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Influence of the Extractant on Strontium Transport from Reprocessing Concentrate Solutions through Flat-Sheet Supported Liquid Membranes

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ABSTRACT

The influence of the extractant on strontium transport through a flat-sheet-supported liquid membrane from nuclear fuel reprocessing concentrate solutions to demineralized water has been studied using two crown ethers of different lipophilicity: dicyclohexano-18-crown-6 (DC18C6) and di-*tert*-butylcyclohexano-18-crown-6 (DtBuC18C6). The distribution coefficients of strontium showed that DC18C6 is a better strontium extractant than DtBuC18C6 in the entire range of crown-ether concentration studied. No effect of association between the DC18C6 molecules was observed even at high concentrations. However, the strong lipophilic character of DtBuC18C6 led to a distribution coefficient of this extractant 10 times higher than the distribution coefficient of DC18C6. Thus, the membrane concentration of DtBuC18C6 was approximately 10 times higher than that of DC18C6. This leads to greater strontium permeability for DtBuC18C6, even though DC18C6 had a greater capacity for strontium extraction and a higher diffusion coefficient in the membrane due to the smaller molar volume of this crown ether. The precipitation of a white solid was observed when the synthetic concentrate was mixed with an organic phase containing DtBuC18C6 dissolved in *n*-hexylbenzene (0.7 mol·L^{-1} isotridecanol), causing a decrease of strontium permeability. In this case, DC18C6 had the greatest strontium permeability.

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INTRODUCTION

Reprocessing operations of nuclear fuels produce medium activity liquid wastes which are treated by evaporation. The distillate is discharged into the environment and all active and inactive salts are concentrated, leading to significant volume of waste. After embedding, this concentrate must be stored in geological formations due to the activity of long-life radionuclides (actinides, cesium, strontium). Removing these radionuclides from the concentrate sharply decreases the volume of wastes to be stored in geological formations. The decontamination of this concentrate can be obtained by coupled transport through supported liquid membranes (SLM) (1–3). An SLM consists of an organic liquid adsorbed onto a microporous support separating two aqueous solutions: the first contains the permeating ions (feed solution), the second is free of these ions (stripping solution). The transport of ions through the membrane occurs when a gradient in the chemical potential is established between the two aqueous solutions. The use of selective neutral extractants (such as crown ethers and CMPO) as membrane carriers leads to coupled transport across the membrane. When an evaporation concentrate (comprised mainly of nitric acid and sodium nitrate in high concentrations) is used as a feed solution, nitrate ions will be cotransported along with the given cation. If a significant concentration difference in nitrate ions exists between the two aqueous solutions (e.g., when demineralized water is used as a stripping solution), the cations can be transferred against their concentration gradient. The main advantage of SLMs over traditional separation technologies is that a low inventory of the organic phase. Hence, very selective and expensive extractants can be used. Other advantages are lower capital and operating costs, low energy consumption, mass transfer in one step, the possibility of attaining high separation factors, and concentration of the recovered species during separation (4).

The solvent extraction of alkali and alkaline earth elements has been throughly studied (5–11), but most of the extraction agents usually used are not available for the decontamination of the concentrate due to the acid and high sodium nitrate content of this type of liquid waste (oxidation and protonation of the extraction agents and high cation competition). Moreover, Cs^+ and Sr^{2+} are cations with a low charge density and thus require special extractants to compensate for their hydration energy (12). Crown ethers, first synthesized by Pedersen in 1967 (13), are macrocyclic compounds which form moderately strong complexes with alkali or alkaline earth cations. In addition to being acid and oxidation resistant, crown ethers are also very size-selective toward cations whose ionic radius most closely matches the cavity radius of the macrocycle (14). Thus, complexing is weak when the crown ether is too small because the cation cannot enter the plane of oxygen atoms where the charge density is highest, or when the crown ether is too large because the cation cannot be simultaneously close to all the oxygen atoms (15).

Considerable work has been performed on strontium extraction from high nitric acid content wastes with crown ethers (16–22). Furthermore, two studies have been carried out using SLMs (23, 24).

According to the relative size of the strontium ions and the crown ethers, 18-crown-6 (18C6) is the most suitable for complexing these ions. However, crown ethers such as 15C5, 18C6, and 21C7 are too soluble in water. Crown ethers with aliphatic or aromatic substituents (such as cyclohexano or benzo) show a more pronounced hydrophobicity that makes them usable in extraction processes. The addition of alkyl or cycloalkyl substituent groups increases the hydrophobicity of the macrocycle with a minimal reduction of its complexing ability. However, benzo or other electron-withdrawing substituent groups reduce macrocycle complexing power (25, 26).

Furthermore, the benzo-substituted crown ethers have a larger binding constant for alkali metals than for alkaline earth metals. The more rigid benzo-substituted crown ethers maintain a configuration in solution that requires relatively little rearrangement of the coordinating oxygens during metal complexation. The smaller dehydration energy of the alkali metals results in an overall free energy change upon complexation that favors the alkali metals. However, the doubly charged alkaline earth ions require a configuration that is more easily attained by the flexible cyclohexano-substituted crown ethers (27).

According to these considerations, the most efficient crown ethers for strontium extraction from the evaporation concentrate are the cyclohexano derivates of 18-crown-6. In this family of crown ethers, dicyclohexano-18-crown-6 (DC18C6) is the most economical and easily available, and hence the most used (17, 18, 20–22). However, DC18C6 is relatively soluble in water [0.036 $\text{mol}\cdot\text{L}^{-1}$ at 26°C (28)]. This results in a low distribution coefficient of the extractant, which can be increased if the extractant becomes more lipophilic. The latter is possible if aliphatic groups are added to the cyclohexano rings of the crown ether (29–31). In cation transport processes through SLMs, these more lipophilic crown ethers show higher cation fluxes (due to a higher carrier concentration in the membrane) and form more stable SLMs (due to less carrier washing by the aqueous solution) (32).

