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12-Membered Crown Ethers. Derivatives of Benzo- and Naphtho-12-crown-4 and their Membrane Electrode Properties. Part II

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Abstract. A series of lipophilic derivatives of benzo-12-crown-4 and naphtho-12-crown-4 has been synthesized. The behavior of the prepared derivatives in membrane ion-selective electrodes has been studied. Selectivity changes dependent on the position and number of substituents have been observed.

Key words: 12-Membered crown ethers, synthesis, ion-selective membrane electrodes.

1. Introduction

The cavity of 12-crown-4 corresponds topologically to the lithium cation [1,2] and forces its complexation with a 1 : 1 metal-to-crown ether stoichiometry. In the solid state the Na^+ cation forms a sandwich-like complex of 1 : 2 sodium to crown ether ratio [3–5]. The larger potassium cation arranges the complex components in perching [6–8] or sandwich type structures [9,10].

A search of the literature shows that data on the structures of sodium or potassium complexes with small crown ethers (12-membered in particular) have a random character; in particular, neither the role of the cation as well as the counter-ion in the creation of different structures are described.

We noted previously [11] that the behavior of benzo- and naphtho-12-crown-4 differs substantially from that of unsubstituted 12-crown-4; for example, the planar aromatic residue decreases the flexibility of the macrocycle leading to conformational differences. The ionic character of benzo-12-crown-4 complexes with sodium and potassium iodides was outlined [12]. Both complexes possess sandwich-like structures with a 2 : 1 ratio of ligand to metal cation. The sodium cation is bonded to all oxygen atoms of both macrocyclic units and is separated from the counter-ion. The potassium cation is also bonded to eight oxygen atoms and, in addition, to iodide ion, forming a tight ionic pair.

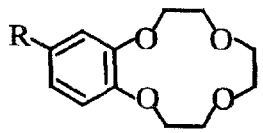
In solution, however, benzo-12-crown-4 forms complexes with both sodium and potassium cations of 1 : 1 and 2 : 1 stoichiometry. Because a lower K_2 value was found for the potassium than for the sodium complex [13,14], and because the sodium cation better fits the cavity of benzo-12-crown-4 than potassium, one

might expect a membrane electrode doped with this crown ether to exhibit sodium selectivity. Some results concerning the behavior of 12-membered crown ethers in ion-selective membrane electrodes have already been presented [12,15,16].

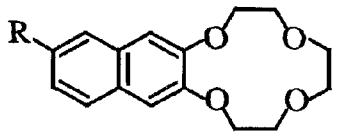
Systematic studies of ion-selective membrane electrode selectivities as a function of the lipophilicity of substituted benzo-15-crown-5, naphtho-15-crown-5 and benzo-18-crown-6 ion carriers have been published [17,18]. The selectivity of ion-selective membrane electrodes is not easy to explain. The selectivity is high when the ionophore forms complexes with various metal cations of highly differentiated stability constants. Such a case is known for the valinomycin-based ion-selective potassium sensitive membrane electrode. With this ionophore potassium and sodium form 1 : 1 complexes with separated charges. The high selectivity for potassium of lipophilic derivatives of benzo-15-crown-5 and naphtho-15-crown-5 in membrane electrodes could be explained as a consequence of the differentiation of the partition coefficient due to the different stoichiometry of the respective complexes, although the stability constants in solution are very similar [17 – 19]. Another factor which should be considered is the formation of complexes with separated charges or complexes in the form of ionic pairs. These latter do not contribute to the membrane electrode potential which enhances the overall selectivity. Such a case was mentioned in our previous paper [12]. The *tert*-alkyl derivatives of benzo-12-crown-4 and naphtho-12-crown-4 studied in ion-selective membrane electrodes [12] show an interesting relationship of selectivity changes with changes in lipophilicity and the character of the complexes with sodium or potassium in the crystalline state. EMF experiments revealed that the membrane electrode containing unsubstituted benzo-12-crown-4 is potassium selective. Introduction of the *tert*-alkyl group onto the benzene ring significantly changes the order of selectivities; the membrane electrodes based on *tert*-alkyl derivatives of benzo-12-crown-4 and naphtho-12-crown-4 are sodium selective with log $K^{pot}_{Na,K}$ values of -0.9 to -1.0.

Bis-crown ethers are better predisposed to form stable complexes with metal cations than are ordinary crown ethers [20]. Such compounds forming intramolecular sandwich complexes with sodium ions were also synthesized. Some of them were applied in sodium selective membrane electrodes [15,21,22]. However, comparing our results and published data we found that bis(benzo-12-crown-4) or bis(naphtho-12-crown-4) ethers in membrane electrodes do not possess significantly higher selectivity for sodium ions than alkyl derivatives of the parent crown ethers.

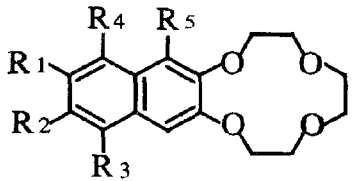
Continuing our former investigation, it seems to be interesting to study the influence of the structure and location of lipophilic alkyl as well as polar substituents in the benzo- or naphthocrown ethers on their sodium selectivity.



