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Synthesis and potentiometric selectivity study of new spiro-14-crown-4 derivatives

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Four new compounds with 14-crown-4 attached to spirocyclopentane or spirocyclohexane were synthesized and tested for potentiometric selectivity for lithium ion in polyvinyl chloride membrane electrodes. Four plasticizers were studied and the addition of trioctylphosphine oxide (TOPO) was investigated. One ionophore exhibited a sodium/lithium selectivity, $K^{pot}_{Li, Na}$ by the matched potential method of 0.0028 in the presence of 1% TOPO, using o-nitrophenylphenyl ether as plasticizer. Selectivities are reported for sodium, potassium, nickel, cobalt, barium and calcium.

INTRODUCTION

The importance of lithium determination in serum in the presence of other interfering ions, especially sodium ion, led to systematic studies using different lithium ion selective electrodes. One important class of ionophores used in such electrodes was found to be derivatives of crown ethers and among them 14-crown-4 derivatives were proved to be the most selective for lithium ion.[1] However, structural variations of the substituent, due to steric effects and/or lipophilicity, alter considerably such selectivities. Several recent reports showed the dependence of lithium selectivity on the substituent in 14-crown-4.[2-10]

These facts prompted the synthesis of the new 14-crown-4 **7** – **10** annelated with spirocyclopentane and spirocyclohexane and their evaluation as neutral carriers in lithium ion selective electrodes.

EXPERIMENTAL

Synthesis of spiro-14-crown-4 derivatives

Two routes were investigated for the synthesis of the spiro-14-crown-4 derivatives **7** – **10** and these are illustrated in Scheme 1. In the first route, cycloalkane-1,1-dimethanol ditosylates **5a,b** were allowed to react with the diols **3a,b** in tetrahydropyran (THP) and NaH under reflux. This route was proved to be completely unsuccessful and the starting materials were recovered completely unchanged even after 120 h of reflux. In the second route each of the cycloalkane-1, 1-dimethanol **6a,b** was reacted with the diol ditosylate **4a,b** in THP and NaH. In the latter route the spirocrown ethers **7** – **10** were obtained in 18 – 20% yield after 120 h of heating the reactants under reflux. In both routes equimolecular amounts of the ditosylate and the diol were dissolved in THP and added dropwise to a refluxing mixture of NaH in THP (modified high dilution procedure).[13] The failure of the first route can be explained on the basis of the difficult nucleophilic attack of the alkoxide anion of **3** on the sterically hindered diol ditosylates **5a,b**. The starting diols **3a,b** were now prepared by $LiAlH_4$ reduction of the esters **2a,b**.[12] Also, the diols **6a,b** and the ditosylate **4a**[4], **4b**[2], **5a,b**[11] were prepared as described in the literature following reaction pathways illustrated in Scheme 1.

Synthesis of the diols 3a,b

To a cold suspension of $LiAlH_4$ (80 mmol) in dry ether (100 mL), each of **2a,b** (50 mmol) in dry ether (200 mL) was added dropwise with stirring over a period of 30 min. The mixture was then refluxed for 20 h. The excess $LiAlH_4$ was decomposed by slow addition of 10 mL of water with cooling and stirring. The etheral solution was then separated by filtration. The solvent was removed in vacuo and the products were used after vacuum distillation in the next step without further purification. *Compound 3a*[4] was obtained in 72% yield. *Compound 3b*[2] was obtained in 70% yield.

Synthesis of spiro-14-crown-4 7 – 10

Sodium hydride (50% suspension in mineral oil) (1.44 gm, 30 mmol) was washed with n-pentane and suspended in tetrahydropyran (THP) (25 mL). To this mixture

