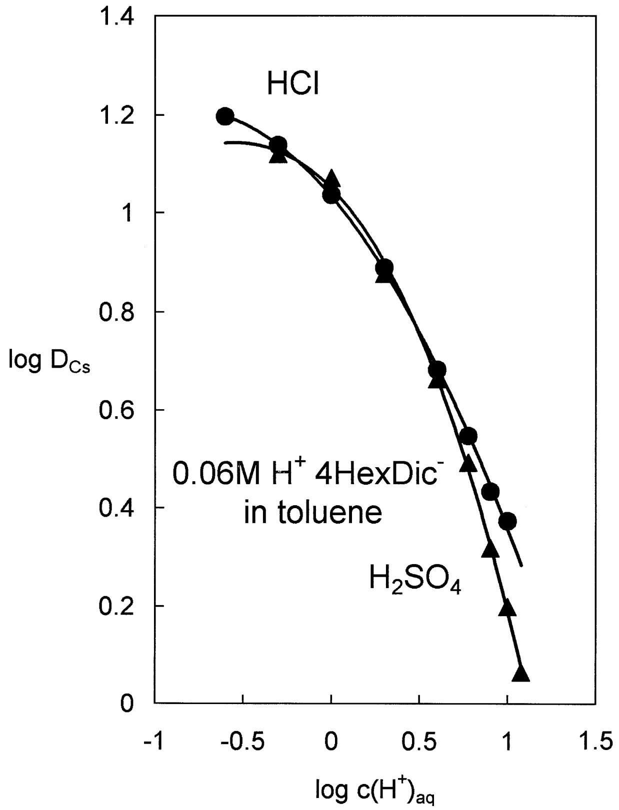

FIG. 3 Influence of aqueous acidity of HCl and H_2SO_4 on extraction of cesium by 0.06 M H^+ 4HexDic$^-$ in toluene.

may partly be explained by the fact that toluene extracts better than dialkyl-substituted benzene (Fig. 5). It is interesting to note that in a pure NaOH environment an increase of D_{Cs} values with c(NaOH) $>$ 2 M was also found for a totally different system [0.2 M sodium tetraphenylborate in 4-chloro-3-nitrobenzene (14)]. Hence, this property seems to be general for Cs and concentrated NaOH solutions, and for lack of a detailed explanation may be tentatively termed a kind of “salting-out” of Cs from $>$ 2 M NaOH solutions.

Choice of Synergist and of Its Concentration for Sr Extraction

p-Nonylphenol nonaethylene glycol under the name Slovafol 909 was chosen as a synergist for classical dicarbollide technology (7). However, the reason for its choice was not its superior extraction ability but rather a need to attain very low losses of synergist in the exiting aqueous phase. Nonsubstituted polyethylene glycol of molecular weight 400 (PEG 400) is the most powerful synergist for Sr in all cases (7). The main reason for this is believed to be that the coordination number 8 of strontium is fully saturated by PEG 400. The same is true for Slovafol 909, but its long alkyl chain may prevent optimal displacement of O atoms around Sr^{2+} due to steric hindrance, hence the stability of the complex is slightly lower (7). Here, due to the very low losses of anion $4HexDic^-$ into the aqueous phase (in fact, in spite of the intensive coloration of the anion in all instances, no traces of anion in equilibrium aqueous phases were detected), it is possible to expect that the losses of PEG 400 (in its protonized form as a counterion of dicarbollide) will also be minimum. Hence, PEG 400 was chosen for further work. The superiority of PEG 400 over Slovafol 909 is apparent from Fig. 4. In Ref. 10 the synergetic effect of hexaethylene glycol and triethylene glycol on the extraction of Sr^{2+} from 1 M HNO_3 by 0.05 M H^+ $4HexDic^-$ into diethylbenzene was reported, but no data were given for extraction from NaOH solutions.