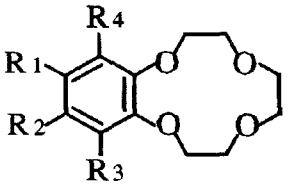
1. R=CH_3CO
2. R=CH_3CHOH
3. R=CH_3CH_2
4. R=$C_7H_{15}CO$
5. R=*n*-C_8H_{17}
6. R=$C_{11}H_{23}CO$
7. R=$C_{11}H_{23}CHOH$
8. R=*n*-$C_{12}H_{25}$
9. R=$C_{17}H_{35}CO$
10. R=$C_{18}H_{37}$



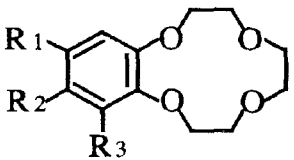
11. R=$C_7H_{15}CO$
12. R=*n*-C_8H_{17}



24. R_1=*s*-butyl
25. R_3=*s*-butyl
26. R_1=R_3=*s*-butyl
27. R_1=R_2=*s*-butyl
28. R_1=R_3=R_4=*s*-butyl
29. R_1=R_3=R_5=*s*-butyl
30. R_1=C_6H_{11}
31. R_1=R_3=C_6H_{11}
32. R_1=R_2=C_6H_{11}
33. R_1=R_3=R_5=C_6H_{11}



13. R_1=*s*-butyl
14. R_1=R_2=*s*-butyl
15. R_1=R_3=*s*-butyl
16. R_1=R_3=R_4=*s*-butyl
17. R_1=C_6H_{11}
18. R_1=R_2=C_6H_{11}
19. R_1=R_3=C_6H_{11}
20. R_3=R_4=C_6H_{11}
21. R_1=R_3=R_4=C_6H_{11}
22. R_1=*s*-C_9H_{19}
23. R_3=*s*-C_9H_{19}



34. R_1=NO_2
35. R_1=NH_2
36. R_1=NO_2; R_2=*t*-butyl
37. R_1=NH_2; R_2=*t*-butyl
38. R_1=NO_2; R_2=*n*-$C_{12}H_{25}$
39. R_1=R_3=*s*-butyl; R_2=NO_2

2. Experimental

2.1. Synthesis of derivatives of benzo- and naphtho-12-crown-4

NMR spectra were recorded on a Varian instrument at 60, 200 or 500 MHz. NOE and TOCSY techniques were used in some cases to determine the positions of substituents in the aromatic rings. Mass spectra were recorded on a Varian MATT 711 instrument using the FD technique or with a AMD–604 apparatus. Melting points [°C] are uncorrected. TLC chromatography was performed on Alufolien F_{254} (Merck) in a solvent system: methylene chloride–acetone (50 : 1 v/v); glass plates F_{254} (Merck) were used for preparative TLC separations. Column chromatography was performed on Silica gel 60 (Fluka). Palladium (10%) on activated alumina (Fluka) and platinum (IV) oxide hydrate (Fluka) were used for hydrogenation.

All materials and solvents were of analytical reagent grade. Benzo–12-crown-4 was prepared according to Wilcox [23]. Naphtho-12-crown-4 was prepared as described in ref [13].

2.1.1. *Synthesis of 4'-acyl, 4'-Hydroxyalkyl and 4'-n-Alkyl Derivatives of Benzo-12-crown-4 and Naphtho-12-crown-4*

4'-Acetylbenzo-12-crown-4 (**1**). A mixture of 1.12 g (5 mmol) benzo-12-crown-4 and 10 mL polyphosphoric acid was maintained at 50° with stirring until dissolution. Then 3 mL acetic anhydride was added with stirring. The mixture was heated at 80° for 18 h. The cooled mixture was diluted with water, the product was extracted with methylene chloride, the organic layer was washed with water and dried ($MgSO_4$). The solution was passed through a short column and the product was eluted with a chloroform–ethyl acetate (5 : 1 v/v) mixture. After evaporation of the solvent 1.3 g of a product was obtained which was crystallized from *n*-hexane. Yield 0.95 g (71%) of acetylderivative **1**, m.p. 56–58° [24]. ^{1}H-NMR (60 MHz), $CDCl_3$, δ [ppm]: 2.53 (3H, s); 3.70–4.40 (12H, m); 6.78–7.05 (1H, m); 7.43–7.68 (2H, m).

4'-(1-Hydroxyethyl)benzo-12-crown-4 (**2**). A solution of 0.8 g (3 mmol) 4'-acetylbenzo-12-crown-4 in 25 mL methanol was hydrogenated in the presence of Pd/Al_2O_3 for 20 h at room temp. The catalyst was removed and the solution was evaporated to dryness. The residue was purified on a column using methylene chloride as an eluent. 0.70 g (87%) of an oily product was obtained. MS: found *m/z* = 268; calcd. m.w. for $C_{14}H_{20}O_5$ = 268. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 1.46 (3H, d, J = 6.5 Hz); 1.90 (1H, broad s); 3.79 (4H, s); 3.82–3.88 (4H, m); 4.14–4.20 (4H, m); 4.82 (1H, q, J = 6.5 Hz); 6.93 (2H, s); 7.02 (1H, s).

4'-Ethylbenzo-12-crown-4 (**3**). A mixture of 0.54 g (2 mmol) hydroxyethylbenzo-12-crown-4 (compound **2**), 40 mL ethanol and 5 g freshly prepared Raney nickel was boiled for 24 h. The solvent was evaporated and the residue was extracted with

hot hexane. Yield 0.41 g (75%) of an oily product. MS: found *m/z* = 252; calcd. m.w. for $C_{14}H_{20}O_4$ = 252. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 1.21 (3H, t, J = 7.5 Hz); 2.58 (2H, q, J = 7.5 Hz); 3.80 (4H, s); 3.80–3.89 (4H, m); 4.14–4.20 (4H, m); 6.78 (1H, dd, J_1 = 1.7 Hz, J_2 = 8 Hz); 6.82 (1H, d, J = 1.7 Hz); 6.91 (1H, d, J = 8 Hz).

