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New Type of Lariat Ethers: Synthesis and Cation Binding Ability of Phosphonoalkyl-Azacrown Ethers

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Abstract. The synthesis of azacrown ethers with phosphonoalkyl side chains of two to five carbon atoms (**3–8, 10**), potentially useful as a new type of cation binding agent, is described. Introduction of the phosphonoalkyl moiety into the parent monoaza-15-crown-5 (**1**) decreases the cation extraction ability, but results in an increase in the selectivity towards the cations examined. The effect of the phosphonoalkyl-azacrown ethers on the properties of membranes used in ion-selective electrodes is also reported.

Key words: azacrown ethers, lariat ethers, phosphonoalkyl side chain, extraction ability.

1. Introduction

It is well known that the complexing ability of the crown ethers can be modified by the introduction of side chains. The effect of phosphorus containing substituents on the complexing ability of azacrown ethers is less studied. Several phosphonomethyl derivatives of monoaza- and diazacrown ethers showing uncommon selectivity

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towards various metal ions have been described [1–3]. Other monoaza- and diazacrown ethers with one or two phosphorus containing side arms have also been synthesized [4]. These lariat ethers include phosphinoethyl or phosphinopropyl derivatives.

In this paper, new azacrown ethers with phosphonoalkyl side chains are described which have been synthesized to test their complex forming ability. We wished to assess the effect of the phosphorus function and the length of the carbon chain on the cation complexing ability of the azacrown moiety.

2. Experimental

The ^{31}P, ^{13}C and ^{1}H NMR spectra were recorded on a Bruker DRX-500 spectrometer operating at 202.4, 125.7 and 500 MHz, respectively. Chemical shifts are downfield relative to 85% H_3PO_4 or TMS. Mass spectra were obtained on an MS-RFA instrument or on a ZAB-2SEQ spectrometer at 70 eV.

General procedure for the preparation of diethyl bromoalkylphosphonates
A mixture of 16.0 mL (0.0933 mol) of triethylphosphite and 0.467 mol of the corresponding dibromoalkane was heated at 160 °C for 24 h. Excess of the dibromoalkane was removed at 20 mmHg and the residue so obtained fractionated at 0.3–0.4 mmHg. The following products were thus synthesized:

Diethyl (2-bromoethyl)phosphonate
Yield: 54%; bp 83–86 °C/0.4 mmHg (lit. [5], 101 °C/0.8 mmHg); ^{31}P NMR ($CDCl_3$) δ 26.1.

Diethyl (3-bromopropyl)phosphonate
Yield: 57%; bp 97–101 °C/0.4 mmHg (lit. [6], 94–95 °C/2 mmHg); ^{31}P NMR ($CDCl_3$) δ 31.3; MS, *m/z* 258 (M^+, 1%), 179 (99), 152 (100).

Diethyl (4-bromobutyl)phosphonate
Yield: 51%; bp 115–120 °C/0.4 mmHg (lit. [7], 120 °C/0.01 mmHg); ^{31}P NMR ($CDCl_3$) δ 31.9; MS, *m/z* 272 (M^+, 5%), 193 (92), 165 (38), 137 (100).

Diethyl (5-bromopentyl)phosphonate
Yield: 43%; bp 120–124 °C/0.3 mmHg; ^{31}P NMR ($CDCl_3$) δ 32.3; MS, *m/z* 286 (M^+, 3%), 207 (42), 179 (21), 152 (100).

Dimethyl (3-bromopropyl)phosphonate was prepared similarly, but by the reaction of trimethylphosphite and 1,3-dibromopropane at 120 °C for 7h. Yield: 41%; bp 94–98 °C/0.4 mmHg (lit. [8], 96 °C/0.05 mmHg); ^{31}P NMR ($CDCl_3$) δ 33.5; MS, *m/z* 230 (M^+, 2%), 151 (48), 124 (100).