The extraction curves for bivalent cations, namely the dependence of $D_{M(2+)}$ vs c_L (concentration of polyethylene glycol in the system) at constant reagent concentration, c_B, generally pass through a maximum. This has been derived theoretically (15) for the case of extractions into polar solvents and

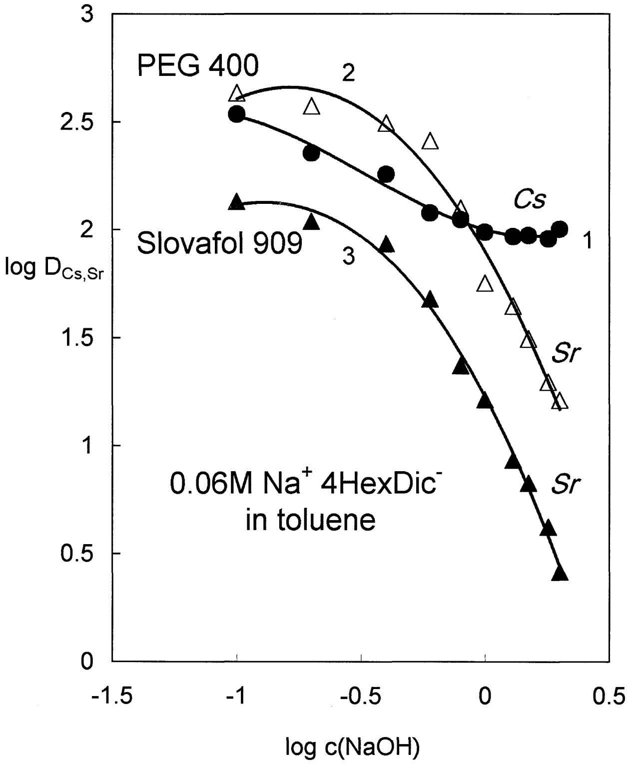

FIG. 4 Extraction of cesium and strontium from NaOH solutions by 0.06 M Na^+ $4HexDic^-$ in toluene. For the extraction of Sr, 1 vol% PEG 400 or 1 vol% Slovafol 909 were added (Curves 2 and 3, respectively).

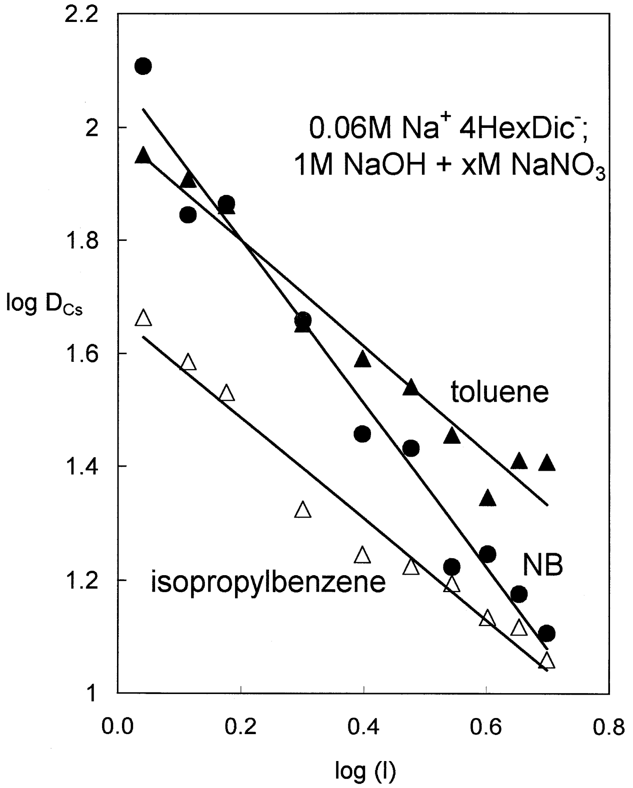

FIG. 5 Comparison of extraction of Cs from NaOH + NaNO$_3$ mixtures by 0.06 M Na$^+$ 4HexDic$^-$ in various solvents.