For the present work we have studied the influence of extractant lipophilicity on strontium transport through SLMs from a given evaporation concentrate to demineralized water, using two crown ethers of different lipophilicities: DC18C6 and the more lipophilic di-*tert*-butylcyclohexano-18-crown-6 (DtBuC18C6). First, we determined the distribution coefficient of strontium and of the crown ether between the aqueous solutions and several solvents, and finally we carried out strontium transport through flat-sheet-supported liquid membranes (FSSLM) with both crown ethers. This type of SLM was used because of easier handling, ease of modeling due to the regular geometry of the system, and hollow fiber membrane data taken under similar conditions are readily predicted from FSSLM data (33).

EXPERIMENTAL

Reagents

The organic solvents used for dissolving the crown ethers were obtained from Aldrich. Isotridecanol, used as a phase modifier with the aromatic solvents, is an Exxon product.

The synthetic concentrate was prepared with the average composition of the evaporation concentrate from medium-activity liquid wastes after nuclear fuel reprocessing operations (see Table 1). The solution was filtered before use to remove insolubles. All the reagents used in this solution and in all the other aqueous feed solutions were analytical-grade products from Prolabo. All these aqueous solutions were doped with ^{85}Sr. The source of ^{85}Sr was an aqueous solution of $SrCl_2$ from Amersham.

The aqueous stripping solution used was demineralized water, purified with a MilliQ system from Millipore.

TABLE 1
Composition of the Synthetic Concentrate

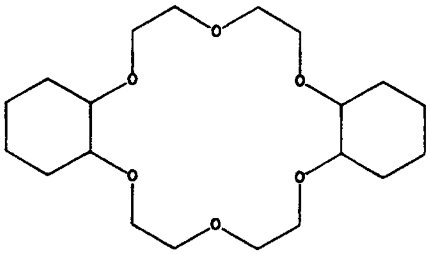
Compound	Concentration (g/L)
HNO_3	63
$NaNO_3$	290
$Mg(NO_3)_2 \cdot 6H_2O$	158
$Ca(NO_3)_2 \cdot 4H_2O$	3.5
$Fe(NO_3)_3 \cdot 9H_2O$	1.1
NaCl	0.7
NaF	0.07
$Na_2O \cdot SiO_2 \cdot 5H_2O$	0.2
$Na_3PO_4 \cdot 12H_2O$	3.4
$Na_2SO_4 \cdot 10H_2O$	3.0
NH_4NO_3	8.0
Tri(*n*-butyl)phosphate	0.15
$UO_2(NO_3)_2 \cdot 6H_2O$	4.7

Dicyclohexano-18-crown-6 (DC18C6) (see Fig. 1a) is an Aldrich product consisting of a mixture of cis-syn-cis and cis-anti-cis isomers with a purity of 99%. Di-*tert*-butylcyclohexano-18-crown-6 (DtBuC18C6) (see Fig. 1b) is a Parish product consisting of a complex mixture of stereo and position isomers, with a total purity of over 97%.

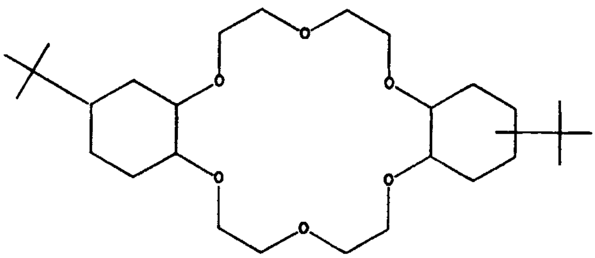
Membranes

The SLMs were prepared by soaking the polymeric support (Celgard 2500) for almost 24 hours in each of the organic solutions used, then letting it drip for a few seconds before placing it in the transport cell.

Celgard 2500 (Celanese Separation Products, Charlotte, North Carolina, USA) is a 2.5×10^{-3} cm thick microporous polypropylene film with a nominal porosity of 45%, an effective pore size of 0.04 μm, a pore tortuosity of 3.44, and a critical surface tension of 35 $mN \cdot m^{-1}$ (34).



a) DC18C6



b) DtBuC18C6

FIG. 1 Chemical structure of dicyclohexano-18-crown-6 (DC18C6) (a) and di-*tert*-butylcyclohexano-18-crown-6 (DtBuC18C6) (b).

Determination of the Strontium Distribution Coefficients

The distribution coefficients of strontium, D_{Sr}, defined as the equilibrium ratio of the strontium species between the organic and the aqueous phases, were determined at room temperature (25°C) by mixing 10 mL of each phase at 100 rpm in a polypropylene test tube, and then measuring the strontium count in each phase by ^{85}Sr gamma spectrometry analysis. Duplicate runs of each experiment were routinely performed.

Determination of Crown-Ether Distribution Coefficients

The distribution coefficients of DC18C6 and DtBuC18C6 between the organic and the aqueous phases (D_E) were determined using two differents methods. In the first method, 8 mL of an organic phase at various crown-ether concentrations previously saturated with the aqueous phase were mixed with the same volume of aqueous phase saturated with the solvent used. The mixture was shaken for 30 minutes at room temperature (25°C). After separation of the phases by centrifugation, 6 mL of the aqueous phase was added to 10 mL of an aqueous solution of KOH ($0.05\ mol{\cdot}L^{-1}$) and picric acid ($0.005\ mol{\cdot}L^{-1}$). A K·E·Pic complex was formed which was extracted quantitatively with 6 mL methylene chloride; then it was analyzed by UV-visible spectroscopy (Beckman DU-64) in order to determine the crown-ether concentration in the aqueous phase. The spectrophotometer calibration was performed with various solutions of the complex in methylene chloride. These solutions were obtained by mixing the aqueous solution of KOH and picric acid with several crown-ether solutions in methylene chloride of known concentration. The crown-ether concentration in the organic phase after partitioning was determined by mass balance of the two phase systems. Finally, the crown-ether concentration in the organic phase was plotted versus the crown-ether concentration in the aqueous phase, and the slope of the straight line obtained was equal to the distribution coefficient.