3-Bromopropyl-diphenylphosphine oxide was prepared by the reaction of ethyl diphenylphosphinite [9] and 1,3-dibromopropane. Yield: 46% after column chromatography (3% methanol in chloroform, silica gel); ^{31}P NMR ($CDCl_3$) δ 32.2; MS, *m/z* 322 (M^+, 2%), 243 (47), 215 (44), 201 (100).

2.1. GENERAL PROCEDURE FOR THE PREPARATION OF LARIAT ETHERS **4–8**

A mixture of 1.5 g (6.85 mmol) of monoaza-15-crown-5 [10], 10.3 mmol of the corresponding bromoalkylphosphonate (or bromoalkylphosphine oxide), 0.95 g (6.85 mmol) of dry potassium carbonate in 30 mL of dry dimethylformamide (DMF) was stirred at 90 °C for 8 h. Solid components were removed by filtration and the filtrate concentrated *in vacuo*. After the addition of 3 mL of water and 50 ml of chloroform, the organic phase was dried ($MgSO_4$). The residue obtained after evaporation was purified by repeated column chromatography (3% methanol in chloroform, silica gel). The following products were thus synthesized:

2.2. DIETHYL (1,4,7,10-TETRAOXA-13-AZA-CYCLOPENTADEC-13-YLPROPYL)PHOSPHONATE (**4**)

Yield: 45%; ^{31}P NMR ($CDCl_3$) δ 33.2; ^{13}C NMR, Table I; ^{1}H NMR ($CDCl_3$) δ 1.27 (t, J = 7.1, 6H, OCH_2CH_3), 1.61–1.82 (m, 4H, C(α)H_2, C(β)H_2), 2.48–2.57 (m, 2H, C(γ)H_2), 2.66–2.74 (m, 4H, C(2)H_2), 3.52-3.69 (m, 16H, C(3)H_2, C(5)H_2, C(6)H_2, C(8)H_2), 3.97–4.10 (m, 4H, OCH_2); MS, *m/z* 396 (M^+-H, 2%), 382 (2), 352 (5), 336 (8), 232 (100) 179 (25); HRMS, $(M\text{-}H)^+_{found}$ = 396.2101, $C_{17}H_{35}NO_7P$ requires 396.2151.

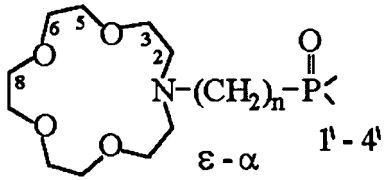
2.3. DIETHYL (1,4,7,10-TETRAOXA-13-AZA-CYCLOPENTADEC-13-YLBUTYL)PHOSPHONATE (**5**)

Yield: 41%; ^{31}P NMR ($CDCl_3$) δ 32.6; ^{13}C NMR, Table I; ^{1}H NMR ($CDCl_3$) δ 1.11 (t, J = 7.1, 6H, OCH_2CH_3), 1.34–1.42 (m, 4H, C(β)H_2, C(γ)H_2), 1.50–1.57 (m, 2H, C(α)H_2), 2.31–2.37 (m, 2H, C(δ)H_2), 2.55 (t, J = 5.7, 4H, C(2)H_2), 3.38–3.48 (m, 16H, C(3)H_2, C(5)H_2, C(6)H_2, C(8)H_2), 3.83–3.91 (m, 4H, OCH_2); MS, *m/z* 411 (M^+, 8%), 410 (M-H, 8), 396 (4), 366 (6), 350 (8) 232 (100), 193 (16); HRMS, M^+_{found} = 411.2332, $C_{18}H_{38}NO_7P$ requires 411.2386.

2.4. DIETHYL (1,4,7,10-TETRAOXA-13-AZA-CYCLOPENTADEC-13-YLPENTYL)PHOSPHONATE (**6**)

Yield: 35%; ^{31}P NMR ($CDCl_3$) δ 32.9; ^{13}C NMR, Table I; MS, *m/z* 425 (M^+, 4%), 410 (3), 380 (3), 364 (4), 232 (100), 207 (10); HRMS, M^+_{found} = 425.2473, $C_{19}H_{40}NO_7P$ requires 425.2542.

