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Cs^+ and Ba^{2+} Selective Transport by a Novel Self-Assembled Isoguanosine Ionophore through Polymer Inclusion and Bulk Liquid Membranes

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Abstract

5′-(Tert-butyldimethylsilyl)-2′,3′-*O*-isopropylidene isoguanosine (isoG 1) serves as a selective Cs^+ carrier in liquid membrane transport. IsoG 1 is a lipophilic nucleoside that self-assembles via hydrogen bonds and cation-dipole interactions to form a stable decamer sandwich complex with Cs^+. Using an acidic receiving phase, Cs^+ transport through polymer inclusion membranes (PIMs) was observed at concentrations of isoG 1 below 21 mM. When isoG 1 was precomplexed with Cs^+ to give the (isoG $1)_{10}$-Cs^+ decamer, flux was observed above 21 mM carrier. The Cs^+ flux increased with increasing carrier concentration of the precomplexed (isoG $1)_{10}$-Cs^+ decamer. The Cs^+ transport selectivity by isoG 1 was investigated in the presence of sodium salt solutions of high concentration. Excellent Cs^+ flux and selectivity over the other alkali metal cations was observed in PIMs and bulk liquid membranes (BLMs). In the absence of Cs^+, this ionophore exhibits good Ba^{2+} selectivity in BLMs.

Introduction

Fifty years of nuclear weapons production by the U.S. Department of Energy (DOE) have left significant waste accumulations: approximately 403 cubic meters of high-level radioactive waste, 2.5 million cubic meters of low-level waste, as well as contaminated groundwater and soils. The current strategy for nuclear waste cleanup is to separate the liquid portion of the waste from the solids. The liquid can be disposed of as low-level waste after removal of fission products such as ^{137}Cs and ^{90}Sr. The solid portion, which contains long-lived actinides, are washed to remove bulk compounds such as salts [1–3].

Nuclear reprocessing operations produce high and medium level liquid wastes in which ^{137}Cs is one of the major radionuclides. Significant effort has been expended throughout the world to reduce the volume and to provide for safe storage of such wastes. ^{137}Cs is the major heat producer and contributor to the radiation field for both calcine and sodium-bearing waste [2, 3]. During the last several decades in the U.S., interest in and application of technology for removing ^{137}Cs from high level wastes has been motivated almost exclusively by waste management needs rather than by potential use of separated nuclear byproducts [4]. Cs^+ separation from alkaline waste is important because Cs^+ is abundant, emits penetrating radiation, and generates substantial decay heat due to its short half life. Over 40% of the radioactivity from nuclear waste tank materials is due to Cs^+. The Cs^+ ion normally exhibits a fairly simple solution chemistry, being present as the unassociated hydrated ion.

Calixarene ionophores are well known as Cs^+ carriers, and membrane chemists have studied Cs^+ separation using calixarene-based carriers. The groups of Reinhoudt and Ungaro have reported selective removal of Cs^+ with calixarenes in supported liquid membrane systems [5–7], Oak Ridge National Laboratory has investigated solvent extraction of Cs^+ from nuclear waste tanks [8, 9], and the group of Shinkai has designed various calixarene-based receptors that show high selectivity for guest molecules and metal cations [10]. Our group has reported excellent membrane permeability and Cs^+ selectivity using calixarene carriers in polymer inclusion membranes (PIMs) [11].

Calixarenes are covalently linked receptors that are pre-organized for cation binding. An alternative approach towards building macrocyclic ionophores is to use non-covalent interactions. Guanine derivatives, including mononucleotides, polynucleotides, and oligonucleotides are able to self-associate to form G-quartet structures [12, 13]. The G-quartet, a cyclic assembly of four hydrogen bonded guanines with four oxygens located within a central cavity, coordinates alkali cations with a selectivity of $K^+ > Na^+, Rb^+ \gg Cs^+, Li^+$ [14]. Using the G-quartet as a basis, we have recently synthesized and studied some lipophilic nucleosides that are able to extract metal cations from water into organic solvents [15, 16]. In particular, 5′-tertbutyl-dimethylsilyl-2′,3′,-di-O-isopropylidene isoguanosine (isoG) 1 (Figure 1), a guanosine isomer with its transposed amino and carbonyl groups, forms a Cs^+ selective ionophore [17]. Its affinity and selectivity for Cs^+ exceeds that of the Cs^+ ionophore 1,3-diisopropylcalix[4]arenecrown-6 [7]. Because of the location of its hydrogen bond donor and acceptor groups isoG 1 prefers to form a hydrogen bonded pentamer [18]. This expanded macrocycle (relative to the G-quartet) is optimal for coordinating the large Cs^+ cation. Indeed, an x-ray structure showed that isoG 1 and Cs^+ interact to form a decamer, (isoG $1)_{10}$-Cs^+, that is composed of 2 hydrogen bonded pentamers sandwiching the bound Cs^+ [18]. While the solid state structure of (isoG $1)_{10}$-Cs^+ showed that the two hydrogen-bonded pentamers encapsulated the Cs^+, our recent dynamic NMR studies demonstrated that both the Cs^+ guest and the isoG 1 sub-unit that makes up the decamer complex are both in dynamic exchange with free species in solution [19]. The above-mentioned structural and mechanistic data suggested that self-assembled ionophores prepared from isoG 1 would be ideal for the efficient transport of Cs^+ across membranes.

