SYNTHESIS AND ELECTROCHEMICAL BEHAVIOUR OF A NEW CLASS OF MACROCYCLIC Li^+-SELECTIVE DIAMIDES

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A series of macrocyclic N-substituted oligomethylenediamides of 4,4,5,5-tetramethyl-3,6-dioxaoctanedioic acid, 5,5-dimethyl-3,7-dioxanonanedioic and *trans*-1,2-cyclohexanedioxydiacetic acid were prepared. Selectivity of these compounds with respect to the structure of the molecule was investigated electrochemically in polymeric (PVC) membranes of ion-selective electrodes.

For many years now, synthetic ionophores (ion carriers) have attracted attention, predominantly due to their ability selectively form ion complexes, especially of alkali and alkaline earth ions. The majority of reported ionophores are selective with respect to potassium, sodium, or calcium ions. On the contrary, only a small number of carriers is able to bind selectively lithium ions. The cause of difficulties involved in designing Li^+-selective ionophores consists in the small ionic radius of Li^+ and the high standard Gibbs' energy of hydration. A number of acyclic Li^+-selective ionophores of the type of diamides of 5,5-dimethyl-3,7-dioxanonanedioic or *cis*-1,2-cyclohexanedicarboxylic acid have been reported in the literature[1,2]. Another type are Li^+-ionophores based on crown-4 derivatives[3,4].

Some time ago we described a new type of macrocyclic carriers – polyether-diamides, which possess a high selectivity for calcium ions[5,6]. Now we have found that by substituting the polyether chain in the 4,4,5,5-tetramethyl-3,6-dioxaoctanedioic acid diamide with the polymethylene chain, a carrier selective for Li^+ can be prepared[7]. In poly(vinylchloride) membranes these compounds have a higher Li^+-selectivity with respect to some ions than ionophores described so far. In this study we have investigated structural effects of this new class of macrocyclic diamides on the selectivity for lithium ions.

EXPERIMENTAL

Melting points were determined with a Kofler hot stage. Mass spectra were recorded with an AEI MS 901 mass spectrometer. ^1H NMR spectra were obtained with a Jeol PS 100 spectrometer at 20 MHz, using the CW techniques in hexadeuteriodimethylsulfoxide and with hexamethyldisiloxane as the internal standard. Chemical shifts are given in ppm. Elemental analyses were performed with a Perkin–Elmer 240 Elemental Analyzer. Column chromatography was

performed on silicagel (Kiselgel 60; Fluka, 70—230 mesh) using solvent systems benzene–methanol (5 : 0·7; diamides *I* and *VII*; 5 : 0·9, *II*; 5 : 0·6, *III*; 5 : 0·5, *VI*; 5 : 0·8, *VIII*) and benzene–acetone (5 : 1, diamide *IV*; 5 : 2, *V*). Alugram SIL G/UV (Macherey–Nagel) plates were used in TLC. The spots were detected under a UV lamp or by spraying with Dragendorff's reagent.

Starting Compounds

Chlorides of 4,4,5,5-tetramethyl-3,6-dioxaoctanedioic, 5,5-dimethyl-3,7-dioxanonanedioic, and *trans*-1,2-cyclohexanedioxydiacetic acid were prepared by a reaction with thionyl chloride each time before the cyclization reaction[6]. 1,14-Diiodotetradecane was prepared according to Nineham[8] from 1,14-dimethoxytetradecane[9]. N-Cyclohexyl-4-toluenesulfonamide was obtained according to Skita et al.[10]

Ethyl 4-(4-*toluenesulfonamido*)*phenylacetate* was prepared by a reaction of ethyl 4-aminophenylacetate[11] with *p*-toluenesulfonylchloride in pyridine, yield 45%, m.p. 88·5°C. Mass spectrum: 333 (M^+), 260, 178, 155, 106, 91. For $C_{17}H_{19}NO_4S$ (333·4) calculated: 61·24% C, 5·74% H, 4·20% N; found: 60·98% C, 5·89% H, 4·12% N.