Table I. ^{13}C NMR data for lariat ethers **3–8** in $CDCl_3$ solutions



Compound	δ_C (J_{PC} in Hz)													
	C_α	C_β	C_γ	C_δ	C_ϵ	C_2	C_3	C_5	C_6	C_8	$C_{1'}$	$C_{2'}$	$C_{3'}$	$C_{4'}$
3	23.3	49.6	–	–	–	53.9	69.7[a]	70.0[a]	70.2[a]	70.8[a]	–	61.4	16.3	
	(136.6)											(6.3)	(5.9)	
4	23.1	20.4	56.8	–	–	54.6	70.0[b]	70.1[b]	70.3[b]	70.9[b]	–	61.4	16.4	
	(141.9)	(4.6)	(18.0)									(6.5)	(5.9)	
5	25.1	20.0	27.6	55.9	–	54.4	69.4[c]	69.8[c]	70.0[c]	70.6[c]		61.2	16.2	
	(140.5)	(5.0)	(16.3)									(6.3)	(6.0)	
6	25.6	22.3	28.3	26.8	56.6	54.5	69.9[d]	70.1[d]	70.4[d]	70.9[d]	–	61.4	16.4	
	(140.5)	(4.9)	(17.1)									(6.6)	(5.8)	
7	21.8	20.1	56.5	–	–	52.1	69.7[e]	69.8[e]	70.1[e]	70.6[e]	–	54.4	–	–
	(142.0)		(17.2)											
8	27.0	19.4	56.7	–	–	54.4	69.7[f]	70.0[f]	70.2[f]	70.8[f]	133.0	130.7[g]	128.5[g]	131.5
	(72.7)		(15.1)								(98.0)	(9.4)	(11.8)	(1.9)

[a–g]Tentative assignments.

2.5. DIMETHYL (1,4,7,10-TETRAOXA-13-AZA-CYCLOPENTADEC-13-YLPROPYL)PHOSPHONATE (**7**)

Yield: 31%; ^{31}P NMR ($CDCl_3$) δ 35.9; ^{13}C NMR, Table I; ^{1}H NMR ($CDCl_3$) δ 1.48-1.85 (m, 4H, C(α)H_2, C(β)H_2), 2.28–2.33 (m, 2H, C(γ)H_2), 2.33–2.57 (m, 4H, C(2)H_2), 3.33–3.62 (m, 22H, C(3)H_2, C(5)H_2, C(6)H_2, C(8)H_2, CH_3O); MS, *m/z* 369 (M^+, 1%), 368 (M^+-H, 1), 338 (3), 232 (100), 180 (39); HRMS, M^+_{found} = 369.1876, $C_{15}H_{32}NO_7P$ requires 369.1916.

2.6. (1,4,7,10-TETRAOXA-13-AZA-CYCLOPENTADEC-13-YLPROPYL)-DIPHENYLPHOSPHINE OXIDE (**8**)

Reaction time: 20h; Yield: 34%; ^{31}P NMR ($CDCl_3$) δ 33.6; ^{13}C NMR, Table I; ^{1}H NMR ($CDCl_3$) δ 1.75–1.86 (m, 2H, C(β)H_2), 2.31–2.38 (m, 2H, C(α)H_2), 2.68–2.82 (m, 6H, C(γ)H_2, C(2)H_2), 3.52–3.69 (m, 16H, C(3)H_2, C(5)H_2, C(6)H_2, C(8)H_2), 7.39–7.76 (m, 10H, Ar); MS, *m/z* 461 (M^+, 2%), 460 (M-H, 2), 400 (7), 311 (100), 243 (85); HRMS, M^+_{found} = 461.2249, $C_{25}H_{36}NO_5P$ requires 461.2331.

The reaction of monoaza 15-crown-5 with diethyl (2-bromoethyl)phosphonate afforded ethyl derivative **2** in 38% yield. ^{13}C NMR ($CDCl_3$) δ 12.0 (CH_2CH_3), 50.4 (CH_2CH_3), 53.9 (N-CH_2CH_2), 69.9 (O–CH_2), 70.0 (O–CH_2), 70.3 (O–CH_2), 70.9 (O–CH_2); MS, *m/z* 247 (M^+–H, 18%), 232 (32), 114 (78), 100 (64), 73 (92), 58 (100), 45 (96) (lit. [11], 247, 232, 114, 100, 73, 58, 45).

