

Proton Ionizable Crown Compounds. 18. Comparison of Alkali Metal Transport in a $\text{H}_2\text{O}-\text{CH}_2\text{Cl}_2-\text{H}_2\text{O}$ Liquid Membrane System by Four Proton-Ionizable Macrocycles Containing the Dialkylhydrogenphosphate Moiety

REED M. IZATT,* GYPZY C. LINDH, PETER HUSZTHY [1], GLEN A. CLARK, R. L. BRUENING, JERALD S. BRADSHAW,* and JAMES J. CHRISTENSEN†
Departments of Chemistry and Chemical Engineering, Brigham Young University, Provo, UT 84602, U.S.A.

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Abstract. The macrocycle-mediated fluxes of alkali, alkaline earth, and several transition metal cations have been determined and compared in a $\text{H}_2\text{O}-\text{CH}_2\text{Cl}_2-\text{H}_2\text{O}$ liquid membrane system using four water-insoluble macrocycles containing a dialkylhydrogenphosphate moiety. Transport of alkali metal cations by these ligands was greatest from a source phase $\text{pH} = 12$ or above into an acid receiving phase ($\text{pH} = 1.5$). Very low fluxes were observed for the transport of the alkaline earth cations and all transition metal ions studied except Ag^+ and Pb^{2+} which were transported reasonably well by these new macrocycles.

Key words. Proton-ionizable crown compounds, metal ion transport, liquid membranes.

1. Introduction

In the past few years, we have described the synthesis and use of various water-insoluble proton-ionizable macrocycles to transport metal cations in a $\text{H}_2\text{O}-\text{CH}_2\text{Cl}_2-\text{H}_2\text{O}$ bulk liquid membrane system [2, 3]. In our previous work with pyridono- ($\text{p}K_a = 10.98$), triazolo- ($\text{p}K_a = 9.55$), and sulfonamido- ($\text{p}K_a \approx 9$ and 12) crown types (**1**, **2**, and **3**), little or no transport of the alkali metal cations was found below source phase pH values of 13 with highest transport occurring between $\text{pH} = 13.5$ and 14 [2–4].

This paper reports on alkali, alkaline earth and transition metal cation transport properties of several recently synthesized [5] dialkylhydrogenphosphate-crown compounds (**4–7**). The $\text{p}K_a$ of phosphate crown **5** was determined to be 4.43 in a 70% dioxane–30% water mixture [6]. This $\text{p}K_a$ value is lower than those of the proton-ionizable macrocycles studied previously by us [2–4]. It was hoped that

* Authors for correspondence.

† Deceased: September 5, 1987.

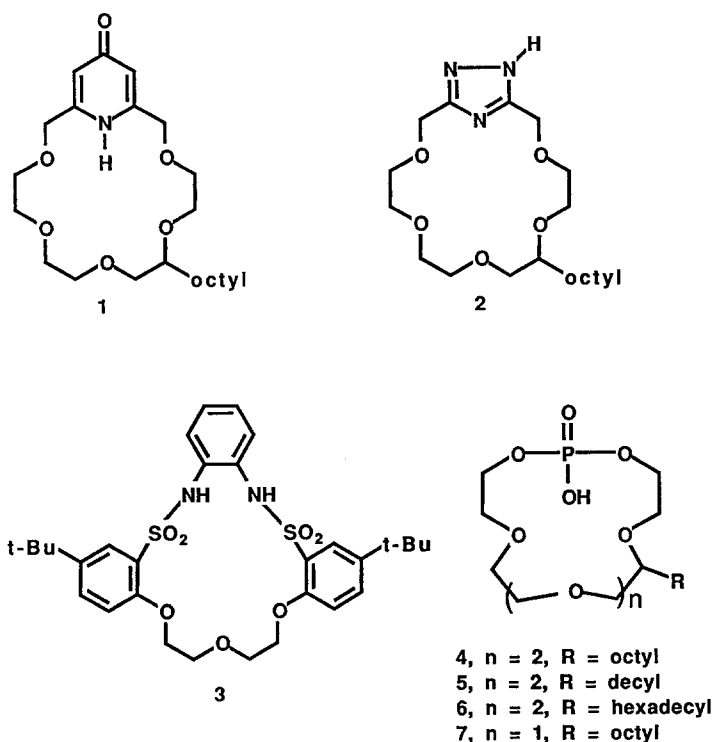


Fig. 1. Macrocyclic compounds.