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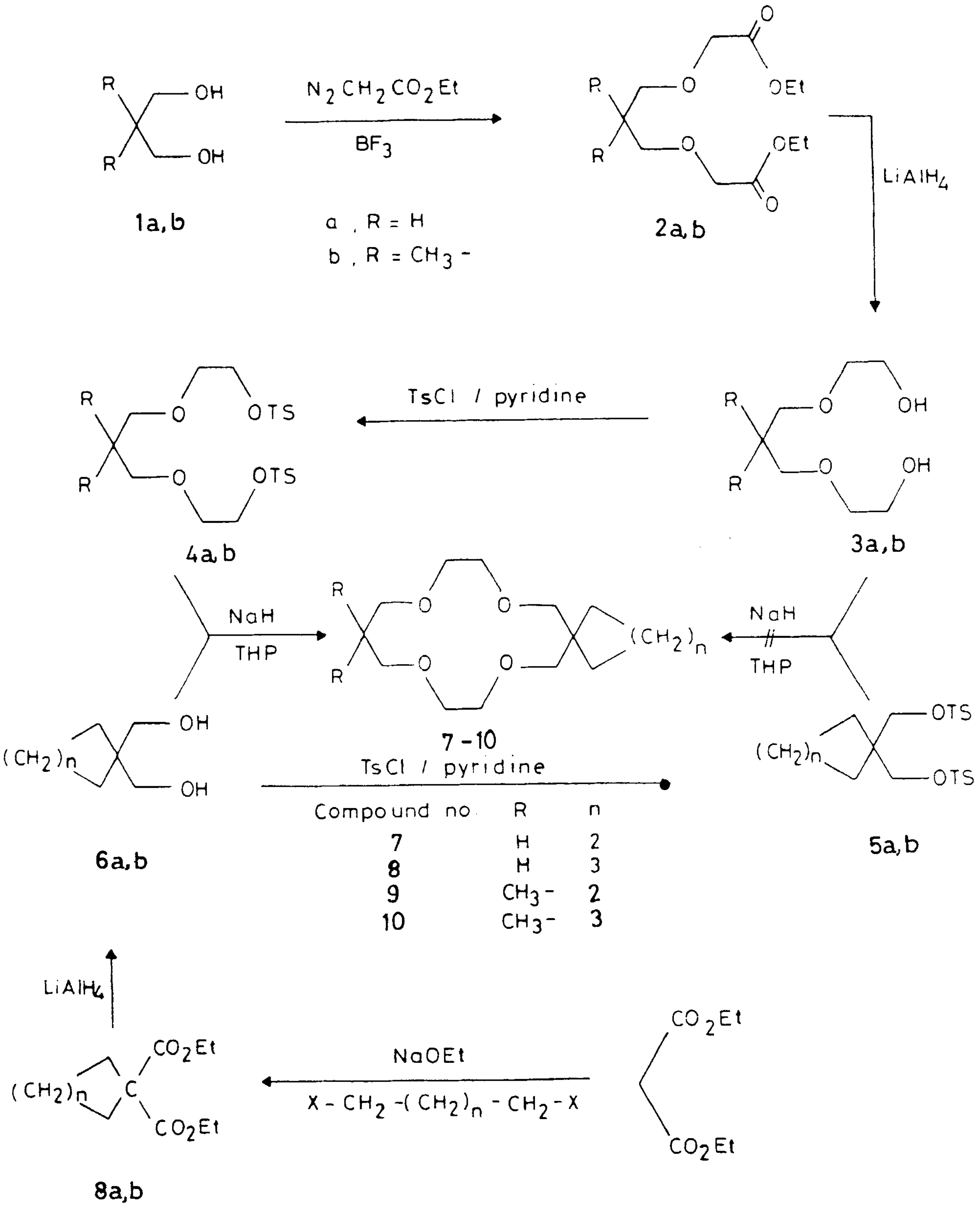

Compound no	R	n
7	H	2
8	H	3
9	CH_3-	2
10	CH_3-	3

Scheme 1

was added a solution containing the appropriate diol **6a,b** (10 mmol) and the appropriate ditosylate **4a,b** (10 mmol) in THP (25 mL) dropwise over a period of 24 h. The reaction mixture was then heated under reflux for 120 h. Water (10 mL) was added and reflux was further continued for 6 h and then extracted with chloroform (3 × 60 mL). The combined extracts were dried over magnesium sulfate and the solvent was evaporated in vacuo to give the crude product which was purified by column chromatography on silica gel with petroleum ether/ethyl acetate (10:1) as an eluent to give the corresponding spiro-14-crown-4 **7** – **10** as pale yellow oils 18 – 20% yield.

Compound 7. MS: m/z = 258 (M^+); ^1H NMR ($CDCl_3$) δ 0.85 – 1.86 (m, 2H, $OCH_2\underline{CH_2}CH_2O$, 8H of cyclopentane); 3.2 – 4.15 (m, 16H, OCH_2) ppm. Analysis: found C, 65.10; H, 9.80. $C_{14}H_{26}O_4$ requires: C, 65.08; H, 10.14.

