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Novel Solvent System for Metal Ion Separation: Improved Solvent Extraction of Strontium(II) and Lead(II) as Dicyclohexano-18-crown-6 Complexes

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ABSTRACT

As a part of our study of hazardous metal ion separations, the extraction of Sr^{2+} and Pb^{2+} from solutions containing nitric acid and various nitrate salts has been investigated. High partition ratios ($D_{Sr} > 100$–10) were observed using comparatively low (10–50 mM) concentrations of dicyclohexano-18-crown-6 in a group of nitrile solvents with relatively high dielectric constants (adiponitrile, glutaronitrile, succinonitrile, malononitrile; $\varepsilon = 30$–60) which are able to participate in coalescence extraction. Equilibria in the solvent extraction system were characterized, with Sr(II) and Pb(II) occurring in the organic phase primarily as partially dissociated ion pairs. A dramatic increase of extraction efficiency over traditional systems is achieved because of the formation of solvated cationic complexes in the organic phase.

Key Words. Strontium(II); Lead(II); Solvent extraction; Crown ethers

INTRODUCTION

Lead compounds and radioactive isotopes of strontium (especially ^{90}Sr) are among the most dangerous of inorganic pollutants. Despite numerous at-

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tempts to create a procedure for Sr^{2+} recovery from wastewater solutions, this problem has still not been fully resolved. It has also been found that Sr^{2+} sorption can be suppressed by Pb^{2+} due to the formation of similar but more stable complexes with the latter.

Since their discovery by Charles Pedersen (1), crown ethers have been applied primarily to alkali metal extraction (2). Among divalent cations, excellent extraction may also be achieved (3–5) for Pb^{2+}, Sr^{2+}, and Ba^{2+}. Eighteen-membered crown ethers, such as dicyclohexano-18-crown-6 (DC18C6), have been found to be most suitable for Sr^{2+} and Pb^{2+} recognition.

There have been several studies of solvent effects in $M(NO_3)_2$ extraction by crown ethers. Exhaustive results were obtained using chlororganic solvents (e.g., $CHCl_3$, CH_2Cl_2) (6, 7) and aliphatic alcohols (e.g., octanol) (8–10). Further improvement of the extraction characteristics is possible by introducing effective solvating agents or even new solvents into the liquid–liquid extraction system. Such solvating molecules should be able to interact strongly with both the $[\text{M-crown ether}]^{2+}$ cation and the nitrate anion, which is most common in nuclear waste solutions, as well as being hydrophobic enough to increase the solubility of the resulting complex in the organic phase. A mixture of tributyl phosphate and kerosene has been used successfully for strontium recovery with 4′,4″(5″)-di-*tert*-butyldicyclohexano-18-crown-6 (11). Solvents with high water content were suggested to be more suitable for strontium extraction (8). Recent results in this area have been reviewed (12, 13).

As a part of a systematic study of hazardous metals separation with crown ethers, we have investigated several new solvents for Sr^{2+} and Pb^{2+} extraction. Here we present the results of liquid–liquid extraction of $Sr(NO_3)_2$ and $Pb(NO_3)_2$ with DC18C6 using nitriles as solvents. The resulting data are compared with extraction for several common diluents such as $CHCl_3$ and CH_2Cl_2. Nitriles [for example, malononitrile (14–17)] are known to form hydrogen bonds with the oxygen atoms of crown ether molecules. These solvents are immiscible with water at common temperatures, but have quite low *upper critical solution temperature* (61–62°C for malononitrile, glutaronitrile, and succinonitrile, and 101°C for adiponitrile) above which they are completely miscible with water. Such behavior makes it possible to apply *the coalescence extraction* procedure of mixing (18) rather than common mechanical agitation.

EXPERIMENTAL

DC18C6 (mixture of isomers) was from Aldrich; pure cis-syn-cis and cis-anti-cis isomers of DC18C6 (98%+) were from Acros. Commercial grade reagents were used without further purification. Main components of simulant solutions were: Al-waste: 0.8 M HNO_3, 1.2 M $Al(NO_3)_3$, 20 mM $NaNO_3$, 20

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mM Fe^{3+}, 3 mM K^+, 10 mM Cl^-, 80 mM F^-, 30 mM SO_4^{2-}; Na-waste: 1 M HNO_3, 0.5 M $Al(NO_3)_3$, 2.0 M $NaNO_3$, 50 mM Fe^{3+}, 0.1 M K^+, 30 mM Cl^-, 100 mM F^-, 50 mM SO_4^{2-}.

Determination of DC18C6 Partition Constants

Equal volumes of aqueous solutions of DC18C6 and organic solvents were shaken for 10 minutes. Phases were allowed to sit for 30 minutes and then centrifuged. The aqueous phase was analyzed for DC18C6 content using either a spectrophotometric (19) or an NMR procedure. For the spectrophotometric determination, the extraction of K^+DC18C6 A^- (where A is 2-naphtholorange anion) into chloroform was used. For the NMR determinations, deuterium oxide solutions of DC18C6 were used as the aqueous phase. Known amounts of CH_3SO_3H or CH_3CN were added as an internal standard, and proton spectra were measured using a 200 MHZ Gemini NMR spectrometer. The integral value for the (CH_2—O) methylene proton signal of DC18C6 was compared to that of the standard. Partition constants for glutaronitrile, malononitrile, and adiponitrile obtained using the NMR procedure agreed well with those obtained using the spectrophotometric method (see Table 1).