In the second method, developed by Horwitz (30), 8 mL of the organic phase containing various crown-ether concentrations ($[E]_0$) was mixed with 40 mL of the aqueous phase for 30 minutes at room temperature (25°C). Thus, the crown ether was partitioned between both phases with a distribution coefficient D_1. After centrifugation, 35 mL of the aqueous phase was mixed, under the same conditions as before, with 7 mL of the solvent. Thus, the crown ether was partitioned between both phases with a distribution coefficient D_2. After centrifugation, 6 mL of the organic phase was mixed with 6 mL of the synthetic concentrate containing ^{85}Sr, and the strontium distribution coefficient (D_{Sr}) was determined following the method indicated above. Since we knew the relation between D_{Sr} and the initial crown-ether concentration in the organic phase, the crown-ether concentration in the second organic phase ($[E]_2$) was determined. Taking into account the two equilibria and considering that $D_1 = D_2 = D_E$, we arrive at the following expression:

$$[E]_2 = \frac{D_E R}{(D_E + R)^2} [E]_0 \tag{1}$$

where R is the phase volume ratio (V_{aq}/V_{org}). In our case $R = 5$. Thus, D_E was determined.

Strontium Transport through an FSSLM

The transport experiments were carried out in a permeation cell consisting of two parallelepiped compartments made of Perspex thermostated at 25 ± 0.1°C. The design of this cell is shown in Fig. 2. The membrane surface area was 29.37 cm^2 (rectangular), and the volumes of the feed and stripping solutions were identical (125 mL).

At the beginning of each experiment the SLM was inserted between the two compartments and the cell was tightly clamped with two Teflon joints with screws. Time $t = 0$ was taken as the moment when the stirring of the aqueous phases was started (with magnetic stirrers). The permeation of strontium across the membrane was measured by periodic sampling of both aqueous solutions. The strontium counts in each phase were determined by gamma spectrometry analyses. The pH of the stripping solution was also monitored regularly.

Strontium permeability through the SLM was determined by plotting ln (C/C_0) versus time for the first 6 or 7 hours. In the transport model proposed by Danesi (4), the permeability is defined by the following equation:

$$\ln (C/C_0) = -(\epsilon S/V)P_{Sr}t \tag{2}$$

where C = feed concentration of strontium at time t
C_0 = feed concentration of strontium at time 0
S = membrane surface area (cm^2)
V = volume of feed solution (cm^3)
ϵ = support porosity
P_{Sr} = strontium permeability (cm·h^{-1})
t = permeation time (h)

Strontium Measurements by Gamma Spectrometry

Strontium counts were determined by gamma spectrometry analyses of ^{85}Sr, using a detection chain from Intertechnique, equipped *with* Ge

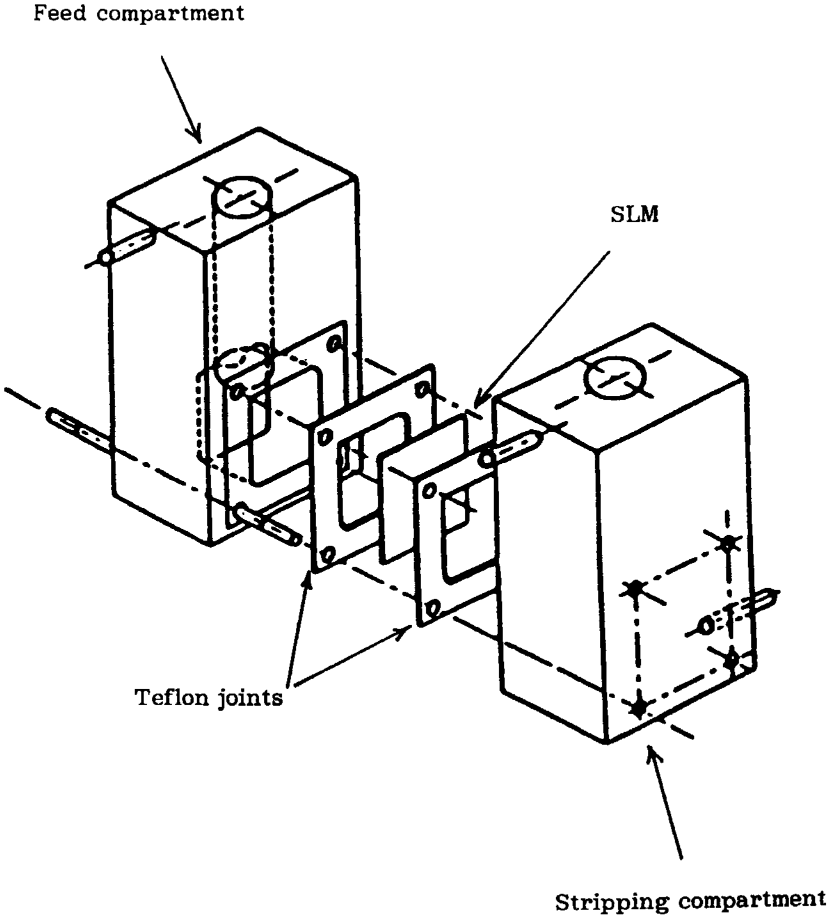


FIG. 2 Exploded view of the transport cell used.

detectors. The counting time was always sufficiently high so as to obtain relative errors in activity measurements of less than 5%.

RESULTS AND DISCUSSION

Distribution Coefficients of Strontium

The distribution coefficients of strontium (D_{Sr}) at various crown-ether concentrations in the organic phase were determined using the two crown ethers studied. *n*-Hexylbenzene (0.7 mol·L^{-1} isotridecanol) and *o*-nitrophenyloctylether, two solvents which allow stable SLMs to be obtained, were used as the organic solvents.

First, we used the synthetic concentrate as the aqueous solution, but precipitation of a white solid was observed between the two phases when DtBuC18C6 dissolved in *n*-hexylbenzene (0.7 mol·L^{-1} isotridecanol) was used. This precipitate may obstruct the support pores and decrease transport kinetics of strontium transport through the SLM. In order to avoid this difficulty, we also used an aqueous solution of $NaNO_3$ (4 mol·L^{-1}) and HNO_3 (1 mol·L^{-1}) (the main constituents of the synthetic concentrate) since no precipitate was observed in this case.

