# Proton-driven Cation Transport through a Polymer Membrane
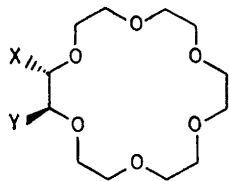
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Membranes formed from polyacrylamide derivatives bearing pendant crown ether-carboxylic acid groups act as proton-driven alkali metal ion pumps.

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Cations may be transported through fluid membranes by natural and synthetic ionophores which form a membrane-soluble complex with the transported ion; of particular interest are coupled transport membranes which permit the transport of one ion to be driven by the co- or counter-transport of another ion.[1] This permits one ion to pump the other against its concentration gradient; numerous model systems exploiting this behaviour have been reported.[2] However, this type of carrier-mediated transport appears not to be widespread in natural systems where transport proteins which create selective 'pores' appear to be more common.[3] These pores may be solvent-filled channels, or more plausibly, may be a series of discrete ion-binding sites which span the membrane.[4] Ion transport would then consist of a series of 'hops' between these sites. In order to mimic this type of behaviour, we have prepared polymers incorporating a crown ether-carboxylic acid along the backbone. Membranes prepared from these polymers were expected to be capable of pumping alkali metal cations from basic to acidic solution by the following sequence of events. At the basic interface, proton loss and cation uptake would occur to form a polymer-bound complex. Ligand exchange reactions of crown ether complexes are known to occur readily in many solvents;[5] should such an exchange occur within the polymer, concomitant proton transfer should also occur to minimize charge separation. Alternatively, proton transfer may precede ligand exchange. In either event, the ion would tend to migrate to the acidic side of the membrane whereupon protonation would induce ion release. The essentials of coupled counter-transport would thus have occurred.

A suitable polymer (1a) to test this hypothesis was prepared from the 18-crown-6 anhydride (2) previously prepared.[2c] Reaction of (2) with the monobenzyloxycarbonyl derivative of 1,3-propanediamine gave (3) which on hydrogenolysis in acidic ethanol gave the crown ether-amino-acid hydrochloride (4). Polyacryloyl chloride (prepared by azobisisobutyronitrile-initiated polymerization, m.wt. ca. 20 000 by viscometry) was treated with (4) in chloroform and an excess of triethylamine and the resultant salt was treated with aqueous acid to give (1a). Copolymers of styrene and acryloyl chloride reacted similarly to give (1b) (from styrene–acryloyl chloride, 1 : 1) and (1c) (from styrene–acryloyl chloride, 5 : 1). The polymers prepared showed the expected

i.r. spectral features for primary amide and carboxylic acid. The amount of free carboxy-group was determined by acid–base titration and agreed well in all cases with the amount of crown ether amide determined by elemental analysis for nitrogen (typically $0.9\text{---}1.8 \times 10^{-3}$ mol g$^{-1}$).

Films cast by solvent evaporation of all samples of (1a—c) prepared were unfortunately too brittle to use directly as membranes. However, suitable membranes incorporating (1a—c) were prepared by soaking microporous Teflon filters (Schleicher and Schuell, 0.2 $\mu$m, 47 mm diam.) in solutions of polymer such that the solution was entirely imbibed into the filter and allowed to evaporate. The amount of polymer taken up was easily controlled, reproducible, and was evenly distributed across the disks as deduced by elemental analysis of portions of various membranes. I.r. spectra of the membrane disks showed the expected reversible changes in the carboxylic acid bands when treated with basic potassium, or acidic aqueous solutions. Some loss of (1a—c) to basic solutions was noted, especially after numerous cycles of acid–base treatment.

Cation–proton coupled counter-transport was studied using a cylindrical cell in which the membrane was mounted vertically between the two halves of the cylinder, running horizontally. The two aqueous compartments were stirred through ports from above and the entire assembly was thermostatted at 25 °C by water circulating in an outer jacket of the cell. Transport was followed by analysis of aliquots withdrawn at various times. Membranes incorporating polymers (1a—c) are capable of pumping cations from basic to acidic solution as shown in Figure 1. Initial transport rates for a number of membranes are given in Table 1.

