Proton Coupled Membrane Transport of Anions Mediated by Cryptate Carriers

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Macrobicyclic diammonium salts mediate the selective membrane symport of bromide ions and protons *via* formation of anion cryptates.

The carrier facilitated transport of anions across liquid membranes has been demonstrated with a range of alkylammonium salts and cationic metal complexes.[1] In all these cases, the transported anion is electrostatically bound to the carrier and transport selectivity is predominantly determined by the free energy of transfer of the anion from the aqueous to the organic membrane phase.[2] As a consequence, lipophilic anions are invariably extracted and transported faster than hydrophilic anions.[1—3]

In contrast, the developing field of anion co-ordination chemistry[4] provides numerous examples of anion inclusion complexation wherein selectivity is governed by a combination of electrostatic factors and ligand-anion complementarity of shape, size, and functionality. One of the simplest and earliest examples is the demonstration by Simmons and Park[5] of the selective complexation of Cl^- by in,in-diprotonated macrobicyclic amines. The extrapolation from anion inclusion *complexes* to anion inclusion *carriers* is hampered by simple electrostatic features: the known anion receptors bear an excess of positive charge with respect to their included substrate.

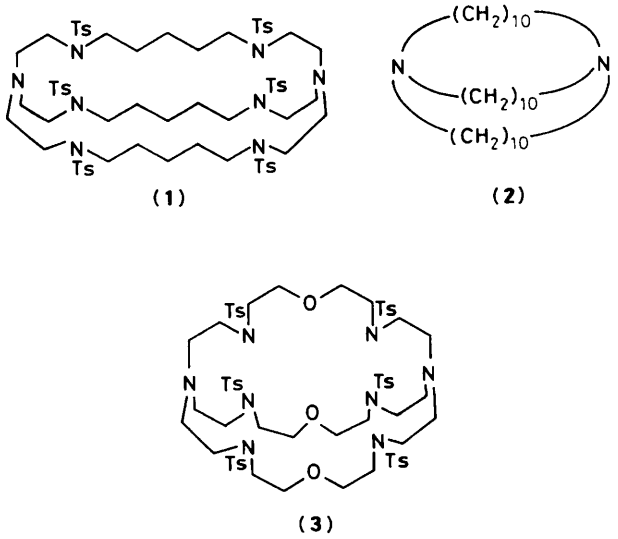
In this report, we demonstrate how this excess positive charge may be neutralized by use of a large lipophilic counterion, dinonyl naphthalene sulphonate ($DNNS^-$). Consequently, macrobicyclic amines can act as anion inclusion carriers in an artifical liquid membrane. Scheme 1 shows a transport cycle for the carriers utilized, (**1**), (**2**), and (**3**).[5,6] The N-tosyl derivatives of the polyamine anion receptors described earlier[6] were employed in order to render the compounds more hydrophobic and to restrict the number of protonation sites to the two bridgehead amine functions. The large lipophilic anion $DNNS^-$ is expected to remain outside the cavity of the carrier but stay within the organic membrane phase. Thus at the acidic (left in Scheme 1) interface protonation/extraction of HX into the membrane can occur to form a ternary complex potentially involving an inclusion complex of X^-. At the neutral (right) interface, deprotonation/loss of HX is favoured but further deprotonation is inhibited by the solution pH relative to the carrier pK_a, and the low aqueous solubility of $DNNS^-$. The membrane was formed in a U-tube from a chloroform solution of the carrier in the base of the U separating two aqueous phases in the arms of the U. The experimental conditions and transport fluxes are summarized in Table 1 for the transport of anions from an acidic mixture of Cl^-, Br^-, NO_3^-, and ClO_4^-.

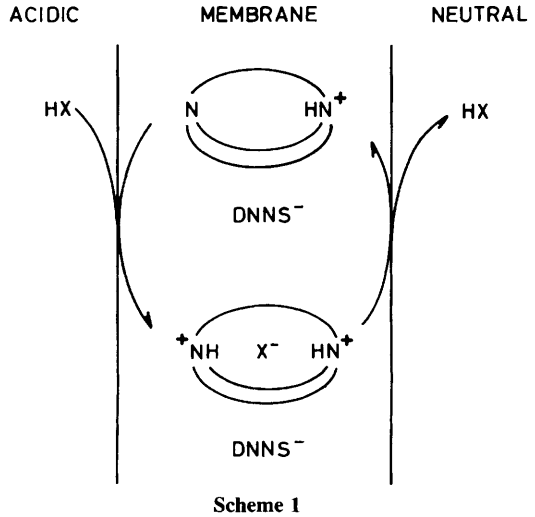
That anion inclusion complexation and transport has occurred is readily demonstrated by the data. Even without added $DNNS^-$, the selectivity of (**1**) is qualitatively different

Table 1. Cryptand carrier mediated anion transport across an artificial membrane.[a]

