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Selective Metal Ion Sorption and Transport Using Polymer Inclusion Membranes Containing Dicyclohexano-18-crown-6

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ABSTRACT

A novel polymer material composed of cellulose triacetate as support, *o*-nitrophenyl octyl ether as plasticizer (solvent), and dicyclohexano-18-crown-6 as carrier was investigated as a solid extractant for metal ion sorption and as a membrane material for ion transport. Selective extraction and transport of Pb(II), Ga(III), and Fe(III) were observed. The influence of the source solution counterion on sorption and transport processes was investigated. The transport mechanism is discussed in terms of diffusion coefficients (D) and extraction constants (K_1). A diffusion-limited transport model has been found to accurately describe metal ion transport by dicyclohexano-18-crown-6 in these systems. The membranes are easy to prepare in the laboratory, and they may be useful in separation and concentration procedures.

INTRODUCTION

Recently we showed the possibility of membrane transport of alkali metals through polymer inclusion membranes (PIMs) containing cellulose triacetate polymer (CTA) as support, a liquid plasticizer, and dicyclohexano-18-crown-6 as a carrier (1). The plasticizer in the membrane acts as an organic solvent similar to that used in liquid extraction systems. Since they were originally proposed, cellulose triacetate films with different plasticizers have been shown to have numerous potential applications (e.g., Ref. 2). They have also been used (3–6) for metal ion transport and determination.

Two main mechanisms of metal ion reactions with crown ethers are known.

1. The crown ether incorporates the metal ion inside its cavity, forming a hydrophobic coating which enables the extraction of the resulting complex cation into an organic phase. For 18-membered crown ethers, Pb^{2+} ion forms the most stable complexes and is preferentially extracted (7, 8).
2. The crown ether molecule solvates a neutral compound or an ion pair, forming a lipophilic associate, and does not incorporate the metal ion. This situation occurs in the case of some *p*-block and transition metal ions, e.g., Fe(III) and Ga(III).

It was of special interest to study the ability of PIMs to extract metal ions by means of both the above-mentioned mechanisms. In this study the PIMs were utilized for metal ion sorption from aqueous solution and for carrier-enhanced selective transport of metal ions between aqueous phases. Based on the results of previous solvent extraction studies (7–10), Pb(II) complexes with different anions and chloride complexes of Fe(III) and Ga(III) were chosen for study.

EXPERIMENTAL

Dicyclohexano-18-crown-6 was purchased from Aldrich as a mixture of cis-syn-cis and cis-anti-cis isomers, and was used without further purification. Cellulose triacetate and *o*-nitrophenyl octyl ether (NOE) were also from Aldrich. HPLC Grade methylene chloride was used for polymer solution preparation. No detectable amount of the latter was found in the prepared PIMs when they were analyzed by proton NMR.

Solution Preparation

Metal nitrate and sodium halogenide solutions were prepared from Analytical Grade reagents. Hydrochloric acid (Mallinckrodt) and picric acid (Aldrich) solutions were standardized by titration with standard NaOH solution (Fisher Scientific).

Solid Extractant and Polymer Inclusion Membrane Preparation

The CTA-NOE membrane was prepared in a fashion similar to the reported procedure (1). 0.2 mL of NOE was mixed with 0.8 mL of CH_2Cl_2

solution of crown ether (usually 0.1 M). To the resulting solution, 4 mL of 1.25% CTA solution in CH_2Cl_2 was added, and the whole mixture was evaporated slowly at atmospheric pressure in a 90-mm diameter flat dish covered by a watch glass to remove CH_2Cl_2. The resulting membrane contained 76% NOE, 18% CTA, and 6–7% DC18C6, and can be assumed to be a 0.32 M solution of DC18C6 in a viscous (4:1) NOE/CTA solvent (assuming that all CH_2Cl_2 was evaporated and all other components remained in the membrane material).

Membrane Transport Experiments

The transparent polymer film 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), Ga(III), and Fe(III) in the source phase were 1.0–0.05 mM. Samples (1–2 mL) were periodically taken by glass pipet.