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In this paper, we report excellent membrane selectivity for Cs^+ over the other alkali metal cations using the lipophilic isoG 1 as a carrier in PIMs and bulk liquid membranes (BLMs). Permeability, permselectivity and flux ratios of Cs^+ and other metal cations through PIMs and BLMs are discussed.

Experimental

Preparation of precomplexed isoG 1: (isoG 1)$_{10}$CsBPh$_4$

IsoG 1 was synthesized as described in Ref. [15]. The ligand was recrystallized from isopropanol prior to use. To prepare (isoG $1)_{10}CsBPh_4$ 1.0 equivalent of pure isoG 1 was mixed with 0.10 equivalent of $CsBPh_4$ in CH_3CN to obtain a clear solution. The solution was evaporated in darkness to yield crystals of (isoG $1)_{10}CsBPh_4$. After all the solvent was evaporated, the pre-complexed (isoG $1)_{10}CsPh_4$ was ready to use. Similarly, using $KBPh_4$, and $NaBPh_4$, isoG 1 complexes of other cations were made.

Polymer inclusion membranes

Membranes were prepared using the method of Sugiura [20, 21] by combining 0.8 mL of carrier in methylene chloride (HPLC grade, Mallinckrodt chemical), 0.2 mL of 10% (v/v) *o*-nitrophenyl octyl ether (NOE) (Aldrich) in methylene chloride, and 4 mL of a cellulose triacetate (CTA) solution made by dissolving 1.25 g of CTA (Aldrich) into 100 mL of methylene chloride. This solution was placed on plate glass in a 9-cm diameter circle and allowed to dry overnight. Following the evaporation of the solvent and the attendant setting of the CTA membrane, a few drops of water were swirled on top of the membrane to help loosen it from the glass. The resulting membrane contained 76% NOE, 18% CTA, and 6–7% carrier, assuming that all the methylene chloride evaporated. The polymer film was then carefully peeled off the glass and placed between two 200 mL cylindrical glass vessels with a sealing rubber O-ring. The side of the film exposed to the air during evaporation was placed so it faced the vessel containing the source solution. The total membrane area exposed to both phases was 20.0 cm^2.

In PIM transport experiments the source aqueous phase contained metal nitrate salts in water, and the receiving phase was 0.5 M nitric acid. Both sides were stirred with three-bladed glass propellers at 600 rpm. Samples of 2 mL were periodically taken from the receiving phase and replaced with 2 mL of receiving phase solution. Blank experiments, in the absence of carrier, yielded no significant flux across the PIM. Analysis to determine the receiving phase concentration of transported Cs^+ was performed on a Perkin-Elmer 5100 atomic absorption spectrophotometer with attached power supply to provide constant current (180 mA) to the EDL (electrodeless discharge lamp). Analysis of other elements was performed on a Perkin-Elmer inductively coupled plasma II emission spectrophotometer.

Bulk liquid membranes

Experiments involving BLM transport were conducted as previously reported, using a membrane apparatus based on the concept of the Schulman bridge [22]. Two water phases were separated by a hydrophobic liquid phase which constituted the membrane. The organic membrane consisted of 3 mL of solution of carrier in chloroform or NOE placed in the bottom of a glass vial (i.d. 18 mm). The phases were stirred using a small Teflon magnetic stirring bar placed in the chloroform layer and driven at 120 rpm by Hurst synchronous motors for 24 hours. The two water phases were placed on top of the chloroform and were separated by a glass tube which extended down into the membrane phase.

One of the two water phases consisted of 0.8-mL aqueous metal nitrate salts (source phase), and the other water phase consisted of a 5.0-mL acidic solution (receiving phase). Each experiment was performed in a room thermostated at 22 °C. After 24 hours a 5 mL sample was removed from the receiving phase and analyzed for the metal ions of interest using a Perkin-Elmer 5100 atomic absorption spectrophotometer or a Perkin-Elmer inductively coupled plasma II emission spectrophotometer.

