Communications to the Editor

Bifunctional Recognition: Simultaneous Transport of Cations and Anions through a Supported Liquid Membrane

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Received November 15, 1994

The design and synthesis of macrocyclic cation receptors is very well documented in supramolecular chemistry.1 Despite anion recognition being a relatively new area of research, both positively charged and neutral receptors for anionic species have been prepared in the last few years.2 Recently we described the synthesis of neutral bifunctional receptors for the simultaneous complexation of hydrophilic anions and cations in organic media.3 In these receptors, the appropriate binding sites for both anionic and cationic species are covalently combined in a neutral molecule.4 In this Communication, we report our preliminary results on simultaneous transport of cations and anions through a supported liquid membrane (SLM) assisted by a novel type of neutral bifunctional receptor. To the best of our knowledge, this is the first example of carrier-assisted cotransport, in which the anion and cation of a hydrophilic salt are bound and transported simultaneously through a membrane.5,6

Our synthetic strategy is based on the attachment of both cation and anion binding sites to the rigid lipopholic calix[4]-

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8 The synthetic platform (Scheme 1). It is known that the covalent combination of a Lewis acidic UO₂⁺ center and amido COONH moieties provides an excellent receptor site for dihydrogen phosphate (H₂PO₄⁻) and chloride (Cl⁻) anions and that the calix[4]arene crown-6 (1,3,alternate) fragment is capable of selective complexation of cesium ion (Cs⁺).10


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Scheme 1

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<Diagram of Scheme 1>
in CH₂Cl₂ gave the corresponding 1,3-bis(chloroacetamido)calix[4]arene 4 in 69% yield. Dihaldehyde 5 was obtained by alkylation of 2-(2-allyloxy)-3-hydroxybenzaldehyde with 4 in the presence of K₂CO₃ and KI in 59% yield. Subsequent palladium-catalyzed deallylation of calixarene 5 afforded dihaldehyde 6 in quantitative yield, which was used without purification for the cyclization step. Reaction of 6 with cia-1,2-cyclohexanediamine and UO₂(AcO)₂H₂O in refluxing methanol under high dilution conditions gave receptor 7, which was isolated in 11% yield after column chromatography. Compound 7 has been used as a carrier to investigate the transport of hydrophilic cationic chloride (CICL) and the more lipophilic cesium nitrate (CICN) across a supported liquid membrane composed of a porous polymeric support (Accurel) impregnated with 0-nitrophenyl-o-cetyl ether (NPPOE). For comparison, the same experiment was performed with the receptors 8 and 9, which have only either anion or cation binding sites, respectively (Chart 1) (Table 1).

The transport processes for CICN and CICl are different: CICN is much more lipophilic than CICl, and only CICl can easily follow the complexed CICl²⁻ cation through the hydrophobic membrane, even in the absence of anion carrier. With the cation carrier 9, a high flux of CICN (5.5 × 10⁻⁷ mol m⁻² s⁻¹) (Table 1) was observed, but the anion receptor 8, which is not selective for CICl²⁻, did not transport CICN. The flux was very low (0.02 × 10⁻⁷ mol m⁻² s⁻¹) and comparable with the (blank) flux obtained without carrier. It implies that, probably, in the case of 9, only the cation binding site is responsible for the transport.

The transport of CICl by the monofunctional carriers 8 (anion) and 9 (cation) exhibits low flux values of 0.07 × 10⁻⁷ and 0.04 × 10⁻⁷ mol m⁻² s⁻¹, respectively (Table 1). Obviously, when one of the ionic species is complexed, the uncomplexed counterion cannot sufficiently penetrate the lipophilic membrane.

However, a significant flux (1.20 × 10⁻⁷ mol m⁻² s⁻¹) was observed for bifunctional carrier 7 with CICl, which is much higher than the corresponding fluxes for the monofunctional carriers 8 and 9. At the same time, carrier 7 showed a surprisingly low flux of CICN (0.89 × 10⁻⁷ mol m⁻² s⁻¹) when compared with that observed for cation receptor 9 (5.50 × 10⁻⁷ mol m⁻² s⁻¹). This proves that (i) both anion and cation binding sites of 7 are involved in the complexation and (ii) the presence of only an anion or a cation binding site in the receptor molecule is not sufficient for effective transport of a hydrophilic salt such as CICl. But more important is that this suggests a preference of hydrophilic CICl over lipophilic CICN.

These results indicate the unique feature of receptors in which both binding sites are covalently linked.

Table 1. Salt Fluxes through a Supported Liquid Membrane Measured for Different Carriers in NPPOE

<table>
<thead>
<tr>
<th>Carrier</th>
<th>CICl flux</th>
<th>CICN flux</th>
</tr>
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<tbody>
<tr>
<td>8</td>
<td>0.02</td>
<td>0.07</td>
</tr>
<tr>
<td>9</td>
<td>5.20</td>
<td>0.42</td>
</tr>
<tr>
<td>7</td>
<td>0.89</td>
<td>1.20</td>
</tr>
</tbody>
</table>

* Salt concentration, 0.1 mol L⁻¹; Fluxes (in units of 10⁻⁷ mol m⁻² s⁻¹) after 24 h at 298 K. Blank fluxes of the salts in NPPOE, for CICl, 0.03 × 10⁻⁷ mol m⁻² s⁻¹; and for CICN, 0.02 × 10⁻⁷ mol m⁻² s⁻¹.

* Carrier in the membrane, 0.01 M. No leakage of receptors was observed in blank experiments.


(14) Selected data for 7: mp 244–245 ºC; IR (NMR (CDCl₃), CD₂OD) 5.2 (9.21, 2H, 7.42 (d, J = 8.2 Hz, 4H), 7.17, 7.11 (2 x d, J = 8.0 Hz, 4H), 7.0–6.8 (m, 10H), 7.11 (t, J = 7.6 Hz, 2H), 7.02 (t, J = 8.0 Hz, 2H), 6.52 (d, J = 8.2 Hz, 4H), 4.69 (4, 4H), 4.6–4.5 (m, 2H), 3.78 (s, 8H), 3.54 (s, 4H), 3.5–3.2 (m, 20H), 3.15 (t, J = 7.0 Hz, 4H), 2.4–2.3 (m, 3H), 1.9 (m, 8H), 1.5–1.3 (m, 6H), MS-FAB m/z 1655.3 [M + H⁺]”, calculated 1656.0. Details of the synthesis will be published in a full article.


(16) In competition experiments with 7, utilizing equimolar quantities of CICl and CICN (0.05 M each), the receiving phases were analyzed, and a [CICl³⁺/NO₃⁻] ratio of ~1:1 was obtained. For comparison, a [CICl³⁺/NO₃⁻] ratio of 0.02:1 was observed in the competitive transport of potassium salts across a chloroform liquid membrane, mediated by dibenzo-18-crown-6.