2.7. DIETHYL (1,4,7,10-TETRAOXA-13-AZA-CYCLOPENTADEC-13-YLETHYL)PHOSPHONATE (**3**)

A solution of 1.5 g (6.85 mmol) of monoaza-15-crown-5 (**1**) and 8.0 g (48.8 mmol) of diethyl vinylphosphonate (prepared from diethyl (2-bromoethyl)phosphonate by a known method [5]) in 7.5 mL of benzene was stirred at the boiling point for 7 days. Volatile components were removed *in vacuo*. Column chromatography (as above) of the residue so obtained led to 0.97 g (37%) of product **3**. ^{31}P NMR ($CDCl_3$) δ 31.2; ^{13}C NMR, Table I; ^{1}H NMR ($CDCl_3$) δ 1.13 (t, J = 7.1, 6H, OCH_2CH_3), 1.74–1.82 (m, 2H, C(α)H_2), 2.53–2.60 (m, 4H, C(2)H_2), 2.66–2.73 (m, 2H, C(β)H_2), 3.42–3.53 (m, 16H, C(3)H_2, C(5)H_2, C(6)H_2, C(8)H_2), 3.87–3.97 (m, 4H, OCH_2); MS, *m/z* 382 (M^+–H, 8%), 368 (5), 338 (20), 322 (33), 232 (100), 166 (28); HRMS, $(M–H)^+_{found}$ = 382.1955, $C_{16}H_{33}NO_7P$ requires 382.1995.

2.8. 7,16-BIS(DIETHYLPHOSPHONOETHYL-)1,4,10,13-TETRAOXA-7,16-DIAZACYCLOOCTADECANE (**10**)

The reaction of 0.5 g (1.90 mmol) of diaza-18-crown-6 (**9**) and 5 g (32.5 mmol) of diethylphosphonate in 5 mL of benzene was carried out as described above for the **1**→**3** transformation. A similar work-up procedure afforded 0.14 g (20%) of

product **10** in a purity of 95%. ^{31}P NMR ($CDCl_3$) δ 31.3; ^{13}C NMR ($CDCl_3$) δ 16.4 ($^3J_{PC}$ = 5.9, OCH_2CH_3), 23.1 ($^1J_{PC}$ = 136.9, CH_2P), 48.5 (CH_2CH_2P), 53.2 (NCH_2CH_2O), 61.4 ($^2J_{PC}$ = 6.3, OCH_2CH_3), 70.5 (OCH_2), 70.4 (OCH_2); ^{1}H NMR ($CDCl_3$) δ 1.18 (t, J = 7.1, 12H, OCH_2CH_3), 1.74–1.87 (m, 4H, CH_2P), 2.55–2.75 (m, 12H, CH_2CH_2P, NCH_2CH_2O), 3.36–3.59 (m, 16H, CH_2OCH_2), 3.89–4.03 (m, 8H, OCH_2CH_3); MS, *m/z* 590 (M^+, 15%), 529 (53), 515 (69), 453 (100); HRMS, M^+_{found} = 590.3001, $C_{24}H_{52}N_2O_{10}P_2$ requires 590.3097.

2.9. PROCEDURE FOR THE DETERMINATION OF THE EXTRACTION ABILITY IN THE PRESENCE OF AZACROWN ETHERS **1**, **3–5** AND **8**

Equal volumes (5 mL) of a dichloromethane solution of the azacrown ether (**1**, **3–5** and **8**) (c = 0.01 mol L^{-1}) and of the aqueous alkali metal picrate (c = 0.005 mol L^{-1}) were introduced into an Erlenmeyer flask, which was then stoppered and shaken for 40 min at 25.0 °C. The mixture was then allowed to stand for at least 2 h in order to complete the phase separation. The phases were separated and the picrate concentration in the aqueous phase determined from its absorption at 354 nm (ϵ = 14600 mol^{-1} cm^{-1}). The extraction ability is given as % of the picrate extracted into the organic phase. In the control experiments carried out in the absence of azacrown ethers no detectable amounts of picrates were extracted into the organic phase.