these lower pK_a values would be indicative of greater ease in exchanging alkali cations for protons in a membrane transport process. Three of the phosphate compounds, with 17 ring members and containing pendant alkyl chains of varying lengths (4–6), were found to be effective transporters of the alkali metal cations Na^+ , K^+ , Rb^+ , and Cs^+ into an acid receiving phase. Several transition and alkaline earth metal ions were also transported by 4–6, but at low transport rates.

2. Experimental

2.1. MATERIALS

Compounds 4–7 were prepared as reported [5]. The following metal compounds were obtained in the highest grade available from the indicated suppliers and were used without further purification: hydroxides of Li^+ and K^+ (Spectrum), Rb^+ and Cs^+ (Aldrich), and Na^+ (Anachemia – carbonate free, Harleco – carbonate free); nitrates of Li^+ and Na^+ (Baker and Mallinckrodt), K^+ (Fisher, Baker, MCB), and Rb^+ and Cs^+ (Fisher, Mallinckrodt, Aldrich). Reagent grade HNO_3 (Fisher, Mallinckrodt, Ashland) and spectroquality methylene chloride (CH_2Cl_2) (EM, B&J) were used. All aqueous solutions were prepared using distilled deionized water.

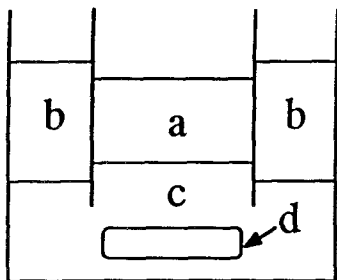


Fig. 2. Liquid membrane cell. (a) Source phase. $M^+(\text{NO}_3^-, \text{OH}^-)$ mixtures, H_2O ; (b) Receiving phase. H_2O or HNO_3 (pH = 1.5); (c) Membrane. CH_2Cl_2 , 1mM macrocycle; (d) Magnetic stirrer. 120 rpm/24 hr.

2.2. PROCEDURE

The membrane transport experiments were carried out using bulk liquid membranes as described previously [3]. Each cell (Figure 2) consisted of a 3.0 mL membrane phase (CH_2Cl_2 , 1.0 mM in carrier, stirred at 120 rpm by a magnetic stirrer) interfaced to both a 0.8 mL source phase (consisting of either 1.00M total cation or an equimolar cation mixture of known pH) and a 5.0 mL receiving phase (consisting of either distilled deionized water or an HNO_3 solution of pH 1.5). Source phases of different pH values were prepared using the appropriate amounts of MNO_3 and MOH . After 24 hours, the receiving phase was sampled and analyzed for cation concentration using a Perkin Elmer model 603 atomic absorption spectrophotometer. The pH values of the aqueous solutions were measured using a Sargent Welch miniature combination pH electrode. The initial source phase pH values were found to correspond closely to the calculated values. The pH values of the solutions listed in the tables are the calculated values based upon the initial MOH concentration.

2.3. CALCULATIONS

Each experiment was repeated at least 3 times, and the results are reported as the average of the three determinations. The standard deviations from the mean among the values in each experiment were less than $\pm 25\%$ except where the flux was below 100 and in a few other cases which are indicated in the Tables. High deviations are a result of sampling uncertainties due to the large concentration gradient in the receiving phase (which was not stirred) when high transport occurred. Experiments performed in which no carrier was present in the membrane showed cation fluxes to be less than $0.003 \times 10^{-6} \text{ mol s}^{-1} \text{ m}^{-2}$.

