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SELECTIVE TRANSPORT OF LEAD(II) AND STRONTIUM(II) THROUGH A CROWN ETHER-BASED POLYMER INCLUSION MEMBRANE CONTAINING DIALKYLNAPHTHALENESULFONIC ACID

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Abstract. New polymer inclusion membranes (PIMs) containing 18-membered crown ethers and dialkylnaphthalenesulfonic acid are proposed for Sr^{2+} and Pb^{2+} removal from nitric acid solutions. The influence of source phase composition and stripping agents was characterized and permeability coefficients were calculated. The PIMs are easy to prepare and may be useful in separation and concentration procedures for these cations from complex mixtures such as nuclear waste. Long-term stability was obtained for at least several weeks of constant use during which no significant change of permeability was observed.

Key words. Crown ether, polymer inclusion membrane, strontium(II), lead(II).

1. Introduction

The separation of Pb and ^{90}Sr from acidic media is an important problem in nuclear waste processing. Numerous procedures based on the methods of solvent extraction [1,2], ion exchange [2], and membrane transport [3] have been developed. Some of these are based on the use of crown ethers as selective reagents for Sr^{2+} and Pb^{2+} recognition.

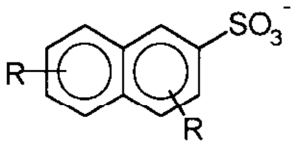
Recently we have proposed a procedure for Pb^{2+} removal using polymer inclusion membranes (PIMs). These membranes are based on cellulose triacetate (CTA) polymer as a support, together with a hydrophobic non-volatile organic solvent (*e.g.*, o-nitrophenyl octyl ether) as plasticizer, and a cation carrier molecule [4-9]. In these systems, the rate of metal ion transfer increases with an increase in counterion hydrophobicity [10]. This result suggests the use of highly hydrophobic counterions in the membrane. It is further possible that such additives may function as effective synergistic agents to improve membrane performance, especially if the counterion has complexing properties of his own.

Here we report the synergistic membrane transport of Sr^{2+} and Pb^{2+} by PIMs which contain different crown ethers in the presence of membrane-bound dialkylnaphthalenesulfonic acid. The properties of similar membranes containing only the crown ether dicyclohexano-18-crown-6 were reported previously [10].

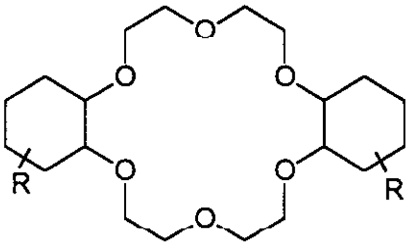
2. Experimental

2.1. MATERIALS

Crown ethers dicyclohexano-18-crown-6 (DC18C6, a mixture of the cis-syn-cis and cis-anti-cis isomers, Aldrich) and bis[4(5)-tert-butylcyclohexano]-18-crown-6 (t-BuDC18C6, a mixture of isomers, Lancaster) were used as received from the manufacturers. Dinonylnaphthalenesulfonic acid (DNNS) was obtained from Alfa as a 50% solution in heptane. The heptane was removed by vacuum evaporation, and the remaining acid was dissolved in methylene chloride. This solution was titrated against alcoholic NaOH. The titrated concentration value was used for the preparation of stock solutions of DNNS in methylene chloride. Didodecylnaphthalenesulfonic acid (DDNS, King Industries, commercial name SYNEX DD-252) was received as a 50% solution in refined kerosene. A procedure similar to that employed for DNNS was used for the preparation of solutions of known concentration in methylene chloride.



R = C_9H_9 (nonyl)
R = $C_{12}H_{25}$ (dodecyl)



R= H DC18C6
R=t-Bu t-BuDC18C6

o-Nitrophenyl octyl ether (NOE) and dioctyl terephthalate (DOTP) were tested as plasticizers with high (ca. 25) and low (ca.5) dielectric constants, respectively. Distilled deionized water of 15 MΩ resistivity (Millipore) was used for the preparation of all aqueous solutions.