The results obtained are shown in Figs. 3, 4, and 5. We can see that D_{Sr} for DC18C6 was always higher than D_{Sr} for DtBuC18C6. This is in agreement with the results of Horwitz et al. (30) who found greater extraction constants for DC18C6 than for DtBuC18C6. However, these authors also observed a plateau of the D_{Sr} values for a certain DC18C6 concentration, probably due to association between DC18C6 molecules at a high crown-ether concentration. On the contrary, the aliphatic groups on the cyclohexano rings of DtBuC18C6 prevent the association between the crown-ether molecules; in this case the D_{Sr} values always increase with the organic concentration of the DtBuC18C6. Thus, there was a crown-ether concentration for which the D_{Sr} value was higher for DtBuC18C6 than for DC18C6.

However, Horwitz et al. used an aqueous solution of only HNO_3 (1 mol·L^{-1}). If we use this same aqueous solution we also observe a plateau in the D_{Sr} values for a certain DC18C6 concentration in contrast to the use of a high $NaNO_3$ content solution, as shown in Fig. 6. The parasitic complexation of the sodium ions by the crown ether may lead to too low a free DC18C6 concentration in the organic phase, and association between the DC18C6 molecules will not be apparent at these concentrations.

Distribution Coefficients of the Crown Ethers

The distribution coefficients of DC18C6 and DtBuC18C6 (D_E) were determined using two different methods. The first uses the UV-visible absorption of the picrate complexes, and thus does not allow the use of a strong acid aqueous solution because of the protonation of the picrate anion. Therefore, only demineralized water was used as the aqueous solution. Nevertheless, the measurement is very sensitive on account of the high molar absorbtivity of the picrate [$\epsilon \approx 15{,}000$ (20)]. On the other hand, the second method uses the radiometric determination of ^{85}Sr and allows the use of acid aqueous solutions. Thus, an aqueous solution of HNO_3 (1 mol·L^{-1}) and another one of $LiNO_3$ (5.8 mol·L^{-1}) and HNO_3 (1 mol·L^{-1}) were used (the latter has an ionic strength similar to the synthetic concentrate, but sodium was replaced by lithium as this cation is scarcely complexed by the crown ethers, unlike sodium).

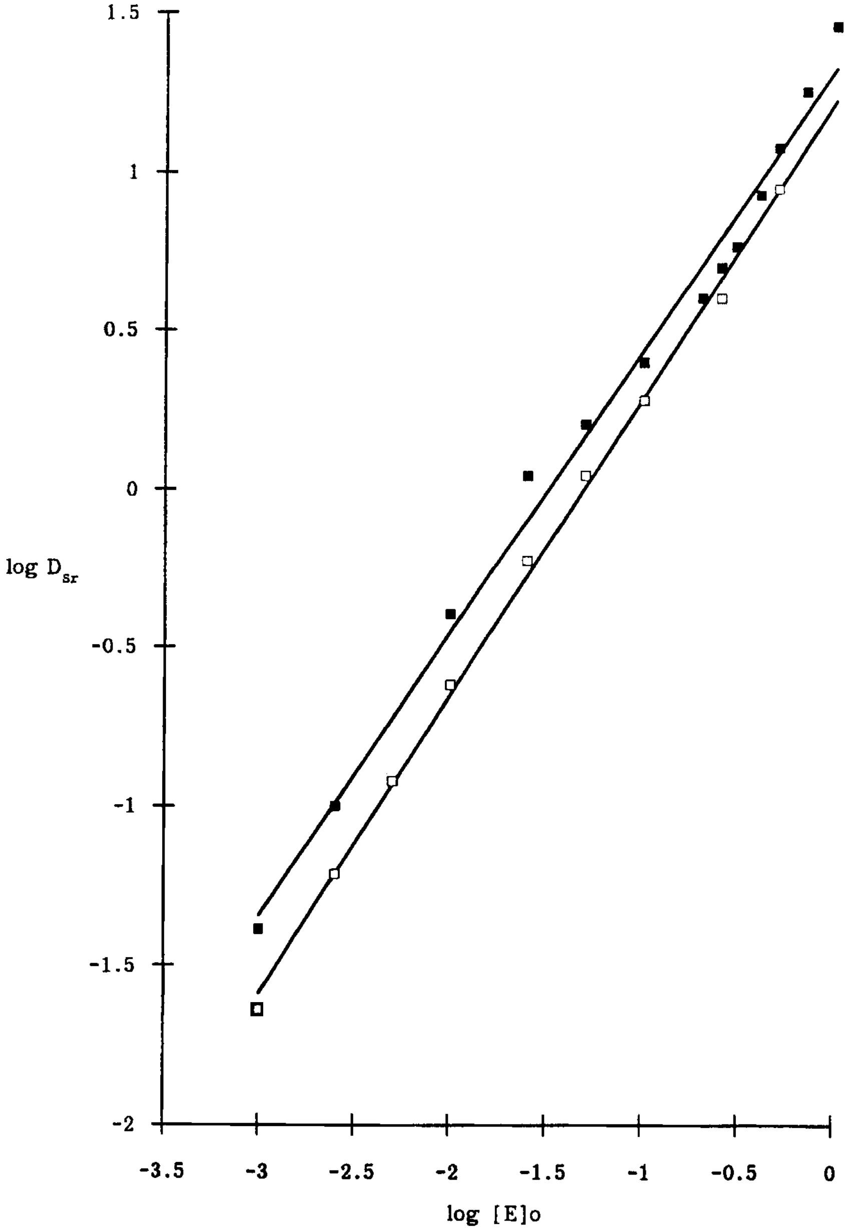


FIG. 3 Distribution coefficients of strontium versus initial crown-ether concentrations in the organic phase for DC18C6 (■) and DtBuC18C6 (□). Solvent: *n*-hexylbenzene (0.7 mol·L^{-1} isotridecanol). Aqueous solution: synthetic concentrate.