Compound 8. ^1H NMR ($CDCl_3$) δ 0.85 – 1.75 (m, 2H, $OCH_2\underline{CH_2}CH_2O$, 10H of cyclohexane); 3.3 – 4.25 (m, 16H, OCH_2.) ppm. Analysis: found: C, 66.30; H, 10.40. $C_{15}H_{28}O_4$ requires: C, 66.14; H, 10.36.

Compound 9. ^1H NMR ($CDCl_3$) δ 0.85 – 1.70 (m, 6H, $2CH_3$, 8H of cyclopentane); 3.18 – 3.80 (m, 16H, O-CH_2) ppm. Analysis: found: C, 67.30; H, 10.30. $C_{16}H_{30}O_4$ requires: C, 67.10; H, 10.56.

Compound 10. MS: m/z = 300 (M^+); ^1H NMR ($CDCl_3$) δ 0.88 – 1.70 (m, 6H, $2CH_3$, 10H of clycohexane), 3.2 – 4.2 (m, 16H, OCH_2) ppm. Analysis: found: C, 68.10; H, 10.80. $C_{17}H_{32}O_4$ requires: C, 67.96; H, 10.74.

Reagent and chemicals

High molecular weight poly(vinyl chloride) (PVC) was obtained from Fluka AG. The plasticizers o-nitrophenyloctyl ether (NPOE), o-nitrophenylphenyl ether (NPPE), o-nitrophenylbutyl ether (NPBE) and o-nitrophenylbenzyl ether (NPBnE) were prepared following reported procedures.[14] Potassium tetrakis-p-chlorophenyl borate (KTpClPB) was obtained from speciality Organics, Inc., Irwindale, California. All salt solutions were prepared from reagent grade compounds using deionized water. The chlorides of the metals were used in all cases.

Electrode measurement system

Measurements were performed by the use of the following cell:

Hg,Hg_2Cl_2, KCl (satd) // sample solution / membrane / AgCl / Ag.

A Beckman digital pH meter (Model 4500) was used for monitoring the voltage.

Electrode membrane solution preparation

Poly(vinyl chloride) (33.0 mg), individual 14-crown-4 **7** – **10** corresponding to a minimum of 4% (W/W) (4.1 mg) of neutral carrier in the membrane, a plasticizer (NPOE, NPPE, NPBE or NPBnE) (65.0 mg), KTpClPB (0.5 mg) and TOPO (1.0 mg) were dissolved in 350 µL tetrahydrofuran (THF).

Electrode fabrication

Two aliquots of 25 µL of the above membrane solution were carefully deposited on a compact silver-silver chloride plug of a Beckman threaded ion selective electrode tip. The second aliquot was deposited after the first aliquot had almost dried. The tip was left to stand for 24 h to allow the THF solvent to evaporate and then it was soaked in 0.1 M LiCl solution for 24 h before use; here we followed a recommended procedure.[1]

Procedure

Selectivity coefficients were determined by the matched potential,[15] the separate solution[16] and the fixed interference methods,[17] as previously described.[18] In the first, a background concentration of the interferant ion was employed that was approximately equal to that found in blood serum, i.e. 140 mM NaCl. Standard solutions of 20, 40, 60, 80 and 110 mM NaCl, KCl, $NiCl_2$, $CoCl_2$, $BaCl_2$ and $CaCl_2$ in 140 mM NaCl were used to prepare calibration curves. Standard solutions (primary ion) of 0.2, 0.5, 2, 5, 10, 20, 50, 100 and 200 mM LiCl prepared in 140 mM NaCl were also used. In the separate solution method, all the standard solutions were prepared in deionized water.

In the mixed solution method or fixed interference method[15,17], the linear portion of the lithium calibration curve (obtained in the presence of a fixed concentration of the secondary ion) is extrapolated to the potential of the background secondary ion solution (method A). The concentration of lithium at that point is equivalent to the concentration of the secondary ion.

In the second form of the mixed solution method, the concentration of lithium ion at which the extrapolated Nernstian line differs by 18 mV (for monovalent ions) from the experimental curve corresponds to the point at which the apparent concentration is theoretically doubled due to the presence of the secondary ion (method B). In cases where the slope of the curve deviated from Nernstian, the amount of deviation from the linear portion was corrected proportionally.