full dissociation in the organic phase. The resulting equation for the maximum position is

$$c_L(\max) = c_B/2 + \beta \tag{2}$$

where β is an equilibrium constant of the organic phase reaction $H_o^+ + SrL_o^{2+} = HL_o^+ + Sr_o^{2+}$. Since the value of β in the studied case with PEG 400 and nitrobenzene could be for higher concentrations of c_B neglected in comparison with $c_B/2$ [actual reported value was $\beta = 10^{-2.73}$ (15)], the maximum occurs at roughly the half concentration of c_B. This is for $c_B = 0.06$ M at the value of 1% PEG 400 (the specific density of the latter is 1.281 g/mL, hence 1 vol% PEG 400 corresponds to its 0.03202 M concentration). We see from Fig. 6 exact agreements with the predictions for extractions from alkaline media both into polar nitrobenzene and into nonpolar cumene.

The existence of conspicuous maxima in Fig. 6 also tells us that Sr is extracted into the organic phase even from 1 M NaOH as a bivalent cation, with all probability as Sr^{2+}. It can be derived theoretically (7) that a maximum does not occur for extractions of univalent cations. This is at variance with the con-

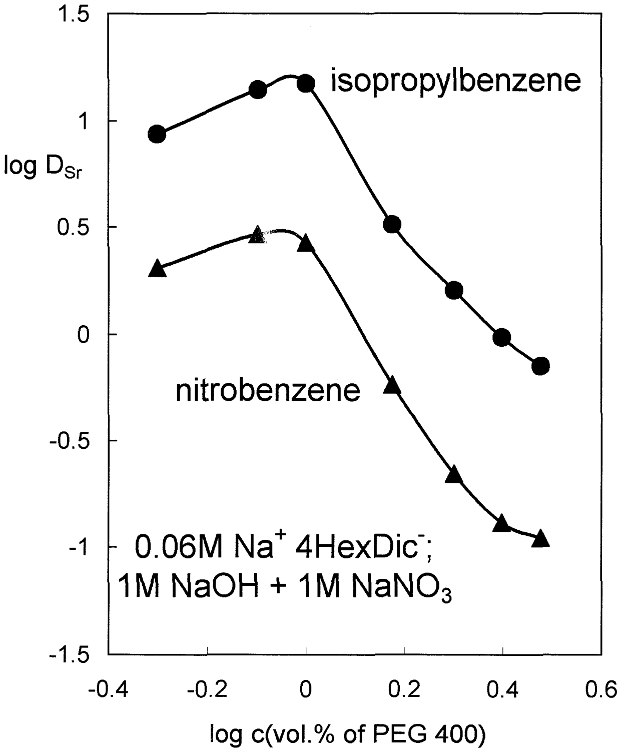

FIG. 6 Extraction of Sr from 1 M NaOH + 1 M $NaNO_3$ by 0.06 M Na^+ $4HexDic^-$ as a function of PEG 400 concentration.

clusions of Ref. 10 where the extraction of $SrOH^+$ is supposed. The Sr^{2+} cation may be the prevailing species in the organic phase, even without neglecting the hydrolysis and formation of $SrOH^+$ in the aqueous phase.

Because a mathematical model for the extraction of nondissociated species has not been created up to now, we performed a simple calculation according to the previously developed iterative algorithm of complex equilibria (7). For a specific case, if all the constants of fully dissociated species in the organic phase were changed for their fully associated counterparts (e.g., instead of H^+, SrL^{2+}, and B^- in the organic phase, the species HB and $SrLB_2$ were considered), the same theoretical curves for the extraction of Sr^{2+} and SrB were obtained. Thus, on a preliminary basis, the same model with a maximum applies if the degree of association in the organic phase is disregarded.