Three separate experimental membrane units were employed in the determination of each cation transport rate. Permeabilities are reported as moles of cation transported per unit time per unit membrane surface area per molar concentration of transported species in the source phase. Permselectivity is defined as the ratio of permeabilities for different species. The standard deviations were less than 10%. Blank tests of transport (no carrier present) were performed for each metal source phase solution. No detectable flux of cation across the chloroform membrane was found in the blank unit.

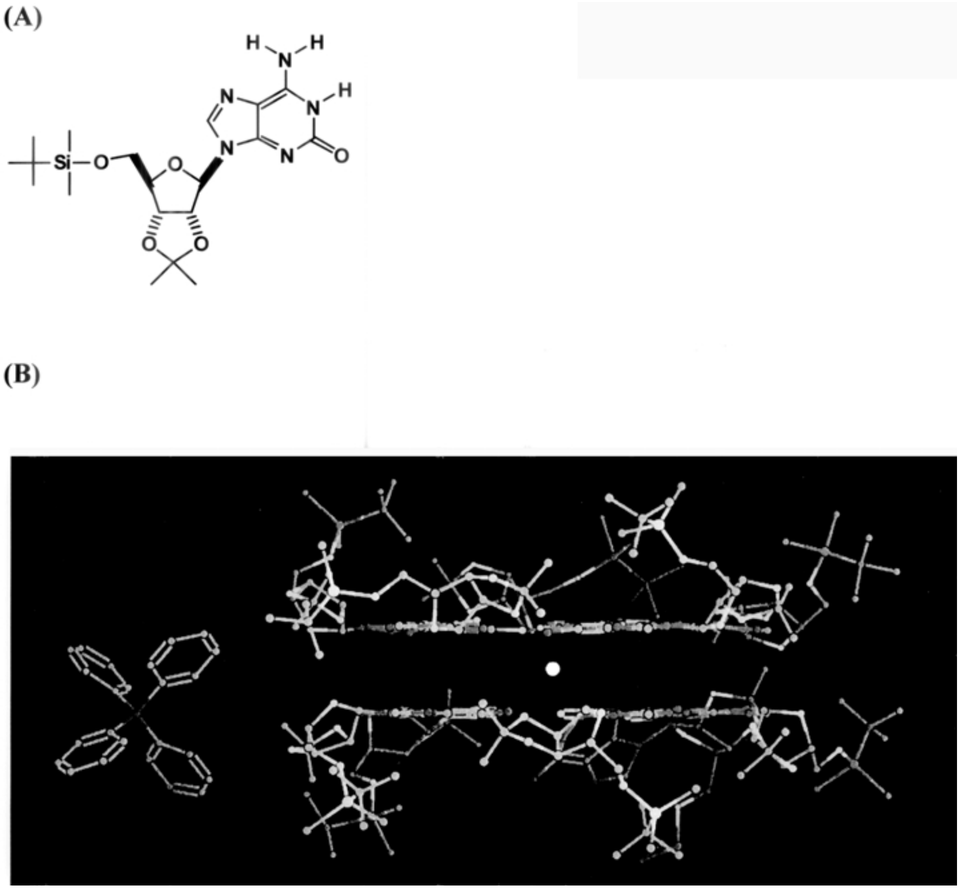

Figure 1. (A) Structure of IsoG 1. (B) X-ray structure of (isoG 1)$_{10}$Cs$^+$BPh$_4^-$.

Results and discussion

Transport through PIMs

Cs$^+$ selectivity

Initially, competitive transport of alkali metal, alkaline earth metal and transition metal cations through PIMs containing isoG 1 carrier was studied. Among these elements, only Cs$^+$ demonstrated high permeability; slow Ba^{2+} transport was observed, and the fluxes of the other elements were extremely low. Therefore, further experiments focused primarily on Cs$^+$ transport.

In an attempt to optimize cation transport, the pH of the receiving phase was varied. With a neutral receiving phase, no significant flux of Cs$^+$ was observed. However, the flux of Cs$^+$ increased with decreasing pH of the receiving phase. Specifically, with 1 mM Cs$^+$ in the source phase, 10% of the Cs$^+$ was transported to a receiving phase of 0.1 M HNO$_3$ in 24 hours, while over 30% was transported to a receiving phase of 0.5 M HNO$_3$. This result implies that the isoG 1 ligand must be protonated at the receiving phase/membrane interface in order to uncouple the hydrogen bonded aggregate and release the cation to the receiving phase. This hypothesis was supported by a series of ^{1}H NMR experiments in CDCl$_3$ that showed that the Cs$^+$ decamer, (isoG 1)$_{10}$-Cs$^+$, readily decomposed to give monomeric isoG 1 upon washing with aqueous solutions of pH below 2. Because the CTA polymer in the membrane is not stable when exposed to higher acidic solution, we did not increase the acid concentration above 0.5 M HNO$_3$. Consequently, a receiving phase of 0.5 M HNO$_3$ was chosen for further study.