4'-Caproylbenzo-12-crown-4 (**4**). A mixture of 1.12 g (5 mmol) benzo-12-crown-4, 10 mL Eaton reagent [25, 26] and 1.44 g (1.6 mL; 10 mmol) caprylic acid was heated for 2 h at 50°. The deep red solution was diluted with ice-water, the product was extracted with chloroform, washed with water and dried ($MgSO_4$). The product was purified chromatographically using methylene chloride–hexane (2 : 1) mixture and methylene chloride as eluent. The yield of a product crystallized from hexane was 1.2 g (69%). M.p. 37–39°. MS: found *m/z* 350; calcd. m.w. for $C_{20}H_{30}O_5$ = 350. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 0.88 (3H, t, J = 6.5 Hz); 1.17–1.43 (8H, m); 1.71 (2H, t, J = 7.2 Hz); 2.90 (2H, t, J = 7.5 Hz); 3.79 (4H, s); 3.81–3.86 (2H, m); 3.87–3.92 (2H, m); 4.21–4.26 (4H, m); 6.97 (1H, d, J = 9 Hz); 7.60–7.66 (2H, m).

4'-Octylbenzo-12-crown-4 (**5**). A solution of 0.35 g (1 mmol) caproyl derivative **4** in 20 mL methanol was hydrogenated over Pd/Al_2O_3 at room temperature for 2 days. The solids were removed, the solvent was evaporated and the product was isolated from the residue on a silica gel column using methylene chloride as an eluent. The product, 0.18 g (54%) melts below 20°. MS: found *m/z* 336; calcd. m.w. for $C_{20}H_{32}O_4$ = 336. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 0.88 (3H, t, J = 6.5 Hz); 1.27 (10H, s); 1.47–1.66 (2H, m); 2.52 (2H, t, J = 7.5 Hz); 3.80 (4H, s); 3.81–3.89 (4H, m); 4.13–4.20 (4H, m); 6.74 (1H, dd, J_1 = 2.1 Hz, J_2 = 8 Hz); 6.79 (1H, d, J = 2 Hz); 6.89 (1H, d, J = 8 Hz).

4'-Lauroylbenzo-12-crown-4 (**6**). This compound was prepared in a similar manner to that for compound **4** from benzo-12-crown-4 and lauric acid with 79% yield. M.p. 44–45°. MS: found *m/z* 406, calcd. m.w. for $C_{24}H_{38}O_5$ = 406. ^{1}H-NMR (60 MHz), $CDCl_3$, δ [ppm]: 0.70–2.10 (21H, m); 2.90 (2H, t, J = 7 Hz); 3.68–4.37 (12H, m); 6.90 (1H, d, J = 8.5 Hz); 7.40–7.70 (2H, m).

4'-(1-Hydroxydodecyl)benzo-12-crown-4 (**7**). 0.41 g (1 mmol) lauroyl derivative **6** was hydrogenated in 20 mL methanol over Pd/Al_2O_3 for 18 h at room temp. After removal of the catalyst the residue was chromatographed on a column to isolate 0.35 g (85%) of a product melting at 47–49°. MS: found *m/z* 408; calcd. m.w. for $C_{24}H_{40}O_5$ = 408. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 0.88 (3H, t, J = 6.5 Hz); 1.25 (18H, m); 1.6–1.8 (2H, m); 1.85 (1H, broad s); 3.80 (4H, s); 3.8–3.88 (4H, m); 4.14–4.21 (4H, m); 4.58 (1H, t, J = 6.6 Hz); 6.93 (1H, dd, J_1 = 1.5 Hz, J_2 = 8.5 Hz); 6.97 (1H, d, J = 8.5 Hz); 7.02 (1H, d, J = 1.5 Hz).

4'-Dodecylbenzo-12-crown-4 (**8**). A mixture of 0.16 g (0.4 mmol) alcohol **7** and Raney nickel in 20 mL ethanol was boiled for 5 h. After crystallization from hexane a product was obtained (0.12 g; 76%), m.p. 37–38°. MS: found *m/z* 392; calcd. for $C_{24}H_{40}O_4$ m.w. = 392. ^{1}H-NMR (60 MHz), $CDCl_3$, δ [ppm]: 0.73–1.80 (23H, m); 2.52 (2H, t, J = 7 Hz); 3.70–4.27 (12H, m); 6.63–6.80 (3H,m).

4'-Stearoylbenzo-12-crown-4 (**9**) was prepared analogously to compound **4** from benzo-12-crown-4 and stearic acid. The product was eluted from a silica gel column with heptane–methylene chloride was crystallized from hexane. Yield 34%, m.p. 46–48°. MS: found *m/z* 490; calcd. for $C_{30}H_{50}O_5$ m.w. = 490. ^{1}H-NMR (60 MHz), $CDCl_3$, δ [ppm]: 0.70–1.93 (33H, m); 2.90 (2H, t, J = 7 Hz); 3.73–4.37 (12H, m); 6.92 (1H, d, J = 9 Hz); 7.47–7.70 (2H, m).

4'-Octadecylbenzo-12-crown-4 (**10**) was obtained analogously to compound **5** from compound **9**. Hydrogenation was performed for 4 days. The yield of product was 64%, m.p. 42–43°. MS: found *m/z* 476; calcd. for $C_{30}H_{52}O_4$ m.w. = 476. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 0.87 (3H, t, J = 6.8 Hz); 1.25 (30H, s); 1.47–1.68 (2H, m); 2.51 (2H, t, J = 7.6 Hz); 3.78–3.89 (8H, m); 4.12–4.20 (4H, m); 6.74 (1H, dd, $J_1$1 = 2 Hz, J_2 = 8 Hz); 6.78 (1H, d, J = 2 Hz); 6.88 (1H, d, J = 8 Hz).