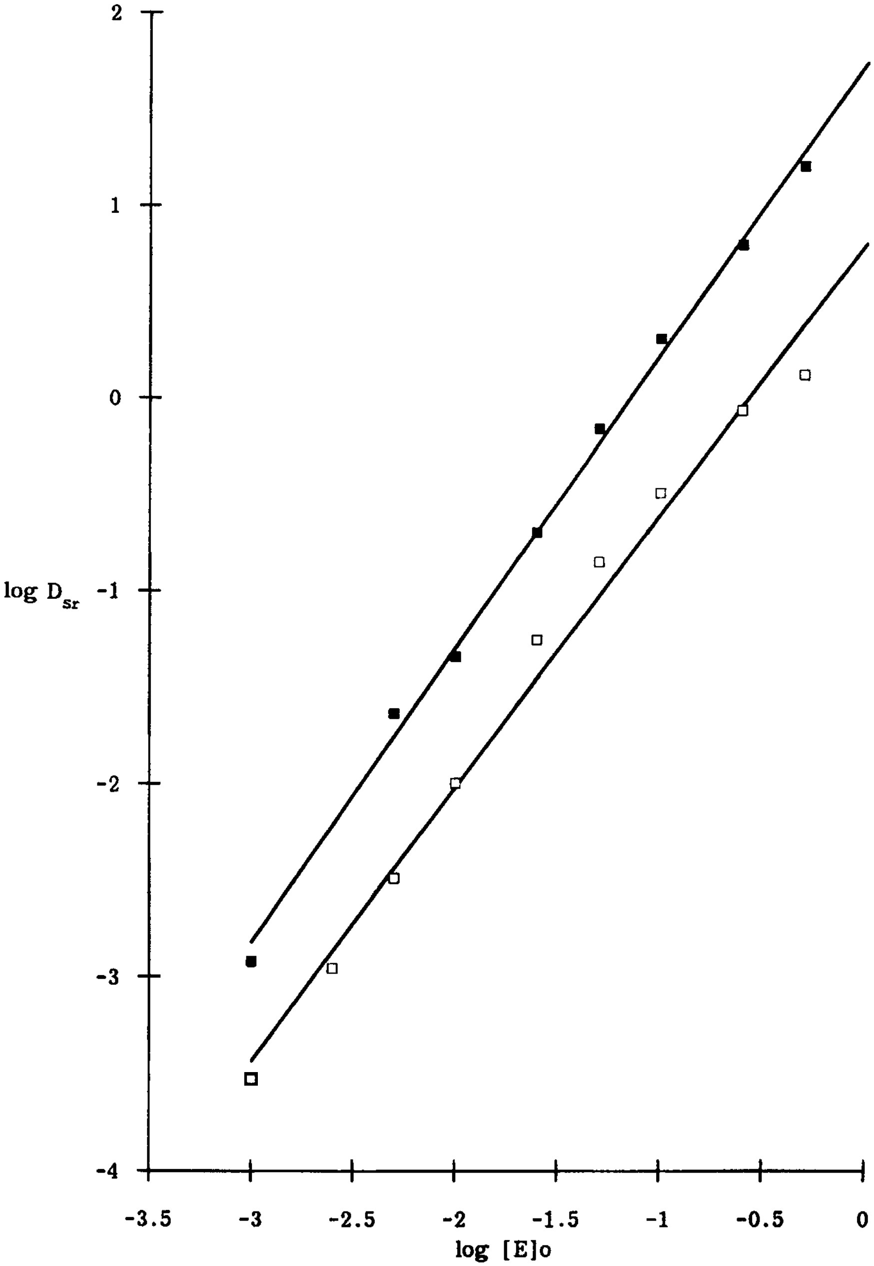


FIG. 4 Distribution coefficients of strontium versus initial crown-ether concentrations in the organic phase for DC18C6 (■) and DtBuC18C6 (□). Solvent: *o*-nitrophenyloctylether. Aqueous solution: synthetic concentrate.

