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Macrocyclic diamide based poly(vinyl chloride) membranes with a high lithium selectivity

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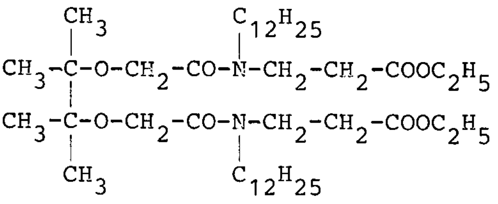
SUMMARY

Macrocyclic diamides 2, 3 and 4 of 4,4,5,5-tetramethyl-3,6-dioxaoctanedioic acid were prepared. These compounds incorporated in poly(vinyl chloride) membranes show a remarkable selectivity for lithium ions.

INTRODUCTION

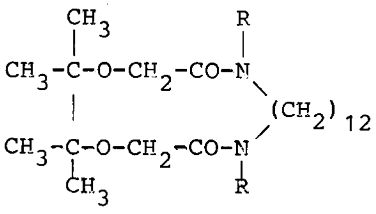
Some acyclic and macrocyclic diamides behave as ionophores and induce remarkable selectivities for alkali metal or alkali earth cations when incorporated in polymeric (PVC) membranes. The design of efficient ionophore for lithium ions presents a considerable problem because of their relatively small ionic diameter with respect to other alkali ions. Two types of lithium ionophores have been described to date. The first is based on acyclic diamides of 5,5-dimethyl-3,7-dioxanonanedioic acid (1,2,3) or cis-1,2-cyclohexanedioic acid (1), the second is based on crown-4 derivatives (4).

We would like to report here the syntheses and properties of a new type of macrocyclic diamides of 4,4,5,5-tetramethyl-3,6-dioxaoctanedioic acid, which show a very high Li$^+$-selectivity in poly(vinyl chloride) membrane systems. The following compounds 1 to 4 were prepared:

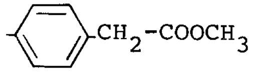


$$\begin{array}{l}
\qquad\;\; CH_3 \qquad\qquad\quad C_{12}H_{25} \\
CH_3-\overset{|}{C}-O-CH_2-CO-\overset{|}{N}-CH_2-CH_2-COOC_2H_5 \\
CH_3-\overset{|}{\underset{|}{C}}-O-CH_2-CO-\underset{|}{N}-CH_2-CH_2-COOC_2H_5 \\
\qquad\;\; CH_3 \qquad\qquad\quad C_{12}H_{25}
\end{array}$$

1



$$\begin{array}{l}
\quad CH_3 \qquad\qquad\quad R \\
CH_3-\overset{|}{C}-O-CH_2-CO-\overset{|}{N}\diagdown \\
\qquad\; | \qquad\qquad\qquad\quad (CH_2)_{12} \\
CH_3-\underset{|}{C}-O-CH_2-CO-\underset{|}{N}\diagup \\
\quad CH_3 \qquad\qquad\quad R
\end{array}$$

2 R = 

3 R = $-CH_2Ph$

4 R = cyclohexyl

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EXPERIMENTAL

The diamides were prepared by the reaction of 4,4,5,5-tetramethyl-3,6-dioxaoctanedioyl dichloride(5) with the respective substituted amine or diamine.

Ethyl 3-(dodecylamino)propionate was obtained by a reaction of 1-dodecylamine with ethyl acrylate. The reaction with acid dichloride was carried out in benzene in the presence of triethylamine.

The diamines were prepared by the alkylation of an appropriate N- substituted p-toluenesulfonamide with 1,12-dibromododecane followed by the cleavage of the tosyl group with sodium in isoamyl alcohol or with 48% HBr and phenol. The reaction with acid dichloride was carried out using the high dilution technique:

Separate solutions of 9 mmol of dichloride in 180 ml of benzene and of 9 mmol of diamine with 27 mmol of triethylamine in 180 ml of benzene were added dropwise at the same rate to 1000 ml of rapidly stirred benzene during 6 - 7 hrs. Triethylamine hydrochloride was filtered off and benzene was removed under reduced pressure. Products were isolated by chromatography on silica gel using benzene - methanol (5:1 or 5:0.6) or benzene - aceton (5:1 or 5:1.6) as eluents; their purity was checked by TLC (detection using Dragendorff´s reagent). The isolated compounds, which were oils or glasses, gave satisfactory elemental analyses and were characterized by their mass (AEI-MS 902 mass spectrometer) and nmr (JEOL PS-100 instrument, 20 MHz - CW technique, hexamethyldisiloxane as internal standard) spectra:

N,N'-Bis[2-(ethoxycarbonyl)ethyl]-N,N'-didodecyl-4,4,5,5-tetramethyl-3,6-dioxaoctanamide (1, 67%). -M.S.: M^+ 768. - ^1H nmr ($CDCl_3$): 0.82 (s, 12H, 4 CH_3), 1.11-1.26 (m, 52H, 2 $(CH_2)_{10}CH_3$, 2 $COOCH_2\underline{CH_3}$), 2.54 (t, 4H, 2 NCH_2), 3.28 (t, 4H, 2 CH_2COO), 3.58 (t, 4H, 2 $N\underline{CH_2}C_{11}H_{23}$), 3.90 (s, 4H, 2 OCH_2CO), 4.10 (m, 4H, 2 $COOCH_2$).

7,20-Bis[4-(methoxycarbonylmethyl)phenyl]-2,2,3,3-tetramethyl-7,20-diaza-1,4-dioxacyclodocosane-6,21-dione (2, 74%). -M.S.: M^+ 694, 679, 663, 635, 611, 604, 593, 546, 535, 522, 504, 473, 430, 416, 371, 355, 229, 191, 178, 146, 132, 130, 118, 106, 84, 69, 55, 41. - ^1H nmr (DMSO - d_6): 0.88 (s, 12 H, 4 CH_3), 1.22 (s, 20 H, 10 CH_2), 3.24 (s, 4 H, 2 CH_2COO), 3.58 (s, 6 H, 2 $COOCH_3$), 3.66 (s, 4H, 2 NCH_2), 3.85 (s, 4H, 2 OCH_2CO), 7.26 (m, 8H, 2 C_6H_4).

7,20-Dibenzyl-2,2,3,3-tetramethyl-7,20-diaza-1,4-dioxacyclodocosane-6,21-dione (3, 48%). -M.S.: M^+ 578, 563, 548, 520, 495, 477, 437, 419, 387, 375, 358, 315, 301, 258, 106, 91, 69, 55, 41. - ^1H nmr ($CDCl_3$): 1.18 (s, 12H, 4 CH_3), 1.24 (s, 20 H, 10 CH_2), 3.26 (m, 4H, 2 NCH_2), 4.16 (m, 4H, 2 OCH_2CO), 4.60 (s, 4H, 2 CH_2Ph), 7.32 (m, 10H, 2 C_6H_5).

7,20-Dicyclohexyl-2,2,3,3-tetramethyl-7,20-diaza-1,4-dioxacyclodocosane-6,21-dione (4, 22%). -M.S.: M^+ 562, 504, 479, 461, 449, 421, 403, 397, 379, 367, 365, 350, 315, 307, 294, 112, 83, 55, 41. - ^1H nmr ($CDCl_3$): 1.20 - 1.80 (m, 54H, 4 CH_3, 2 C_6H_{11}, 10 CH_2), 3.20 (m, 4H, 2 NCH_2), 4.08 (m, 4H, 2 OCH_2CO).

The selectivities of synthesized ionophores were investigated potentiometrically by measuring emf of the cell: Hg, Hg_2Cl_2, KCl_{sat} / measured solution // polymeric membrane // internal filling solution 0.1M $CaCl_2$ or LiCl / AgCl; Ag. The membranes were prepared by casting the solution of high molecular poly(vinyl chloride) in cyclohexanone containing plasticizer and carrier on a glass plate and allowing it to dry for at least 24 hrs at room temperature (6). The composition of the membranes was: 33% of PVC, 66% of dipentyl phthalate (DPP) as a plasticizer, 1% of carrier 2,3 and 4. Carrier 1 was used in o-nitrophenyl octyl ether (NPOE) in the presence of potassium tetrakis(p-chlorophenyl)borate (KTpClPB, 0.3%). The potentiometric selectivity coefficients K^{pot}_{CaM} resp. K^{pot}_{LiM} were determined by the separate solution method in 0.1M aqueous solutions of the respective chlorides.