Accordingly, for further experiments with 0.06 M Na^+ $4HexDic^-$ the concentration of PEG 400 chosen was 1 vol% ($c_L/c_B = 0.5$). In Ref. 10, $c_B = 0.05$ M and $c_L = 0.1$ M ($c_L/c_B = 2$). Hence, it is possible to suppose that the experiments performed in Ref. 10 correspond to some position along the right branch of the curve with a maximum and that a higher D_{Sr} could have been reached if 0.025 M PEG 400 had been used. However, the dependence of D_{Sr} vs c(PEG 400) is not reported in Ref. 10.

Extraction of Sr^{2+} in the Presence of PEG 400

The results of this extraction are given in Fig. 4. It is seen that use of PEG 400 instead of Slovafol 909 increases D_{Sr} by about half of order of magnitude. The overall steep decrease of D_{Sr} with c(NaOH) was also reported in Ref. 10. However, the absolute values of D_{Sr} reported here are higher (e.g., ~11 for 1 M NaOH in Ref. 10, 55 here). One reason may be optimalization of the $c_{\mathrm{L}}/c_{\mathrm{B}}$ ratio discussed just above.

It should be noted that although Slovafol 909 and PEG 400 are surface-active compounds, no problems concerning the formation of emulsions occur in extraction systems. In fact, the compounds pass mainly in their H^+ forms into the organic phase, which may be the reason for the absence of their surface-active properties.

Extractions from 1 M NaOH + $NaNO_3$ Solutions

We decided to study extractions from mixtures of NaOH + $NaNO_3$ for two reasons. First, due to the reported good stability of the reagent in alkaline solutions. Second, we wanted to simulate more closely actual conditions which may be encountered during practical separations. The results obtained here are thus not directly comparable to those in Ref. 10 where extractions from simple $NaNO_3$ and KNO_3 were studied.

Both for Cs and Sr the dependences gave the best linear plots in coordinates of log D vs log(I), where I is the ionic strength of the aqueous phase (see Figs. 5 and 7). This is the same representation as in Ref. 10.

Extraction of Cs^+ in the Absence of Synergist

The data of this extraction are given at Fig. 5 and the regression coefficients are presented in Table 5. For comparison, the extraction with 4HexDic$^-$ into nitrobenzene is also given. The distribution coefficients are generally very high; even for cumene and 1 M NaOH + 4 M $NaNO_3$ the D_{Cs} is higher than 10, thus enabling efficient extraction. As compared to the nitrobenzene system, efficient extraction at high ionic strengths is given largely by the lower slopes of log D_{Cs} vs log (I) dependences for nonnitrated aromatic solvents. In Ref. 10 the maximum D_{Cs} reported for conditions analogous to ours (0.05 M 4HexDic$^-$, diethylbenzene) was $D_{\mathrm{Cs}} = 10$ for extraction from 1 M $NaNO_3$.

Extraction of Sr^{2+} in the Presence of PEG 400

The data of this extraction are given at Fig. 7 and regression coefficients of straight lines are presented in Table 5. Since the measured D_{Sr} are generally lower than for Cs, we also studied an extractant with higher concentrations of 4HexDic$^-$ and PEG 400. Again, lower efficacy of cumene compared to toluene