6'-Caproylnaphtho-12-crown-4 (**11**) was obtained analogously to compound **4** starting from 0.68 g (2.5 mmol) naphtho-12-crown-4, 5 mL of Eaton reagent and 0.8 mL caprylic acid. The mixture was heated for 3 h at 40° and diluted with ice-water. The product was extracted with chloroform and purified on a column using chloroform as an eluent. The yield of compound **11** after crystallization from hexane was 0.6 g (60%), m.p. 58–59°. MS: found *m/z* 400, m.w. calcd. for $C_{24}H_{32}O_5$ = 400. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 0.89 (3H, t, J = 6.5 Hz); 1.20–1.46 (8H, m); 1.70–1.87 (2H, m); 3.06 (2H, t, J = 7.5 Hz); 3.83 (4H, s); 3.89–3.97 (4H, m); 4.28–4.33 (4H, m); 7.29 (1H, s); 7.43 (1H, s); 7.72 (1H, d, J = 8.7 Hz); 7.92 (1H, dd, J_1 = 1.7 Hz, J_2 = 8.5 Hz); 8.32 (1H, d, J = 1.1 Hz).

6'-Octylnaphtho-12-crown-4 (**12**) was obtained analogously to compound **5** by hydrogenation (5 days) of compound **11**. After crystallization from hexane 70% of compound **12** was obtained M.p. 36–39°. MS: found *m/z* 386; m.w. calcd. for $C_{24}H_{34}O_4$ = 386. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 0.80–0.93 (3H, m); 1.18–1.43 (10H, m); 1.57–1.77 (2H, m); 2.72 (2H, t, J = 7.6 Hz); 3.83 (4H, s); 3.88–3.94 (4H, m); 4.24–4.29 (4H, m); 7.17–7.63 (5H, m).

2.1.2. *Synthesis of Alkyl Derivatives of Benzo-12-crown-4 by Reaction of the Parent Compound with Secondary Alcohols*

Reaction of benzo-12-crown-4 with s-butanol. A mixture of 2.24 g (10 mmol) benzo-12-crown-4, polyphosphoric acid (20 mL) and *s*-butanol (3 mL) was heated at 60° for 2, 4 and 20 h, resp. The cooled mixture was diluted with water and the product was extracted with methylene chloride. The crude material was chromatographed on a column using hexane – methylene chloride mixture of increasing polarity. Yields:

	Reaction time		
Product	2 h	4 h	20 h
4′-alkyl derivative **13**	0.09 g	0.3 g	–
4′,5′-dialkyl derivative **14**	0.18 g	0.6 g	0.2 g
3′,5′-dialkyl derivative **15**	0.84 g	1.22 g	1.1 g
3′,4′,6′-trialkyl derivative **16**	–	0.15 g	0.9 g

Compound **13**, oil. MS: found *m/z* 280; m.w. calcd. for $C_{16}H_{24}O_4$= 280. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 0.80 (3H, t, J = 7.3 Hz); 1.19 (3H, d, J = 7 Hz); 1.54 (2H, qu, J = 7.3 Hz); 2.51 (1H, sextet, J = 7 Hz); 3.80 (4H, s); 3.81–3.89 (4H, m); 4.13–4.21 (4H, m); 6.75 (1H, dd, J_1 = 2.2 Hz, J_2 = 8.1 Hz); 6.79 (1H, d, J = 2 Hz); 6.89 (1H, d, J = 8.1 Hz). TLC R_f = 0.19

Compound **14**, oil. MS: found *m/z* 336; m.w. calcd. for $C_{20}H_{32}O_4$ = 336. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 0.81 and 0.83 (6H, 2t, J_1 = J_2 = 7.4 Hz); 1.15 and 1.18 (6H, 2d, J_1 = J_2 = 6.9 Hz); 1.45–1.65 (4H, m); 2.90 (2H, sextet, J = 7 Hz); 3.81 (4H, s); 3.82–3.89 (4H, m); 4.13–4.20 (4H, m); 6.78 (2H, s). TLC R_f = 0.25.

Compound **15**, oil. MS: found *m/z* 336; m.w. calcd. for $C_{20}H_{32}O_4$ = 336. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 0.76–0.89 (6H, m); 1.12–1.24 (6H, m); 1.46–1.65 (4H, m); 2.50 (1H, sextet, J = 7 Hz); 3.06 (1H, sextet, J = 7 Hz); 3.69–4.0 (8H, m); 4.0–4.16 (4H, m); 6.56 (1H, d, J = 2 Hz); 6.59 (1H, d, J = 2 Hz). TLC R_f = 0.34.

Compound **16**, oil. MS: found *m/z* 392; m.w. calcd. for $C_{24}H_{40}O_4$ = 392. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 0.77–0.92 (9H, m); 1.10–1.22 (6H, m); 1.30 (3H, d, J = 7.2 Hz); 1.45–1.84 (6H, m); 2.80–3.10 (3H, m); 3.75–4.35 (12H, m); 6.74 (1H, s). TLC R_f = 0.56.

Reactions of benzo-12-crown-4 with cyclohexanol. A mixture of 1.12 g (5 mmol) benzo-12-crown-4, 10 mL polyphosphoric acid and 1.5 g cyclohexanol was heated at 75° for 4 and 20 h. The product was isolated similarly to the *s*-butyl derivatives. The following amounts of products were obtained:

Product	Reaction time 4 h	20 h
Compound **17**	0.4 g	–
Compound **18**	0.3 g	0.6 g
Compound **19**	0.55 g	0.7 g
Fraction containing compound **20** and **21**	0.1 g	0.2 g

Compound **17**, m.p. 40–42°; MS: found *m/z* 306; m.w. calcd. for $C_{18}H_{26}O_4$ = 306. ^{1}H-NMR (60 MHz), $CDCl_3$, δ [ppm]: 1.0–2.0 (10H, m); 2.0–2.65 (1H, m); 3.70–4.30 (12H, m); 6.75 (3H, s). TLC R_f = 0.42.