Oligomethylenediamines

These compounds were prepared by reacting the corresponding N-substituted 4-toluenesulfonamides with oligomethylenedihalides, with a subsequent detosylation of the products with a mixture HBr–phenol.

N,N′-*Bis*[4-(*methoxycarbonylmethyl*)*phenyl*]-1,6-*diaminohexane*. A mixture of ethyl 4-(4-toluenesulfonamido)phenylacetate (18 mmol), 1,6-dibromohexane (9 mmol, Fluka), 18 ml acetone, and 6 g anhydrous K_2CO_3 was refluxed 5 h with vigorous stirring. The course of the reaction was checked by TLC. The reaction mixture was poured out on 50 g ice, the N,N′-bis[4-(ethoxycarbonylmethyl)phenyl]-N,N′-di-*p*-toluenesulfonyl-1,6-diaminohexane precipitate was filtered with suction and recrystallized from ethanol (57%), m.p. 132—133°C. The compound (3·6 g) was detosylated by boiling 4 h with 29 ml of freshly distilled 48% HBr and 5·7 g phenol. On cooling, 13 ml diethyl ether was added, the dihydrobromide diamine was filtered with suction and washed with diethyl ether. The base was obtained after the compound had been dissolved in 35 ml hot water by adding potassium acetate. Recrystallization from ethanol gave N,N′-bis-[4-(carboxymethyl)phenyl]-1,6-diaminohexane (30%) in the form of white flakes, m.p. 171°. Esterification with methanol was performed by introducing hydrogen chloride into a suspension of 1·5 g diamine in 17 ml methanol. After the hot solution had been cooled, 15 ml diethyl ether was added, and crystalline diamine dihydrochloride separated from the solution. The base was obtained after dissolution in 35 ml hot water by adding aqueous ammonia. The product was recrystallized from methanol (62%), m.p. 87°C. For $C_{24}H_{32}N_2O_4$ (412·5) calculated: 69·88% C, 7·82% H, 6·79% N; found: 69·46% C, 8·12% H, 6·65% N. Mass spectrum: 412 (M^+), 381, 353, 234, 178, 119, 106. ^{1}H NMR spectrum: 1·28—1·60 m, 8 H (4 CH_2); 2·95 t, 2 H (2 NH); 3·14 s, 4 H (2 CH_2N); 3·40 s, 4 H (2 CH_2COO); 3·55 s, 6 H (2 CH_3); 6·74 q, 8 H (2 C_6H_4).

N,N′-*Bis*[4-(*methoxycarbonyl*)*phenyl*]-1,10-*diaminodecane* was prepared from 1,10-dibromodecane through intermediates, namely, N,N′-bis[4-(ethoxycarbonylmethyl)phenyl]-N,N′-di-*p*-toluenesulfonyl-1,10-diaminodecane (76%), m.p. 84—86°C, and N,N′-bis[4-(carboxymethyl)-phenyl]-1,10-diaminodecane (45%), m.p. 153°C. The final product was obtained in a yield of 64%, m.p. 81·5—82°C. For $C_{28}H_{40}N_2O_4$ (468·8) calculated: 71·76% C, 8·60% H, 5·98% N; found: 71·49% C, 8·76% H, 5·96% N. Mass spectrum: 468 (M^+), 437, 409, 178, 120, 106. ^{1}H NMR spec-

trum: 1·25 m, 16 H (8 CH_2); 2·94 t, 2 H (2 NH); 3·15 s, 4 H (2 CH_2N); 3·41 s, 4 H (2 CH_2COO); 3·55 s, 6 H (2 CH_3); 6·70 q, 8 H (2 C_6H_4).