2.10. PROCEDURE FOR THE ION-SELECTIVITY MEASUREMENTS

Membrane preparation: 5 mg of the azacrown ether (**1**, **4** and **8**) compound (ionophore), 66 mg of PVC powder of high molecular weight and 120 mg of *o*-nitrophenyl octyl ether were dissolved in 2 mL tetrahydrofuran (THF) and poured into a glass ring (diameter 28 mm) fixed on a glass plate [12]. A flexible membrane of ca. 0.2 mm thickness remained after the slow (ca. 24 h) evaporation of THF.

All membrane components except the azacrown ethers were purchased from Fluka AG, Buchs, Switzerland.

Electrodes: The membranes with diameter of 7 mm were incorporated into Philips IS 561 electrode bodies (Eindhoven, The Netherlands). As the inner electrolyte, 0.001 mol L^{-1} potassium chloride solution, while as the external reference electrode, Ag/AgCl electrode with 0.1 mol L^{-1} lithium acetate salt bridge electrolyte (Type 8201, Radelkis, Hungary) was used.

Selectivity determination: The potentiometric selectivity coefficients were determined by the separate solution method (SSM) [13] from the electromotive force (EMF) data measured in 0.1 mol L^{-1} chloride solutions of Li^+, Na^+, K^+ and NH_4^+. The EMF measurements were carried out at 25.0 °C with a Radiometer pHM 64 digital pH-meter (Coppenhagen, Denmark).

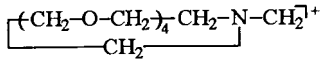
All solutions were prepared from chemicals of analytical grade and doubly quartz distilled water.

The activity coefficients of the solutions were calculated by the extended Debye-Hückel equation [14], while the liquid junction potential was estimated with the help of the Henderson formalism [14].

3. Results and Discussion

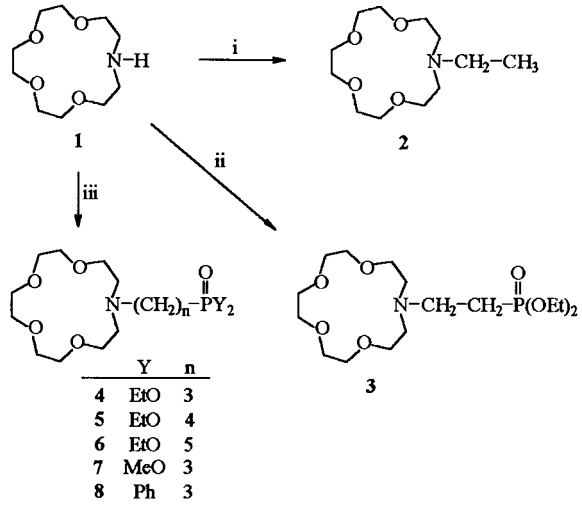
3.1. SYNTHESIS AND SPECTRAL CHARACTERIZATION OF *N*-PHOSPHONOALKYL-MONOAZA-15-CROWN-5 ETHERS AND AN *N*,*N*-DI(PHOSPHONOALKYL)-DIAZA 18-CROWN-6-ETHER