Compound **18**, m.p. 115–117°; MS: found *m/z* 388; m.w. calcd. for $C_{24}H_{36}O_4$ = 388. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 1.27–1.88 (20H, m); 2.68–2.76 (2H, m); 3.83 (4H, m); 3.84–3.88 (4H, m); 4.18–4.21 (4H, m); 6.85 (2H, s). TLC R_f = 0.49.

Compound **19**, m.p. 105–106°; MS: found *m/z* 388; m.w. calcd. for $C_{24}H_{36}O_4$ = 388. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 1.24–1.89 (20H, m); 2.42–2.47 (1H, m); 2.92–2.97 (1H, m); 3.83–3.85 (2H, m); 3.90–3.96 (6H, m); 4.09–4.12 (4H, m); 6.63 (1H, s); 6.70 (1H, s). TLC R_f = 0.54.

Compounds **20** and **21** were isolated on glass TLC plates in a hexane–acetone (10 : 1) solvent system from a mixture containing both these compounds in a 4 : 5 ratio.

Compound **20**, m.p. 166–167°. MS: found *m/z* 388; m.w. calcd. for $C_{24}H_{36}O_4$ = 388. ^{1}H-NMR (500 MHz), $CDCl_3$, δ [ppm]: 1.24–1.88 (20H, m); 2.89–2.95 (2H, m); 3.86 (4H, s); 3.97 (4H, t, J = 3.9 Hz); 4.15 (4H, t, J = 3.9 Hz); 6.96 (2H, s). TLC R_f = 0.68.

Compound **21**, m.p. 159–161°. MS: found *m/z* 470; m.w. calcd. for $C_{32}H_{46}O_4$ = 470. ^{1}H-NMR (500 MHz), $CDCl_3$, δ [ppm]: 1.24–1.45 (12H, m); 1.6–2.12 (18H, m); 2.65–3.43 (3H, m); 3.76–4.38 (12H, m); 6.84 (1H, s). TLC R_f 0.78.

Reactions of benzo-12-crown-4 with secondary nonanol. A mixture of 0.76 g (3.4 mmol) benzo-12-crown-4, 7 mL polyphosphoric acid and 1.8 mL (10 mmol) 2-nonanol was heated at 45° for 3 days. The products were isolated on a column. The column was washed with hexane. A small amount of compound **23** was washed out with a methylene chloride – hexane mixture. The dominant product was eluted with methylene chloride. The yield of the monoderivative **22** was 0.9 g (80%).

Compound **22**, oil (mixture of isomers). MS: found *m/z* 350; m.w. calcd. for $C_{21}H_{34}O_4$ = 350. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 0.6–1.7 (~18.H, m); 2.2–2.67 (0.8H, m); 3.80–3.90 (8H, m); 4.13–4.20 (4H, m); 6.67–6.95 (3H, m). TLC R_f = 0.26.

Compound **23**, m.p. 62–66° (mixture of isomers). MS: found *m/z* 350; m.w. calcd. for $C_{21}H_{34}O_4$ =350. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 0.73–1.70 (18H,

m); 2.94–3.22 (1H, m); 3.80–3.92 (6H, s + m); 3.92–3.98 (2H, m); 4.04–4.13 (4H, m); 6.69–6.84 (2H, m); 6.95–7.05 (1H, m). TLC R_f = 0.44.

2.1.3. *Reactions of Naphtho-12-crown-4 with Secondary Alcohols*

Reaction of naphtho-12-crown-4 with s-butanol. A mixture of 1.37 (5 mmol) naphtho-12-crown-4, 10 mL polyphosphoric acid and 3 mL *s*-butanol was maintained at 40° for 6 h or 60° for 20 h. Six main products are formed, which were isolated. Yields:

	Reaction conditions	
Product	40°. 6 h	60°, 20 h
Compound **24**	0.3 g	–
Compound **25**	0.13 g	–
Compound **26**	0.2 g	0.2 g
Compound **27**	0.25 g	–
Mixture of **27** and **28**	–	0.7 g
Compound **29**	–	1.0 g

The mixture of compounds **27** and **28** was partially separated using preparative TLC in a methylene chloride–acetone (50 : 1) system.

Compound **24**, oil. MS: found *m/z* 330; m.w. calcd. for $C_{20}H_{26}O_4$ = 330. ^{1}H-NMR (500 MHz), $CDCl_3$, δ [ppm]: 0.87 (3H, t, J = 7.5 Hz); 1.32 (3H, d, J = 6.9 Hz); 1.65–1.73 (2H, m); 2.74 (1H, sextet, J = 7 Hz); 3.86 (4H, s); 3.93–3.96 (4H, m); 4.28–4.31 (4H, m); 7.24 (1H, dd, J_1 = 8.3 Hz; J_2= 1.9 Hz); 7.27 (1H, s); 7.30 (1H, s), 7.48 (1H, d, J = 2 Hz); 7.64 (1H, d, J = 8.3 Hz). TLC R_f = 0.29.