Sorption Experiments

These were performed in the batch mode, using 0.30–0.50 g of solid extractant material (PIM) and 25.0 mL of aqueous solution containing metal ions with some lithium or sodium salt of the appropriate anion added. In all experiments the initial total metal concentration was 0.1–0.8 mM (0.04 mM for PbI_2 sorption), which allowed for an excess of macrocycle in the system. The whole system was left overnight (ca. 15 hours) after gentle shaking and then analyzed. Distribution ratios, $k_d = C_{org}/C_{aq}$ (in g/mL), were calculated.

Analysis to determine the metal ion concentration in both sorption and membrane experiments was performed on a Perkin-Elmer ICP Plasma II Spectrometer.

RESULTS AND DISCUSSION

Sorption

Crown-containing PIMs served to extract metal ions effectively in a fashion comparable to that observed with the usual liquid–liquid extraction systems (e.g., with chloroform as a solvent). Quantitative ($k_d > 10^4$) extraction of Pb(II) was observed from picrate solutions, while partial sorption of Pb(II) was observed from nitrate, bromide, iodide, and thiocyanate solutions (Fig. 1). The same order of extraction ability was observed for lead complex extraction with DC18C6 in chloroform (7). After sorption

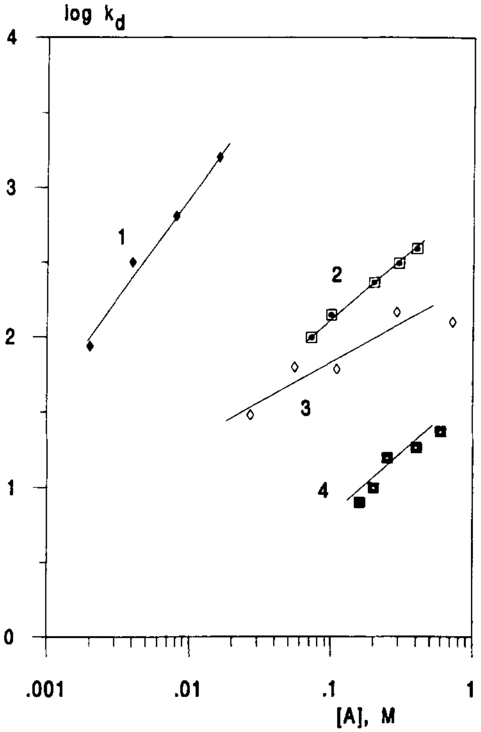

FIG. 1 Distribution of lead species between PIM and aqueous phase vs anion concentration in aqueous phase. V_{aq} = 25 mL. Organic (PIM) phase: 0.32 M DC18C6 in 4:1 w/w NOE/CTA, m = 0.3–0.5g. Distribution ratio $k_d = C_{org}/C_{aq}$ in mL/g. A: (1) I^-, (2) SCN^-, (3) Br^-, (4) NO_3^-.

by PIM, nearly all the lead (>96%) was stripped out of the sorbent with EDTA solution.

The distribution of neutral lead complex between organic and aqueous phases can be described using an extraction constant K_1 as follows:

$$PbA_{2aq} + DC18C6 \leftrightarrows Pb(DC18C6)A_{2org} \qquad (1)$$

$$K_1 = [Pb(DC18C6)A_2]_{org}/[PbA_2]_{aq}[DC18C6]_{org}$$

The concentration of PbA_2 in the aqueous phase can be calculated for known total concentration of lead, C_{Pb}, using stability constant values and counterion concentration [A]:

$$[PbA_2]_{aq} = \alpha_2 C_{Pb} = C_{Pb} \frac{\beta_2[A]^2}{1 + \sum_{i=1}^{N} \beta_i[A]^i} \qquad (2)$$