3. Results and Discussion

Flux values are given in Table I for the transport of single alkali metal cations by ligands 4–7 at varying source and receiving phases pH values. Ligands 4–6 were also tested for the competitive transport of two cations from a source phase

Table I. Single M^+ fluxes^a in a bulk $H_2O-CH_2Cl_2-H_2O$ liquid membrane^b system using 4-7 as carriers

| M^+ | Receiving phase pH | Source phase pH | | | | |
|-----------------|--------------------|-----------------|------|------|------|------|
| | | 11 | 12 | 13 | 13.5 | 14 |
| Ligand 4 | | | | | | |
| Li^+ | 7 | 0.07 | 0.11 | 0.11 | 0.18 | 0.29 |
| | 1.5 | 0.18 | 0.27 | 0.35 | 0.34 | 0.26 |
| Na^+ | 7 | 0.27 | 0.38 | 0.35 | 0.53 | 0.43 |
| | 1.5 | 0.87 | 2.2 | 2.5 | 3.1 | 1.9 |
| K^+ | 7 | 0.37 | 0.49 | 0.52 | 0.55 | 0.52 |
| | 1.5 | 0.94 | 1.9 | 6.2 | 7.5 | 11 |
| Rb^+ | 7 | 0.39 | 0.57 | 0.70 | 0.54 | 0.53 |
| | 1.5 | 0.55 | 2.0 | 3.4 | 8.5 | 6.6 |
| Cs^+ | 7 | 0.36 | 0.51 | 0.50 | 0.84 | 0.36 |
| | 1.5 | 0.80 | 0.84 | 1.7 | 2.4 | 6.2 |
| Ligand 5 | | | | | | |
| Li^+ | 7 | 0.17 | 0.16 | 0.25 | 0.44 | 0.36 |
| | 1.5 | 0.10 | 0.38 | 0.19 | 0.25 | 0.11 |
| Na^+ | 7 | 0.37 | 0.43 | 0.45 | 0.65 | 0.42 |
| | 1.5 | 0.69 | 1.8 | 2.9 | 3.9 | 3.1 |
| K^+ | 7 | 0.34 | 0.80 | 0.45 | 0.47 | 0.44 |
| | 1.5 | 1.09 | 2.4 | 4.8 | 8.1 | 14 |
| Rb^+ | 7 | 0.39 | 0.55 | 0.60 | 0.71 | 0.58 |
| | 1.5 | 0.52 | 1.6 | 4.6 | 7.3 | 24 |
| Cs^+ | 7 | 0.28 | 0.47 | 0.49 | 0.55 | 0.44 |
| | 1.5 | 0.81 | 2.6 | 1.8 | 6.6 | 11 |
| Ligand 6 | | | | | | |
| Li^+ | 7 | 0.41 | 1.2 | 1.3 | 0.56 | 0.48 |
| | 1.5 | 0.26 | 3.4 | 1.8 | 0.88 | 0.76 |
| Na^+ | 7 | 0.26 | 0.50 | 0.52 | 0.30 | 0.35 |
| | 1.5 | 0.59 | 1.9 | 8.3 | 24 | 21 |
| K^+ | 7 | 0.86 | 1.4 | 1.7 | 1.1 | 0.48 |
| | 1.5 | 0.84 | 3.7 | 18 | 34 | 19 |
| Rb^+ | 7 | 0.39 | 0.89 | 3.8 | 1.0 | 0.55 |
| | 1.5 | 0.43 | 6.2 | 26 | 32 | 28 |
| Cs^+ | 7 | 0.40 | 0.53 | 2.5 | 0.30 | 0.04 |
| | 1.5 | 0.79 | 4.0 | 4.2 | 39 | 22 |