Compound **25**, oil. MS: found *m/z* 330; m.w. calcd. for $C_{20}H_{26}O_4$ = 330. ^{1}H-NMR (500 MHz), $CDCl_3$, δ [ppm]: 0.95 (3H, t, J = 7.3 Hz); 1.37 (3H, d, J = 6.9 Hz); 1.68–1.76 (2H, m); 3.37 (1H, sextet, J = 6.8 Hz); 3.87 (4H, s); 3.93–3.98 (4H, m); 4.28–4.35 (4H, m); 7.28 (1H, d, J = 7.8 Hz); 7.31 (1H, s); 7.36 (1H, t, J = 7.9 Hz); 7.56 (1H, d, J = 8.3 Hz); 7.62 (1H, s). TLC R_f = 0.33.

Compound **26**, oil. MS: found *m/z* 386; m.w. calcd. for $C_{24}H_{34}O_4$ = 386. ^{1}H-NMR (500 MHz), $CDCl_3$, δ [ppm]: 0.87 (3H, t, J = 7.3 Hz); 0.96 (3H, 2t, J = 8 Hz); 1.32 (3H, 2d, J = 7.3 Hz); 1.37 (3H, 2d, J = 6.8 Hz); 1.64–1.75 (4H, m); 2.72 (1H, sextet, J = 7 Hz); 3.35 (1H, sextet, J = 7 Hz); 3.87 (4H, s); 3.93–3.98 (4H, m); 4.28–4.35 (4H, m); 7.12 (1H, s); 7.26 (1H, s); 7.34 (1H, s); 7.58 (1H, s). TLC R_f = 0.36.

Compound **27**, oil. MS: found *m/z* 386; m.w. calcd. for $C_{24}H_{34}O_4$ = 386. ^{1}H-NMR (500 MHz), $CDCl_3$, δ [ppm]: 0.96 (6H, 2t, J = 7.5 Hz); 1.37 and 1.38 (6H, 2d, J = 6.8 Hz); 1.66–1.74 (2H, m); 1.82–1.89 (2H, m); 3.34 (2H, sextet, J = 6.8 Hz); 3.88 (4H, s); 3.97 (4H, t, J = 4.1 Hz); 4.37 (4H, t, J = 4 Hz); 7.26 (2H, s); 7.63 (2H, s). TLC R_f = 0.39.

Compound **28**, oil. MS: found *m/z* 442; m.w. calcd. for $C_{28}H_{42}O_4$ = 442. ^{1}H-NMR (500 MHz), $CDCl_3$, δ [ppm]: 0.83–0.97 (9H, m); 1.26–1.30 (3H, m); 1.34–1.38 (3H, m); 1.53–1.57 (3H, m); 1.64–1.76 (2H, m); 1.80–1.92 (2H, m); 1.96–2.09 (2H, m); 3.20–3.37 (2H, m); 3.55–3.62 (1H, m); 3.87 (4H, s); 3.93–3.99 (4H, m); 4.28–4.35 (4H, m); 7.15 (1H, s); 7.58 (1H, s); 7.80 (1H, s). TLC R_f = 0.42.

Compound **29**, m.p. 75–77°. MS: found *m/z* 442; m.w. calcd. for $C_{28}H_{42}O_4$ = 442. ^{1}H-NMR (500 MHz), $CDCl_3$, δ [ppm]: 0.89 (3H, t, J = 7.3 Hz); 0.92 (3H, t, J = 7.3 Hz); 0.97 and 0.98 (3H, 2t, J = 7.3 Hz); 1.34 (3H, d, J = 6.8 Hz); 1.38 (3H, d, J = 6.8 Hz); 1.49–1.59 3H, broad); 1.62–1.76 (4H, m); 1.92–2.08 (2H, broad); 2.74 (1H, sextet, J = 6.8Hz); 3.36 (1H, sextet, J = 6.8Hz); 3.86–4.26 (13H, m); 7.15 (1H, s); 7.32 (1H, s); 7.80 (1H, broad s). TLC R_f = 0.54.

Reaction of naphtho-12-crown-4 with cyclohexanol. A mixture of 1.37 g (5 mmol) naphtho-12-crown-4, 10 mL polyphosphoric acid and 5 mL cyclohexanol was maintained at 60° for 24 h. Of the numerous products, four compounds were isolated: 0.03 g compound **30**, 0.05 g compound **31**, 0.95 g compound **32** and 0.5 g compound **33**.

Compound **30**, oil. MS: found *m/z* 356 calcd. m.w for $C_{22}H_{28}O_4$ = 356. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 1.2–2.0 (10H, m); 2.51–2.70 (1H, m); 3.83 (4H, s); 3.88–3.94 (4H, m); 4.23–4.31 (4H, m); 7.20–7.30 (3H, m); 7.46–7.49 (1H, s); 7.61 (1H, d, J = 8.6 Hz). TLC R_f = 0.33.

Compound **31**, oil. MS: found *m/z* 438; m.w. calcd. for $C_{28}H_{38}O_4$ = 438. ^{1}H-NMR (500 MHz), $CDCl_3$, δ [ppm]: 1.27–2.08 (20H, m); 2.59–2.65 (1H, m); 3.13–3.18 (1H, m); 3.85–3.88 (4H, m); 3.94 (2H, t, J = 4 Hz); 3.97 (2H, t, J = 4 Hz); 4.28 (2H, t, J = 4 Hz); 4.32 (2H, t, J = 4 Hz); 7.18 (1H, s); 7.26 (1H, s); 7.37 (1H, s); 7.58 (1H, s). TLC R_f = 0.44.

Compound **32**, oil. MS: found *m/z* 438; m.w. calcd. for $C_{28}H_{38}O_4$ = 438. ^{1}H-NMR (200 MHz), $CDCl_3$,δ [ppm]: 1.2–2.1 (20H, m); 3.05–3.21 (2H, m); 3.86 (4H, s); 3.9–4.0 (4H, m); 4.27–4.38 (4H, m); 7.26 (2H, s); 7.61 (2H, s). TLC R_f = 0.51.