The monoaza-15-crown-5-based lariat ethers with phosphonyl function were synthesized by the *N*-alkylation of azacrown **1**. The reaction of azacrown **1** with diethyl (2-bromoethyl)phosphonate in DMF in the presence of potassium carbonate at 90 °C led to ethyl derivative **2** (Scheme 1). Under the conditions applied, the bromoethylphosphonate acted as an ethylating agent instead of phosphonoethylating the nitrogen atom. The expected product (**3**) could, however, be prepared in acceptable yield by reaction with diethyl vinylphosphonate (Scheme 1). In contrast to the bromoethylphosphonate, the bromoalkylphosphonates with three to five carbon atoms could be well utilized in the synthesis of the corresponding lariat ethers (**4–6**). The alkylating ω-bromoalkylphosphonates were prepared by the Arbuzov reaction of dibromoalkanes and triethyl phosphite according to our procedure. The synthesis had to be optimized to avoid the formation of the diphosphonates. *N*-Alkylation of azacrown **1** by the bromoalkylphosphonates afforded the lariat ethers (**4–6**) in 35–45% yield after repeated column chromatography (Scheme 1). The structure of the products was supported and characterized by ^{31}P, ^{13}C and ^{1}H NMR data, as well as MS and HRMS. The ^{31}C NMR spectral parameters are listed in Table I. The J_{PC} couplings are as large as ca. 140 Hz on C_α of the side chain of the lariat ethers (**3–6**); while values of ca. 5 Hz and 17 Hz were detected on C_β and C_γ, respectively. Protons of the CH_2N and CH_2O units appeared in the expected region, around δ_H 2.7 and 3.5, respectively. The EI mass spectra of the lariat ethers revealed the molecular ion only for **5** and **6**; in the case of **3** and **4** the molecular ion appeared in a deprotonated form. The



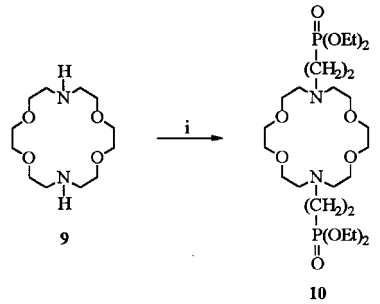
fragment (*m/z* = 232) was the base peak in all cases. Elemental composition of the products (**3–6**) was confirmed by HRMS.

To extend the range of the phosphonoalkyl-azacrown ethers, dimethylphosphonate **7** and diphenylphosphine oxide **8** were also synthesized using the bromoalkylation method (Scheme 1). The products isolated in ca. 33% yield were characterized by NMR and MS data (for ^{13}C NMR parameters see Table I). Lariat ethers **7** and **8** displayed similar NMR and mass spectroscopic features, as the other derivatives (**3–6**).



	Y	n
4	EtO	3
5	EtO	4
6	EtO	5
7	MeO	3
8	Ph	3

Scheme 1. Reagents and conditions: (i) $BrCH_2CH_2P(O)(OEt)_2$, K_2CO_3, DMFA, 90 °C; (ii) CH_2=CHP(O)$(OEt)_2$ (7.1 equiv.), C_6H_6, 80 °C; (iii) $Br(CH_2)_nP(O)Y_2$, K_2CO_3, DMFA, 90 °C.



Scheme 2. Reagent and conditions: (i) CH_2=CHP(O)$(OEt)_2$ (8.5 equiv.), C_6H_6, reflux.

A diazacrown ether with side chains on the two nitrogen atoms was also prepared. The reaction of 7,16-diaza-18-crown-6-ether (**9**) with diethyl vinylphosphonate afforded di(phosphonoethyl) derivative **10** in moderate yield (Scheme 2). The structure of the product (**10**) was confirmed by ^{31}P, ^{13}C and ^{1}H NMR, as well as mass spectrometry.

It is noted that the phosphonic acid derivatives of lariat ethers **3** and **10** are known compounds [15, 16]; their utilization as components of layered ion-exchangers has also been reported [15, 16].

3.2. EXTRACTION ABILITY OF THE PHOSPHONOALKYL-AZACROWN ETHERS

The complex forming ability of the lariat ethers (**3–5** and **8**) were characterized by the extracting ability (EA) of picrate salts (lithium, sodium, potassium and