A number of points are of interest. All membranes bearing 10 mg of polymer tend to give sustained ion pumping (Figure 1, curve A). For these membranes the amount of potassium ion transported is a linear function of time, transport rates are equal on both sides of the cell, and the pH changes associated with transport are consistent with a cation–proton stoicheiometry of 1 : 1. As the amount of



(1a,b,c) X = polymer-C(:O)NH[CH$_2$]$_3$NHC(:O)–, Y = –CO$_2$H
a; polymer from acryloyl chloride. b; polymer from styrene–acryloyl chloride (1 : 1). c; polymer from styrene–acryloyl chloride (5 : 1).
(2) X, Y = –C(:O)OC(:O)–
(3) X = PhCH$_2$OCONH[CH$_2$]$_3$NHC(:O)– , Y = –CO$_2$H
(4) X = HCl.H$_2$N[CH$_2$]$_3$NHC(:O)– , Y = –CO$_2$H
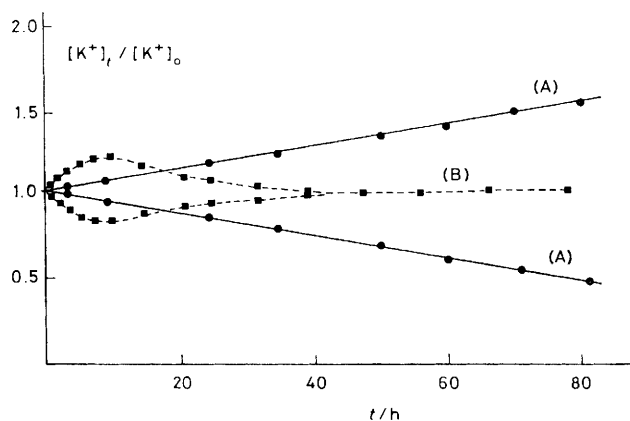(5) X = Me[CH$_2$]$_{13}$NHC(:O)– , Y = –CO$_2$H

**Figure 1.** Potassium ion concentration as a function of time for membranes incorporating (1a). Curve A, cell of entry 1; curve B, cell of entry 2.

**Table 1.** Initial transport rates for polymer membranes prepared.[a]

| Entry | Polymer | wt/disk (mg) | moles/disk ($\times 10^5$ mol) | Initial potassium concentration ($\times 10^3$ mol dm$^{-3}$) | Initial rate ($\times 10^6$ mol h$^{-1}$) | Type[b] |
|---|---|---|---|---|---|---|
| 1 | (1a) | 10 | 1.75 | 1.0 | 0.33 | A |
| 2 | (1a) | 20 | 3.50 | 1.0 | 0.41 | B |
| 3 | (1a) | 40 | 7.00 | 1.0 | 0.45 | B |
| 4 | (1a) | 10 | 1.75 | 5.0 | 0.57 | A |
| 5 | (1a) | 10 | 1.75 | 0.5 | 0.20 | A |
| 6 | (1a) | 10 | 1.75 | 1.0[c] | 0.06 | A |
| 7 | (1b) | 5 | 0.80 | 1.0 | 0.14 | A |
| 8 | (1b) | 10 | 1.60 | 1.0 | 0.23 | A |
| 9 | (1b) | 30 | 4.80 | 1.0 | 0.24 | B |
| 10 | (1b) | 10 | 1.60 | 0.5 | 0.13 | A |
| 11 | (1b) | 10 | 1.60 | 1.0[c] | 0.07 | A |
| 12 | (1c) | 5 | 0.45 | 1.0 | 0.08 | A |
| 13 | (1c) | 10 | 0.90 | 1.0 | 0.13 | A |
| 14 | (1c) | 20 | 1.80 | 1.0 | 0.19 | B |
| 15 | (1c) | 40 | 3.60 | 1.0 | 0.25 | B |