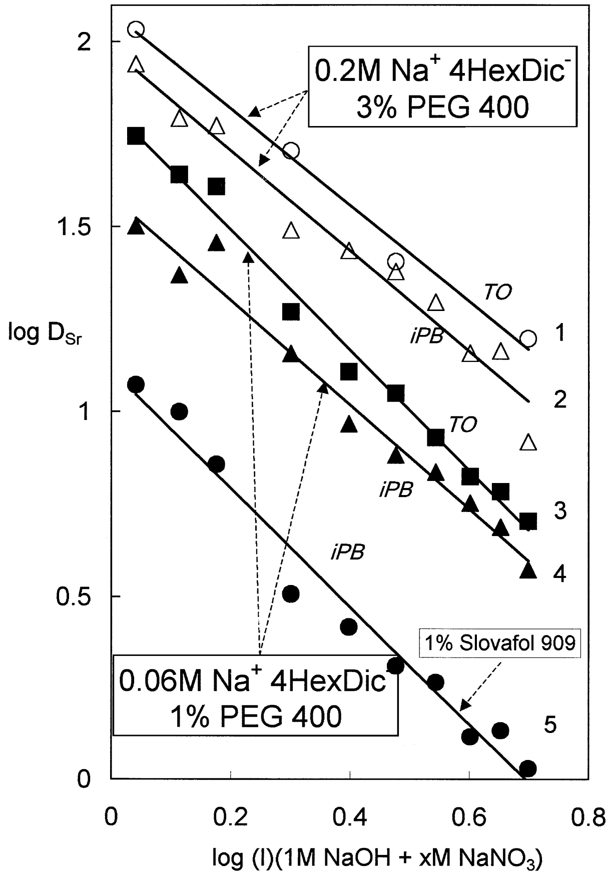

FIG. 7 Extraction of Sr from mixtures of 1 M NaOH + *x* M $NaNO_3$ into toluene (TO) and isopropylbenzene (PB) at different Na^+ $4HexDic^-$ concentrations. Curves 1 and 2: 0.2 M Na^+ $4HexDic^-$ + 3% PEG 400. Curves 3 and 4: 0.06 M Na^+ $4HexDic^-$ + 1% PEG 400. Curve 5 0.06 M Na^+ $4HexDic^-$ + 1% Slovafol 909.

TABLE 5

Parameters of Straight Lines of Log D_{Cs} and Log D_{Sr} vs Log(*I*) for Fig. 5 and Fig. 7[a]

Cation	System[b]	*a*	*b*	R^2
Cs^+	0.06 M R, toluene	−0.9386	1.9884	0.9574
Cs^+	0.06 M R, isopropylbenzene	−0.8914	1.6653	0.9656
Cs^+	0.06 M R, nitrobenzene	−1.4453	2.0908	0.9751
Sr^{2+}	0.06 M R, 1% P, toluene	−1.6298	1.8186	0.9885
Sr^{2+}	0.06 M R, 1% P, isopropylbenzene	−1.4111	1.5824	0.976
Sr^{2+}	0.06 M R, 1% S, isopropylbenzene	−1.6009	1.1123	0.9741
Sr^{2+}	0.2 M R, 3% P, toluene	−1.3046	2.08	0.9898
Sr^{2+}	0.2 M R, 3% P, isopropylbenzene	−1.3605	1.9788	0.9665

[a] Parameters of straight lines plotted as $\log D = a \log(I) + b$; *R* is the correlation coefficient.
[b] R denotes Na+ $4HexDic^-$, P is PEG 400, and S is Slovafol 909.

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as well as the ineffectiveness of Slovafol 909 in comparison with PEG 400 are well seen. Still, even with 0.06 M extractant and cumene and the highest concentrations studied (1 M NaOH + 4 M $NaNO_3$) a technologically acceptable $D_{Sr} = 3.7$ was measured. It seems that use of a three times more concentrated reagent (0.2 M) does not have much effect since the concentration of PEG 400 is increased 3.33 times whereas the value of D_{Sr} is increased only 2.21 times. In Ref. 10 for 0.05 M $4HexDic^-$, 0.1 M PEG 400, and diethylbenzene, a value of $D_{Sr} = 1–2$ was measured for 4 M $NaNO_3$, in general agreement with our results.

