Alkali Cation Transport by Proton-ionizable Macrocycles in a H_2O–CH_2Cl_2–H_2O Bulk Liquid Membrane System

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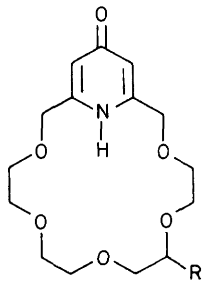
Coupled H^+–M^+ (M = Na, K, Rb, or Cs) transport of individual M^+ and binary M^+ mixtures in which K^+ is transported selectively in a 1 M MOH–CH_2Cl_2–HNO_3/H_2O (pH 1.5 and ~6) bulk liquid membrane system has been accomplished using a proton-ionizable 4-pyridone-fused-18-crown-6 macrocycle with an attached C_8H_{17} chain (**2**).

Cation transport through liquid membranes by ionizable macrocyclic carriers has been achieved by several workers. In previous studies, the ionizable proton was attached either to a group exterior to the macrocycle ring of donor atoms[1—3] or to an atom that extends from the macrocycle ring towards the interior cavity of the macrocycle.[4—6] Our purpose in designing the present set of macrocycles was to place the site of proton ionization at one of the ring donor atoms thereby making it possible to control whether H^+ or M^+ is bound by the macrocycle through adjustment of the pH of the source phase. We report here the use of a proton ionizable macrocycle (**2**), which was prepared in the same manner as that described for (**1**).[7]

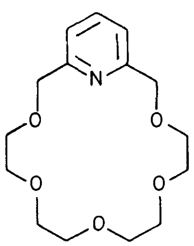
The *X*-ray crystal structure of (**1**) shows the ionizable proton to be attached directly to the nitrogen atom of the ring.[7] Values of p*K* for proton dissociation from the protonated and neutral forms of (**1**) are 3.10 and 10.98, respectively.[7] Values of *K* for proton dissociation from (**2**) were not determined, but should be similar to those for (**1**). Both (**1**) and (**2**) were tested as carriers for cations in a H_2O–CH_2Cl_2–H_2O bulk liquid membrane system at room temperature (23—25 °C), see Figure 1, insert (B), using transport cells patterned after the Shulman bridge and which have been described.[8] The receiving phase was analysed after 24 h for alkali metals by atomic absorption spectroscopy. Small temperature variations of a few degrees have no effect upon cation fluxes over a period of 24 h. In order to provide reproducible stirring of the membrane phase, Hurst synchronous motors were used to turn small magnetic stirrer bars at 120 r.p.m.

The transport of M^+ was at the blank level for both (**1**) and (**2**) using neutral (pH ~6) MNO_3 source phases. As the pH of the source phase was increased by the replacement of MOH for MNO_3, M^+ transport increased rapidly with (**2**) above pH ~12 as shown in Figure 1 for K^+ using H_2O as the receiving phase. However, transport of M^+ with (**1**) remained low even with increasing source phase pH for all cations studied, as seen in Figure 1 for the case of K^+.

The large difference in the abilities of (**1**) and (**2**) to effect M^+ transport at high pH values despite their expected similar co-ordination behaviour towards these cations is probably a result of the expected much larger partitioning of the M^+–(**2**)$^-$ complex into the CH_2Cl_2. The increase in cation transport by (**2**) with increasing source phase pH is consistent with observed cation transport in similar systems containing proton-ionizable calixarene carriers.[5,6] It can be reasoned that cation transport with (**2**) increases rapidly when the source phase pH is high enough to allow deprotonation of the carrier and subsequent formation of a neutral cation–carrier complex that partitions easily to the membrane phase. Diffusion of the complex ion pair to the receiving phase–membrane interface is followed by exchange of alkali cation for H^+ from H_2O. This exchange occurs because of the strong basicity of the anionic form of the carrier and because of a large cation concentration gradient. This scheme is depicted in insert (A) in Figure 1. Substantiation of this process is seen when the aqueous receiving phase is adjusted to pH 1.5 with HNO_3. Under these conditions, the flux of K^+ at high source phase pH values is increased markedly, J_M = 1631 mol × 10^{-8} s^{-1} m^{-2} at pH 14 (Figure 1), apparently because of the large H^+ gradient. Similar results were found for other M^+ (at pH 14, J_M = 617, 1601, and 799 mol × 10^{-8} s^{-1} m^{-2} for Na^+, Rb^+, and Cs^+, respectively).



(**1**) R = H
(**2**) R = C_8H_{17}



(**3**)

The ability of (**2**) to partition M^+ into CH_2Cl_2 should be related directly to the equilibrium constant, *K*, for the reaction: $M^+ + (\mathbf{2})^- = M$–(**2**). Values of *K* for this reaction have not been determined. However, log *K*(MeOH) values for the 1 : 1 reaction of M^+ with the similar macrocycle (**3**) are 4.09 (Na^+), 5.35 (K^+), and 4.56 (Rb^+).[9] For Cs^+, a reaction of stoicheiometry other than 1 : 1 was present. The order of the

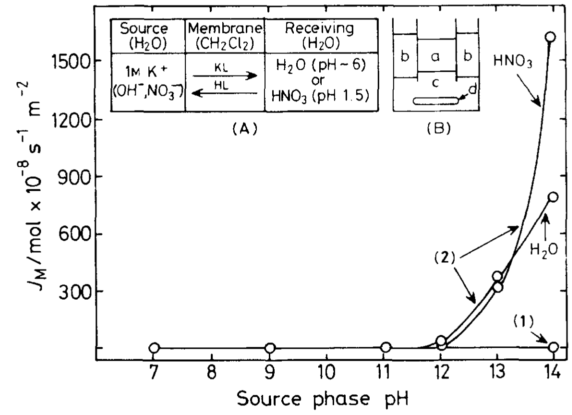


Figure 1. Plot of J_M *vs.* source phase pH using K^+ and the indicated macrocycle. (A) Scheme of coupled K^+–H^+ transport. (B) Transport cell. In (B), the aqueous source phase, a (0.8 ml), containing the cation(s) to be transported and the aqueous receiving phase, b (5 ml), are separated by a CH_2Cl_2 membrane, c (3.0 ml), which is 0.001 M in macrocycle. A small magnetic stirrer bar (d) is driven at 120 r.p.m. for 24 h. J_M represents the flux values across the CH_2Cl_2–source phase boundary. Flux values across the CH_2Cl_2-receiving phase boundary can be calculated by multiplying the values in the figure by 0.286. The cell dimensions are given in ref. 8. Each J_M value is the average of three determinations. The standard deviations average ±15% with none being greater than ±20%.

flux values is that expected from these log K values. Competitive transport experiments were carried out using binary mixtures of the alkali cations. In each mixture, selectivity was found for K^+ over the second cation. For example, the selectivity of K^+ at source phase pH 14 and receiving phase water is 4.6 fold over Na^+, 2.7 fold over Rb^+, and 6.3 fold over Cs^+. The results are consistent with the greater partitioning of K^+ owing to its expected preferential complexation by (**2**)$^-$ as estimated from the relative stabilities of the M^+–(**3**) complexes.[9]

These results demonstrate the selectivity of (**2**) for K^+ over other M^+ in competitive transport and suggest that selective coupled H^+–M^+ transport of other cations may be accomplished by appropriate macrocycle design.

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