where α_2 represents the partial fraction of neutral PbA_2 complex, and β_i is the stability constant of the PbA_i complex. Using known β_i values from Ref. 11, α_2 values were obtained and extraction constants K_1 were calculated. An activity correction μ was applied using the extended Debye–Huckel equation for activity coefficients γ_i in approximate form:

$$\log \gamma_i = -0.51Z^2\sqrt{\mu}/(1 + 1.6\sqrt{\mu}) \tag{3}$$

Because of the high dielectric constant of NOE, there is the possibility of PbA_2 dissociation in the organic phase. From solvent extraction experiments and x-ray structural data, it is known that $Pb(DC18C6)^{2+}$ cation forms stable complexes with nitrate, thiocyanate, and halides, where Pb–A interactions are stronger than just electrostatic attraction (7). These results confirm that we can neglect the dissociation of these compounds under our experimental conditions (at least as a first approximation).

Representative results of calculations for $Pb(NO_3)_2$ and $Pb(SCN)_2$, determined from these data at various anion concentrations, are shown in Table 1. The resulting log K_1 values for all anions are collected in Table 2. They change in the same order as extraction constants K_{ex} for common

TABLE 1
Determination of Extraction Constant K_1 of Pb(II) Compounds.
$[DC18C6]_0 = 0.32$ M
$Pb(NO_3)_2$ $\log \beta_1 = 1.17$, $\log \beta_2 = 1.4$ (11)

$[NO_3^-]$, M	log k_d	$-\log \alpha_2$	log K_1
0.16	1.04	1.31	2.85
0.19	0.91	1.25	2.66
0.20	1.09	1.23	2.82
0.25	1.22	1.14	2.85
0.40	1.33	0.98	2.81
0.60	1.43	0.85	2.78
0.61	1.45	0.85	2.80

$Pb(SCN)_2$ $\log \beta_1 = 1.08$, $\log \beta_2 = 1.48$, $\log \beta_3 = 1.5$ (11)

$[SCN^-]$, M	log k_d	$-\log \alpha_2$	log K_1
0.012	0.85	2.69	4.04
0.072	2.02	1.57	4.09
0.10	2.16	1.41	3.98
0.20	2.37	1.11	3.94
0.30	2.48	0.96	3.94
0.40	2.60	0.87	3.97

TABLE 2
Extraction Constants of Pb(II) Complexes with DC18C6

Compound	log K_1[b]	log β_2 [11]	log K_{cx}(PIM)[a]	log K_{cx}($CHCl_3$)[a] (7a)
$Pb(NO_3)_2$	2.80 (7)	1.4	4.2	6.6
$PbBr_2$	3.3 (1)	2.6	5.9	8.4
$Pb(SCN)_2$	4.01 (8)	1.5	6.5	8.5
PbI_2	4.8 (1)	3.2	8.0	11.4
Pb(picrate)$_2$	>5[c]	?	>10	12.1

[a] $K_{cx} = [PbDC18C6A_2]_{org}/[[Pb^{2+}]_{aq}[DC18C6]_{org}[A^-]^2_{aq}$.
[b] Standard deviation in parentheses.
[c] Log k_d, at [picrate] > 1 mM.

solvents like chloroform using DC18C6 as extractant:

$$NO_3^- < Br^- < SCN^- < I^- < \text{picrate}$$

This enables us to suggest that the structure and properties of Pb^{2+}–DC18C6 complexes in the PIM material are the same as in known extraction systems. The crown ether incorporates Pb^{2+} into its cavity, and two counterions are coordinated in axial positions, forming a lipophilic neutral complex which is suitable for transfer into the organic phase. Thus, the degree of extraction increases with the hydrophobicity of the anion.

Crown complexes which form through a solvation mechanism without incorporating the metal ion in the macrocycle cavity were also extractable into the PIM solvent. Good sorption of Fe(III) and Ga(III) was observed from HCl solutions of various concentrations (Fig. 2). Distribution coefficients k_d increased with HCl concentration in a fashion similar to that observed with other extraction systems using DC18C6 as extractant and chloroform as solvent (9, 10). The degree of sorption coincided with the existence of anionic chloride complexes of Fe(III) and Ga(III). Some higher k_d values were obtained in our experiments compared to solvent extraction with chloroform (9, 10), which leads us to propose that PIMs are also convenient for metal ion extraction via a solvation mechanism (Mechanism 2 from the Introduction).