RESULTS AND DISCUSSION

Selectivity coefficients

Tables 1 – 4 list the selectivity coefficients of sodium, potassium, nickel, cobalt, barium and calcium ions with respect to lithium ion, using the matched potential methods and the separate solution methods, for ionophores **7**

Table 1 Selectivity coefficients $K^{pot}_{Li,M}/^{l}/K^{pot}_{Li,M}$ determined by two methods[a] for **7** – **10** ionophores using o-nitrophenyloctyl ether (NPOE) plasticizer. Electrode matrix includes 1% TOPO.

Neutral carrier	$K^{pot}_{Li,Na}/^{l}/_{K}$		$K^{pot}_{Li,K}/^{l}/_{K}$		$K^{pot}_{Li,Ni}/^{l}/_{K}$		$K^{pot}_{Li,Co}/^{l}/_{K}$		$K^{pot}_{Li,Ba}/^{l}/_{K}$		$K^{pot}_{Li,Cd}/^{l}/_{K}$	
	M.P.	*S.S.*	*M.P.*	*S.S.*	*M.P.*	*S.S.*	*M.P.*	*S.S.*	*M.P.*	*S.S.*	*M.P.*	*S.S.*
7	0.041	0.33	1.69	0.6	0.035	0.22	0.485	1.96	0.051	1.2	0.063	1.15
	24.3	3.0	0.59	1.7	28.6	4.5	2.06	0.5	19.5	0.83	15.82	0.87
8	0.038	0.286	0.33	1.7	0.00616	0.07	0.2	1.25	0.123	1.1	0.099	0.59
	26.4	3.5	3	0.6	162.4	14.2	5	0.8	8.1	0.9	10.06	1.69
9	0.053	0.2	0.45	0.25	0.00477	0.078	0.206	0.34	0.017	0.12	0.24	0.079
	19	5	2.2	4	209.6	12.8	4.8	2.9	58.3	8.3	4.1	12.5
10	0.027	0.09	0.137	0.13	0.0206	0.024	0.07	0.13	0.024	0.063	1.38	0.04
	36.1	11.1	7.3	7.6	48.5	41.5	14.2	7.5	41.05	15.8	0.725	22.78

[a] M.P., matched potential method; S.S., separate solution method

Table 2 Selectivity coefficients $K^{pot}_{Li,M}/^{l}/K^{pot}_{Li,M}$ determined by two methods[a] for **7** – **10** ionophores using o-nitrophenylphenyl ether (NPPE) plasticizer. Electrode matrix includes 1% TOPO.

Neutral carrier	$K^{pot}_{Li,Na}/^{l}/_{K}$		$K^{pot}_{Li,K}/^{l}/_{K}$		$K^{pot}_{Li,Ni}/^{l}/_{K}$		$K^{pot}_{Li,Co}/^{l}/_{K}$		$K^{pot}_{Li,Ba}/^{l}/_{K}$		$K^{pot}_{Li,Cd}/^{l}/_{K}$	
	M.P.	*S.S.*	*M.P.*	*S.S.*	*M.P.*	*S.S.*	*M.P.*	*S.S.*	*M.P.*	*S.S.*	*M.P.*	*S.S.*
7	0.021	0.075	0.046	0.11	0.115	0.097	0.77	0.6	0.14	0.14	0.537	0.69
	46.5	13.2	21.46	8.5	8.65	10.2	1.3	1.6	7.1	6.9	1.86	1.4
8	0.0028	0.0217	0.0105	0.035	0.0146	0.065	0.083	0.29	0.076	0.43	0.058	0.24
	356.4	46.0	95.4	28.5	68.43	15.25	12	3.4	13	2.3	17.24	4.17
9	0.037	0.11	0.167	0.13	0.057	0.061	0.32	0.296	0.056	0.09	0.417	0.3
	26.7	9	6	7.65	17.6	16.4	3.1	3.37	17.8	11.0	2.4	3.33
10	0.0271	0.091	0.024	0.049	0.67	1.98	1.12	1.1	0.26	0.438	9	4.9
	36.8	11.0	41.67	20.4	1.49	0.5	0.9	0.91	3.9	2.28	0.11	0.204

[a] M.P., matched potential method; S.S., separate solution method

Table 3 Selectivity coefficients $K^{pot}_{Li,M}/^{l}/K^{pot}_{Li,M}$ determined by two methods[a] for **7** – **10** ionophores using o-nitrophenylbutyl ether (NPBE) plasticizer. Electrode matrix includes 1% TOPO.