The effect of concentration of isoG 1 on Cs$^+$ flux was investigated using five PIMs of different isoG 1 concentration. An unexpected result was obtained as seen in Figure 2. With 1 mM Cs$^+$ in the source phase, increasing transport was observed through PIMs containing 7–21 mM isoG 1 (corresponding to 0.7–2.1 mM (isoG 1)$_{10}$). However, no Cs$^+$ transport was observed through PIMs with isoG 1 concentrations of 41–62 mM. We hypothesized that these unusual transport results may be due to non-specific aggregation of isoG 1 in the NOE solvent. Without a cation to template formation of the macrocyclic pentamer, little Cs$^+$ transport may occur if non-specific aggregation of the ligand is occurring in the membrane. To test this hypothesis, we precomplexed isoG 1 with Cs$^+$ to form (isoG 1)$_{10}$-Cs$^+$ Ph$_4$B$^-$ before introducing the carrier into the membrane. Using equivalent amounts of carrier in the membrane as in former experiments, five PIMs were made with the precomplexed isoG 1. The flux of Cs$^+$ through these five PIMs of different carrier concentration was determined. As shown in Figure 3, Cs$^+$ flux was observed in all cases, even at high carrier concentrations. This figure also serves to illustrate the form of raw data obtained in membrane experiments of this type. A

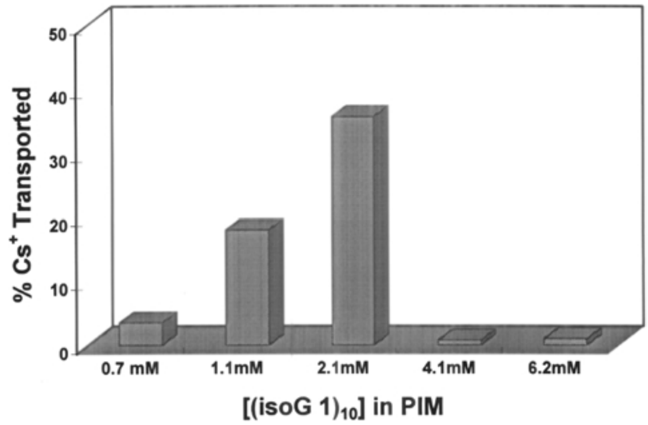

Figure 2. Percentage Cs^+ transported across PIMs with isoG 1 in 24 h. Source phase 1.0 mM $CsNO_3$. Receiving phase 0.5 M HNO_3.

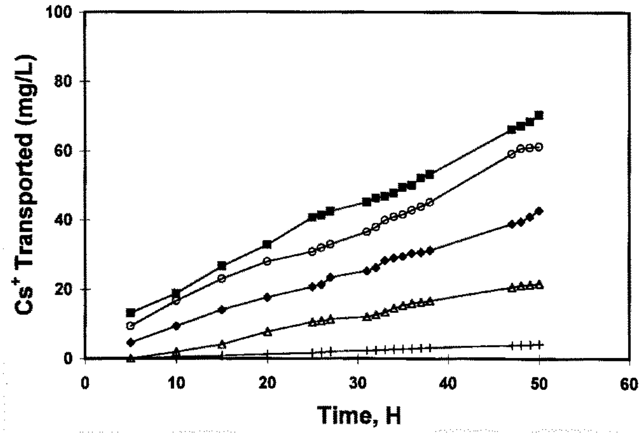

Figure 3. Plots of Cs^+ transported across five PIMs of different concentration of isoG 1 precomplexed with Cs^+. Source phase 1.0 mM $CsNO_3$. Receiving phase 0.5 M HNO_3. Membrane concentration of (isoG $1)_{10}Cs^+$. ■: 6.2 mM, ○: 4.1 mM, ◆: 2.1 mM, △: 1.1 mM, +: 0.7 mM.

comparison of fluxes obtained with the membrane prepared in these two different ways is given in Table 1.

Reinhoudt *et al.* observed a gradual drop in Cs^+ flux with increasing carrier concentration at high carrier concentration when Cs^+ was transported in NOE supported liquid membranes using a calix[4]arene-crown-6 conformer as carrier. They reported that the phenomenon was due to the high viscosity of NOE in their supported liquid membrane. It has been shown that the properties of the membrane solvent affect membrane transport to a significant degree; i.e., the diffusion velocity of the carrier complex is inversely related to the solvent viscosity [23, 24]. This phenomenon differs from the one reported in our work in that with isoG 1, flux drops to a value near zero above a certain critical concentration, consistent with the aggregation of carrier ligand to form species which do not serve as carriers.