Metal Ion Distribution

Solvent extraction experiments were performed in 10–20 mL glass vessels fitted with Teflon stoppers. Initial volumes of aqueous and organic phases were equal to 4 mL. Phases were shaken gently for 10 minutes, although no detectable change of extraction was observed after 5 minutes of shaking. Solutions were allowed to separate, then centrifuged, and samples of both aqueous and organic phases were taken. All the resulting solutions were analyzed for metal ion concentrations using a Perkin-Elmer Plasma 1000/2000 ICP spectrometer.

Nitric acid distribution was studied in the same way as described above. The sample of organic phase was diluted by ethanol and water and then titrated with 10 mM standard solution of NaOH using methylthymol blue as indicator.

All extraction studies were carried out at 23°C.

RESULTS AND DISCUSSION

There are a number of chemical reactions which contribute to the overall equilibrium process occurring in the extraction system. These individual reactions are treated in the following sections.

TABLE 1

Properties of Solvents and Partition Constants of DC18C6 (cis-syn-cis isomer)

Solvent	Dielectric constant (20)	Solubility (20–22) in water (%)	Solubility of water in solvent (20–22)		P_{DC18C6}[a]
			%	Mole ratio	
Chloroform	4.9	0.7	0.072	0.0048	2500 (Ref. 19)
Dichloromethane	9.14	1.3	0.198	0.009	>1000 (Ref. 12)
Dichloroethane	10	0.81	0.187	0.010	4000 (Ref. 12)
Octanol	10.3	0.03	0.1	0.007	120 (Ref. 23)
Benzyl alcohol	13.1	3.9			306 (Ref. 23)
Tributyl phosphate	8.05	0.04	6.4	1.1	
Tributyl phosphine oxide		4.0	33	4	
Nitrobenzene	34.8	0.19	0.25	0.0171	182 (10)
Benzyl cyanide, $PhCH_2CN$		0.14	1.65	0.11	*120* (10)
Benzonitrile, PhCN	25.2	0.2	1	0.05	
Butyronitrile, C_3H_7CN	23	3.35	1.99	0.08	51 (10)
Adiponitrile, $NC—(CH_2)_4—CN$	32.5	5.5	5.9	0.40	14.6 (8), *16* (1)
Glutaronitrile, $NC—(CH_2)_3—CN$		10.5	10	0.57	11.5 (8), *10* (1)
Succinonitrile, $NC—(CH_2)_2—CN$	57.3	11	8.5	0.41	17 (1)
Malononitrile, $NC—CH_2—CN$	46.3	11.8	12	0.50	700, *400*

[a] This work, if no reference (NMR data are shown in italics). Standard deviations in parentheses.

Crown Ether Distribution between Aqueous and Organic Phases

The distribution of the extraction reagent between the aqueous phase and the organic solvent plays an important role in the description of solvent extraction equilibria. The partition constants obtained in this work and elsewhere for most of the dinitrile solvents are comparatively low (10–20, see Table 1). The only exception is malononitrile, which forms stable complexes with DC18C6 (15) even in aqueous solutions. These complexes are responsible for significantly higher partition constants for malononitrile (Table 1). We observed no evidence of association between any other nitriles and DC18C6 molecules in D_2O using proton NMR.

Nitric Acid Extraction by Crown Ether Solutions

In the liquid–liquid extraction systems studied, detectable amounts of nitric acid were extracted into the organic phase (see Fig. 1). The experimental data fit the equilibrium:

$$H^{+}_{aq} + NO^{-}_{3,aq} \xleftrightarrow{K_1} HNO_{3,org}$$

$$K_1 = \frac{[HNO_3]_{org}}{[H^+]_{aq}[NO_3^-]_{aq}} \tag{1}$$

Nitric acid molecules in the organic phase react with dicyclohexano-18-crown-6, forming associates:

$$HNO_{3,org} + DC18C6_{org} \xleftrightarrow{K_{11}} \{HNO_3{\cdot}DC18C6\}_{org}$$

$$K_{11} = \frac{[HNO_3{\cdot}DC18C6]_{org}}{[HNO_3]_{org}\,[DC18C6]_{org}} \tag{2}$$

Example K_1 and K_{11} values are shown for only the adiponitrile system in Tables 2 and 3. Nitric acid appears to be a weak acid in the adiponitrile–water system, in agreement with the weakness of HNO_3 in acetonitrile [p$K = 8$, pre-