Because of an uncertainty in the stability constants at high HCl concentrations, no attempts to calculate the actual values of extraction constants were made in these cases. The solvation of the $H_3O^+MCl_4^-$ ion pair or MCl_3 neutral complex by the DC18C6 molecule, forming $[DC18C6{\cdot}H_3O^+]MCl_4^-$ or DC18C6·MCl_3 solvates, can be proposed as a possible explanation of this extraction process.

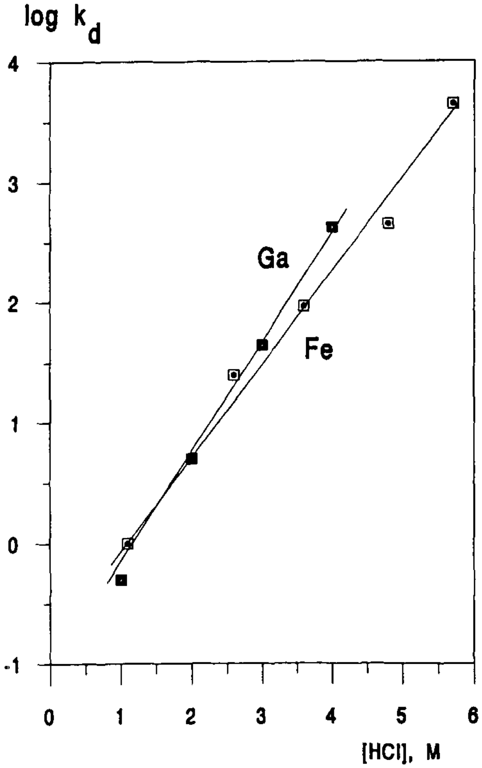

FIG. 2 Distribution of Ga(III) and Fe(III) between PIM and HCl solutions. V_{aq} = 25 mL. Organic (PIM) phase: 0.32 M DC18C6 in 4:1 NOE/CTA, m = 0.3–0.5g. Distribution ratio $k_d = C_{org}/C_{aq}$ in mL/g.

While Ga(III) can easily be stripped out of the sorbent using pure water, stripping of Fe(III) was difficult even with EDTA solution because of the formation of a rusty layer of Fe(III) hydroxo complexes at the stripping side of the membrane. Satisfactory stripping of Fe(III) was performed by dilute (ca. 0.2 M) HCl solution.

Membrane Transport

The same metal ions which may be extracted into the PIM when used as a solid extractant were transferred through the PIM when used as a membrane. The kinetics of the transport process may be described within the observed experimental standard deviation as a first-order reaction in metal ion concentration (Fig. 3).

$$J = kC_sV/S \tag{4}$$

where J is the metal ion flux, k is the first-order reaction rate constant for the transport process, C_g is the total concentration of metal species in the source solution as a function of time t, V is the source solution volume, and S is the membrane area. Permeability coefficients, $P = J/C_s$, were calculated from the first-order kinetic rate constants by plotting the logarithm of C_s/C_0 vs time:

$$\ln(C_s/C_0) = -kt \tag{5}$$

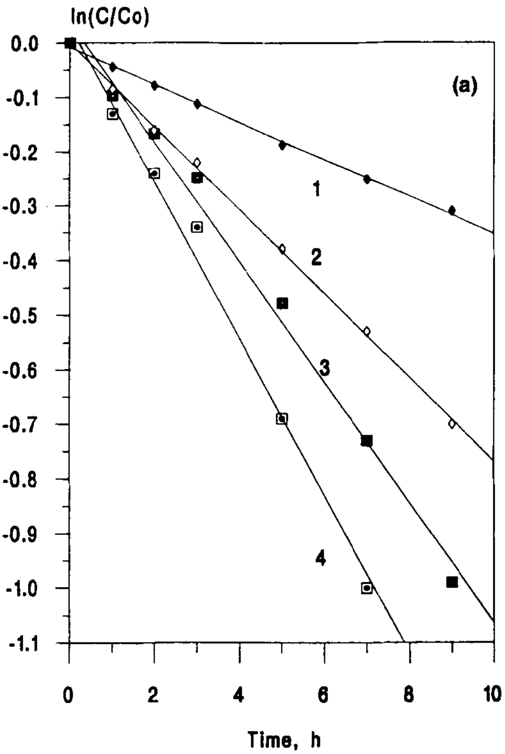

FIG. 3 First-order kinetics of metal complex transport through PIMs. (a) Pb(II) transport from picrate solutions. 5 mM EDTA in receiving phase, equal concentrations of picrate ion in both source and receiving phases [Picr], mM: (1) 0.5, (2) 1.0, (3) 2.5, (4) 4.0. (b) Ga(III) transport from HCl solutions; [HCl] M: (1) 2.5, (2) 4.5. Receiving phase: pure water.

since $k = PS/V$ and $P = kV/S$. Here, C_0 is the initial total concentration of cation in the source solution.

Transport of Lead Complexes

Permeability coefficients of Pb(II) complexes depend on the counterion and its concentration (Fig. 4). The increase in permeability coefficient is very similar to that for the distribution ratio of complexes with the same anions (Table 2):

$$NO_3^- < ClO_4^- < Br^- < SCN^- < I^-$$

Very poor transport was observed with chloride and trichloroacetate anions.

For picrate complexes, the distribution ratio k_d is too high for successful stripping of Pb(II) into the receiving phase. After the stripping of a small

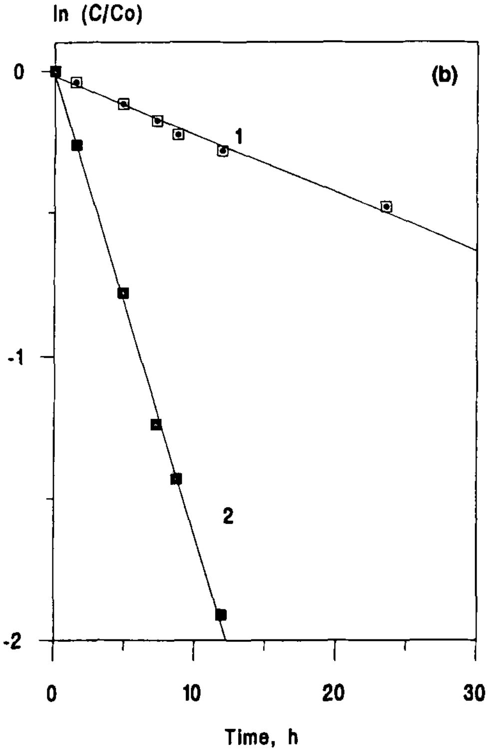

FIG. 3. Continued.

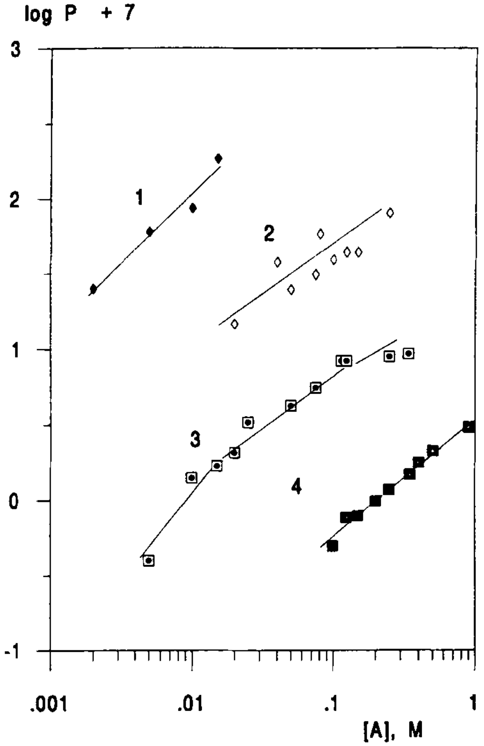

FIG. 4 Permeability coefficients P (in m/s) vs anion concentration. (1) I^-, (2) SCN^-, (3) Br^-, (4) NO_3^-.