Table 1. Permeability of Cs^+ through PIMs containing isoG 1 or precomplexed isoG 1[a]

[(isoG $1)_{10}$] (mM)[b]	Permeability (m/s)	[Precomplexed isoG 1 & Cs^+] (mM)[b]	Permeability (m/s)
0.7	1.7×10^{-8}	0.7	1.9×10^{-8}
1.1	8.3×10^{-8}	1.1	1.1×10^{-7}
2.1	1.5×10^{-7}	2.1	2.0×10^{-7}
4.1	2.5×10^{-9}	4.1	3.2×10^{-7}
6.2	2.8×10^{-9}	6.2	3.8×10^{-7}

[a] Transport conditions: Source phase: 1.0 mM $CsNO_3$ in water. Receiving phase: 0.5 M HNO_3; experiments completed in 50 h.
[b] Concentration in 1 mL solution in CH_2C_2 from which the membrane was made. The membrane volume is ~1/5 mL, so the concentration of carrier in the membrane itself is approximately 5× this value.

Cs^+ selectivity over high concentration Na^+

In order to investigate Cs^+ selectivity when Na^+ was present at high concentration, as in most nuclear waste solutions, we studied transport from a source phase of 1 mM Cs^+ and 50 mM Na^+. To avoid loss of carrier effectiveness at high concentration, precomplexed isoG 1&Cs^+, i.e., (isoG $1)_{10}Cs^+$, was used as carrier. Under these conditions, high Cs^+ permeability was obtained with very low flux of Na^+. These results show promise for removing trace Cs^+ from solutions of high sodium concentration. Within 24 h, 3.4–53% of the source phase Cs^+ was transported depending on the concentration of the precomplexed decamer (isoG $1)_{10}Cs^+$ in the PIM, and permselectivity (Cs^+/Na^+) ranged from 1300 to 9600. Because the amount of Na^+ transport was very small, these selectivity values are not very precise, and reflect only the order of magnitude of the selectivity. The percentage of transported Cs^+ increased with increasing carrier concentration, as seen in Table 2. The amount of Cs^+ ion in the precomplexed ligand in the membrane represents only 0.6% of the Cs^+ ion transported in the experiment using the lowest carrier concentration, 0.7 mM (isoG $1)_{10}Cs^+$. Thus, the vast majority of Cs^+ appearing in the receiving phase represents transfer from the source phase. Cs^+ transport using isoG 1 carrier was as effective as the best Cs^+ carrier we have investigated to date, namely the crown-ether-capped calix[4]arene, didodecyl-calix[4]arene-crown-6 [11]. With both carriers, Cs^+ permeabilities on the order of 10^{-6} m/s were obtained, which is close to the diffusion-based theoretical limit. Selectivities were also high in both cases. One significant advantage of the isoG 1 carrier, relative to the more structurally complex covalent ionophores, is its ease of preparation and its potential as a low cost and recyclable Cs^+ ionophore.

Ba^{2+} selectivity in the absence of Cs^+

We investigated fluxes of Ba^{2+} in PIMs containing 7–62 mM isoG 1. Fluxes of Ba^{2+} increased with increasing carrier concentration from 7 mM through 21 mM. However, no flux was observed in PIMs containing 41 mM or more isoG 1, similar to the effect observed for Cs^+.

Two different precomplexed forms of isoG 1 were prepared as carrier, one precomplexed with Cs^+, (isoG $1)_{10}Cs^+Ph_4B^-$, and the other precomplexed with Na^+, (isoG $1)_{10}Na^+Ph_4B^-$. PIMs were made with 0.7–6.2 mM of these carriers, and the source phase consisted of 1 mM Ba^{2+}, Sr^{2+}, 50 mM Na^+, K^+ and 100 mM Ca^{2+}, Mg^{2+}. In this competitive transport, only Ba^{2+} and

Table 2. Percentage and permeability of transported cations and permselectivity (Cs^+/Na^+)[a] through PIMs containing isoG 1 precomplexed with Cs^+

$[(isoG\ 1)_{10}Cs^+]$ (mM)	Transport (%)		Permeability (m/s)		Permselectivity
	Cs^+	Na^+	Cs^+	Na^+	(Cs^+/Na^+)
0.7	3.4	0.002	3.6×10^{-8}	2.8×10^{-11}	1300
1.1	16.5	0.002	2.1×10^{-7}	2.8×10^{-11}	7500
2.1	31	0.004	4.4×10^{-7}	8.3×10^{-11}	5300
4.1	44.5	0.004	6.4×10^{-7}	8.3×10^{-11}	7700
6.2	53	0.004	8.0×10^{-7}	8.3×10^{-11}	9600

[a] Transport conditions: Source phase: {1.0 mM $CsNO_3$ + 50 mM $NaNO_3$} in water. Carrier = precomplexed iso 1&Cs^+. Receiving phase: 0.5 M HNO_3. (Total transport time 24 h.)