N,N′-*Bis*[4-(*methoxycarbonylmethyl*)*phenyl*]-1,12-*diaminododecane* was prepared from 1,12-dibromododecane through intermediates, N,N′-bis[4-(ethoxycarbonylmethyl)phenyl]-N,N′-di-*p*-toluenesulfonyl-1,12-diaminododecane (56%) with an unsharp m.p. and N,N′-bis [4-(carboxymethyl)phenyl]-1,12-diaminododecane (89%) m.p. 144—145°C. The final product was obtained in a yield of 45%, m.p. 77—78°C. For $C_{30}H_{44}N_2O_4$ (496·7) calculated: 72·55% C, 8·93% H, 5·64% N; found: 72·39% C, 9·15% H, 5·68% N. Mass spectrum: 496 (M^+), 465, 437, 318, 178, 120, 119, 106. ^{1}H NMR spectrum 1·22 m, 20 H (10 CH_2); 2·94 t, 2 H (2 NH); 3·32 s, 4 H (2 CH_2N); 3·40 s, 4 H (2 CH_2COO); 3·54 s, 6 H (2 CH_3); 6·72 q, 8 H (2 C_6H_4).

N,N′-*Bis*[4-(*methoxycarbonylmethyl*)*phenyl*]-1,14-*diaminotetradecane* was prepared from 1,14-diiodotetradecane through intermediates, N,N′-bis[4-(ethoxycarbonylmethyl)phenyl]-N,N′-di-*p*-toluenesulfonyl-1,14-diaminotetradecane (76%) with an indistinct m.p. and N,N′-bis[4-(carboxymethyl)phenyl]-1,14-diaminotetradecane (isolated as dihydrobromide, 78%, m.p. 193—194°C). The final product was obtained in a yield of 85%, m.p. 82·5—83°C. For $C_{32}H_{48}N_2O_4$ (524·7) calculated: 73·25% C, 9·22% H, 5·34% N; found: 73·13% C, 9·38% H, 5·26% N. Mass spectrum: 524 (M^+), 492, 465, 178, 120, 106. ^{1}H NMR spectrum: 1·22 m, 24 H (12 CH_2); 2·95 t, 2 H (2 NH); 3·44 m, 8 H (2 CH_2N, 2 CH_2COO); 3·57 s, 6 H (2 CH_3); 6·60 q, 8 H (2 C_6H_4).

N,N′-Dibenzyl-1,12-diaminododecane was prepared according to Petránek and Ryba[6].

N,N′-*Dicyclohexyl*-1,12-*diaminododecane* was prepared from 1,12-dibromododecane through N,N′-di-*p*-toluenesulfonyl-N,N′-dicyclohexyl-1,12-diaminododecane as the intermediate. In this case, dimethylformamide was used instead of acetone, and the product (oil) was isolated by column chromatography using a mixture of solvents CCl_4–acetone (5 : 0·3) in a yield of 81%. The final product was obtained in a yield of 60%, m.p. 41°C. For $C_{24}H_{48}N_2$ (364·6) calculated: 79·06% C, 13·27% H, 7·68% N; found: 78·65% C, 13·51% H, 7·88% N. Mass spectrum: 364 (M^+), 363, 362, 320, 306, 292, 280, 266, 238, 223, 209, 195, 181, 153, 138, 111, 97.

Macrocyclic Diamides

Oligomethylenediamides were prepared by a reaction of benzene solutions of the corresponding chlorides of dicarboxylic acids with the respective oligomethylenediamines by the high dilution techniques. The products were purified by column chromatography. With the exception of diamide *I* all oligomethylenediamides described here were obtained as viscous oils or glasses.

7,14-*Bis*[4-(*methoxycarbonylmethyl*)*phenyl*]-2,2,3,3-*tetramethyl*-7,14-*diaza*-1,4-*dioxacyclohexadecane*-6,15-*dione* (I): 61%, m.p. 90—91°C (ethanol–water). For $C_{34}H_{46}N_2O_8$ (610·7) calculated: 66·86% C, 7·59% H, 4·58% N; found: 67·16% C, 7·49% H, 4·43% N. Mass spectrum: 610 (M^+), 595, 579, 568, 551, 527, 509, 470, 462, 451, 433, 389, 246, 191, 187, 178, 146, 132, 130, 118, 106, 84, 69, 55, 41. ^{1}H NMR spectrum: 1·02 s, 12 H (4 CH_3); 1·36 s, 8 H (4 CH_2); 3·22 s, 4 H (2 CH_2COO); 3·66 s, 6 H (2 $COOCH_3$); 3·74 s, 4 H (2 NCH_2); 4·01 s, 4 H (2 OCH_2CO); 7·35 s, 8 H (2 C_6H_4).