		Flux/10^6 mol m^{-2} s^{-1}				
Entry	Carrier	Cl^-	Br^-	NO_3^-	ClO_4^-	Total
1	(**1**)·$DNNS^-$	0.8	2.4	<0.1	2.3	5.5
2	(**1**)	1.3	4.0	2.6	4.9	12.8
3	Trioctylamine	0.4	2.2	2.3	4.0	8.9
4	Trioctylamine·0.5 $DNNS^-$	0.6	1.2	1.2	2.3	5.3
5	(**2**)·$DNNS^-$	0.7	2.0	<0.1	4.4	7.1
6	(**3**)·DNNS	0.4	0.7	1.7	5.6	8.4
$\Delta G_{tr}^{X^-}$ ($H_2O \rightarrow CHCl_3$)[7]/ kJ mol^{-1}		64.4	49.3	44.7	22.6	

[a] U-tube cell containing 8×10^{-3} dm^3 of HCl 0.1 M, NaBr 0.1 M, $NaNO_3$ 0.1 M, and $NaClO_4$ 0.1 M ‖ 12×10^{-3} dm^3 of carrier 1.0×10^{-3} M in $CHCl_3$ ‖ 8×10^{-3} dm^3 of NaH_2PO_4/Na_2HPO_4 buffer (0.02 M, pH 7.0). All three phases stirred at 400 ± 1 r.p.m.; 25.0 ± 0.2 °C; anion analysis by ion chromatography; reproducibility ± 10%; no transport in the absence of carrier.





Scheme 1

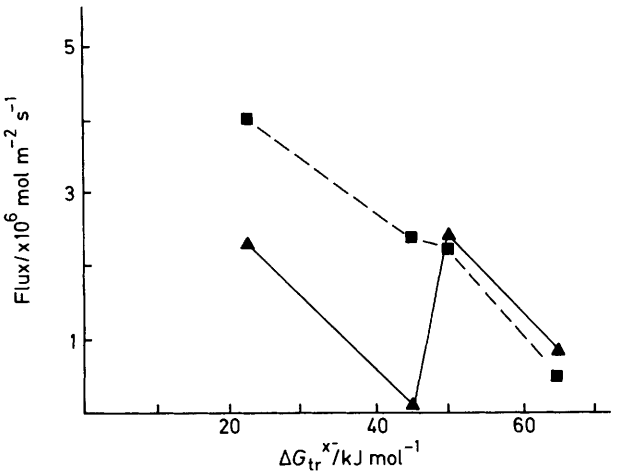


Figure 1. Anion flux as a function of $\Delta G_{tr}^{X^-}$ ($H_2O \rightarrow CHCl_3$) for (**1**)·$DNNS^-$ (▲, ———) and trioctylamine (■, – – –).

from trioctylamine (entries 2 and 3). Upon addition of $DNNS^-$ (0.5 equiv.), the trioctylamine selectivities remain constant (entries 3 and 4) while a similar addition of $DNNS^-$ to (**1**) results in a greatly enhanced Br^-/NO_3^- selectivity. These differences are illustrated more clearly in Figure 1 which relates transport flux to calculated free energies of transfer of the anions from water to chloroform ($\Delta G_{tr}^{X^-}$).[7] The anion flux *via* ion pairs with the carrier trioctylamine is a linear function of $\Delta G_{tr}^{X^-}$. In contrast, the carrier system (**1**)·$DNNS^-$ is clearly able to discriminate between Br^- and NO_3^- despite their closely similar $\Delta G_{tr}^{X^-}$. A similar discrimination is evident with the (**2**)·$DNNS^-$ carrier system. The Br^-/ClO_4^- selectivities are not high in any case, indicating that exclusive complexes of the bicyclic amines probably also participate in competition with inclusive complexes. From the differences in $\Delta G_{tr}^{X^-}$, the Br^- cryptate of (**1**) is about 10^4 times more stable than the ClO_4^- (exclusive) complex in chloroform.

Other features of the transport support the schematic mechanism. The fluxes are dependent upon the stirring rates in the three phases implying that the process is limited by diffusion in the unstirred boundary layers adjacent to the interfaces.[8] The proton/anion stoicheiometry assessed in the three cases is one proton per anion transferred as required by Scheme 1. The transport flux is independent of the Na^+ concentration and no Na^+ is transferred (using $DNNS^-$ as a carrier for example). The flux is a function of the acid concentration of the source phase but the Br^-/ClO_4^- selectivity is independent of the acid concentration. Finally, late in an experiment (t >1500 min) the 'neutral' phase buffer is exhausted and the pH drops to 4—5. The total anion flux remains constant but the relative fluxes of individual anions begin to alter. This indicates that the transport is dominated by events at the extraction interface. The extraction constants for all systems thus apparently lie below the optimum value for maximum flux.[8]

Although some of the selectivities exhibited by this system are modest this may only reflect the rather low inherent selectivity of these macrobicyclic amines as anion receptors. The competition with exclusive complexes is a further complicating factor. Even so, these results indicate some of the features required for an anion transporter based on the selectivity of anion cryptates and show how anion transport systems may be simply derived from known anion receptors.

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