Table I. (continued)

| M ⁺ | Receiving phase pH | Source phase pH | | | | |
|-----------------|--------------------|-----------------|------|------|------|------|
| | | 11 | 12 | 13 | 13.5 | 14 |
| Ligand 7 | | | | | | |
| Li ⁺ | 7 | 0.08 | 0.20 | 0.22 | 0.14 | 0.06 |
| | 1.5 | 0.14 | 0.43 | 0.35 | 0.16 | 0.03 |
| Na ⁺ | 7 | 0.18 | 0.34 | 0.42 | 0.29 | 0.06 |
| | 1.5 | 0.12 | 0.26 | 0.54 | 0.24 | 0.02 |
| K ⁺ | 7 | 0.16 | 0.08 | 0.08 | 0.08 | 0.06 |
| | 1.5 | 0.39 | 0.52 | 0.23 | 0.07 | 0.04 |
| Rb ⁺ | 7 | 0.21 | 0.16 | 0.10 | 0.08 | 0.05 |
| | 1.5 | 0.89 | 0.47 | 0.08 | 0.04 | 0.03 |
| Cs ⁺ | 7 | 0.24 | 0.11 | 0.11 | 0.07 | 0.05 |
| | 1.5 | 0.27 | 0.39 | 0.42 | 0.06 | 0.04 |

^a $J_M = (\text{mol s}^{-1} \text{m}^{-2}) 10^6$.

^b Phase compositions: Source: 1.0M in each metal cation using appropriate amounts of MNO₃ and MOH to achieve the initial source phase pH. Membrane: 0.001M ligand (4–7) in CH₂Cl₂. Receiving: initial pH of 7 (H₂O) or 1.5 (HNO₃), as indicated.

pH = 14 into an HNO₃ (pH = 1.5) receiving phase. Data for the competitive experiments using 4, 5, and 6 are given in Tables II, III, and IV, respectively.

The data in Table I show little transport of the alkali metal cations by these ligands into a neutral receiving phase. The increased flux when an acid (pH = 1.5) receiving phase was present indicates that transport by these systems is proton driven. In general, transport into the acidic receiving phase was about as good as transport by pyridono-crown 1 [3, 7] but not as good as transport by triazalo-crown 2 and bis-sulfonamido-crown 3 where fluxes of 30 to 50 × 10⁻⁶ mol s⁻¹ m⁻² were observed [2, 4]. Ligand 6 exhibited high fluxes for K⁺, Rb⁺ and Cs⁺ at a source phase pH value of 13.5 (see Table I). It is important to note that considerable transport of the alkali metal cations (up to 6 × 10⁻⁶ mol s⁻¹ m⁻² for Rb⁺) by ligands 5 and 6 was observed from a source phase of pH = 12 to an aqueous receiving phase of pH = 1.5. Transport by 5 and 6 from a source phase of pH = 11 was at a lower rate. Ligands 1–3, all with pK_a values at 9.5 or higher [7–9] did not transport the alkali cations at source phase pH values below about 13 [2–4]. The pK_a value for 5 in 70% aqueous dioxane was determined to be 4.43 [6], thus transport by 5 and 6 at a lower source phase pH value would be expected. These results show that comparison of ligand pK_a values can be useful in estimating whether new ligands will be capable of membrane transport of cations from less basic source phases than ligands previously studied. However, these results also demonstrate the potential danger of quantitatively predicting complexation behavior in multi-solvent systems from single solvent data such as pK_a values.

Table II. Competitive M^+ fluxes^a in a bulk $H_2O-CH_2Cl_2-H_2O$ liquid membrane^b system using **4** as carrier.

| Metal Ions $\frac{M_1^+}{M_2^+}$ | Aqueous Receiving Phase (pH = 1.5) | | | | |
|----------------------------------|------------------------------------|--------------|----|-------------|--------------|
| | <i>Flux</i> | <i>Ratio</i> | | <i>Flux</i> | <i>Ratio</i> |
| $\frac{Li}{Na}$ | 0.11 | 0.05 | Na | 1.2 | 0.48 |
| | 2.2 | | Rb | 2.5 | |
| $\frac{Li}{K}$ | 0.40 | 0.06 | Na | 1.4 | 1.3 |
| | 6.4 | | Cs | 1.1 | |
| $\frac{Li}{Rb}$ | 0.39 | 0.08 | K | 2.9 | 1.5 |
| | 5.0 | | Rb | 2.0 | |
| $\frac{Li}{Cs}$ | 0.30 | 0.12 | K | 4.0 | 4.0 |
| | 2.5 | | Cs | 1.0 | |
| $\frac{Na}{K}$ | 1.0 | 0.48 | Rb | 4.0 | 3.6 |
| | 2.1 | | Cs | 1.1 | |

^a $J_M = (\text{mol s}^{-1} \text{m}^{-2}) 10^6$.