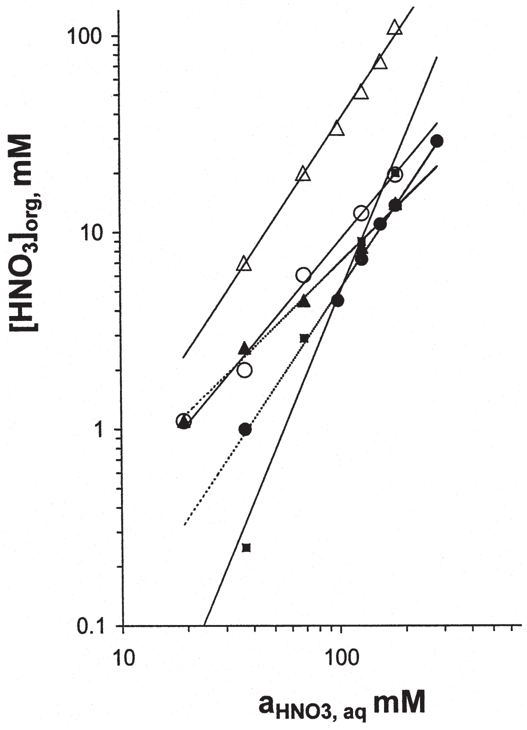

FIG. 1 Nitric acid distribution between water and various organic solvents: (▲) malononitrile, (■) benzyl alcohol, (△) tributyl phosphate, (○) glutaronitrile, (●) adiponitrile. [cis-syn-cis-DC18C6] = 10 mM.

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TABLE 2
Nitric Acid Extraction from Water into
Adiponitrile at Varying Concentrations

$[HNO_3]_{aq}$(mM)	$[HNO_3]_{org}$ (mM)		K_1 (M^{-1})
45	0.2		0.10
89	−1.1		0.14
133	2.2		0.13
174	6.3		0.20
341	19		0.16
423	26.7		0.15
		Average:	0.14(4) M^{-1}

viously shown (24)]. In keeping with the results shown for adiponitrile, the distribution ratios $[HNO_3]_{org}/[HNO_3]_{aq}$ were lower than 0.2–0.3 for each of the nitrile solvents tested.

Alkali Metal Nitrate Extraction by Crown Ether Solutions

Lithium nitrate distribution between the nitrile solvents and the aqueous phase was observed. The distribution ratio is constant within the concentration

TABLE 3
Association of Nitric Acid with DC18C6 in the Adiponitrile Extraction System under Varying Concentration Conditions. All Concentrations in mM

$[HNO_3]_{aq}$[a]	$[DC18C6]_{org}$	$[HNO_3]_{org}$[b]	$[HNO_3]_{org}$[c]	$[HNO_3]_{org}$[d]	$\log(K_1K_{11})$[e]
45	10	1	0.3	0.7	1.6
180	10	7.3	4.3	3.0	1.18
270	10	13.7	9.4	4.3	1.07
225	7	10	6.7	3.3	1.28
225	15	12	6.6	5.4	1.10
225	10	11	6.6	4.4	1.23
225	25	16.4	6.3	10.1	1.17
225	50	21.4	6.0	15.4	1.03
135	10	4.5	2.5	2.0	1.19
135	20	6.7	2.4	4.3	1.23
135	30	8.5	2.3	6.2	1.21
135	40	9.4	2.3	7.1	1.14
135	50	11.3	2.2	9.1	1.16
				Average:	1.17(6)

[a] Total concentration.
[b] Total concentration in organic phase.
[c] Free nitric acid, calculated using Eq.
[d] Associate with DC18C6.
[e] $\log K_{11} = 1.16$, $\log K_1 = 2.01(8)$.

TABLE 4
Lithium Nitrate Extraction from Water into Adiponitrile at Varying Concentrations

$[LiNO_3]_{aq}$ (mM)	$[LiNO_3]_{org}$ (mM)		*P*
9.9	0.133		0.013
19.8	0.19		0.0096
29.7	0.304		0.010
34.7	0.30		0.009
49.4	0.58		0.012
49.4	0.59		0.012
64.1	0.86		0.013
79.1	0.90		0.011
98.9	1.14		0.012
98.8	1.21		0.012
		Average:	0.011(2)

range 10–500 mM $LiNO_3$ in the aqueous phase (see Table 4). Complete dissociation of lithium nitrate occurs in the aqueous phase at these concentrations; hence, complete dissociation in the organic phase was assumed, in agreement with the low association constant of lithium nitrate in acetonitrile (24). There was no detectable influence of DC18C6 on lithium nitrate distribution, in keeping with the low affinity of crown ethers for this cation. For example, at any concentration of DC18C6 in malononitrile from 0 to 3 mM we received the partition coefficient of 0.02(2) with no trend vs DC18C6 concentration.

Sodium and potassium nitrates are distributed to the nitrile solvent phase, but less so than lithium. However, contrary to lithium, the presence of DC18C6 increases the amounts of sodium and potassium which are extracted into the organic phase. Distribution ratios in all cases studied, with or without DC18C6, were less than 0.1.