Comparison with Nitrobenzene System

Because poor efficacies of extractions of Sr from mixtures containing a high content of $NaNO_3$ were attained in the acidic side of the dicarbollide process (7), it is important to know whether $4HexDic^-$ anion plays any specific role in extracting this element. For this we compared the extraction data reported in the above paragraph with those of $[(C_2B_9H_{11})_2Co]^-$ anion. The latter is insoluble in nonnitrated aromatic solvents, hence nitrobenzene was chosen as the reference solvent. Pertinent data are given at Fig. 8 as ratios of

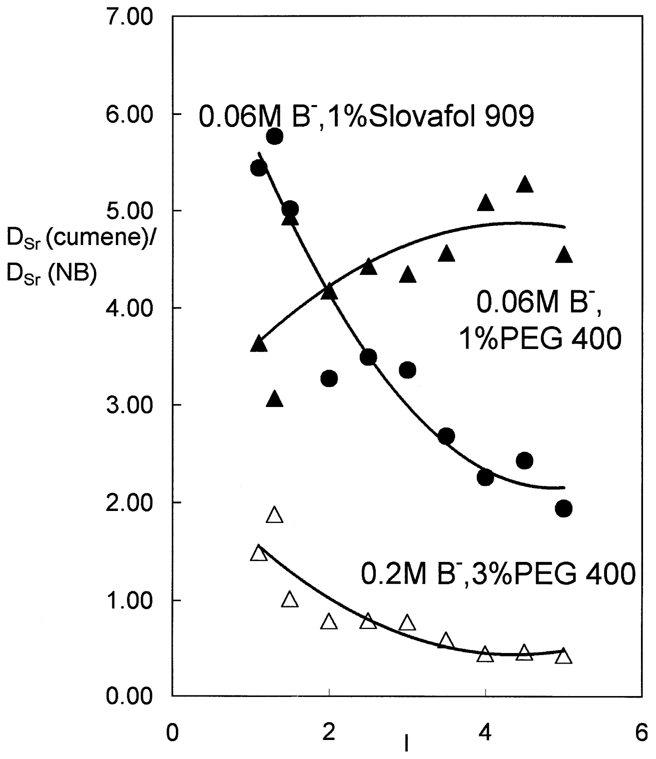

FIG. 8 Comparison of extraction of Sr from 1 M NaOH + x M $NaNO_3$ mixtures by 0.06 M and 0.2 M Na^+ $4HexDic^-$ in isopropylbenzene and nitrobenzene and in the presence of two Sr synergists.

D_{Sr}(cumene)/D_{Sr}(nitrobenzene) at otherwise identical conditions. There is an enhancement of D_{Sr} values in the 4–5 range for the cumene + 4HexDic$^-$ system as compared to the nitrobenzene + $[(C_2B_9H_{11})_2Co]^-$ system when extracting with PEG 400 as synergist. However, this is so only for lower concentrations of reagents, whereas for higher concentration the systems are nearly identical. Hence, we do not detect any effective role for 4HexDic$^-$ in promoting the extraction of Sr. For Slovafol 909 the dependence is more complicated, but this system is not of particular interest here. As noted before, the D_{Sr} values are too small for practical use at high concentrations of $NaNO_3$.

Selectivity of Extraction and Losses of Reagent

It may be reasonably assumed that the majority of hydrolyzable multivalent elements will not be extracted into the organic phase from a medium of 1 M or higher NaOH. A rough estimate of the selectivities toward K^+ may be made from the K(Cs/K) constant determined for Table 2. The selectivity of the Sr/K pair was not studied here, but $D_{Sr} \sim 10$ has been measured for 1 M KNO_3 (10).