^b Phase compositions. Source: initial pH of 14, 0.5M in each metal hydroxide. Membrane: 0.001M (**4**) in CH_2Cl_2 . Receiving: initial pH of 1.5 (HNO_3).

Table III. Competitive M^+ fluxes^a in a bulk $H_2O-CH_2Cl_2-H_2O$ liquid membrane^b system using **5** as carrier

| Metal Ions $\frac{M_1^+}{M_2^+}$ | Aqueous Receiving Phase (pH = 1.5) | | | | |
|----------------------------------|------------------------------------|--------------|----|-------------------|--------------|
| | <i>Flux</i> | <i>Ratio</i> | | <i>Flux</i> | <i>Ratio</i> |
| $\frac{Li}{Na}$ | 0.12 | 0.05 | Na | 5.4 ^c | 0.44 |
| | 2.3 | | Rb | 12.3 ^c | |
| $\frac{Li}{K}$ | 1.4 ^c | 0.19 | Na | 1.7 | 0.94 |
| | 7.5 | | Cs | 1.8 | |
| $\frac{Li}{Rb}$ | 1.3 | 0.12 | K | 11.8 | 0.94 |
| | 10.6 | | Rb | 12.5 | |
| $\frac{Li}{Cs}$ | 27 | 1.04 | K | 4.1 | 1.3 |
| | 26 | | Cs | 3.2 | |
| $\frac{Na}{K}$ | 1.3 ^c | 0.40 | Rb | 7.0 | 1.04 |
| | 3.3 | | Cs | 6.7 | |

^a $J_M = (\text{mol s}^{-1} \text{m}^{-2}) 10^6$.

^b Phase compositions. Source: initial pH of 14, 0.5M in each metal hydroxide. Membrane: 0.001 **5** in CH_2Cl_2 . Receiving: initial pH of 1.5 (HNO_3).

^c Deviation $> \pm 25\%$.

Table IV. Competitive M^+ fluxes^a in a bulk $H_2O-CH_2Cl_2-H_2O$ liquid membrane^b system using **6** as carrier

| Metal Ions $\frac{M_1^+}{M_2^+}$ | Aqueous Receiving Phase (pH = 1.5) | | | | |
|----------------------------------|------------------------------------|--------------|-----------------|--------------------|--------------|
| | <i>Flux</i> | <i>Ratio</i> | | <i>Flux</i> | <i>Ratio</i> |
| $\frac{Li}{Na}$ | $\frac{0.69}{6.3}$ | 0.11 | $\frac{Na}{Rb}$ | $\frac{9.0}{10.8}$ | 0.83 |
| $\frac{Li}{K}$ | $\frac{0.77}{9.9}$ | 0.08 | $\frac{K}{Rb}$ | $\frac{16}{13}$ | 1.2 |
| $\frac{Li}{Rb}$ | $\frac{1.0}{2.3}$ | 0.04 | $\frac{K}{Cs}$ | $\frac{14}{13}$ | 1.1 |
| $\frac{Li}{Cs}$ | $\frac{0.66}{6.2}$ | 0.11 | $\frac{Rb}{Cs}$ | $\frac{19}{13}$ | 1.5 |
| $\frac{Na}{K}$ | $\frac{7.9}{14}$ | 0.56 | | | |

^a $J_M = (\text{mol s}^{-1} \text{m}^{-2}) 10^6$.