Table 3. Permeability of alkali metal and alkaline earth metal cations and permselectivity (Ba^{2+}/Na^+) through PIMs containing isoG 1 precomplexed with Na^+ [a]

$[(isoG\ 1)_{10}Cs^+]$ (mM)	Permeability (m/s)					Permselectivity
	Ba^{2+}	Sr^{2+}	K^+	Na^+	(Ca^{2+}, Mg^{2+})	(Ba^{2+}/Na^+
0.7	0	0	0	0	0	
1.1	0	0	0	0	0	
2.1	1.1×10^{-7}	8.3×10^{-9}	2.8×10^{-11}	2.8×10^{-11}	2.3×10^{-11}	4000
4.1	2.3×10^{-7}	3.6×10^{-8}	2.8×10^{-11}	5.6×10^{-11}	3.5×10^{-11}	4100
6.2	4.2×10^{-7}	4.2×10^{-8}	5.6×10^{-11}	8.3×10^{-11}	4.6×10^{-11}	5100

[a] Transport conditions: Source phase: {1.0 mM $Ba(NO_3)_2$ + 1.0 mM $Sr(NO_3)_2$ + 50 mM $NaNO_3$ + 50 mM KNO_3 + 100 mM $Ca(NO_3)_2$ + 100 mM $Mg(NO_3)_2$} in water. Receiving phase: 0.5 M HNO_3.

Sr^{2+} showed measurable flux while most of other metal ions showed virtually no flux. High selectivity for Ba^{2+} was observed; maximum flux was 32%; permeability was 10^{-6} m/s after 24 hours and permselectivity of Ba^{2+}/Na^+ was from 4000 to 5100 (Table 3). When PIMs of 0.7–1.1 mM carrier were used, no elements showed measurable flux. Transport results for membranes using precomplexed isoG 1&Cs^+ are given in Table 4. In this case, the maximum flux of Ba^{2+} after 24 hours was 20%, and permselectivity of Ba^{2+}/Na^+ was from 2000 to 3900.

The permselectivity (P_{Ba^{2+}/Na^+}) values obtained using precomplexed isoG 1 were quite high. Clearly, precomplexed isoG 1 is a useful carrier for removing traces of Ba^{2+} ions from solutions of high sodium concentration. Fluxes of Ba^{2+} increased with increasing carrier concentration, and there was no loss of transport character in the PIMs of high carrier concentration. While Ba^{2+} flux using precomplexed isoG 1&Na^+ was slightly higher than that using precomplexed isoG 1&Cs^+, clearly either ligand is effective and the choice of precomplexing cation is not crucial.

Transport through BLMs

In an attempt to understand why uncomplexed isoG 1 showed no flux in PIMs above 21 mM, we investigated Cs^+ transport in chloroform bulk liquid membrane systems using this ligand. We expected that if proper self-assembly of isoG 1 in NOE was the determining factor, the effect would be different in a different membrane solvent.

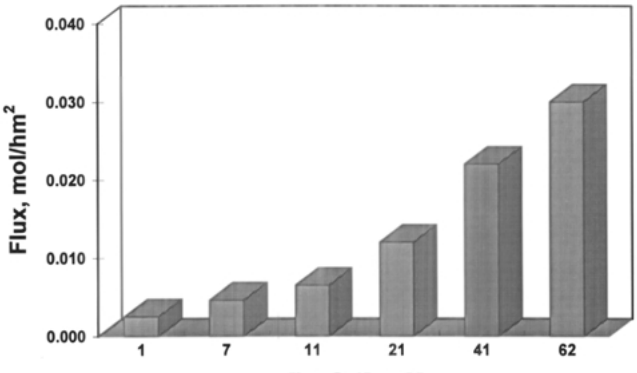

Figure 4. Fluxes of Cs^+ transported through chloroform BLMs containing varying concentrations of isoG 1. Source phase 1.0 mM $CsNO_3$ in water. Membrane phase isoG 1 in $CHCl_3$. Receiving phase 0.1 M HNO_3.

Cs^+ transport

With isoG 1 as carrier in a $CHCl_3$ bulk liquid membrane phase, Cs^+ was transported from a water source phase to an acidic receiving phase (pH 1). Fluxes obtained at different carrier concentrations did not show the same trends as those obtained in PIM experiments. As shown in Figure 4, fluxes increased with increasing carrier concentration, with no loss of flux above a certain critical concentration limit.