ammonium picrate) from water into dichloromethane by the method of Kimura et al. [17]. The extraction ability may not accurately reflect the complexation ability in homogeneous solution, still it can be regarded as a good indicator of the cation binding ability. Concentrations of the picrates in water were determined by UV spectroscopy. The experimental data are shown in Table II. The unsubstituted azacrown ether (**1**) used as reference compound transports 56–67% of the picrate salts into the organic phase, but it does not show a notable selectivity with any of the alkali or ammonium ions. As can be seen, introduction of the phosphonoalkyl side arms results in a decreased extracting ability. The crown ether with the phosphonopropyl group (**4**) has the lowest values (except for potassium ion). A probable explanation for this effect may be that the bending side arms display a steric hindrance towards the cations. A change in the conformation of the azacrown ethers after introducing the side arms and protonation may also play important roles in the decreased extracting ability. On the other hand, selectivity of the monoazacrown ether (**1**) was improved significantly by introducing the phosphonoalkyl side chain: compound **3** transports two times more ammonium picrate and three times more lithium picrate into the organic phase, than potassium picrate. Lariat ether **4** extracts three times more ammonium picrate than lithium picrate. A similar trend can be observed for azacrown ether **5** and **8**. It is interesting to compare the extraction ability of the phosphonoalkyl azacrown ethers (**3**, **4**, **5**) with that of the diphenylphosphine oxide derivative (**8**): phosphonoalkyl species **3**, **4**, **5** form a relatively weak complex with the sodium ion (their EA values are 36%, 20% and 34%, respectively), while phosphine oxide **8** displays a better complex forming ability (EA = 50%) for the same cation. The sequence of selectivity was also changed by the substituents at the nitrogen atom: in the case of the unsubstituted azacrown ether (**1**) it is $K^+ \sim Li^+ > NH_4^+ > Na^+$. Compound **3** shows the order $Li^+ > NH_4^+ > Na^+ > K^+$, while derivatives **4** and **5** follow the order $NH_4^+ > K^+ > Na^+ > Li^+$. For phosphine oxide **8** the order of selectivity is $Na^+ > NH_4^+ > K^+ > Li^+$.

3.3. SELECTIVITY OF PVC MEMBRANE ELECTRODE CONTAINING PHOSPHONOALKYL-AZACROWN ETHERS (**1, 4, 8**)

The ion-selectivity of azacrown ethers **1**, **4**, **8** based on plasticized PVC membranes [12] was studied potentiometrically by the separate solution method [13] in 0.1 mol L^{-1} metal (M) chloride solutions. The selectivity coefficient values obtained by considering potassium as the primary ion are shown in Table III. From the data it is clear that the membrane with the unsubstituted azacrown ether (**1**) is selective for the ammonium ion and the order of selectivity is $NH_4^+ > K^+ > Na^+ > Li^+$. It is also seen that the membranes with the substituted azacrown ethers (**4** and **8**) lose the selectivity for the ammonium ion, and the sequence of selectivity changes in slight favour of the lithium ion.

Our research to synthesize new azacrown ethers with phosphinoalkyl side chains and to test their complex forming ability towards different cations is continuing.

Table II. Data for the extraction of alkali metal and ammonium picrates by crown ethers **1**, **3–5** and **8**[a]

Compound	Extractability (%)[b]			
	Li^+	Na^+	K^+	NH_4^+
1	65	56	67	60
3	68	36	25	48
4	13	20	31	40
5	25	34	51	62
8	21	50	30	46

[a]Temperature 25 °C; aqueous phase (5 mL); [picrate] = 5×10^{-3} M; organic phase (CH_2Cl_2, 5 mL); [crown ether] = 1×10^{-2} M.
[b]Defined as % picrate extracted into the organic phase. Determined by UV spectroscopy. Error limit: 5%.

Table III. Selectivity properties of azacrown ether (**1**, **4**, **8**) incorporated PVC membranes

Component of the membrane[a]	Potentiometric selectivity coefficient ($K^{Pot}_{K,M}$)			
	Li^+	Na^+	K^+	NH_4^+
1	0.60	0.95	1.00	8.51
4	1.20	0.93	1.00	0.83
8	1.26	1.02	1.00	1.10

[a]Composition of the membranes: 2.5 w/w% of substituted azacrown ether, 33 w/w% of PVC and 64.5 w/w% of 2-nitrophenyloctylether.

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