Metal nitrate solutions were prepared from Analytical Grade reagents. Nitric acid (Mallinckrodt) solutions were standardized by titration with standard NaOH solution (Fisher). The compositions of the nuclear waste mimics used in this work are shown in Table I.

2.2. PREPARATION OF POLYMER INCLUSION MEMBRANES

NOE (1.00 mL) was mixed with 4.00 mL of a 0.10 M crown ether solution in CH_2Cl_2. To the resulting solution, 0.17 mL of 50% DNNS in CH_2Cl_2 and 20 mL of 1.25% CTA in CH_2Cl_2 were added. A 5.0 mL aliquot of this solution was evaporated slowly in a 90-mm diameter flat dish (bottom formed of plate glass) which was covered by a watch glass. The resulting membrane can be assumed to be a 0.3 M solution of crown ether and 0.1 M solution of DNNS in a viscous (4:1) NOE/CTA solvent. A similar procedure was used for preparation of membranes with different compositions.

Table I. Nuclear Waste Simulants

Ion	Sodium Mixture (mM)	Aluminum Mixture (mM)
Acidity (H^+)	1000	1000
Al^{3+}	0	1000
Na^+	1000	0.02
Pb^{2+}	0.1	0.1
NO_3^-	2000	4000
Sr^{2+}	0.05	0.05

2.3. MEMBRANE TRANSPORT EXPERIMENTS

The transparent polymer film (PIM) was placed between two cylindrical 200 mL glass vessels. The total membrane area exposed to the aqueous phases was 20 cm^2. Both source and receiving aqueous solutions were stirred with glass stirrers at 600 rpm by synchronous motors. The initial concentrations of Pb(II) and Sr(II) in the source phase were 0.10 and 0.05 mM respectively. Samples (1-2 mL) were periodically removed with a glass pipette and analyzed for metal ion concentration with a Perkin-Elmer ICP Plasma II Spectrometer.

3. Results and Discussion

The kinetics of the transport process may be described within the observed experimental standard deviation by Equation 1 as a first-order reaction in metal ion concentration for both Sr^{2+} and Pb^{2+} transport.

$$\ln(C_s/C_0) = -(PS/V)t \qquad (1)$$

Here, C_o is the initial total concentration of the cation in the source phase, C_s is the total concentration of metal species in the source phase as a function of time t, V is the volume of the source phase, and S is the membrane area. Permeability coefficients P were calculated by plotting the logarithm of C_s/C_o vs t. First order kinetic plots of six transport experiments are shown in Figure 1.

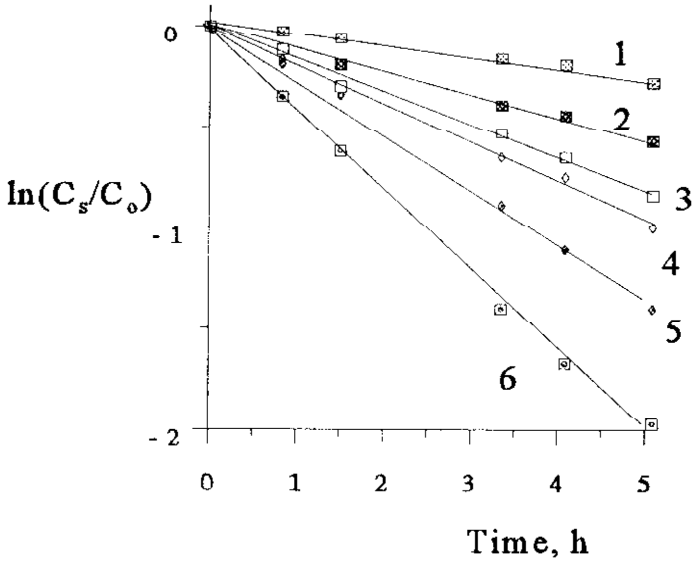


Figure 1. First-order kinetic plots of Sr^{2+} transport through a DC18C6/DDNS membrane. Plasticizer: NOE - runs 2,4,6; DOTP - runs 1,3,5. Source phase: 0.3 M HNO_3 and 0.5 M $NaNO_3$ (runs 1,2), 0.1 M HNO_3 and 0.5 M $NaNO_3$ (runs 3,4), 0.5 M $NaNO_3$ (runs 5,6).