Compound **33**, m.p. 170–173°. MS: found *m/z* 520; m.w. calcd. for $C_{34}H_{48}O_4$ = 520. ^{1}H-NMR (500 MHz), $CDCl_3$, δ [ppm]: 1.25–2.20 (~30H, m); 2.24–3.85 (~3H, m); 3.89 (2H, s); 3.90–4.03 (4H, m); 4.03–4.18 (4H, m); 4.18–4.27 (2H, m); 7.20–7.37 (~2H, m); ~7.7–~8.3 (~1H, m). TLC R_f = 0.56.

2.1.4. *Synthesis of Nitro and Amino Derivatives of Benzo-12-crown-4*

4′-Nitrobenzo-12-crown-4 (**34**). Nitric acid (conc., 5 mL) was added to a mixture of 1.12 g (5 mmol) benzo-12-crown-4, 25 mL chloroform and 25 mL acetic acid. The mixture was stirred at room temp. for 24 h. Then 10 mL water was added and the mixture was neutralized with small portions of solid sodium carbonate. The chloroform layer was separated and the aqueous solution was extracted with chloroform. The combined organic solutions were evaporated and the residue was

chromatographed on a column with a methylene chloride–ethyl acetate (4 : 1) mixture. The eluent was evaporated and the residue crystallized from ethyl ether – hexane. 1.2 g (89%) nitroderivative **34** was obtained, m.p. 103–105° (Lit. m.p. 105–108° [27]). ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 3.78 (4H, s); 3.85 (2H, t, J = 4.1 Hz); 3.91 (2H, t, J = 4.2 Hz); 4.24–4.30 (4H, m); 7.00 (1H, d, J = 8.8 Hz); 7.88 (1H, d, J = 2.7 Hz); 7.94 (1H, dd, J_1 = 8.8 Hz, J_2 = 2.5 Hz).

4′-Aminobenzo-12-crown-4 (**35**). 0.1 g (0.37 mmol) 4′-nitrobenzo-12-crown-4 in 15 mL methanol was hydrogenated over PtO_2 for 4 h. The catalyst was removed and the solution evaporated. The oily residue was washed with hexane. Yield 0.084 g (95%), cf. [28]. MS: found *m/z* 239; m.w. calcd. for $C_{12}H_{17}O_4N$ = 239. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 2.8–3.3 (2H, broad s); 3.77–3.82 (6H, m); 3.86–3.91 (2H, m); 4.08–4.14 (4H, m); 6.25 (1H, dd, J_1 = 8.5 Hz, J_2 = 2.5 Hz); 6.33 (1H, d, J = 2.5 Hz); 6.83 (1H, d, J = 8.5 Hz).

4′-tert-Butyl-5′-nitrobenzo-12-crown-4 (**36**). Nitric acid (1 g) was added to a solution of 0.84 g (3 mmol) 4′-*tert*-butylbenzo-12-crown-4 [12] in a mixture of chloroform (30 mL) and acetic acid (5 mL) and the mixture was maintained at 40° for 4 h. Then ice-cooled water was added. The solution was adjusted to pH = 4 using solid sodium carbonate. The product was extracted with chloroform, the organic layer was washed with water and dried ($MgSO_4$). The product was purified by column chromatography using methylene chloride as an eluent. Crystallization from hexane gave 0.3 g (31%) of a desired product, m.p. 79–81°. MS: found *m/z* 325; m.w. calcd. for $C_{16}H_{23}O_6N$= 325. ^{1}H-NMR (60 MHz), $CDCl_3$, δ [ppm]: 1.30 (9H, s); 3.70–3.96 (8H, m); 4.05–4.30 (4H, m); 6.98 (1H, s); 7.05 (1H, s).

5′-Amino-4′-tert-butylbenzo-12-crown-4 (**37**). This compound was obtained analogously to **35** from compound **36**. Yield 98%; m.p. 133–135°. MS: found *m/z* 295; m.w. calcd. for $C_{16}H_{25}NO_4$ = 295. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 1.39 (9H, s); 2.1–2.4 (2H, broad s); 3.79–3.82 (2H, m); 3.81 (4H, s); 3.85–3.91 (2H, m); 4.09–4.16 (4H, m); 6.32 (1H, s); 6.94 (1H, s).

4′-Dodecyl-5′-nitrobenzo-12-crown-4 (**38**) was prepared analogously to compound **36** from compound **8**. Yield 46%; m.p. 46–48°. MS: found *m/z* 437; m.w. calcd. for $C_{24}H_{39}NO_6$ = 437. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 0.88 (3H, t, J = 6.5 Hz); 1.26 (16H, s); 1.57–1.7 (4H, m); 2.87 (2H, t, J = 7.7 Hz); 3.78 (4H, s); 3.81–3.86 (2H, m); 3.88–3.93 (2H, m); 4.20–4.28 (4H, m); 6.80 (1H, s); 7.70 (1H, s).

3′,5′-di-s-Butyl-4′-nitrobenzo-12-crown-4 (**39**) was obtained analogously to compound **36** starting from 3′,5′-di-*s*-butylbenzo-12-crown-4. The product was eluted from a chromatographic column with a methylene chloride–hexane mixture. The product was crystallized from hexane. Yield 36%; m.p. 77–79°. MS: found *m/z*

381; m.w. calcd. for $C_{20}H_{31}NO_6$ = 381. ^{1}H-NMR (200 MHz), $CDCl_3$, δ [ppm]: 0.79–0.86 (6H, m); 1.21 and 1.22 (3H, 2d, J_1 and J_2 = 6.8 Hz); 1.34 (3H, d, J = 6.8 Hz); 1.54–1.72 (4H, m); 1.78–1.89 (1H, m); 2.46 (1H, sextet, J = 6.8 Hz); 3.84 (4H, s); 3.90–3.95 (2H, m); 3.99–4.02 (2H, m); 4.11–4.15 (2H, m); 4.20–4.26 (2H, m); 6.68 (1H, s).