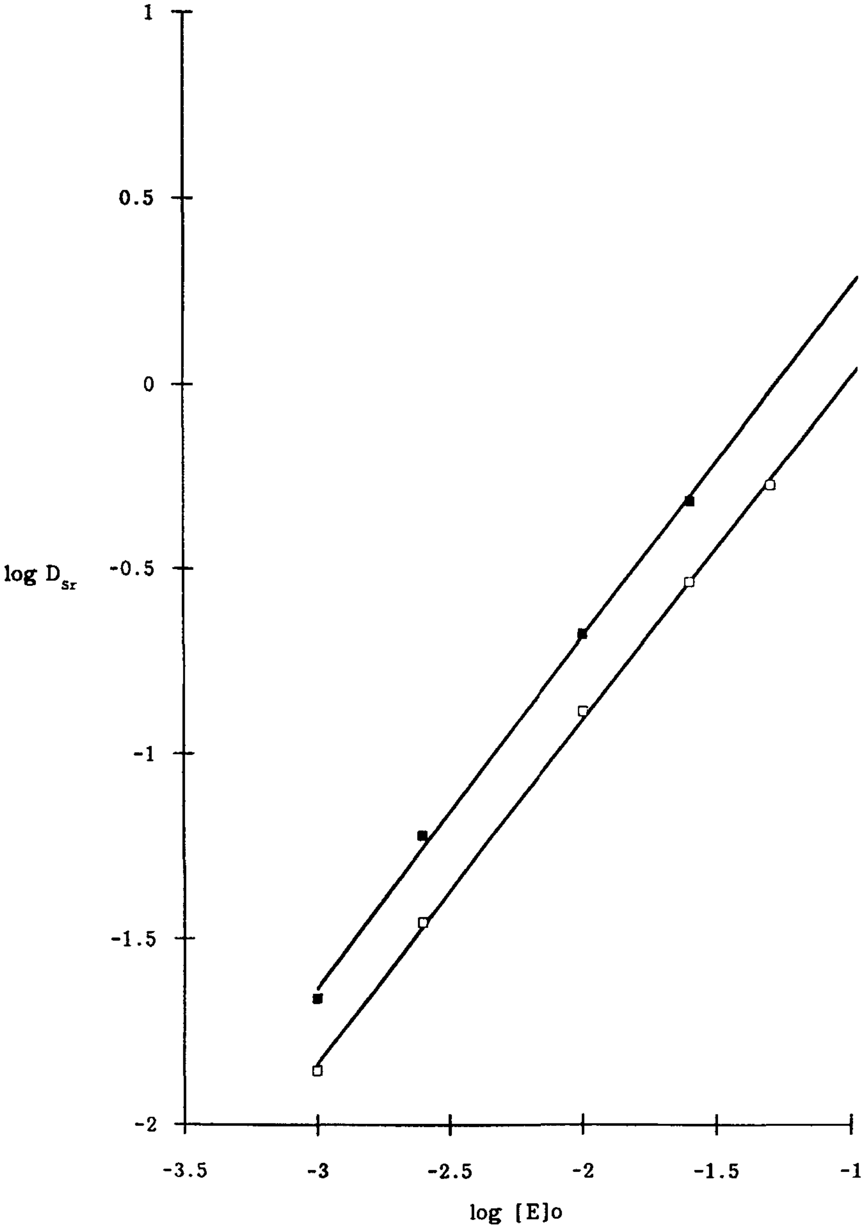


FIG. 5 Distribution coefficients of strontium versus initial crown-ether concentration in the organic phase for DC18C6 (■) and DtBuC18C6 (□). Solvent: *n*-hexylbenzene (0.7 mol·L^{-1} isotridecanol). Aqueous solution: sodium nitrate (4 mol·L^{-1}) + nitric acid (1 mol·L^{-1}).

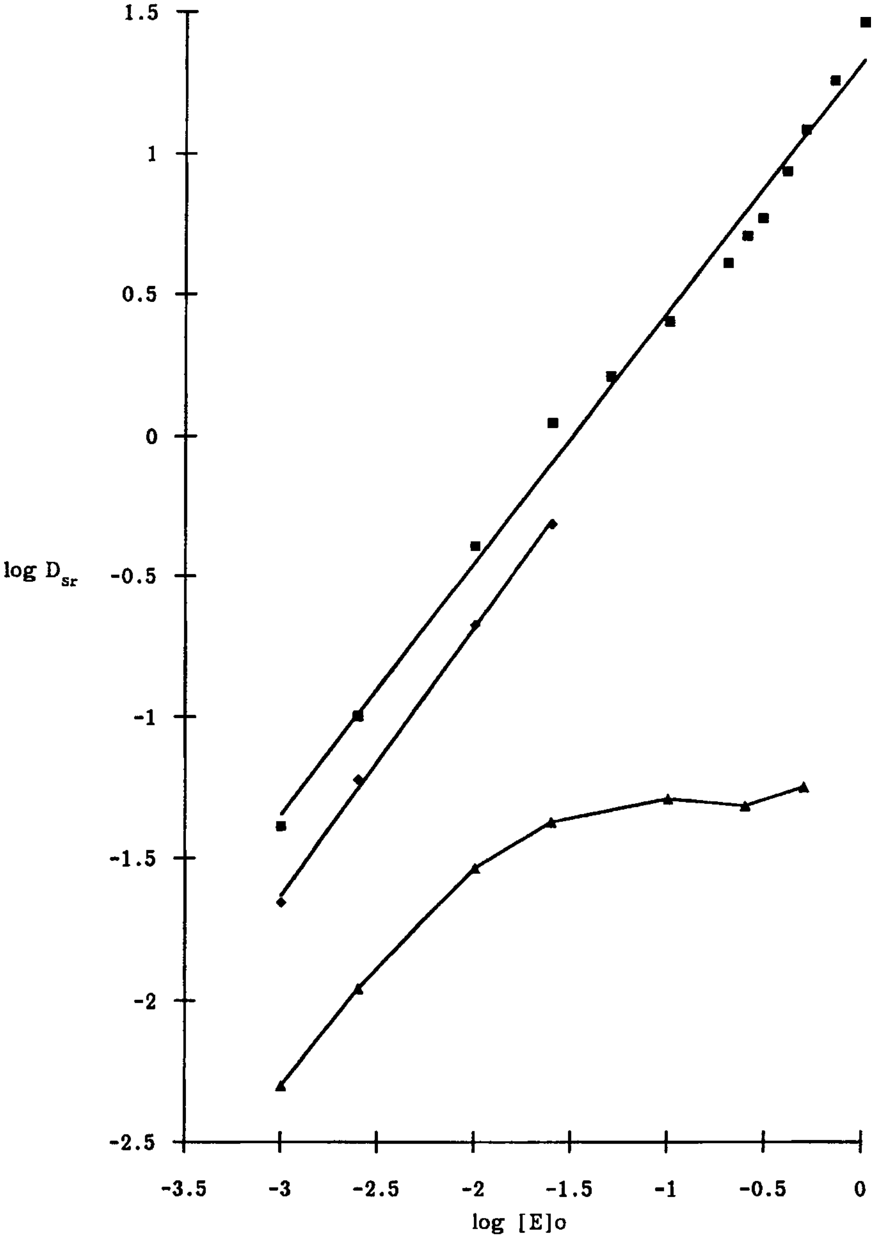


FIG. 6 Influence of the composition of the aqueous solution on the distribution coefficient of strontium. (■) Synthetic concentrate; (◆) sodium nitrate (4 mol·L^{-1}) + nitric acid (1 mol·L^{-1}); (▲) nitric acid (1 mol·L^{-1}). Extractant: DC18C6. Solvent: *n*-hexylbenzene (0.7 mol·L^{-1} isotridecanol).

The results obtained are shown in Table 2. We can see that the distribution coefficients of DtBuC18C6 were approximately 10 times higher than those of DC18C6 due to the greater lipophilic character of the former. We can also observe that the influence of the aqueous solution composition was relatively weak in comparison of the effect of crown-ether lipophilicity. On the other hand, the isotridecanol content in the organic phase led to a considerable increase in the distribution coefficients of the extractant. Finally, the D_E values obtained by both methods were found to be of the same order despite the difficulties in the methods.