The extraction of Ba was studied with Na^+ 4HexDic$^-$ and Slovafol 909 or PEG 400 in cumene. The results for extraction from NaOH + $NaNO_3$ mixtures are given in Fig. 9. It is seen that Ba^{2+} cation is still better extracted than

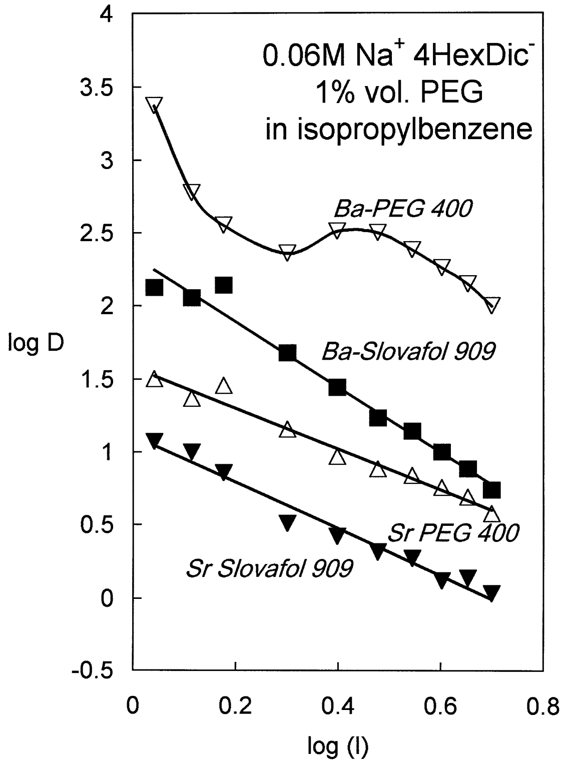

FIG. 9 Comparison of Ba and Sr extractions from 1 M NaOH + x M $NaNO_3$ mixtures by 0.06 M Na^+ 4HexDic$^-$ + 1% Slovafol 909 and 1% PEG 400 in isopropylbenzene.

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Sr^{2+}, analogously to the "classical" chlorinated dicarbollide system (7), and in an actual extraction scheme the need to wash it out of the organic phase would arise.

The reagent losses in the exiting aqueous phase are minimal. In fact, in no experiment during this study were any losses into the aqueous phase observed. The dramatic increase of extractibility of anion as compared to the chlorinated dicarbollide + nitrobenzene system is probably connected with the effect of ion association in the organic phase. In fact, the formation of noncharged Na 4HexDic in the organic phase would increase its transfer to the organic phase according to the reaction $Na^+_a + 4HexDic^-_a = (Na\ 4HexDic)_o$.

Stripping and Regeneration

Due to the long-term chemical instability of $4HexDic^-$ anion in strong acids, backextraction by a strong acid is not practicable. Using any ion other than H^+ at a high concentration would load raffinate with a nonacceptable amount of inert trash material. We have studied two other variants.

As seen from Fig. 6, the extraction of Sr^{2+} decreases with an increasing content of PEG 400. Consequently, we checked the distribution ratios of Sr^{2+} at concentrations of PEG 400 of 5 and 10% (5 and 10 times larger than at maximum extraction) and various other conditions. The results are given in Table 6. It is seen that Sr can be backextracted, e.g., by 1 M NH_4NO_3 or a mixture of 1 M NaOH + 1 M $NaNO_3$. However, the inert material content in the backextract would be high. Unfortunately, no promising distribution ratios were found when using H_2SO_4 as a possible backextractant. A mixture of HNO_3 + PEG 400 + hydrazine seems to be very effective for backextraction (it was

TABLE 6
Backextraction of Sr^{2+} in the Presence of Excess of PEG 400, D_{Sr}

Medium	Concentration (M)	Vol % of PEG 400	D_{Sr}
H_2SO_4	1	5	3.72
H_2SO_4	1	10	3.17
H_2SO_4	2	5	1.43
H_2SO_4	2	10	1.22
NaOH	1	5	1.14
NaOH	1	10	0.947
NaOH + $NaNO_3$	1 + 1	5	0.339
NaOH + $NaNO_3$	1 + 1	10	0.248
NH_4NO_3	1	5	0.178
NH_4NO_3	1	10	0.119
$HNO_3 + N_2H_4$	2 + 0.5	10	0.085
$HNO_3 + N_2H_4$	2 + 1	10	0.030

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supposed that hydrazine could also have a stabilizing effect on anion decomposition in nitric acid). However, after one cycle of extraction from $I = 4$ ($NaOH + NaNO_3$, $D_{Sr} = 6.43$), backextraction with the given mixture and washing the organic phase three times with 0.1 M NaOH, the D_{Sr} from $I = 4$ dropped to a value of 0.126–0.164. Hence, complete transfer to the original extractant was not accomplished.