3.1. DIALKYLNAPHTHALENESUFONATE MEMBRANES

Membranes containing 8% DNNS but no macrocyclic carrier provided detectable transport of Sr^{2+} ions from neutral or weakly acidic solutions into a 1 M HNO_3 receiving phase. Permeability coefficients were between 2×10^{-6} and 4×10^{-6} m/s depending upon the percentage of DNNS in the membrane and decreased significantly with increasing source phase acidity. Those with 8% DNNS were stable for at least several days of continuous use. Increasing the DNNS content to 50% improved permeability, but the resulting membranes were unstable and failed in a couple of hours.

3.2. DIALKYLNAPHTHALENESUFONATE - CROWN ETHER MEMBRANES

Incorporation of the crown ether DC18C6 into a PIM containing DDNS or DNNS dramatically improved the permeability of Sr^{2+} (Figures 2 and 3), in the best cases from 4×10^{-6} m/s up to 30×10^{-6}m/s. The DC18C6/DNNS/NOE membranes facilitated removal of 99% of the Sr^{2+} from the source phase (originally 0.050 mM) into the receiving phase within several hours. When the same membrane was reused with new source and receiving solutions, there was a detectable decrease in transport from the first experiment, due to loss of macrocyclic carrier to the aqueous phases. However, even after 5 such changes, permeability was still much higher than that of the dinonylnaphthalenesulfonate membranes without macrocyclic carrier. When DC18C6 was used in NOE-containing PIMs without dialkylnaphthalenesulfonic acid, a second use of the same membrane showed a 80-90% decrease of the M^{2+} flux. This result suggests that dinonylnaphthalenesulfonic acid decreases the macrocyclic carrier loss because of association with crown ether in the organic phase.

Use of o-nitrophenyl octyl ether (NOE) as plasticizer provided better transport than dioctyl terephthalate (DOTP) (see Figure 1). Therefore, NOE was used in all further experiments.

The use of HNO_3 as the receiving solution did not permit transport of metal ions from strong acidic media. Therefore, 0.05 M Na_4EDTA was adopted as a receiving solution (Figure 3). The use of EDTA actually improved transport rates a little, but simultaneously decreased the stability of the membrane. In this system, the membrane could be used only a few times. (Compare the permeabilities for consecutive reuse of a membrane with an acid receiving phase (Figure 2) with an EDTA receiving phase(Figure 3)).

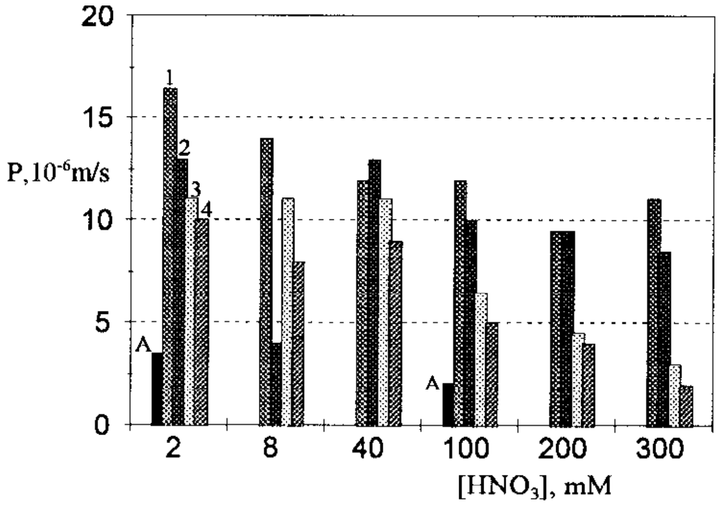


Figure 2. Permeabilities in consecutive runs (1-4) *vs* the acidity of the source phase for Sr^{2+} transport through a DC18C6/DNNS/NOE PIM. A- run for an analagous PIM without DC18C6. Receiving phase: 1 M HNO_3.

