

Molecularly imprinted ionically permeable membrane for uranyl ion

Anael Kimaro,^a Lisa A. Kelly^a and George M. Murray^{*b}

^a Department of Chemistry and Biochemistry, University of Maryland, Baltimore County, Baltimore, MD, USA

^b Johns Hopkins University Applied Physics Laboratory, Laurel, MD, USA.
E-mail: george.murray@jhuapl.edu

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A polymeric membrane for the separation of specific metal ions can be designed by the application of the molecular imprinting technique.

The transport of metal ions through membranes has been studied as a means of separation, concentration and recovery of both valued and toxic metal ions.^{1–5} These efforts are driven by environmental concerns and dwindling natural resources. The development of efficient and selective metal ion transporting systems for use in such operations is of great interest. Two types of membranes are predominant in membrane transport systems: supported liquid membranes and polymeric membranes. The convenience and high flux characteristics of supported liquid membranes have made popular these types of membranes.^{5–7} However, the low stability, strength and finite solubility of the active agent used in liquid supported membranes limit their practical application. Polymeric membranes have the physical and chemical stability for practical applications, but are often hampered by low transport flux. In many applications, selectivity is the most important function. The most selective membrane will have a specific transporting or penetrating path, pore or matrix through which only the desired substrate is able to pass. Specific receptor sites in polymeric membranes can be introduced by the molecular imprinting technique.⁸

Molecular imprinting is a process for making selective recognition sites in synthetic polymers. The process employs a target molecule as the template. The template is surrounded by molecular compliments that possess polymerisable functionalities. The template complex is typically copolymerised with a matrix monomer and a cross-linking monomer in the presence of a suitable solvent. The cross-linking monomers add rigidity to the finished polymer and the solvent provides site accessibility. Removal of the template molecules leaves behind cavities that exhibit enhanced affinity for rebinding the target molecule. Previously, using vinylbenzoic acid and vinylsalicyladoxime, we used the molecular imprinting technique to prepare ion exchange resins that are selective for the sequestration of uranyl ions.⁹ Recently, Saunders *et al.* reported an imprinted polymer extractant based on chloroacetic acid.¹⁰ However, the utility of a permeable membrane for the selective transport of metal ions has remained relatively unexplored. In this communication, we report our initial results and observations concerning the transport of uranyl ions through an imprinted polymer membrane. The molecular imprinting technique has been exploited in preparing membranes with molecular recognition sites for low weight organic molecules, as reported in a recent review.¹¹ Mathew-Krotz and Shea¹² reported imprinted polymer membranes for the selective transport of targeted neutral (organic) molecules with fluxes up to 0.5 nmol cm⁻² h⁻¹. The highest selectivity factor was 3.4 for adenosine vs. guanosine with 9-ethyladenine imprinted membrane.

The polymeric membranes were synthesized with ingredients for both selective binding and improved permeability. The selective binding site was prepared by using uranyl ion imprinting. Permeability was addressed using a polyester that

associates with the metal ions. The length of the alkyl chain in the diol that was used to make the polyester controlled the spacing of association sites. The polyester was removed from the membrane by the same acid treatment used to remove the uranyl ion. Removal was detected by GC-MS of the membrane acid-wash solutions. The polyester is intended to create channels, directing ion migration to the imprinted sites, thus increasing flux but maintaining selectivity. The addition of polyester to the formula had two significant results: the amount of swelling of the membrane in aqueous solutions was dramatically increased, and in the absence of the polyester there was no detectable migration of ions.

Membranes were prepared using uranyl vinylbenzoate, UO₂(VBA)₂, as the ion imprinting complex. Styrene was used as the matrix monomer and divinylbenzene was used as the cross-linking monomer. Membrane synthesis was carried out in a screw-top vial by dissolving the uranyl vinylbenzoate complex (20–150 mg) in 400 μL of 2-methoxyethanol. Nitrophenyl octyl ether (NPOE) as a plasticizer and 22 mg of a polyester, prepared from diglycolic acid and 1,6-hexanediol, was added to the polymerisation mixture. After deaeration with dry nitrogen, 20 mg of a free radical initiator, 2,2'-azobisisobutyronitrile (AIBN) were added. The vial was sealed and placed in a sonicator at 60 °C. The solution was sonicated until viscous and then poured into a Teflon mold. The resultant sample was kept in a sealed container and placed in an oven at 60 °C for 18 h to complete the polymerisation. The thickness of the resulting membranes was approximately 100 microns. Table 1 summarizes the composition of membranes A, Q and R. A reference membrane imprinted with Ni²⁺ was prepared in the same manner as membrane Q. The metal templates and the polyester were removed using a 0.1 M acetic acid solution followed by a 5% nitric acid solution. Metal ions were removed using acid until the entire template was recovered. The membrane was then washed with deionised water until the acid was removed.

Transport studies were carried out in a U-shaped tube consisting of two detachable parts. The membrane, with an exposed cross-sectional area of 0.613 cm², was placed between the two halves of the tube. The halves were held together with a screw-actuated clamp that compresses an o-ring seal to tightly secure the connection. Experiments were performed under quiescent conditions and also by stirring the solutions. The time-dependence of uranyl ion transport in quiescent solution is

Table 1 The composition of the membrane in wt% of the total components in the original mixture

Reagent	Membrane A	Membrane Q	Membrane R
UO ₂ (VBA) ₂ ^a	6.7	1.5	1.5
Divinylbenzene	2.0	14.5	24.5
Polyester	1.8	1.8	1.8
AIBN	0.9	1.6	1.6
NPOE	4.6	8.3	8.3
Styrene	84.0	72.3	62.3

^a UO₂(VBA)₂ was dissolved in 0.4 ml of 2-methoxyethanol in each case.