7,18-*Bis*[4-(*methoxycarbonylmethyl*)*phenyl*]-2,2,3,3-*tetramethyl*-7,18-*diaza*-1,4-*dioxacycloicosane*-6,19-*dione*(II): 85%. For $C_{38}H_{54}N_2O_8$ (666·8) calculated: 68·39% C, 8·16% H, 4·20% N; 68·03% C, 8·49% H, 4·32% N. Mass spectrum: 666 (M^+), 635, 607, 583, 565, 518, 494, 402, 388, 343, 327, 191, 178, 146, 132, 130, 118, 106, 84, 69, 55, 41. ^{1}H NMR spectrum: 0·95 s, 12 H (4 CH_3); 1·29 s, 16 H (8 CH_2); 3·28 s, 4 H (2 CH_2COO); 3·64 s, 6 H (2 $COOCH_3$); 3·72 s, 4 H (2 NCH_2); 4·00 s, 4 H (2 OCH_2CO); 7·32 m, 8 H (2 C_6H_4).

7,20-Bis[4-(methoxycarbonylmethyl)phenyl]-2,2,3,3-tetramethyl-7,20-diaza-1,4-dioxacyclodocosane-6,21-dione (*III*): cf. ref.[7].

7,22-*Bis*[4-(*methoxycarbonylmethyl*)*phenyl*]-2,2,3,3-*tetramethyl*-7,22-*diaza*-1,4-*dioxacyclotetracosane*-6,23-*dione* (IV): 73%. For $C_{42}H_{62}N_2O_8$ (722·9) calculated: 69·78% C, 8·64% H, 3·87% N; found: 69·38% C, 7·81% H, 3·70% N. Mass spectrum: 722 (M^+), 707, 691, 664, 663, 639, 368, 279, 178, 172, 167, 149, 132, 84, 69, 55, 41. ^{1}H NMR spectrum: 0·94 s, 12 H (4 CH_3); 1·26 s, 24 H (12 CH_2); 3·50 s, 4 H (2 CH_2COO); 3·63 s, 6 H (2 $COOCH_3$); 3·73 s, 4 H (2 NCH_2); 3·83 s, 4 H (2 OCH_2CO); 7·33 q, 8 H (2 C_6H_4).

8,19-*Bis*[4-(*methoxycarbonylmethyl*)*phenyl*]-3,3-*dimethyl*-8,19-*diaza*-1,5-*dioxacyclohenicosane*-7,20-*dione* (V): 62%. For $C_{37}H_{52}N_2O_8$ (652·8) calculated: 68·07% C, 8·03% H, 4·29% N; found: 67·92% C, 8·03% H, 4·29% N. Mass spectrum: 652 (M^+), 621, 593, 569, 504, 478, 446, 432, 420, 345, 207, 192, 178, 146, 132, 130, 118, 106, 69, 55, 41. ^{1}H NMR spectrum: 0·73 s, 6 H (2 CH_3C); 1·28 s, 16 H (8 CH_2); 3·11—3·13 m, 8 H (2 CCH_2O, 2 CH_2COO); 3·63 s, 6 H (2 $COOCH_3$); 3·70 s, 4 H (2 NCH_2); 3·88 s, 4 H (2 OCH_2CO); 7·32 m, 8 H (2 C_6H_4).

8,21-*Bis*[4-(*methoxycarbonylmethyl*)*phenyl*]-3,3-*dimethyl*-8,21-*diaza*-1,5-*dioxacyclotricosane*-7,22-*dione* (VI): 58%. For $C_{39}H_{56}N_2O_8$ (680·6) calculated: 68·80% C, 8·29% H, 4·11% N; found: 69·15% C, 8·57% H, 3·87% N. Mass spectrum: 680 (M^+), 649, 621, 597, 506, 474, 373, 207, 191, 178, 149, 146, 132, 130, 118, 106, 69, 55, 41. ^{1}H NMR spectrum: 0·70 s, 6 H (2 CH_3C); 1·26 s, 20 H (10 CH_2); 3·11—3·14 m, 8 H (2 CH_2COO, 2 CCH_2O); 3·61 s, 6 H (2 $COOCH_3$); 3·68 s, 4 H (2 NCH_2); 3·81 s, 4 H (2 OCH_2CO); 7·32 m, 8 H (2 C_6H_4).