Lead and Strontium Extraction from Nitric Acid and Lithium Nitrate Solutions

Use of nitrile solvents dramatically improves the extraction of $Sr(NO_3)_2$ and $Pb(NO_3)_2$ by DC18C6 over that obtained with traditional solvents. As shown in Figs. 2A, 2B, and 2C, the extraction isotherms measured at constant crown ether concentration reflect almost no extraction using octanol as solvent, while 95–98% extraction was observed using either malononitrile or succinonitrile. The order of extraction efficiency may be described as:

$$\text{octanol} < \text{tributylphosphate} < \text{benzyl alcohol} < \text{benzyl cyanide} < \text{adiponitrile} < \text{glutaronitrile} < \text{succinonitrile} = \text{malononitrile}$$

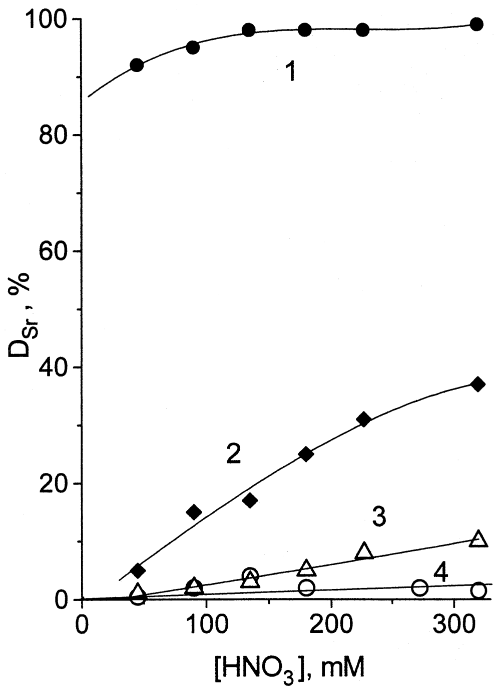

FIG. 2A Effect of nitric acid concentration on Sr^{2+} distribution: (1) malononitrile, (2) butyronitrile, (3) tributylphosphate, (4) octanol. [cis-syn-cis-DC18C6] = 10 mM.

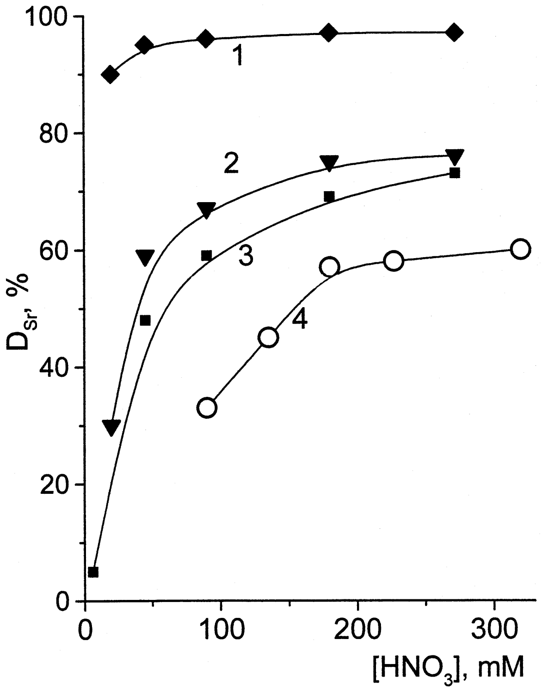

FIG. 2B Effect of nitric acid concentration on Sr^{2+} distribution: (1) succinonitrile, (2) glutaronitrile, (3) adiponitrile, (4) benzyl cyanaide. [cis-syn-cis-DC18C6] = 10 mM.

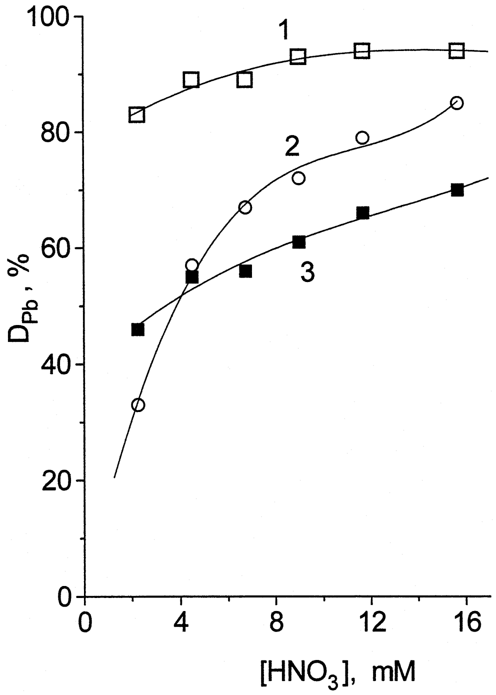

FIG. 2C Effect of nitric acid concentration on Pb^{2+} distribution: (1) glutaronitrile, (2) adiponitrile, (3) butryonitrile. [cis-syn-cis-DC18C6] = 10 mM.