Strontium Transport through FSSLMs

Strontium transport through an FSSLM was carried out using each crown ether studied dissolved in *n*-hexylbenzene (0.7 mol·L^{-1} isotridecanol) at a concentration of 0.5 and 0.25 mol·L^{-1} whereas the aqueous feed solution used was, respectively, the synthetic concentrate and a solution consisting of $NaNO_3$ (4 mol·L^{-1}) and HNO_3 (1 mol·L^{-1}). Demineralized water was always used as the aqueous stripping solution. In all cases we determined the strontium permeability of the membrane, as Fig. 7 shows. Under our conditions, strontium permeability (P_{Sr}) can be expressed by the following equation (4):

$$P_{Sr} = \frac{D_{Sr}}{D_{Sr}\Delta_a + \Delta_0} \tag{3}$$

Transport resistance due to diffusion by the aqueous feed boundary (Δ_a) has a value of 0.66 h·cm^{-1}, obtained in previous experiments (35).

TABLE 2

Distribution Coefficients of the Crown Ethers between the Organic and Aqueous Phases

	DC18C6		DtBuC18C6		
Solvent	Demineralized water	Nitric acid (1 M)	Demineralized water	Nitric acid (1 M)	$LiNO_3$ (5.8 M), HNO_3 (1 M)
n-Hexylbenzene			140^a		
n-Hexylbenzene (0.7 M isotridecanol)	59^a 25^b	15^b	200^a 260^b	390^b	320^b
n-Hexylbenzene (1.5 M isotridecanol)	88^a				
o-Nitrophenyloctylether	17^b	9^b			260^b

[a] Visible-UV absorption method.

[b] Spectrometric method.

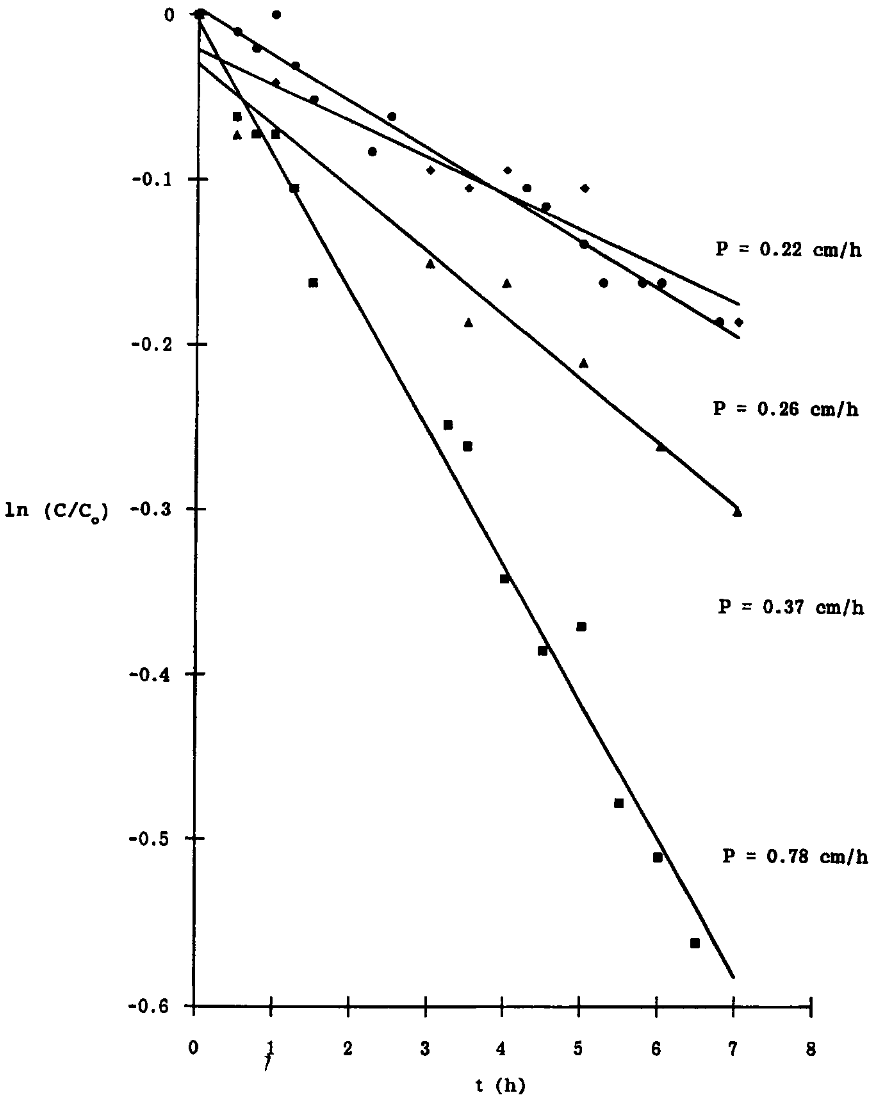


FIG. 7 Influence of the extractant and the composition of the aqueous feed solution on the strontium permeability of the SLM. (■) DC18C6 (0.5 mol·L^{-1})/synthetic concentrate; (◆) DC18C6 (0.5 mol·L^{-1})/sodium nitrate (4 mol·L^{-1}) + nitric acid (1 mol·L^{-1}); (●) DtBuC18C6 (0.5 mol·L^{-1})/synthetic concentrate; (▲) DtBuC18C6 (0.5 mol·L^{-1})/sodium nitrate (4 mol·L^{-1}) + nitric acid (1 mol·L^{-1}). Membrane solvent: *n*-hexylbenzene (0.7 mol·L^{-1} isotridecanol). Aqueous stripping solution: demineralized water.

The transport resistance due to diffusion by the membrane (Δ_0) can be expressed as

$$\Delta_0 = \tau d_0 / D_0 \tag{4}$$

where τ = tortuosity of the support pores
d_0 = thickness of the membrane
D_0 = membrane diffusion coefficient of the strontium-containing species

The value of the support parameters, τ and d_0, are known (2 and 25×10^{-4} cm, respectively). The D_0 value can be evaluated by means of the Wilkie and Chang equation (36):

$$D_0 = \frac{7.4 \times 10^{-8} X^{0.5} T M^{0.5} 3600}{\mu V^{0.6}} \tag{5}$$

where X = association parameter of the solvent (1)
T = absolute temperature (298 K)
M = molecular weight of the solvent (167.45 g·mol^{-1})
μ = dynamic viscosity of the solvent (1.95 cP)

The only parameter of Δ_0 which depends on the extractant nature is the molar volume of the extractant (V). In our case, a V value of 458.6 cm^3·mol^{-1} for DC18C6 and 636.2 cm^3·mol^{-1} for DtBuC18C6 were evaluated using the group contribution method of Le Bas (37). Thus, we found Δ_0 values of 0.38 and 0.46 h·cm^{-1} for DC18C6 and DtBuC18C6, respectively.