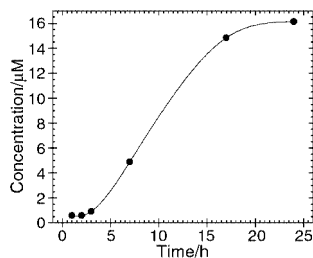


Fig. 1 Transport of uranyl ions across the membrane with time.

given in Fig. 1. The concentration of uranium in the receiving phase was determined by ICP-MS. An experiment performed while stirring the solutions (both the source and the receiving solution) showed that higher fluxes could be obtained by convection. After 24 h of stirring, 25% of UO_2^{2+} in the source solution containing $42 \mu\text{M}$ UO_2^{2+} was transported through the membrane, compared to 6.5% when the solution was un-stirred.

The selectivity of the membrane was evaluated by carrying out competitive transport experiments. A solution containing 0.2 mM of UO_2^{2+} , Ni^{2+} , Cd^{2+} , Cu^{2+} and Zn^{2+} was used as a source solution. After 22 h, a portion of the receiving solution was analysed by ICP-MS to determine the amount of each ion that was transported across the membrane. Fluxes of the competing ions were found to be very small (Table 2). UO_2^{2+} was transported at higher rate, with a selectivity factor (α) ranging from 114 to 152. The selectivity factor is defined as the ratio of the molar concentration of uranyl ion to the molar concentration of the competing metal ions measured in the receiving solution.

Table 2 Transport of uranyl ion through the membrane in the presence of competitors; selectivity

Metal ion	Amount diffused/ μM	Flux/ $\text{nmol cm}^{-2} \text{ h}^{-1}$
UO_2^{2+}	11.8 ± 0.1	2.74
Ni^{2+}	0.104 ± 0.002	0.024
Cd^{2+}	0.086 ± 0.001	0.019
Zn^{2+}	0.076 ± 0.001	0.018
Cu^{2+}	none detected	

Membrane A, composition: 6.7 wt% complex, 2 wt% cross-linker.

The origin of selective transport can be attributed to the selective binding of uranyl ion to imprinted sites along channels that span the membrane. The reference membrane prepared by imprinting with nickel showed little permeation of uranyl ions, but higher permeation of some of the competing metal ions. The transport fluxes of UO_2^{2+} , Cu^{2+} and Co^{2+} through the reference membrane were 0.015 ± 0.002 , 0.142 ± 0.003 and $0.045 \pm 0.001 \text{ nmol cm}^{-2} \text{ h}^{-1}$ respectively. No Ni^{2+} or Zn^{2+} was detected in the effluent, suggesting that the conditions for membrane preparation may need to be established on a case by case basis. The results do show that the Ni^{2+} ion imprinted membrane does not have sites selective for uranyl ions. The selective transport observed in the uranyl ion imprinted membrane arises from a process that involves preferential and reversible complexation for uranyl ion. Metal ion transport across the membrane requires a counter flow of cations in the reverse direction to maintain electroneutrality. A surplus of protons was maintained in the receiving solution by the addition of acid. A scanning electron micrograph of the membrane shows that the surface of the membrane has pores in the micron and submicron range (Fig. 2). Micrographs of the inside of the membranes show an open porous structure. Energy dispersive X-ray emission spectra of the pore area show larger amounts of uranium in the pores relative to the surrounding area, suggesting that the pores are involved in metal ion transport.

The effects of the imprinting conditions on the membrane performance were investigated by preparing membranes with different degrees of cross-linking. Each membrane's perform-

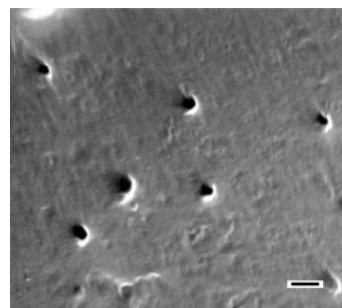


Fig. 2 Scanning electron micrograph of the membrane (bar = $1 \mu\text{m}$).

ance towards uranyl ion was examined. Using source solutions that contained a range of UO_2^{2+} concentrations from 0.25 to 0.42 mM , the transport fluxes were measured and compared. These results are shown in Table 3.

Table 3 Effects of cross-linker and concentration of the source solution on the transport flux

UO_2^{2+} (source)/mM	Flux/ $\text{nmol cm}^{-2} \text{ h}^{-1}$	
	Membrane Q ^a	Membrane R ^b
0.25	0.83 ± 0.03	0.34 ± 0.02
0.34	0.96 ± 0.04	0.68 ± 0.02
0.42	1.21 ± 0.02	0.91 ± 0.03

^a 1.5 wt% complex, 14.5 wt% cross-linker. ^b 1.5 wt% complex, 24.5 wt% cross-linker.

The membrane with a lower degree of cross linking (Q) exhibited higher fluxes than the membrane with a higher degree of cross-linking (R). The selectivity of the two membranes was verified by the competitive transport test described above. The results show that the membrane with the higher flux also exhibits higher selectivity (α_{Cd} for Q = 56 and for R = 10). Repeated uses of the membranes did not show a loss of selectivity. This result is in agreement with previous work on Pb^{2+} imprinted ion-exchange resins.¹³

In conclusion, the present study demonstrates that a polymeric membrane can be designed for the separation of a specific metal ion from a mixed metal ion solution. The selectivity imparted by the imprinting technique is high.

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