5,18-*Bis*[4-(*methoxycarbonylmethyl*)*phenyl*]-5,18-*diaza*-2,21-*dioxabicyclo*[20,4,0]-*hexacosane*-4,19-*dione* (VII): 45%. For $C_{40}H_{56}N_2O_8$ (692·8) calculated: 69·34% C, 8·15% H, 4·04% N; found: 69·08% C, 8·13% H, 4·05% N. Mass spectrum: 692 (M^+), 661, 633, 611, 595, 564, 553, 535, 522, 506, 486, 477, 460, 433, 390, 223, 207, 191, 178, 165, 146, 132, 130, 118, 106, 81, 69, 55, 41. ^{1}H NMR spectrum: 1·27 m, 20 H (10 CH_2); 1·36—1·62 m, 8 H (C_6H_8); 3·14 m, 6 H (2 C_6H_2, 2 CH_2COO); 3·61 s, 6 H (2 $COOCH_3$); 3·69 s, 4 H (2 NCH_2); 3·95 s, 4 H (2 OCH_2CO); 7·27 m, 8 H (2 C_6H_4).

7,20-Dibenzyl-2,2,3,3-tetramethyl-7,20-diaza-1,4-dioxacyclodocosane-6,21-dione (*VIII*): cf. ref.[7].

7,20-Dicyclohexyl-2,2,3,3-tetramethyl-7,20-diaza-1,4-dioxacyclodocosane-6,21-dione (*IX*): cf. ref.[7].

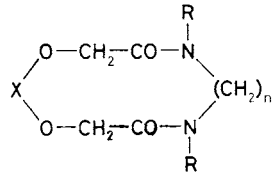
Preparation of Membrane Electrodes and *EMF* Measurements

The membranes were prepared by casting a solution of high-molecular weight PVC in cyclohexanone containing a plasticizer and ionophore employing a procedure reported earlier[5]. From a membrane, c. 0·15 mm thick, a disc of suitable size was cut out and welded to a PVC tube, i.d. 5 mm. The electrode unit was completed by inserting an internal wire silver–chloride electrode and filled with a 0·1M-LiCl solution.

The *EMF* of the cell was measured at 25°C with an Ionanalyzer 901 electrometer (Orion). In all cases the following cell was used: Hg; Hg_2Cl_2/KCl_{sat}/0·1M-NH_4NO_3/measured solution/ /polymeric membrane/internal filling solution 0·1M-LiCl/AgCl; Ag. The selectivity coefficients K^{pot}_{LiM} were determined by the separate solution method in 0·1M chloride solutions of the respective cations.

RESULTS AND DISCUSSION

A series of macrocyclic diamides *I*–*IX* was prepared, containing various numbers of methylene groups in the polymethylene part of the ring and with the structure-modified group X in the dioxadiacyl part of the macroring. The ion-selective pro-



I, X = $C(CH_2)_2C(CH_3)_2$; R = *p*-$C_6H_4CH_2COOCH_3$; *n* = 6
II, X = $C(CH_3)_2C(CH_3)_2$; R = *p*-$C_6H_4CH_2COOCH_3$; *n* = 10
III, X = $C(CH_3)_2C(CH_3)_2$; R = *p*-$C_6H_4CH_2COOCH_3$; *n* = 12
IV, X = $C(CH_3)_2C(CH_3)_2$; R = *p*-$C_6H_4CH_2COOCH_3$; *n* = 14
V, X = $CH_2C(CH_3)_2CH_2$; R = *p*-$C_6H_4CH_2COOCH_3$; *n* = 10
VI, X = $CH_2C(CH_3)_2CH_2$; R = *p*-$C_6H_4CH_2COOCH_3$; *n* = 12
VII, X = 1,2-cyclohexanediyl; R = *p*-$C_6H_4CH_2COOCH_3$; *n* = 12
VIII, X = $C(CH_3)_2C(CH_3)_2$; R = benzyl; *n* = 12
IX, X = $C(CH_3)_2C(CH_3)_2$; R = cyclohexyl; *n* = 12