The equilibria taking place in these two-phase systems can be represented by the following equations:

$$M^{2+}_{aq} + L_{org} + 2^{A-}_{aq} \xrightarrow{K_{ex}} \{MLA_2\}_{org}$$

$$K_{ex} = \frac{[MLA_2]_{org}}{[M^{2+}]_{aq}[L\ ]_{org}[A^-]^2_{aq}} \qquad (3)$$

$$M^{2+}_{aq} + L_{org} + 2^{A-}_{aq} \xrightarrow{K_{ex2}} \{MLA^+\}_{org} + A^-_{org}$$

$$K_{ex2} = \frac{[MLA_{n-1}]_{org}[A^-]_{org}}{[M^{2+}]_{aq}[L]_{org}[A^-]^2_{aq}} \qquad (4)$$

$$M^{2+}_{aq} + L_{org} + 2A^-_{aq} \xrightarrow{K_{ex3}} \{ML^{2+}\}_{org} + 2A^-_{org}$$

$$K_{ex3} = \frac{[ML^{2+}]_{org}[A^-]^2_{org}}{[M^{2+}]_{aq}[L]_{org}[A^-]^2_{aq}} \qquad (5)$$

Equation (3) describes the extraction of neutral ion pairs into the organic solvent, Eq. (4) describes extraction of partly dissociated ion pairs, and Eq. (5)

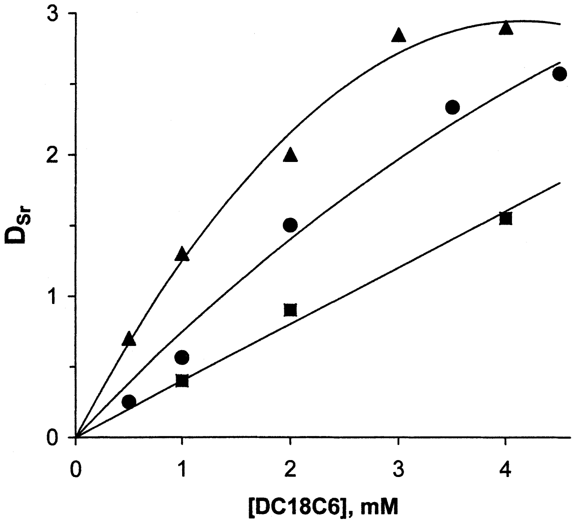

FIG. 3 Effect of DC18C6 (cis-syn-cis isomer) concentration on Sr^{2+} distribution. [$LiNO_3$] = 50 mM C_{Sr}: (■) 1.0 mM, (●) 0.50 mM, (▲) 0.10 mM.

TABLE 5
Extraction of $Pb(NO_3)_2$ and $Sr(NO_3)_2$ using DC18C6 from Water into Various Solvents

	log $C_{org}/([M][L][NO_3]^2)$			
	Pb			Sr
Solvent	cis-syn-cis	cis-anti-cis	Mixture of cis isomers	cis-syn-cis
Chloroform	6.6	6.2		3.7(1)
Dichloromethane	6.90(2)	6.44(3)	6.65(4)	3.86(4)
Nitrobenzene	6.8(1)		6.5(1)	3.63(1)
Dichloroethane	6.8(1)		6.6(2)	
Benzonitrile			6.5(1)	
Nitrobenzene–succinonitrile (1:1)	8.1(1)		8.1(1)	5.1(3)
Succinonitrile	10–11			8.5–9.1
Glutaronitrile	10.6(3)			7.3(5)
Butoxyethanol			6.5–7	
Tributyl phosphate				3.5
Tributyl phosphine oxide			6	
Malononitrile	11		11	9–8
Adiponitrile	9.3–8.8			5.6
Butyronitrile	8.2(4)			4.2
Benzyl alcohol	7.0(1)			4.5(1)
Pentanol	6.04(1)			
Octanol	5.60(4)			>3.0
Benzyl cyanide	8–9			4.7(1)

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describes extraction of fully dissociated ionic species. M represents the metal ion, L the crown ether, and A the NO_3^- anion.

Subscripts "aq" and "org" indicate the aqueous and organic phase, respectively, and square brackets indicate equilibrium molar concentrations.

Experiments performed at constant nitrate concentration confirm that only one crown ether molecule reacts with each metal ion, in keeping with the results shown in Fig. 3.

Because different equilibria apply to the different extraction systems studied, an empirical value of $C_{M,org}/[M]_{aq}[L]_{org}[NO_3]^2$ was used as a measure to compare extraction effectiveness. This expression corresponds to K_{ex} for solvents with no ion pair dissociation (Eq. 3). Corresponding values are shown in Table 5 and in Fig. 4. In almost all cases the difference between log K_{ex} values for lead and strontium remains equal to 3.0 ± 0.2. A mixture of cis isomers extracts metal ion slightly less than pure cis-syn-cis isomer itself. The explanation is based on the fact that quite often (e.g., Refs. 2, 12, 15, 19) the