Neutral carrier	$K^{pot}_{Li,Na}/^{l}/_{K}$		$K^{pot}_{Li,K}/^{l}/_{K}$		$K^{pot}_{Li,Ni}/^{l}/_{K}$		$K^{pot}_{Li,Co}/^{l}/_{K}$		$K^{pot}_{Li,Ba}/^{l}/_{K}$		$K^{pot}_{Li,Cd}/^{l}/_{K}$	
	M.P.	*S.S.*	*M.P.*	*S.S.*	*M.P.*	*S.S.*	*M.P.*	*S.S.*	*M.P.*	*S.S.*	*M.P.*	*S.S.*
7	0.016	0.06	0.038	0.114	0.188	0.18	0.435	1.16	0.162	0.64	2.04	4.46
	61.6	15.9	26.3	8.77	5.3	5.55	2.3	0.86	6.17	1.57	0.49	0.22
8	0.0148	0.05	0.07	0.113	0.018	0.055	0.15	0.48	0.113	0.76	0.041	0.19
	67.5	20	14.4	8.8	54.7	18.2	6.6	2.1	8.8	1.3	24.2	5.2
9	0.041	0.07	0.042	0.127	0.259	0.29	0.77	0.93	0.169	0.4	2.14	1.66
	24.4	14	23.8	7.88	3.85	3.45	1.3	1.07	5.9	2.5	0.47	0.6
10	0.076	0.09	0.194	0.187	0.16	0.49	1.42	5.3	0.564	1.89	4	3.49
	13	11	5.16	5.34	6.17	2.04	0.7	0.188	1.77	0.53	0.25	0.286

[a] M.P., matched potential method; S.S., separate solution method

– **10** with 1% TOPO in the electrode matrices. Tables 5 – 8 list the selectivity coefficients determined with and without TOPO using the matched potential method, the separate solution methods and the fixed interference methods. A comparison of relative selectivities with different plasticizers (with 1% TOPO) is given in Table 9. The selectivity coefficient $K^{pot}_{Li,Na}$ were calculated from the calibration curves using the matched potential method[15,19] and the separate solution or fixed interference methods. It is known that the selectivity coefficient varies with the method used to measure it and experimental[15] conditions. Hence, several methods were employed. The separate solution and fixed interference methods are standard comparison methods, while the matched potential method often better reflects analytical experimental conditions. It should be noted that, espe-

Table 4 Selectivity coefficients $K^{pot}_{Li,M}/{}^{1}/K^{pot}_{Li,M}$ determined by two methods[a] for **7 – 10** ionophores using o-nitrophenylbenzyl ether (NPBnE) plasticizer. Electrode matrix includes 1% TOPO.

Neutral carrier	$K^{pot}_{Li,Na}/{}^{1}/_{K}$		$K^{pot}_{Li,K}/{}^{1}/_{K}$		$K^{pot}_{Li,Ni}/{}^{1}/_{K}$		$K^{pot}_{Li,Co}/{}^{1}/_{K}$		$K^{pot}_{Li,Ba}/{}^{1}/_{K}$		$K^{pot}_{Li,Ca}/{}^{1}/_{K}$	
	M.P.	*S.S.*	*M.P.*	*S.S.*	*M.P.*	*S.S.*	*M.P.*	*S.S.*	*M.P.*	*S.S.*	*M.P.*	*S.S.*
7	0.018	0.093	0.099	0.105	0.22	0.145	0.31	0.9	0.31	0.27	6.67	2.3
	54.4	10.75	10.12	9.5	4.5	6.89	3.2	1.1	3.2	3.7	0.15	0.43
8	0.00485	0.052	0.0149	0.083	0.028	0.093	0.137	0.63	0.157	0.63	0.08	0.33
	206	19	67	12	35.5	10.7	7.3	1.6	6.3	1.6	12.4	3.0
9	0.137	0.145	0.88	0.526	0.494	0.142	2.25	1.02	0.82	0.49	2.4	1.88
	7.3	6.9	1.1	1.9	2.02	7.04	0.44	0.98	1.2	2.03	0.417	0.53
10	0.063	0.08	0.3	0.465	0.46	1.25	2.75	2.04	1.01	0.258	16	4.8
	15.8	12.08	3.33	2.15	2.17	0.8	0.36	0.49	0.99	3.87	0.06	0.208

[a] M.P., matched potential method; S.S., separate solution method

Table 5 Selectivity coefficients for **7** using NPBE plasticizer with and without TOPO.