portion of Pb(II) by pure water, equilibrium between membrane and stripping solution was reached and no more metal ions were released into the receiving phase. When dilute EDTA solutions (6–20 mM) were used to strip metal ion, Pb(II) transport was observed (Fig. 3a).

Flux of other metal ions under these same conditions is much smaller than for Pb^{2+}, making it possible to separate Pb^{2+} from other cations in a manner comparable to that accomplished by solvent extraction. Only small fluxes of Na^+ and Sr^{2+} cations through the membrane were measured (Fig. 5). The selectivity of Pb^{2+} transport toward Sr^{2+} and Na^+ is P_{Pb}/P_{Sr} = 300–500 and P_{Pb}/P_{Na} = 2000–3000 for all anions studied.

The same approach used for the calculation of K_p can be used to explain the membrane transport data. The mechanism of neutral compound (ion

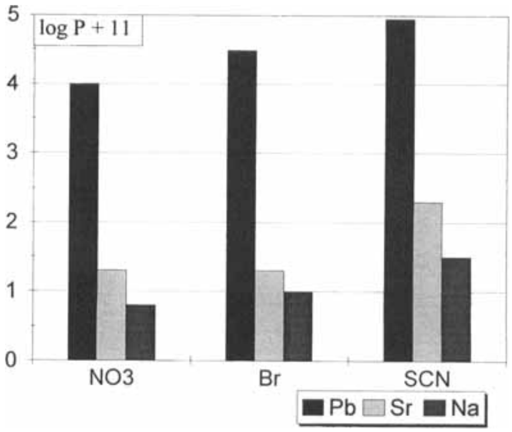

FIG. 5 Permeability coefficients of Pb^{2+}, Sr^{2+}, and Na^{+} (in logarithmic scale) for different counterions at parallel transport conditions. Starting concentrations: Pb^{2+}, 1.0 mM; Sr^{2+}, 10 mM; Na^{+}, 1 M.

pair) PbA_2 transport through the PIM can thus be written

$$\{PbA_2\}_{aq,s} \rightarrow \{PbA_2\}_{org,1} \quad (I)$$

$$\{PbA_2\}_{org,1} \rightarrow \{PbA_2\}_{org,2} \quad (II)$$

$$\{PbA_2\}_{orb,2} \rightarrow \{PbA_2\}_{aq,r} \quad (III)$$

where subscripts "aq" and "org" describe aqueous and organic phases respectively, "s" and "r" are source and receiving aqueous phases, respectively, and "1" and "2" are surfaces of the membrane in contact with the source and receiving phase, respectively. Step II, transport through the viscous PIM, determines the rate of the process. Flux at this stage can be written as

$$J = \frac{D}{l}([Pb(DC18C6)A_2]_{org,1} - [Pb(DC18C6)A_2]_{org,2}) \quad (6)$$

The concentration of lead complex in the organic phase is a function of DC18C6 concentration in the organic phase and the composition of the aqueous phase.

$$[Pb(DC18C6)A_2]_{org} = K_1[PbA_2]_{aq}[DC18C6]_{org} \quad (7)$$

If we assume that $[PbA_2]_{aq,r} = \alpha_2 C_{Pb,r}$ is very low because the anion concentration generates little ion pairing, we can neglect