To evaluate the strontium permeability, we need to know the distribution coefficient of strontium between the membrane and the aqueous feed solution.

The distribution coefficient can be estimated using the relationship between D_{Sr} and the initial organic concentration of the extractant previously found (Figs. 3 and 5). The real organic concentration of the crown ether in the SLM has been determined taking into account the Sr–crown ether complex in the aqueous phase using the mass balance equation for the crown ether:

$$[E]_{\mathrm{org}} = [E]_{\mathrm{org,tot}}(1 + 2VV_{\mathrm{org}}^{-1}D_{\mathrm{E}}^{-1} + VV_{\mathrm{org}}^{-1}D_{\mathrm{E}}^{-1}K[\mathrm{Sr}^{2+}])^{-1} \tag{6}$$

where V_{org} is the membrane volume measured by weight (the volume ratio VV_{org}^{-1} is 960), $[\mathrm{Sr}^{2+}]$ is the free strontium concentration in the feed solution, and K is the formation constant of Sr–crown ether in aqueous phase.

The value for the Sr–crown ether formation constant used was log K

= 3.2 for both extractants since the macrocycle substituent groups have a minimal effect on cation macrocycle interaction (38).

The D_E values used were the average of all values obtained for each crown ether, 33 and 300 for DC18C6 and DtBuC18C6, respectively.

The estimated D_{Sr} values are shown in Table 3.

Finally, as D_{Sr}, Δ_a, and Δ_0 values were known, the strontium permeability of the membrane was estimated by means of Eq. (3). The results obtained and the experimental values are shown in Table 4.

In addition, calculation of the permeability was performed using the following equation proposed by Izatt et al. (39, 40):

$$J = \frac{D_0 K_{ex}[E]_{org}[\mathrm{Sr(NO_3)_2}]}{\tau d_0(1 + K_{ex}[\mathrm{Sr(NO_3)_2}])} \tag{7}$$

where J is the flux and K_{ex} is the strontium extraction constant, defined as

$$K_{ex} = \frac{[\mathrm{Sr(NO_3)_2}E]_{org}}{[\mathrm{Sr}^{2+}][\mathrm{NO_3^-}]^2[E]_{org}} \tag{8}$$

The values of the extraction constant were evaluated from the ordinate of the straight lines from Figs. 3 and 5, and were found to be log K_{ex} = 1.78 and 0.98 for DC18C6 and DtBuC18C6, respectively.

The values of the permeability calculated from Eq. (7) are given in Table

TABLE 3

Distribution Coefficients of Strontium in the Membrane. Solvent: *n*-Hexylbenzene (0.7 M isotridecanol)

Aqueous phase	Crown ether	Initial concentration of the crown ether in the organic phase (M)	Equilibrium concentration of the crown ether in the organic phase (M)	Distribution coefficient of strontium
Synthetic concentrate	DC18C6	0.5	0.0084	0.31
Sodium nitrate (4 M), nitric acid (1 M)	DC18C6	0.25	0.0038	0.081
Synthetic concentrate	DtBuC18C6	0.5	0.067	1.3
Sodium nitrate (4 M), nitric acid (1 M)	DtBuC18C6	0.25	0.053	0.35

TABLE 4
Evaluated and Experimental Strontium Permeabilities. Solvent: *n*-Hexylbenzene (0.7 M isotridecanol). Aqueous Stripping Solution: Demineralized Water

Aqueous feed solution	Crown ether	Experimental P_{Sr} (cm/h)	Evaluated P_{Sr} (cm/h) from Eq. (3)	Evaluated P_{Sr} (cm/h) from Eq. (7)
Synthetic concentrate	DC18C6 (0.5 M)	0.78	0.53	0.51
$NaNO_3$ (4 M), HNO_3 (1 M)	DC18C6 (0.25 M)	0.22	0.20	0.37
Synthetic concentrate	DtBuC18C6 (0.5 M)	0.26	1.01	1.30
$NaNO_3$ (4 M), HNO_3 (1 M)	DtBuC18C6 (0.25 M)	0.37	0.50	0.44

4. As seen from this table, the values of the evaluated permeability using a model for diffusion-limited transport which involves distribution coefficients (Eq. 3) and extraction constants (Eq. 7) are in good agreement.

According to the estimated values, strontium permeability of DtBuC18C6 is twice the value obtained for the DC18C6 because the D_E values for DtBuC18C6 are larger, which leads to a higher crown ether concentration in the membrane. Thus, DtBuC18C6 must have a higher strontium permeability even though DC18C6 has a greater capacity for strontium extraction and a higher diffusion coefficient in the membrane due to its smaller molar volume. Experimental values of P_{Sr} showed this trend when the aqueous feed solution was the solution comparing only $NaNO_3$ (4 mol·L^{-1}) and HNO_3 (1 mol·L^{-1}). However, higher strontium permeability was found with DC18C6 than with DtBuC18C6 when the synthetic concentrate was used as the aqueous feed solution. The lower value of P_{Sr} obtained with DtBuC18C6 is due to precipitation of a white solid in the aqueous feed solution–membrane interface which probably obstructs the support pores.

In the other cases, the differences between the estimated and experimental values could be due to the uncertainty in the estimation of the diffusion coefficients in the membrane and errors in the determination of the D_E and V_{org} values.

CONCLUSIONS

Although DC18C6 has a greater diffusion coefficient in the organic phase due to its smaller molar volume, and leads to higher D_{Sr} values in a wide range of organic concentrations of crown ethers, faster strontium transport through FSSLMs was obtained with DtBuC18C6 as the extractant due to its greater lipophilic character which led to a concentration in the membrane 10 times higher than with DC18C6. However, the white solid which appears at the synthetic concentrate–organic phase interface when DtBuC18C6 is used must obstruct the support pores because we observed strontium permeability to be much lower than expected. Hence, DC18C6 leads to the highest strontium permeability.

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