RESULTS AND DISCUSSION

The selectivity coefficients of the membrane systems expressed as log K^{pot}_{CaM} resp. log K^{pot}_{LiM} are shown in Figure 1.

It is obvious from Figure 1 that the acyclic diamide of 4,4,5,5-tetramethyl-3,6-dioxaoctanedioic acid shows a considerable preference for Ca^{2+} ions similarly as described for ionophores prepared in our laboratory earlier (7). On the other

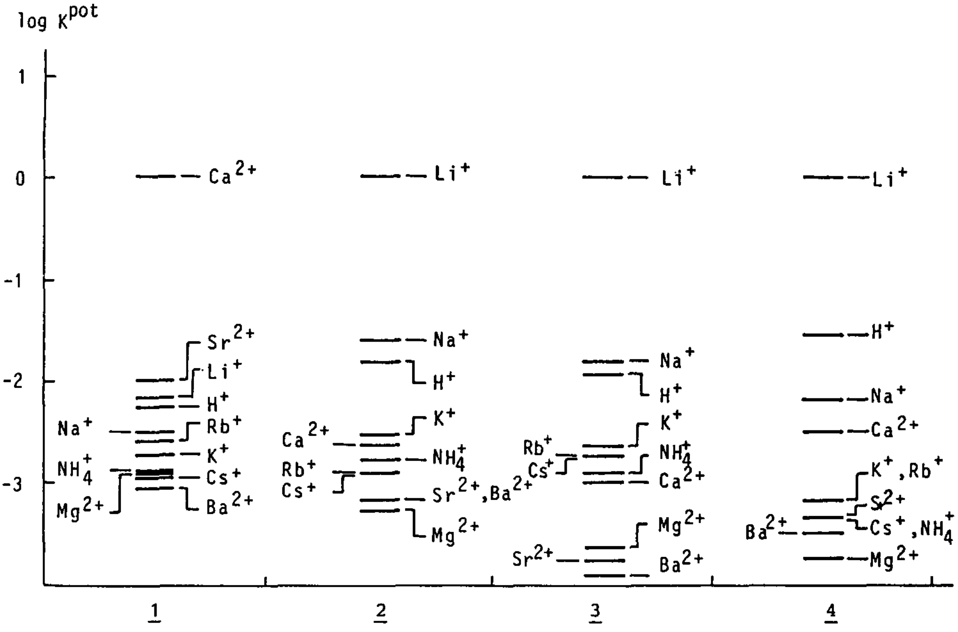

Figure 1. Potentiometric selectivity coefficients log K^{pot}_{CaM} for ionophore 1 (PVC - NPOE - KTpClPB membrane) and log K^{pot}_{LiM} for ionophore 2-4 (PVC - DPP membrane)

hand, the macrocyclic structure of diamides 2 - 4 with the aliphatic (polymethylene) chain brings about a dramatic increase in the selectivity for lithium ions, the Ca^{2+} preference being suppressed simultaneously. We suppose that the main reason for the preferable binding of small lithium ions is the cavity of suitable geometry formed by the macrocyclic ligand as a result of the steric effect of four CH_3 groups and of the cyclic structure.

The observed Li^+ - Na^+ selectivity which is important in biological applications is equivalent to the selectivities attained by the ionophores published earlier.

The Li^+ - selectivity relative to other alkaline cations is better by about one to one and a half order of magnitude. This is more evident with compounds 3 and 4, where the substituents on amidic nitrogens are more lipophilic and bulky. Unlike the acyclic ionophores, they are relatively independent of pH similarly to crown-4 derivatives. The Li^+ - selective PVC membrane electrode based on diamides 3 or 4 showed a linear Nernstian response in a wide activity range from 10^{-1} - to 10^{-5} M Li^+. The ionophoric character of 3 was proved in transport experiments. A potential gradient across the studied polymeric membranes led to the efficient transport of Li^+ ions. No transport was observed in the absence of ionophore.

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