$[Pb(DC18C6)A_2]_{org,2}$ and write a simplified version of Eq. (6):

$$J = \frac{D}{l}[Pb(DC18C6)A_2]_{org,1} = \frac{D}{l}K_1[PbA_2]_{aq}[DC18C6]_{org} \qquad (8)$$

showing that flux (and permeability coefficient) is a linear function of crown ether concentration. In the case of complex dissociation in the organic phase, the equilibrium is described by

$$[Pb(DC18C6)A]_{org,1}[A]_{org,1} = K_2[PbA_2]_{aq}[DC18C6]_{org} \qquad (9)$$

and, from the conditions of electroneutrality,

$$[Pb(DC18C6)A]_{org,1} = [A]_{org,1} \qquad (10)$$

and flux becomes a function of the square root of the carrier concentration as follows:

$$[Pb(DC18C6)A]_{org,1} = \sqrt{K_2[PbA_2]_{aq}[DC18C6]_{org}} \qquad (11)$$

(This mechanism is also in agreement with more detail calculations in Refs. 12–14.) However, in our case, for all anions studied we observed

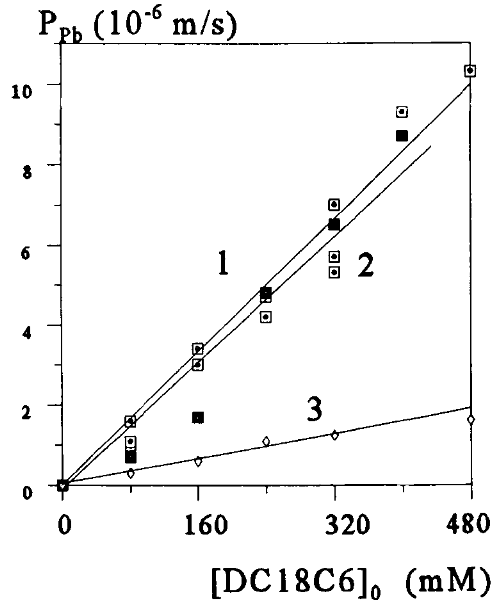

FIG. 6 Permeability coefficients P (in m/s) vs DC18C6 concentration. (1) SCN^- (0.25 M); (2) I^- (4 mM); (3) Br^- (0.25 M).

linear dependence of permeability coefficients vs carrier concentration (see Fig. 6) confirming the model based on formation of the neutral complex. Thus, the model which describes our results is

$$J = \frac{D}{l} K_1 \alpha_2 C_{\mathrm{Pb,s}}[\mathrm{DC18C6}]_{\mathrm{org}} \tag{12}$$

This expression allows us to correct the experimental values of the permeability coefficient for the α_2 value, yielding P values for the neutral PbA_2 species. It also makes possible estimation of diffusion coefficients D from known K_1, l, and P values (i.e., from $D = Pl/K_1$ [DC18C6]). An example of calculations of P for $Pb(NO_3)_2$ is shown in Table 3.

The resulting P and D values are summarized in Table 4. These data are of the same magnitude (10^{-4}–10^{-6} m/s for P and 10^{-11}–10^{-12} m^2/s for D) as was observed for different supported liquid (SLM) membranes with NOE as the solvent (12–14). It should be underscored that for the SLM results, a correction for membrane porosity was applied, which effectively increases the resulting D values 2–5 times. Much more viscous than pure solvent, the PIM possesses lower diffusion coefficients but makes available the whole volume of membrane (no inert support), increasing the resulting permeability. The PIM also has proven superiority in long-term stability (1).

Metal Ion Transport from HCl Solutions

While chloride appeared to be a poor counterion for lead sorption or transport, chloride complexes of Fe(III) and Ga(III) were transported

TABLE 3
Determination of Permeability Coefficient P of $Pb(NO_3)_2$:
$\log \beta_1 = 1.17$, $\log \beta_2 = 1.4$ (11)