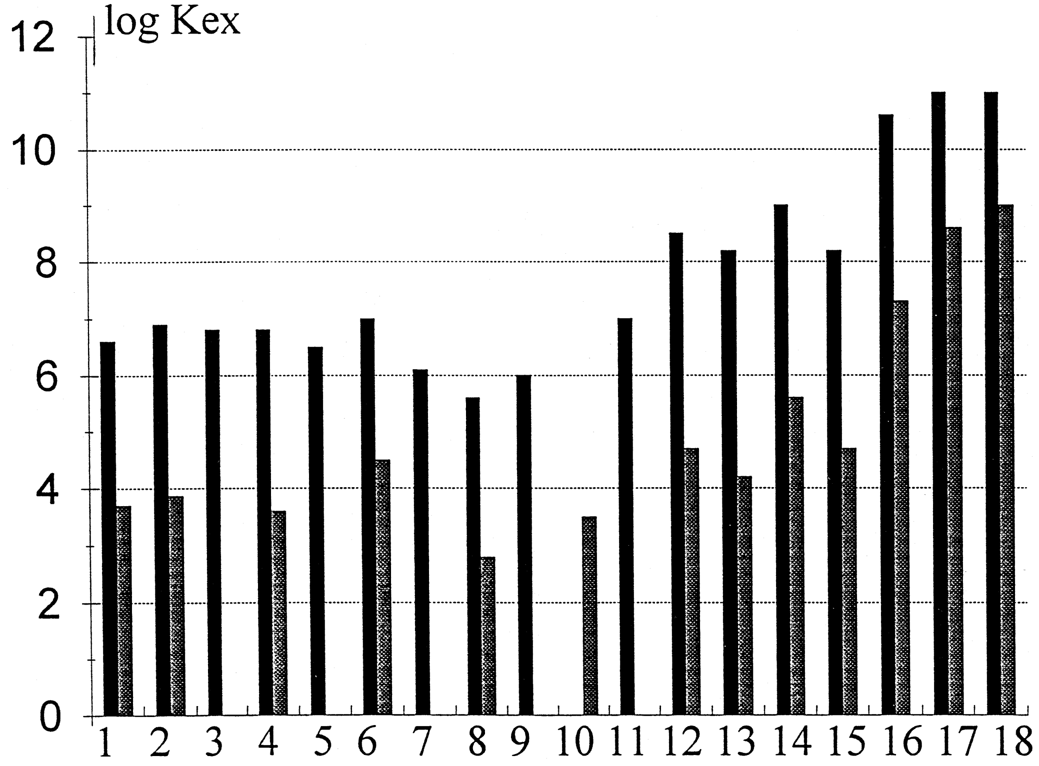

FIG. 4 Extraction of $Pb(NO_3)_2$ (solid bar) and $Sr(NO_3)_2$ (shaded bar) using DC18C6 for various solvents. Log K_{ex} = log $C_{org}/([M][L][NO_3]^2)$. Solvents: (1) chloroform, (2) dichloromethane, (3) dichloroethane, (4) nitrobenzene, (5) benzonitrile, (6) benzyl alcohol, (7) pentanol, (8) octanol, (9) tributyl phosphine oxide, (10) tributyl phosphate, (11) butoxyethanol, (12) benzyl cyanide, (13) butyronitrile, (14) adiponitrile, (15) methylglutaronitrile, (16) glutaronitrile, (17) succinonitrile, (18) malononitrile.

cis-anti-cis isomer shows much lower extraction, so that when excess macrocyclic reagent is present, reaction occurs with cis-syn-cis isomer only. This in turn results in the decrease of the overall effective constant by 50% (a decrease in log K_{ex} of log $2 = 0.3$). For this reason, we have used the pure cis-syn-cis isomer of dicyclohexano-18-crown-6 in almost all experiments.

From Fig. 4 it is clear that one group of solvents has significantly better extraction performance: nitriles containing the —CH_2—CN group. The cyano group alone does not satisfy the requirements, since benzonitrile extracts the complexes no better than any other solvent of similar dielectric constant. A high dielectric constant, which is characteristic for nitriles, apparently is not enough alone to achieve good extraction. For example, nitrobenzene possesses a high dielectric constant but is only a fair extraction solvent. High water content in the solvent also does not seem to be a requirement: solvents such as tributyl phosphate and butoxyethanol achieve high water concentration (see Table 1) but are relatively weaker extracting solvents. The best results were achieved with the dinitrile solvents having two cyanomethylene groups —CH_2—CN. Butyronitrile and benzyl cyanide show much lower extraction constants. And extra methylene groups between cyano groups decrease extraction of Sr and Pb macrocyclic complexes, as seen by comparing glutaronitrile and adiponitrile with succinonitrile.

Mechanism of Improved Extraction with Dinitrile Solvents

It is interesting to consider possible sources of the observed improved extraction with dinitrile solvents. The first factor to consider is solvation of the metal ion. Solvents which are known to solvate metal ions effectively (e.g., tributyl phosphate and tributyl phosphine oxide) did not yield high values of log K_{ex}. The nitrile group itself could be a good solvating group, but the low extraction constant observed in benzonitrile confirms that this feature is not sufficient to cause the effect.