Method[a]	*TOPO*	*Slope mV decade*	*Selectivity coefficients*					
			$K^{pot}_{Li,Na}$ 1/K	$K^{pot}_{Li,K}$ 1/K	$K^{pot}_{Li,Ni}$ 1/K	$K^{pot}_{Li,Co}$ 1/K	$K^{pot}_{Li,Ba}$ 1/K	$K^{pot}_{Li,Ca}$ 1/K
1	1	49.2	0.016	0.038	0.188	0.435	0.162	2.04
			61.6	26.3	5.3	2.3	6.17	0.49
1	0	56.6	0.037	0.04	0.33	0.52	0.17	3.1
			26.9	25	3	1.9	5.8	0.32
2	1	53.5	0.06	0.114	0.18	1.16	0.64	4.46
			15.9	8.77	5.55	0.86	1.57	0.22
2	0	60.0	0.147	0.175	0.208	2.56	0.714	5.0
			6.78	5.7	4.8	0.39	1.4	0.2
3	1		0.056					
			17.62					
3	0		0.100					
			10					
4	1		0.0505					
			19.8					
4	0		0.095					
			10.5					

[a] 1, Matched potential method; 2, separate solution method; 3, fixed interference method (method A); 4, fixed interference method (method B)

cially with TOPO in the membrane, the slopes of the calibration curves are less than Nernstian. Hence, the selectivity coefficient results obtained by the separate solution method should not be considered true values, but only relative.

It is known[6,20] that the presence of TOPO in the electrode matrix has a variety of effects and increases the selectivity coefficients of lithium over sodium and most cations. In the present electrode matrices, TOPO almost always increases the selectivity for lithium over sodium from two to five times and the best selectivity ($1/K^{pot}_{Li,Na}$ up to 356.4) was achieved with ionophore **8** incorporated in the electrode containing 1% TOPO and NPPE plasticizer.

The present study shows that compounds with cyclohexane moieties show higher selectivity for lithium over sodium than those with cyclopentane derivatives. This may be attributed to the change in the cavity size of the 14-crown-4. Also, spiro derivatives with no other substituents in the macrocycle show higher selectivities over those with additional substituents. Thus the lithium selectivity (matched potential methods) decreases from 356.4 for compound **8** to 36.8 for the dimethyl derivative **10**. Similar behavior is observed for the spirocyclopentane **7** and its substituted derivatives **9**. Apparently, the steric effect caused by these substituents decreases the complexing ability of the macrocycle toward the desired ion and hence its selectivity.

Table 6 Selectivity coefficients for **8** using NPPE plasticizer with and without TOPO.

Method[a]	*TOPO*	*Slope*	*Selectivity coefficients*					
		mV	$K^{pot}_{Li,\,Na}$	$K^{pot}_{Li,\,K}$	$K^{pot}_{Li,\,Ni}$	$K^{pot}_{Li,\,Co}$	$K^{pot}_{Li,\,Ba}$	$K^{pot}_{Li,\,Ca}$
		decade	*1/K*	*1/K*	*1/K*	*1/K*	*1/K*	*1/K*
1	1	40.0	0.0028 356.4	0.0105 95.4	0.0146 68.43	0.083 12	0.076 13	0.058 17.24
1	0	53.3	0.0147 68.0	0.065 15.3	0.0176 56.6	0.102 9.8	0.128 7.8	0.0763 13.1
2	1	48.3	0.0217 46.0	0.035 28.5	0.065 15.25	0.29 3.4	0.43 2.3	0.24 4.17
2	0	58.3	0.04 25	0.08 12.5	0.1 10	0.8 1.25	1 1	0.32 3.125
3	1		0.033 29.59					
3	0		0.10 10					
4	1		0.0268 37.25					
4	0		0.090 11.11					

[a] 1, Matched potential method; 2, separate solution method; 3, fixed interference method (method A); 4, fixed interference method (method B)

Table 7 Selectivity coefficients for **9** using NPPE plasticizer with and without TOPO.