A second approach to backextraction uses the fact that for any protonized base H, B^+ functions as a competitive particle for Cs^+ and Sr^{2+}. In contact with alkaline aqueous solution, the base would switch back to the unprotonized form B, with presumably no effect on the extraction. Thus, adding some strong base to the organic phase could promote the backextraction of Cs and Sr, simultaneously enabling the return of the system to the properties of pure extractant on the alkaline side. Moreover, some hydrophobic base like tributyl phosphate (TBP) would stay permanently in the organic phase.

This reasoning is largely true, as seen from Fig. 10 where dependences on the concentration of TBP for both the acidic and alkaline side are plotted. However, two points are to be noticed. As seen from the figure, extraction from acid media is generally much higher than from alkaline media at zero

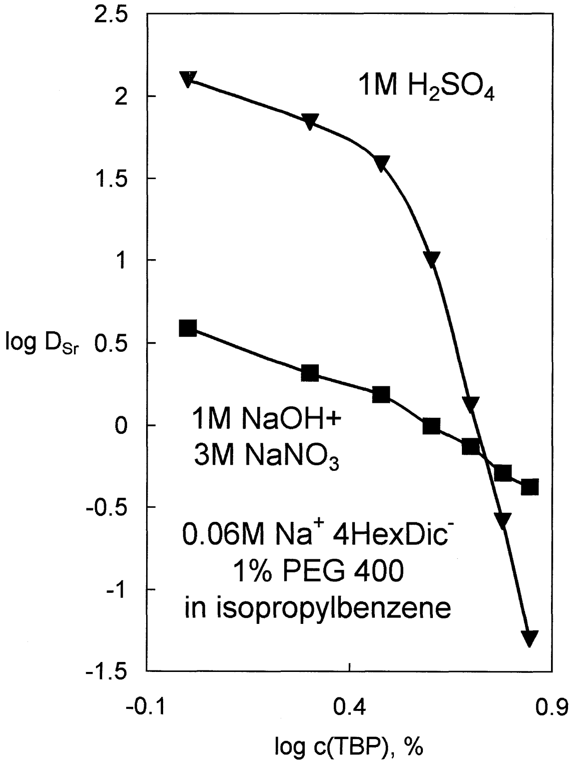

FIG. 10 Extraction of Sr from 1 M H_2SO_4 and 1 M $NaOH + 3$ M $NaNO_3$ by 0.06 M Na^+ 4HexDic$^-$ + 1% PEG 400 in isopropylbenzene vs the concentration of TBP in the organic phase.

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concentration of TBP. Furthermore, there is also a slight effect of TBP on Sr^{2+} extraction on the alkaline side. This can be easily explained by the formation of particles of Na, B^+ also competing for extraction of Cs^+ and Sr^{2+}. In fact, for the conditions given in Fig. 10 the cycle extraction/backextraction/regeneration is not accomplished, but we believe it would be possible to fine-tune to the desired conditions.

CONCLUSIONS

Tetrahexyldicarbollide, initially proposed at LANL (8–10), is a powerful extraction reagent for the separation of ^{137}Cs and ^{90}Sr from alkaline highly radioactive waste. Suitable distribution ratios are attained when extracting from a medium of 1 M NaOH + 4 M $NaNO_3$ by 0.06 M extractant in the absence or presence of 1 vol% PEG 400, respectively, into isopropylbenzene as solvent. The chemical stability of the reagent in alkaline solutions is good. Further studies should concentrate on ways to optimize the backextraction/regeneration of the extractant.

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