perties of the compounds (ligands) thus prepared were studied electrochemically. The ionophores were incorporated in membranes from high-molecular weight poly(vinyl chloride) plasticized with dipentylphthalate. The selectivity coefficients with respect to Li^+ obtained from *EMF* measurements are plotted in Fig. 1. The numerical values of selectivity coefficients with respect to sodium and potassium ions which are of importance for practical applications are given in Table I. With macrocyclic diamides of 4,4,5,5-tetramethyl-3,6-dioxaoctanedioic acid the effect of the number of methylene groups in the closing amide chain was investigated. Ligand *I* with six methylene groups virtually does not show any preference of lithium ions. An increase in the ring size in ligand *II* by the extension of the methylene chain to ten members led to an increase in the Li^+-selectivity by an order of magnitude. Further increase in selectivity, especially with respect to alkali metal ions, was achieved with diamide *III* having 12 methylene groups in the chain. Courtauld's atomic models of ligands show that in the sixteen-membered ring of ligand *I* ($n = 6$) the donor oxygen atoms possess only a limited mobility due to steric strain, and cannot therefore occupy the optimal position for binding Li^+. This may explain the low Li^+-selectivity of the ionophore. An increase in the ring size of ligands *II*, *III* gives the molecule of the ligand a better possibility of reaching the optimal conformation, which also results in a higher selectivity of the ligand. Additional increase in the ring size by adding two methylene groups in ligand *IV* ($n = 14$) did not cause further improvement in Li^+-selectivity.

In order to verify the effect of structure of the carbon bridge **X** between oxygen atoms of the macrocycle on the Li^+-selectivity, macrocyclic diamides of 5,5-dimethyl-3,7-dioxanonanedioic (ligands *V*, *VI*) and *trans*-1,2-cyclohexanedioxydiacetic (*VII*) acid were also prepared. The Li^+-selectivity of these ligands, however, is lower by as much as an order of magnitude than that of similar diamides of 4,4,5,5-tetramethyl-3,6-dioxaoctanedioic acid (ligands *II*–*IV*). Thus, the presence of four methyl groups near the donor oxygen atoms is just the important factor affecting the Li^+--selectivity of the ionophore. It can also be seen in Fig. 1 that a ring increase of ligand *V* ($n = 10$) in the linking chain of amide groups by two methylene groups resulted in ligand *VI* ($n = 12$) in the reduction of Li^+-preference. Compared with ligands *II* and *III*, this effect is just an opposite one.

The effect of a change in the substituent on amide nitrogen atoms can be seen in the selectivity behaviour of ionophores *VIII* and *IX*. In ligand *VIII* the original N-substituents containing ester groups have been substituted with lipophilic benzyl substitents, in order to remove the possibility of coordination of ester oxygen atoms with the interfering cations. This change had a favourable effect on the Li^+-selectivity of the ligand. The highest selectivity with respect to alkali metals (cf. Table I) was