In light of this result, transport of Cs^+ was measured in an NOE bulk liquid membrane to determine if either the solvent or presence of CTA in the PIMs was the causative factor for the ligand concentration effect observed in the PIM experiments. In the NOE BLM, Cs^+ flux through the membrane phase was low. Cs^+ flux increased with increasing carrier concentration up to 21 mM, then dropped off, just

Table 4. Permeability of alkali metal and alkaline earth metal cations and permselectivity (Ba^{2+}/Na^{+}) through PIMs containing isoG 1 precomplexed with Cs^{+}[a]

$[(\text{isoG 1})_{10}Cs^{+}]$	Permeability (m/s)					Permselectivity
(mM)	Ba^{2+}	Sr^{2+}	K^{+}	Na^{+}	(Ca^{2+}, Mg^{2+})	(Ba^{2+}/Na^{+})
0.7	0	0	0	0	0	
1.1	0	0	0	0	0	
2.1	1.1×10^{-7}	8.3×10^{-9}	2.0×10^{-11}	2.8×10^{-11}	1.5×10^{-11}	3900
4.1	1.7×10^{-7}	1.1×10^{-8}	2.8×10^{-11}	8.3×10^{-11}	3.1×10^{-11}	2000
6.2	2.4×10^{-7}	1.9×10^{-8}	5.8×10^{-11}	8.3×10^{-11}	4.6×10^{-11}	2900

[a] Transport conditions: Source phase: {1.0 mM $Ba(NO_3)_2$ + 1.0 mM $Sr(NO_3)_2$ + 50 mM $NaNO_3$ + 50 mM KNO_3 + 100 mM $Ca(NO_3)_2$ + 100 mM $Mg(NO_3)_2$} in water. Receiving phase: 0.5 M HNO_3.

Table 5. Fluxes and selectivities of transported cations in chloroform BLMs

Flux (10^{-6} mol h^{-1} m^{-2})			Selectivity (flux ratio)	
Cs^{+}	Na^{+}	K^{+}	Cs^{+}/Na^{+}	Cs^{+}/K^{+}
2100	5.4	6.4	390	328

Transport conditions: Source phase: 0.1 M {$CsNO_3$ + $NaNO_3$ + KNO_3} in water, 0.8 mL. Membrane phase: $CHCl_3$ saturated with water, 3 mL; [isoG 1] = 1.0 mM. Receiving phase: 0.1 M HNO_3, 5.0 mL.

as it did in the PIMs. We believe this is further evidence that isoG 1 forms ineffective aggregates in NOE above a certain concentration. We conclude that the reason for the drop in flux above a certain critical carrier concentration is formation of isoG 1 aggregates not suited for the binding of Cs^{+}. The nature of these aggregates will be the topic of future study.

Competitive transport: Cs^{+} and Ba^{2+}

Selectivity of Cs^{+} over Na^{+} and K^{+} was investigated in chloroform BLMs. This transport was carried out competitively by placing equimolar amounts of Cs^{+}, Na^{+}, and K^{+} in the aqueous source phase. In this case, Cs^{+} was selectively transported over the other alkali metal cations in the presence of isoG 1. As seen in Table 5 the flux ratio values were low compared to the selectivities obtained in PIM experiments.

To investigate Ba^{2+} selectivity in BLMs, competitive transport of Ba^{2+}/K^{+}, Na^{+}, Ca^{2+}, Mg^{2+} was investigated. As seen in Table 6, good selectivity for Ba^{2+} over K^{+} and Na^{+} was obtained. The concentration of isoG 1 in five chloroform membrane phases ranged from 7 mM to 62 mM, and the selectivity varied from 200 to 430. When K^{+} and Na^{+} were present in large excess in the source phase, excellent selectivity of Ba^{2+} over K^{+} and Na^{+} was achieved (Table 7). Clearly Ba^{2+} recovery from solutions of alkali metal salts of high concentration is possible as long as Cs^{+} is not present.

Competitive transport experiments were carried out, with Cs^{+} present in the BLM source phase, with fluxes reported in Table 8 and selectivities in Table 9. Excellent selectivity of Cs^{+} over the other metal cations was obtained. There was a great difference in the Ba^{2+}/Na^{2+} selectivity in the presence or absence of Cs^{+} (compare Table 6 and Table 9).

Table 6. Competitive Ba^{2+} transport of alkali metal and alkaline earth metal cations in chloroform BLMs from equimolar source phase[a]

[isoG 1]	Flux × 10^{-6} mol h^{-1} m^{-2}					Selectivity
(mM)						(flux ratio)
	Ba^{2+}	K^{+}	Na^{+}	Ca^{2+}	Mg^{2+}	Ba^{2+}/Na^{+}
7	1100	5.4	5.4	0	0	200
11	2300	5.4	5.4	0	0	430
21	3500	11	16	0	0	220
41	4400	11	16	0	0	280
62	4700	16	22	0	0	210

[a] Transport conditions: Source phase: 0.1 M {$Ba(NO_3)_2$ + KNO_3 + $NaNO_3$ + $Ca(NO_3)_2$ + $Mg(NO_3)_2$} in water, 0.8 mL. Membrane phase: $CHCl_3$ saturated with water, 3 mL. Receiving phase: 0.1 M HNO_3, 5.0 mL.