Method[a]	*TOPO*	*Slope*	*Selectivity coefficients*					
		mV	$K^{pot}_{Li,\,Na}$	$K^{pot}_{Li,\,K}$	$K^{pot}_{Li,\,Ni}$	$K^{pot}_{Li,\,Co}$	$K^{pot}_{Li,\,Ba}$	$K^{pot}_{Li,\,Ca}$
		decade	*1/K*	*1/K*	*1/K*	*1/K*	*1/K*	*1/K*
1	1	35.7	0.037 26.7	0.167 6	0.057 17.6	0.32 3.1	0.056 17.8	0.417 2.4
1	0	46.7	0.074 13.5	0.37 2.7	0.055 18	0.2 5	0.048 20.8	0.31 3.2
2	1	47.3	0.11 9.0	0.13 7.65	0.061 16.4	0.296 3.37	0.09 11.0	0.3 3.33
2	0	61.5	0.25 4.0	0.32 3.16	0.1 10	0.398 2.5	0.126 7.94	0.416 2.4
3	1		0.056 17.9					
3	0		0.16 6.25					
4	1		0.036 27.8					
4	0		0.169 5.91					

[a] 1, Matched potential method; 2, separate solution method; 3, fixed interference method (method A); 4, fixed interference method (method B)

Table 8 Selectivity coefficients for **10** using NPPE plasticizer with and without TOPO.

Method[a]	*TOPO*	*Slope*	*Selectivity coefficients*					
		mV	$K^{pot}_{Li, Na}$	$K^{pot}_{Li, K}$	$K^{pot}_{Li, Ni}$	$K^{pot}_{Li, Co}$	$K^{pot}_{Li, Ba}$	$K^{pot}_{Li, Ca}$
		decade	*1/K*	*1/K*	*1/K*	*1/K*	*1/K*	*1/K*
1	1	33.7	0.0271	0.024	0.67	1.12	0.26	9.0
			36.8	41.67	1.49	0.9	3.9	0.11
1	0	53.3	0.033	0.034	0.49	0.94	0.30	16.66
			30.2	29.4	2.04	1.06	3.32	0.06
2	1	47.3	0.091	0.049	1.98	1.1	0.438	4.9
			11.0	20.4	0.5	0.91	2.28	0.204
2	0	58.3	0.204	0.196	2.5	1.15	0.735	8.33
			4.9	5.09	0.4	0.87	1.36	0.12
3	1		0.015					
			66.2					
3	0		0.042					
			23.5					
4	1		0.0127					
			78.7					
4	0		0.0357					
			27.9					

[a] 1, Matched potential method; 2, separate solution method; 3, fixed interference method (method A); 4, fixed interference method (method B)

Table 9 Comparison of selectivities for lithium over sodium ($1/K^{pot}_{Li, Na}$) determined by four methods[a] with different plasticizers[b].

Ionophore	*Plasticizer 1*				*Plasticizer 2*				*Plasticizer 3*				*Plasticizer 4*			
	m_1	m_2	m_3	m_4	m_1	m_2	m_3	m_4	m_1	m_2	m_3	m_4	m_1	m_2	m_3	m_4
7	24.3	3.0	33.3	35.7	46.5	13.2	20	28.6	61.1	15.9	17.6	19.8	54.4	10.75	7.4	8.8
8	26.4	3.5	20	28.6	356.4	46	29.6	37.25	67.5	20	25	43.5	206	19	63.6	78.1
9	19	5	18.66	20.9	26.7	9.0	17.9	27.8	24.4	14	17.6	19.77	7.3	6.9	8.8	9.9
10	36.1	11.1	33.3	34.5	36.8	11	66.2	78.7	13	11	16.6	18.7	15.8	12.08	28	46.9

The electrode matrix includes 1% TOPO.

[a] m_1, matched potential method; m_2, separate solution method; m_3, fixed interference method (method A); m_4, fixed interference method (method B).

[b] Plasticizer 1, o-nitrophenyloctyl ether (NPOE); plasticizer 2, o-nitrophenylphenyll ether (NPPE); plasticizer 3, o-nitrophenylbutyl ether (NPBE); plasticizer 4, o-nitrophenylbenzyl ether (NPBnE).

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