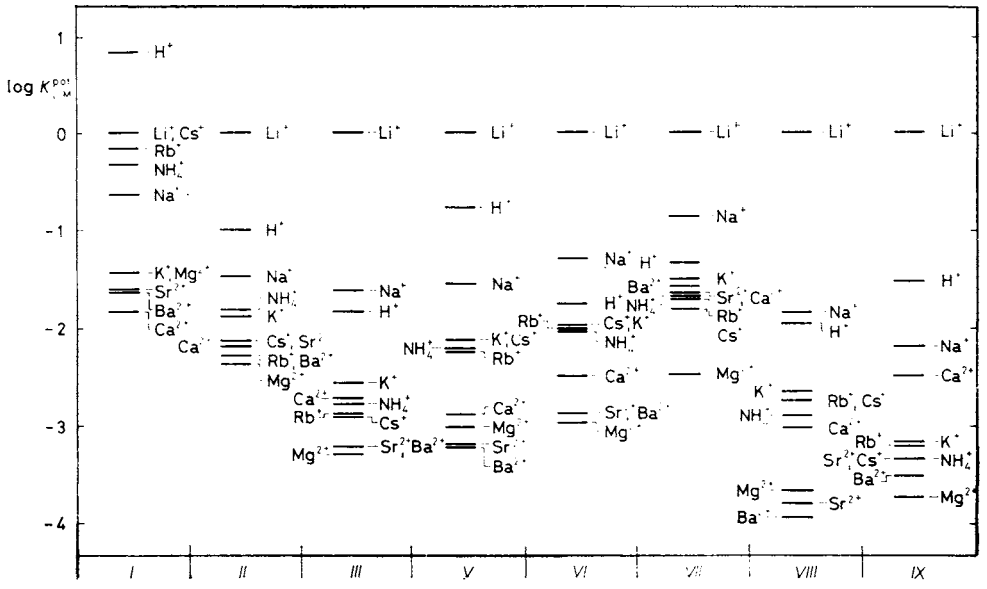


FIG. 1

Selectivity coefficients $\log K^{pot}_{LiM}$ of membranes containing macrocyclic diamides. Dipentylphthalate used as the plasticizer of the polymeric membrane

achieved with ligand *IX* containing bulky cyclohexyl N-substituents. The Li^+-Na^+ selectivity observed is equivalent to the Li^+-Na^+ selectivities by Simon[2] and Kimura[4]. For the other alkali metal ions the selectivity is even higher by an order of magnitude.

The course of the electrode function of the membrane with ionophore *VIII* and dipentylphthalate as the plasticizer is linear within the Li^+ activity range from 10^{-1} to 10^{-4} mol l^{-1} with the theoretical slope 59·2 ± 1 mV (Fig. 2). The use of a plasti-

TABLE I

Selectivity coefficients for Li^+ with respect to Na^+ and K^+ of membranes containing macrocyclic diamides *I*—*IX* in dipentylphthalate

Diamide	$K^{pot}_{LiM} \cdot 10^2$		$1/K^{pot}_{LiM}$	
	Na^+	K^+	Na^+	K^+
I	23	3·7	4	27
II	3·4	1·3	30	78
III	2·4	0·28	42	355
IV	4·7	3·3	21	304
V	2·9	0·74	35	135
VI	4·9	1·1	20	96
VII	14	3·2	7	32
VIII	1·5	0·22	68	447
IX	0·68	0·069	148	1 445

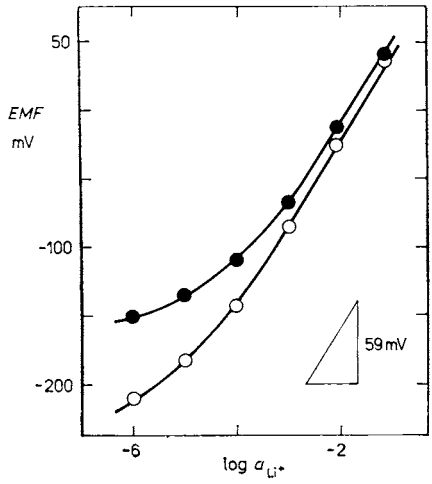


FIG. 2

Dependence of *EMF* of the membrane electrode with ionophore *VIII* on the logarithm of Li^+ activity in solution. Plasticizer of the polymeric membrane: ● *o*-nitrophenyloctyl ether, ○ dipentyl phthalate

cizer having a higher dielectric constant (*o*-nitrophenyloctyl ether) restricted the linear character of this dependence to the range between 10^{-1} and 10^{-3} mol l^{-1}. At the same time, the Li^+ selectivity of the system dropped considerably, especially with respect to alkaline earth metal ions. The potential of the membrane electrode with dipentylphthalate as plasticizer of the polymeric membrane with a change in the Li^+ activity in solution was established within c. 30 s and was very stable. The electrode functions of ligands *III* and *IX* were virtually the same. Hence, the characteristics of the polymeric membranes investigated in this study which contain macrocyclic diamides *III*, *VIII*, and *IX* suggest that the membranes may be used for analytical purposes.

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