$[NO_3^-]$, M	P, 10^{-7} m/s	$-\log \alpha_2$	$-\log P$ $(Pb(NO_3)_2)$
0.1	0.5	1.52	5.78
0.11	0.8	1.48	5.68
0.125	0.77	1.42	5.70
0.15	0.8	1.34	5.76
0.20	1.4	1.22	5.64
0.25	1.2	1.14	5.78
0.35	1.5	1.02	5.80
0.40	1.8	0.97	5.77
0.50	2.2	0.90	5.76
0.90	3.2	0.73	5.76

TABLE 4
Permeability Coefficients for the Transport of Pb(II) Complexes through Polymer Inclusion Membranes with DC18C6. Thickness of Membrane ca. 3×10^{-5} m. $[\mathrm{DC18C6}]_0 = 0.32$ M

Compound	$-\log P^a$ (P in m/s)	$\log K_1$	$-\log D$ (D in m^2/s)
$Pb(NO_3)_2$	5.74 (6)	2.8	12.5
$PbBr_2$	5.2 (1)	3.3	12.5
$Pb(SCN)_2$	3.7 (2)	4.0	11.7
PbI_2	3.4 (2)	4.8	12.2

[a] Standard deviation in parentheses.

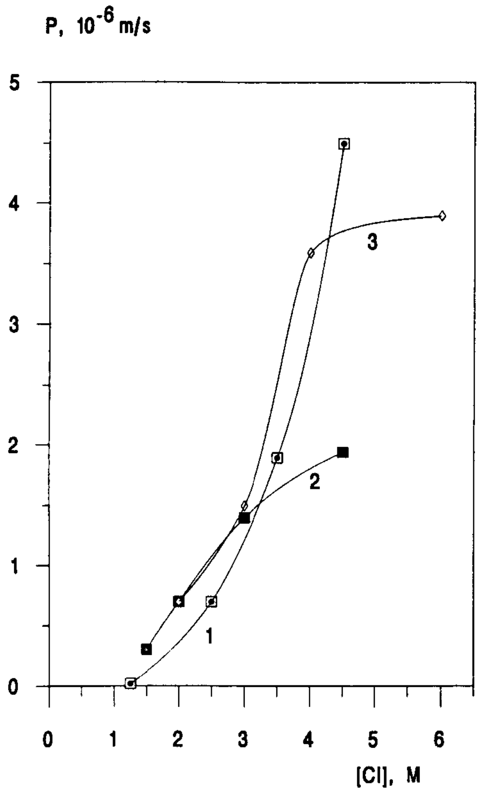

FIG. 7 Permeability coefficients P (in 10^{-6} m/s) as a function of chloride ion concentration. (1) Ga(III), vs HCl concentration; (2) Fe(III), vs HCl concentration; (3) Fe(III), vs total Cl^- concentration (2M HCl plus different LiCl concentrations).

from HCl solution through DC18C6–NOE PIMs at high rates. No detectable transport of Fe(III) and Ga(III) chloride complexes was observed through PIM membranes without DC18C6 carrier. As in the case of Pb(II), first order was observed through PIM membranes without DC18C6 carrier. As in the case of Pb(II), first-order kinetics was observed (Fig. 3b). The metal ion permeability increased with chloride ion concentration along with the distribution ratio of the same metals into the membrane material (Fig. 7). The addition of lithium chloride to the source phase improved iron transport even more (Fig. 7, Curve 3), while addition of the same amount of aluminum chloride led to only a slight increase of flux. No detectable amounts of Al were observed in the receiving phase, which confirms the high selectivity of transport. As in the case of sorption of Ga(III) and Fe(III), no attempts to quantify the species being transported were made because of uncertainty in complex composition.

Gallium ions were successfully stripped out of the polymer material with pure water, while for iron ions recovery using 0.1 M HCl or 0.01 M EDTA as stripping agent was necessary.

CONCLUSIONS

Polymer inclusion membranes with macrocyclic carriers are convenient for metal ion separations from solutions of different compositions. The order of permeability coefficients correlates with the extraction constants of the same complexes, which allows prediction of membrane permeation from solvent extraction data. The membranes are easy to prepare in the laboratory, and may be used in separation and concentration procedures.

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