Table 7. Competitive transport of alkali and alkaline earth metal cations in chloroform BLMs from source phase with high concentrations of competing cations[a]

[isoG 1]	Flux × 10^{-6} mol h^{-1} m^{-2}					Flux ratio
(mM)	Ba^{2+}	K^{+}	Na^{+}	Ca^{2+}	Mg^{2+}	Ba^{2+}/Na^{+}
7	1400	5.4	6.4	0	0	220
11	2100	11	6.4	0	0	330
21	2800	16	13	0	0	220
41	3400	22	13	0	0	260
62	4300	27	19	0	0	480

[a] Transport conditions: Source phase: {0.05 M $Ba(NO_3)_2$ + 0.50 M KNO_3 + 0.50 M $NaNO_3$ + 0.50 M $Ca(NO_3)_2$ + 0.50 M $Mg(NO_3)_2$} in water, 0.8 mL. Membrane phase: $CHCl_3$ saturated with water, 3 mL. Receiving phase: 0.1 M HNO_3, 5.0 mL.

Table 8. Competitive transport of alkali and alkaline earth metal cations in BLMs[a]

[isoG 1]	Flux (10^{-6} mol h^{-1} m^{-2})					
(mM)	Cs^{+}	Ba^{2+}	K^{+}	Na^{+}	Ca^{2+}	Mg^{2+}
7	1800	220	6	5	0	0
11	2600	450	8	7	0	0
21	4600	710	17	14	0	0
41	8700	1000	20	19	0	0
62	12000	1100	28	25	0	0

[a] Transport conditions: Source phase: 0.1 M {$CsNO_3$ + $Ba(NO_3)_2$ + KNO_3 + $NaNO_3$ + $Ca(NO_3)_2$ + $Mg(NO_3)_2$} in water, 0.8 mL. Membrane phase: $CHCl_3$ saturated with water, 3 mL. Receiving phase: 0.1 M HNO_3, 5.0 mL.

Table 9. Selectivities in the competitive transport of alkali metal and alkaline earth metal cations in chloroform BLMs[a]

[isoG 1] (mM)	Selectivity (flux ratio)				
	Cs^+/Ba^{2+}	Cs^+/K^+	Cs^+/Na^+	Ba^{2+}/K^+	Ba^{2+}/Na^+
7	8.2	300	360	37	44
11	5.8	330	370	56	31
21	6.5	270	330	42	51
41	8.7	440	460	50	53
62	11	430	480	39	44

[a] Transport conditions: Source phase: 0.1 M $\{CsNO_3 + Ba(NO_3)_2 + KNO_3 + NaNO_3 + Ca(NO_3)_2 + Mg(NO_3)_2\}$ in water, 0.8 mL. Membrane phase: $CHCl_3$ saturated with water, 3 mL. Receiving phase: 0.1 M HNO_3, 5.0 mL.

Ba^{2+} selectivity over Na^+ and K^+ decreased markedly due to the predominant Cs^+ flux, as seen in Table 9.

Conclusions

When using the precomplexed decamer, $(\text{isoG }1)_{10}Cs^+$-Ph_4B^-, as carrier for ion transport through PIMs, highly selective transport of Cs^+ was observed at all carrier concentrations. Excellent permselectivity (Cs^+/Na^+) was obtained in PIMs, with promise for removing trace Cs^+ from solutions of high background sodium concentration. Competitive transport experiments with Cs^+, Na^+, and K^+ gave excellent Cs^+ selectively over the other alkali metal cations in BLMs. Good selectivity was obtained for Ba^{2+} over the other alkaline earth metal cations when Cs^+ was not present in PIMs and BLMs. However, Ba^{2+} could not be removed effectively in isoG 1-mediated transport when Cs^+ was present at equimolar concentration in the source phase. Cs^+ permeability with isoG 1 was comparable in scale to that obtained with calixcrowns used previously in our research [11]. Specifically, permeability of Cs^+ with isoG 1 was as high (above 10^{-6} m/s) as with the calixcrown.

These PIM and BLM transport results using the lipophilic nucleoside isoG 1 clearly demonstrate that self-assembled ionophores have great potential as useful ion carriers. The supramolecular synthesis of self-assembled ionophores can be straightforward and efficient, as relatively simple building blocks provide exquisite receptors under thermodynamic conditions. Moreover, the monomer-aggregate equilibrium can be perturbed by factors such as pH, temperature, solvent polarity, etc, thus providing a reversible system for ion binding and release. The further development of self-assembled ionophores as selective ion transporters is being pursued in our laboratories.

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