[a] Cell as described in the text with the initial potassium ion concentration equal on both sides of the cell. Buffers used: basic side, pH 8.25, tris(hydroxymethyl)aminomethane (Tris)/HCl, [Tris] = 0.25 M; acidic side, pH 2.30, triethanolamine–phosphoric acid, [phosphate] = 0.25 M. Temp. = 25.0 ± 0.20 °C. Most values are an average of duplicates; rates ± 15%. [b] A, linear with time see Figure 1, curve A; B, nonlinear, in most cases similar to Figure 1, curve B. [c] Sodium used in place of potassium.

polymer is increased, the membranes tend to degrade during the experiment (Figure 1, curve B); an initially created ion gradient collapses to equilibrium. This degradation is accompanied by a rapid collapse of the proton gradient indicating that free pores have appeared in the membrane. This may be due to dissolution of the polymer from the support matrix. At lower loads the polymer is presumed to be more intimately held in the support allowing fewer 'free ends' for the onset of dissolution. However, at much lower loadings (2 mg/disk) there is insufficient coverage of the support for an intact membrane; in these cases the proton gradient collapses without ion pumping.

Even in cases where ion pumping is not sustained, the initial transport rates can be determined. For a given polymer, increasing the load eventually causes a plateau in transport rate (entries 1—3, 7—9, 12—15). This is consistent with the view that a certain coverage is necessary but that once coverage is complete, no further rate increase should be expected. The optimal stability of the membrane depends on the amount of polymer (10 mg) rather than on the amount of carrier incorporated.

Variation in the potassium ion concentration results in a variation in transport rate which may be treated by a standard kinetic analysis for transport systems.[3] An Eadie–Hofstee plot of initial rate as a function of (initial rate/initial potassium concentration) gave a line of slope $-9.9 \times 10^{-4}$ mol dm$^{-3}$ ($-K_m$) and an intercept of $0.66 \times 10^{-6}$ mol h$^{-1}$ ($V_{max}$) for (1a). Comparable data for (1b) are $K_m = 3.3 \times 10^{-3}$ mol dm$^{-3}$ and $V_{max} = 0.99 \times 10^{-6}$ mol h$^{-1}$. These may be compared with a mobile carrier system using the carrier (5) ($5 \times 10^{-4}$ mol dm$^{-3}$ in chloroform) where $K_m = 6.1 \times 10^{-4}$ mol dm$^{-3}$ and $V_{max} = 4.1 \times 10^{-6}$ mol h$^{-1}$.[6] These results are consistent with the physical properties of the various polymers; the more hydrophobic polymer (1b) exhibits the lower tendency to take up ions while the more rigid polymer (1a) shows the lower maximum transport rate. Binding to polymer reduces the maximum rate of transport and somewhat impairs ion uptake. Most of the bulk of these membranes is the support, hence substantially higher transport rates may be anticipated for self-supporting films.

Copolymers containing styrene (1b—c) appear to be somewhat less selective than (1a). The potassium–sodium selectivity of (1a) is 5.5 (entries 1, 6) while for (1b) it is 3.2

(entries 8, 11). The mobile carrier (5) exhibits a potassium–sodium selectivity of 3.5.[2c] Thus the ability of the crown ether to discriminate is not substantially impaired on binding to a polymer. Despite the different amounts of styrene incorporated into (1b) and (1c), resulting in different amounts of carrier per weight of polymer, these two materials are remarkably similar for a given amount of crown ether in the membrane. By this criterion however, (1c) is inferior to (1b) since the optimal membrane loading of 10 mg of polymer per disk results in more carrier per disk for (1b) than (1c) and hence results in a higher transport rate.

In summary, this study introduces a new type of model membrane for ion pumping. The principles of coupled counter-transport and the close analogies with mobile carrier membranes are retained but the additional features of discrete ion binding sites immobilized across the membrane[7] provide closer ties to mechanisms presumed to be important in biological transport. In addition, the physical resistance and multiple uses of these polymeric ion pumps will be of additional benefit in practical applications of this separation strategy.

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