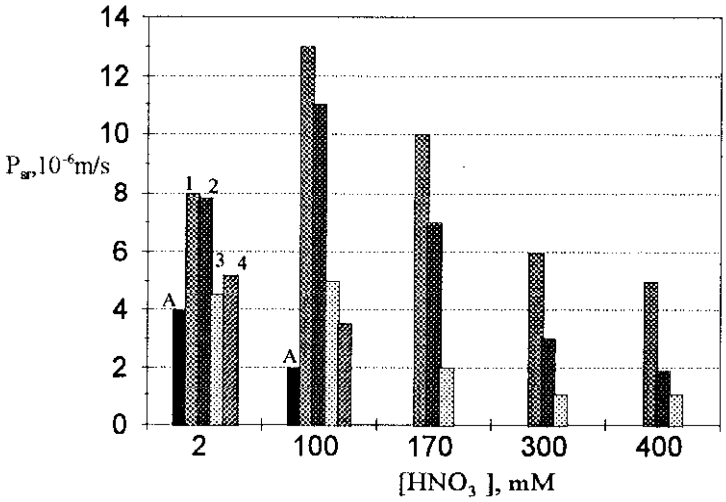


Figure 3. Permeabilities in consecutive runs (1-4) *vs* the acidity of the source phase for Sr^{2+} transport through a DC18C6/DNNS/NOE PIM. A- run for an analogous PIM without DC18C6. Receiving phase: 50 mM Na_4EDTA.

The problem associated with loss of membrane permeability upon reuse was resolved by use of t-BuDC18C6 instead of DC18C6 as a macrocyclic carrier. The resulting membranes are stable for at least several weeks of continuous use and exhibit the same flux after numerous uses (Figure 4). The use of both HNO_3 and Na_4EDTA in the receiving phase is possible (Figure 5).

The combination of a crown ether with DNNS in the membrane also significantly improved the sorption of metal ions when the PIM material was used as a solid extractant. An increase in the concentration of nitric acid and/or different nitrates in the source phase suppressed the sorption of Pb^{2+} and Sr^{2+}, but even at high nitrate concentration the distribution ratios remained high (Table II).

Table II. Distribution ratios (K_d) for Pb^{2+} and Sr^{2+} sorption by DC18C6/DNNS/NOE PIM.

$[HNO_3]$,M	log K_d	
	Pb^{2+}	Sr^{2+}
0	>3.9	>3.7
0.3	3.21	2.88
0.6	2.64	2.54
0.9	2.27	
1.2	2.04	
1.5	1.93	1.8[a]

a) From sodium mixture nuclear waste simulant (see Table I)

A counter-transport mechanism [3] can be used to describe membrane transport of metal ions from water into HNO_3 in the PIM system. In this case, the difference in distribution ratios of the metal ion between the source and receiving interfaces is achieved by the proton concentration gradient between the two phases. While the metal ions are moving from a less acidic solution into a more acidic one, protons are simultaneously transported in the opposite direction, following the proton concentration gradient:

$$M^{2+}_s + 2\,HDNNS_{PIM} + DC18C6_{PIM} \rightleftharpoons [M\,(DC18C6)(DNNS)_2]_{PIM} + 2\,H^+_s \quad \text{(source interface)}$$

$$[M\,(DC18C6)(DNNS)_2]_{PIM} + 2H^+_r \rightleftharpoons M^{2+}_r + 2HDNNS_{PIM} + DC18C6_{PIM} \quad \text{(receiving interface)}$$