A clue to the source of the effect may be found using known structural information about Pb (and Sr) complexes with 18-membered crown ethers (25). In all known crystal structures, the central atom is fully coated by the crown ether molecule and accompanying anions or water molecules. There is no free space for extra solvation of the central ion without removal of the counterions, water molecules, or crown ether. However, some sites on the periphery of the complex are hydrophilic—e.g., there are two oxygen atoms of the nitrate anion in an apical position of the complex as well as six oxygens of the crown ether, some of which are partially exposed for extra solvation. The best opportunity for solvation can be provided by strong hydrogen bond donors, e.g., water itself. But this would prevent hydrophobic solvation of the complex as its exterior shell becomes more hydrophilic. Dinitriles are able to solvate the complex but maintain the hydrophobic character of the resulting outer shell. They are known as strong donors in C—H...X hydrogen bonds. Malononitrile is known to form very stable associates with crown ether molecules in this same way.

The associate formation enhances the retention of the crown ether in the organic phase, decreasing the loss of reagent. As good donors but poor acceptors of hydrogen bonding, these dinitrile solvents can extrasolvate the complex cation through the system of C—H...O hydrogen bonds which enhance the overall extraction process.

Speciation Analysis in the Dinitrile Solvent Systems

Effective extraction constant values ($C_{M,org}/[M]_{aq}[L]_{org}[NO_3]^2$) which describe the extraction processes into alcohols and chlorohydrocarbons are not appropriate to the dinitrile systems because they are not sufficiently stable versus concentration. These effective parameters are quite stable while the nitrate concentration in the aqueous phase is the same (Table 6), but they vary dramatically with counterion concentration. High concentration of nitrate ion (from nitric acid or lithium nitrate) in the organic phase suppresses complete dissociation of complexed strontium or lead nitrates despite the high dielectric constants of the nitriles. For this reason, Eq. (4) better describes the distribution of metal complexes under our experimental conditions.

TABLE 6

Extraction Constant K_{ex2} Determination for Sr(DC18C6)$(NO_3)_2$ Extraction from Water into Adiponitrile. cis-syn-cis isomer of DC18C6

C_{Sr} (mM)	C_{NO_3} (mM)	C_{DC18C6} (mM)	R_{Sr} (%)		$\log(C_{org}/[Sr][L][NO_3]^2)$	$\log K_{ex2}$ (M^{-2})
1	50	1	30		6.01	2.88
1	50	2	48		6.05	2.99
1	50	4	62		6.00	3.02
0.5	50	1	36		6.07	2.87
0.5	50	2	60		6.21	3.08
0.5	50	3.5	72		6.22	3.13
0.5	50	4.5	68		6.05	2.95
0.1	50	2	67		6.30	3.04
0.1	50	3	74		6.29	3.05
0.1	50	4	74		6.19	2.95
0.25	5	20	40		6.77	2.94
0.25	10	20	60		6.62	3.01
0.25	15	20	64		6.40	2.89
0.2	5	5	35		7.00	3.05
0.2	5	10	40		6.90	3.01
0.2	5	15	40		6.83	2.93
				Average:	6.36(33)	2.97(9)

A complete description of the equilibria includes concentrations of all species in both aqueous and organic phases. Both Sr^{2+} and Pb^{2+} form stable complexes with DC18C6 in aqueous solution: $\log K = 4.95$ for Pb (26) and 3.27 for Sr (26). We have obtained a similar value ($\log K = 3.3$ for Sr^{2+}) using proton NMR in D_2O. In our extraction experiments we have used comparatively low concentrations of both metal ions (<1 mM) and crown ether (<10 mM). Taking into account the partition constants of DC18C6 between the organic and aqueous phases and the stability constants of complexes in the aqueous phase, one can estimate the concentrations of $SrDC18C6^{2+}$ and $PbDC18C6^{2+}$ in the aqueous phase and make appropriate corrections to the extraction constants. Ion pair formation in the aqueous phase is described by the following equations (27):

$$Pb^{2+} + NO_3^- \rightarrow PbNO_3^+ \qquad K_1 = [PbNO_3^+]/[Pb^{2+}][NO_3^-] \qquad \log K_1 = 1.17$$

$$Sr^{2+} + NO_3^- \rightarrow SrNO_3^+ \qquad K_1 = [SrNO_3^+]/[Sr^{2+}][NO_3^-] \qquad \log K_1 = 0.8$$

The extended Debye–Hückel equation was used to apply ion strength (μ) corrections in the form

$$\log \gamma = 0.51Z^2\sqrt{\mu}/(1 + 1.6\sqrt{\mu})$$

To calculate the activity coefficients in the organic phase, a similar equation can be applied (28) using parameters which depend on the dielectric constant of the solvent. Because of low concentrations of ions in the organic phase, the correction to $\log \gamma$ was never larger than 0.1 in our experiments. No corrections were made on the activities of neutral compounds because in the comparatively low ionic strengths of our systems, corrections would be less than the standard deviations of our experimental results.