^b Phase compositions. Source: initial pH of 14, 0.5M in each metal hydroxide. Membrane: 0.001 M (**6**) in CH_2Cl_2 . Receiving: initial pH of 1.5 (HNO_3).

Comparison of single alkali metal cation fluxes in Table I, shows that little transport of Li^+ occurred into an acidic receiving phase using any of the four hydrogenphosphate ligands. Compound **4**, with the shortest alkyl substituent, transported K^+ the best among the other alkali metals at a source phase pH = 14. Compound **5**, with a slightly longer alkyl chain, transported Rb^+ best with K^+ and Cs^+ also transporting well at a source phase pH = 14 (Table I). Compound **6**, with the longest alkyl chain, transported all alkali metal ions at the fastest rate of the three compounds into an acidic receiving phase. Even Li^+ was transported by **6** at pH = 12. It is interesting that Na^+ , K^+ , Rb^+ , and Cs^+ were transported at the fastest rate by **6** at a source phase pH value of 13.5. The ability of **6** to transport at a faster rate than **4** and **5** is probably due to the longer alkyl substituent which decreases water partitioning, thus increasing crown availability in the organic phase for the transport of metal ions.

Competitive experiments where two alkali metal ions were transported by **4-6** indicated that there was low selectivity among the cations Na^+ , K^+ , Rb^+ and Cs^+ with selectivity ratios varying between about 0.5 and 3. High selectivity for all other M^+ over Li^+ was observed (Tables II-IV). Selectivity by **6** for Na^+ over Li^+ was the largest yet observed by us for proton-ionizable crown compounds. Lithium is almost certainly too small to be transported by the seventeen-membered rings. Furthermore, compound **7**, which contains a fourteen-membered ring, also did not transport Li^+ (Table I). The phosphate group appears to have enlarged the ring size

compared to that of normal crown ethers to the point where Li^+ would not be transported. The oxygen on the proton-ionizable site of the fourteen-membered ring system (**7**) could be directed into the ring cavity causing severe steric hindrance thereby reducing the ability of **7** to complex with small cations which are highly solvated by water. This steric hindrance would not be as important with larger seventeen-membered ring ligands and they should form stronger complexes as was observed.

Transport of the alkaline earth and certain heavy metal cations by **4–7** was also studied. Transport of the alkaline earth cations from a source phase of $\text{pH} = 14$ to a receiving phase of $\text{pH} = 1.5$ was very small ($0.1\text{--}0.2 \times 10^{-6} \text{ mol s}^{-1} \text{ m}^{-2}$). All four ligands transported Pb^{2+} ($0.74\text{--}2.1 \times 10^{-6} \text{ mol s}^{-1} \text{ m}^{-2}$) and Ag^+ ($1.8\text{--}5.3 \times 10^{-6} \text{ mol s}^{-1} \text{ m}^{-2}$) from a neutral or slightly acidic source phase to a receiving phase of $\text{pH} = 1.5$. Other heavy metal cations studied (Cd^{2+} , Ni^{2+} and Zn^{2+}) were only minimally transported by these ligands ($0.20\text{--}0.70 \times 10^{-6} \text{ mol s}^{-1} \text{ m}^{-2}$). These transport values are very low when compared to the transport of the alkali metal cations by these ligands as shown in Table I or the transport of Ag^+ by **2** ($12 \times 10^{-6} \text{ mol s}^{-1} \text{ m}^{-2}$) [10].

4. Conclusions

The four hydrogenphosphate-containing macrocycles were poor transporters for the alkali metal cations into a neutral receiving phase. Transport of all alkali metal ions except Li^+ into an acid receiving phase by these materials increased with increasing source phase pH values to $\text{pH} = 13.5$ or 14 for carriers **4–6**. Macrocycle **6** was the best transporter. Compound **7** exhibited poor transport for the alkali metal ions possibly due to a steric problem by the intra-annular oxygen atom. All four ligands transported Ag^+ and Pb^{2+} reasonably well, but very low fluxes were observed for Zn^{2+} , Cd^{2+} and Ni^{2+} .

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