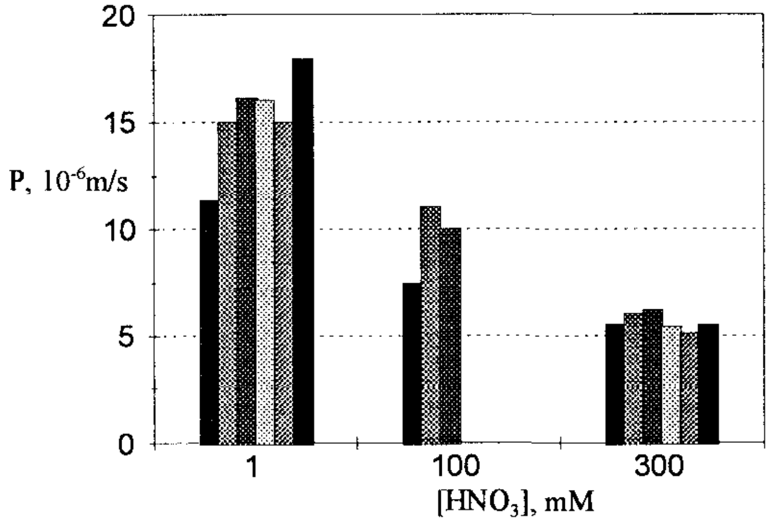


Figure 4. Permeabilities in consecutive runs versus the acidity of the source phase for Sr^{2+} transport through a t-BuDC18C6/DNNS/NOE PIM. Receiving phase: 1 M HNO_3.

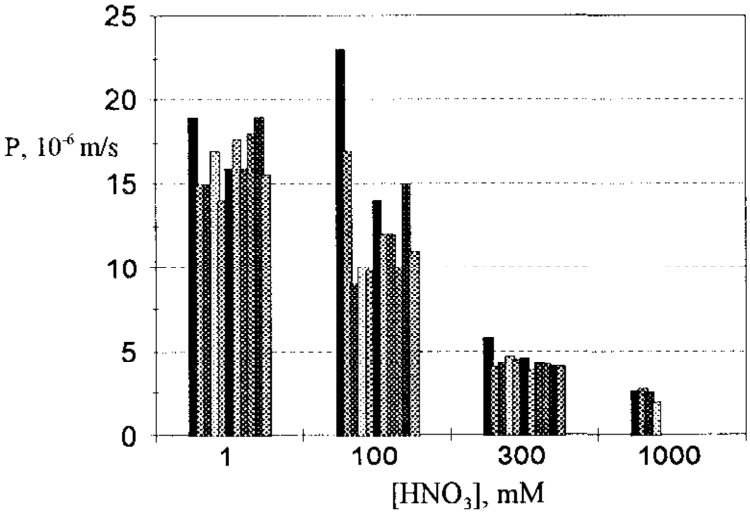


Figure 5. Permeabilities in consecutive runs versus the acidity of the source phase for Sr^{2+} transport through a t-BuDC18C6/DNNS/NOE PIM. Receiving phase: 50 mM Na_4EDTA.

Transport rate is limited by the rate of diffusion of $[M(DC18C6)(DNNS)_2]$ through the PIM.

3.3. t-BuDC18C6 MEMBRANES

Because of its extremely low solubility in water t-BuDC18C6, unlike DC18C6, can be used for membrane preparation without DNNS. Under these conditions, pure water can be used as a receiving phase. The transport mechanism can be described as formation of a neutral complex ion pair with the source phase anion at the source phase interface of the membrane, its diffusion to the receiving phase interface, followed by complete dissociation of the complex into the receiving phase. A high counterion concentration in the source phase provides the driving force for transport in this case (the so called co-transport mechanism).

$$M^{2+}{}_s + 2A^-{}_s + \text{t-BuDC18C6}_{PIM} \rightleftarrows [M(\text{t-BuDC18C6})A_2]_{PIM} \rightarrow \\ M^{2+}{}_r + 2A^-{}_r + \text{t-BuDC18C6}_{PIM}$$

Increased extraction of the metal ion by the PIM from the source phase produces a higher concentration at the source phase side of the membrane and concommitantly a higher flux through the membrane. This mechanism suggests a correlation between the sorption and transport properties of the PIM as has been demonstrated [10].