A sample set of results for the adiponitrile extraction system is shown in Table 6. The resulting constant is quite stable to concentration changes over a wide range of concentrations of all components of the system. However, the high standard deviation suggests the possibility of other complex forms in the system with a relative content less than 10–20% of the total.

The extraction constants K_{ex2} for dinitrile systems which have been studied are collected in Table 7. The difference between $\log K_{ex}$ for Sr^{2+} and Pb^{2+} remained around 3 and is the same as it would be for neutral complexes (compare with Table 5).

Changing the nitric acid or the lithium nitrate concentration in the aqueous phase also causes changes in the organic phase. An increase of nitrate ion concentration in the organic solvent decreases the extraction of the target complex cation. This effect is quite detectable for nitric acid because it is extracted more effectively into the organic solvent. Furthermore, due to the formation of associates in the organic phase, nitric acid decreases the concentration of free crown ether molecules.

TABLE 7
Equlibrium Constants log K_{ex2}. Extraction of $Sr(NO_3)_2$ and $Pb(NO_3)_2$ using cis-syn-cis-DC18C6 from Water in Various Dinitrile Solvents

	log K_{ex2}		
Solvent	P_{LiNO_3}	Sr	Pb
Adiponitrile	0.012	2.97(9)	5.1(1)
2-Methylglutaronitrile	0.01	1.8(1)	4.40(6)
Glutaronitrile	0.016	3.2(1)	6.0(1)
Succinonitrile	0.03	5.3(1)	7.1(1)
Malononitrile	0.02	4.2(1)	7.2(1)

Sr^{2+} and Pb^{2+} Extraction from Nuclear Waste Mimics

The chemistry described above can be exploited in the design of superior systems for Sr^{2+} and Pb^{2+} extraction from nuclear waste. With adiponitrile as solvent, we were able to recover 90% of the Sr^{2+} in one extraction step using a 8 mM solution of commercial DC18C6 (mixture of isomers) from an Al-containing waste simulant. The partition ratio of Sr^{2+} increases linearly with

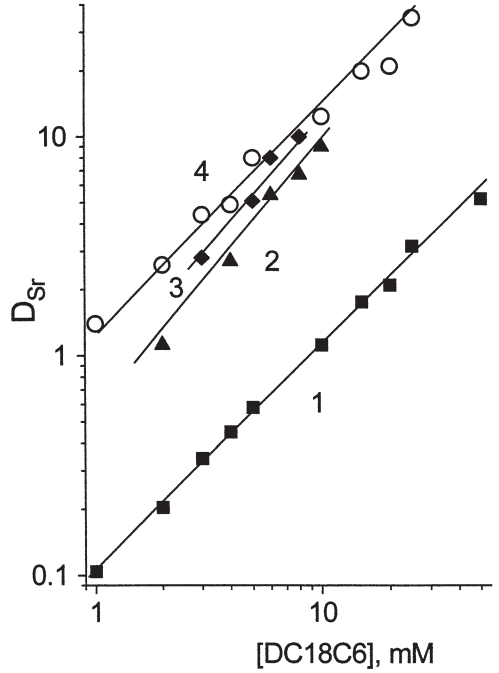

FIG. 5 Effect of DC18C6 concentration (commercial mixture of isomers) on Sr^{2+} distribution from Al- (4) and Na- (1–3) bearing waste simulants. Solvents: (1) adiponitrile, (2) malononitrile, (3) succinonitrile, (4) adiponitrile.

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crown ether concentration (Fig. 5). A 10 mM DC18C6 solution in succinonitrile or malononitrile is necessary to achieve the same extraction from the Na-containing waste. Both of these results are a significant improvement over those obtained in the common SREX process, for which $D_{sr} = 3.6$ for the sodium-bearing waste using 150 mM crown ether solution (10).

CONCLUSIONS

Solvent extraction using most common solvents (hydrocarbons, chlororganics, aliphatic alcohols, and ketones) requires the formation of dehydrated neutral compounds because of the low dielectric constant ($\varepsilon < 10$) of the organic phase. This requirement may be avoided by the use of dinitrile solvents with high dielectric constants ($\varepsilon = 30$–50). A dramatic increase of extraction efficiency is achieved because of the formation of solvated cationic complexes in the organic phase.

Solvents containing the NC—CH_2— group show several properties which enhance metal ion extraction.

- Because of high water content, these solvents do not require complete dehydration of the metal ions, a feature which is thermodynamically favorable.
- Because of the high dielectric constant, metal ions in the organic phase exist mainly in the form of complex cations instead of the neutral species. This obviates the necessity of counterion attachment to a metal ion which might require extra energy. This feature may be of importance to alkali and alkaline earth metal ions which do not favor complex formation.
- The NC—CH_2— group is a good donor but poor acceptor of hydrogen bonding. It can extra solvate the complex cation through a system of weak C—H...O hydrogen bonds.

The low upper critical solution temperature of dinitriles makes it possible to apply the coalescent extraction procedure for metal ion separations. Another possible approach to exploit these findings is to include solvents with active methylene groups as synergistic additives to existing diluent systems. These principles will be tested for application to facilitated membrane transport and ion chromatography separations.

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