One attractive feature of t-BuDC18C6 PIMs is their stability. In our lab, they have been used for one month of continuous operation (Figure 6). Permeabilities are quite high for Pb^{2+} while those for Sr^{2+} are significantly lower (Table III) indicating excellent selectivity for Pb^{2+}.

These data are in a good agreement with results from sorption experiments using the same t-BuDC18C6/NOE membrane material (Table IV). All of the distribution ratios are much higher for lead compounds. This observation supports the proposed mechanism of ion transport.

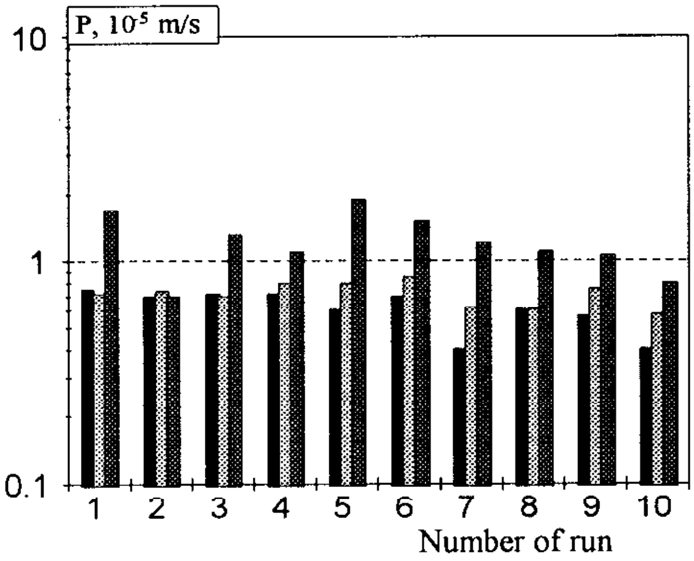


Figure 6. Long-term experiment (20 days). Pb^{2+} permeabilities through t-BuDC18C6/NOE PIMs versus the run number. Receiving phase: pure water. Source phase: 0.1 M (left bar), 0.2 M(middle), 0.3 M (right) $NaNO_3$.

Table III. Permeabilities of Pb^{2+} through t-BuDC18C6/NOE membranes

Counter-ion	P, 10^{-6} m/s
I^-	23
Br^-	15
SCN^-	20
NO_3^- (0.3M $NaNO_3$)	17
NO_3^-(a)	6.2
NO_3^-(b)	9.5

Permeabilities of Sr^{2+} through t-BuDC18C6/NOE membranes

Counterion	P, 10^{-6} m/s
NO_3^-(a)	1.5
NO_3^-(0.3M $NaNO_3$)	0.5

a)Aluminum mixture nuclear waste simulant(Table I) b) Sodium mixture nuclear waste simulant(Table I)

Table IV. Distribution ratios (K_d) for Pb^{2+} and Sr^{2+} sorption by t-BuDC18C6/NOE PIM

$[HNO_3]$,M	log K_d	
	Pb	Sr
0.16	3.4	1.0
0.32	2.8	0.9
0.48	2.9	
0.64	2.8	1.3
0.83	2.9	
1.28	2.9	1.5

4. Conclusions

Polymer inclusion membranes containing dialkylnaphthalenesulfonic acid and a hydrophobic 18-membered crown ether as carrier show stable and high fluxes of Sr^{2+} and Pb^{2+} ions from nitric acid solution into various stripping solutions. A counter-transport mechanism describes the process with strong HNO_3 as a stripping solution, while a co-transport model is sufficient for neutral and alkaline stripping solutions. Experiments using nuclear waste simulants demonstrate the potential to recover target metal ions. The possible use of PIMs as solid sorbents has been demonstrated.

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