2.2. Membrane electrodes and EMF measurements

The membranes were prepared and the membrane electrodes were characterized analogously to that described previously [12]. A typical composition (w/w) of a membrane was as follows: 9% of the respective ionophore, 30.2% of poly(vinyl chloride), 60.5% of 2-nitrophenyl-octyl ether and 0.3% potassium tetrakis(4-chlorophenyl) borate (KTClPB). For comparison in some cases the lipophilic salt was omitted. The selectivity coefficients $\log K^{pot}_{Na,M}$ were determined by the separate solution method (SSM) at a 10^{-2} mol dm^{-3} concentration of the corresponding metal chlorides. The fixed (10^{-2} mol dm^{-3} KCl) interference method (FIM) [29] was used to determine the $\log K^{pot}_{Na,K}$. The representative, selected properties ($\log L_{DNa}$, $\log K^{pot}_{Na,K}$) are summarized in Table I. The influence of the location and number of substituents on the selectivities of ion-selective membrane electrodes is shown in Figure 1 (for all studied cations). The influence of polar groups on electrode behavior is shown in Figure 2.

3. Results and Discussion

3.1. Synthesis

Recently the synthesis and membrane electrode properties of mono-*tert*-alkyl derivatives of benzo- and naphtho-12-crown-4 were described [12]. These compounds were easily and unambiguously synthesized in a reaction of *tert*-alcohols with aromatic nuclei of the respective crown ethers in the presence of polyphosphoric acid. Now derivatives with primary or secondary alkyl residues are described. Monoderivatives with primary alkyl groups were obtained in an unambiguous way by acylation of the aromatic residue of the crown ether with carboxylic acid followed by reduction of the acyl derivative in one or two steps (position 4′ for benzo- and 6′ for naphtho-12-crown-4). In the case of short acyl residues the reduction with hydrogen over Pd/Al_2O_3 catalyst in methanol under atmospheric pressure leads to the respective alcohols. The reduction of alcohols to alkyl residues was performed on Raney nickel in boiling ethanol. In the case of longer acyl residues reduction to the intermediate alcohols or to the respective *n*-alkyl derivatives was completed with hydrogen over Pd/Al_2O_3 selecting the reaction time.

Reaction with secondary alcohols like *s*-butanol and cyclohexanol with aromatic residues of crown ethers do not lead to a sole product [30]. Double and triple substituted benzo-12-crown-4 compounds and up to tetrakis substituted naphtho-

Table I. Selected properties of ion-selective membrane electrodes.

Compound	log L_{DNa}	S (mV)	log $K_{Na,K}$	Compound	log L_{DNa}	S (mV)	log $K_{Na,K}$
0.[1]	−3.35	59	+1.46	15.*	−4.40	57	+0.20
1.	−4.10	52	+0.49	16.	−5.00	59	−0.60
2.	−3.95	57	+1.50	16.*	−4.00	56	+0.91
3.	−5.30	56	−0.80	17.	−5.52	57	−0.90
4.	−4.95	61	−0.67	17.*	−4.90	59	−0.80
5.	−5.10	60	−0.95	18.	−5.00	62	−0.95
5.*	−5.10	58	−0.97	19.	−5.00	62	−0.75
6.	−4.85	60	−0.65	20.	−4.80	60	−0.67
7.	−5.25	58	−0.85	21.	−4.70	60	−0.65
8.	−5.20	61	−0.95	22.	−5.00	63	−0.90
9.	−5.45	58	−0.80	26.	−4.65	60	−0.65
10.	−5.22	60	−0.90	27.	−5.05	62	−0.76
11.	−5.15	59	−0.62	29.	−4.95	60	−0.65
12.	−5.40	59	−0.90	34.	−4.35	57	+0.97
12.*	−5.15	59	−0.90	35.	−4.20	55	+0.22
13.	−5.15	58	−0.82	36.	−5.35	58	−0.45
14.	−5.00	61	−0.90	37.	−4.10	61	−0.72
14.*	−4.90	59	−0.80	38.	−4.95	60	−0.55
15.	−5.10	60	−0.70	39.	−4.90	54	+0.35

[1] Without ionophore.
* Without KTClPB.

12-crown-4 compounds are formed. Only some of the products were isolated from the reaction mixture and obtained in a pure state.

Introduction of a nitro group into the position *ortho* to the alkyl groups of 4′-alkylbenzo-12-crown-4 should be performed under possibly mild conditions [27] to avoid release of alkyl residues. Under the described conditions the nitro residue is easily reduced to the amino group when there is only one alkyl group in its vicinity.

3.2. Membrane electrodes

PVC membrane electrodes containing benzo- or naphtho-12-crown-4 derivatives as ionophores, *o*-nitrophenyl-octyl ether as selected plasticizer, and KTClPB as a lipophilic salt were studied. Comparing the behavior of benzo-12-crown-4 and naphtho-12-crown-4 in ion selective electrodes it is seen that alkyl substituents increase their sodium selectivity. The differences in log $K^{pot}_{Na,K}$ are up to 1.8 for benzo-12-crown-4 and its derivatives and up to 0.25 for naphtho crown ethers. In this respect the best systems are lipophilic monosubstituted 12-membered crown ethers, e.g., 4′-derivatives of benzo-12-crown-4 and 6′-derivatives of naphtho-12-

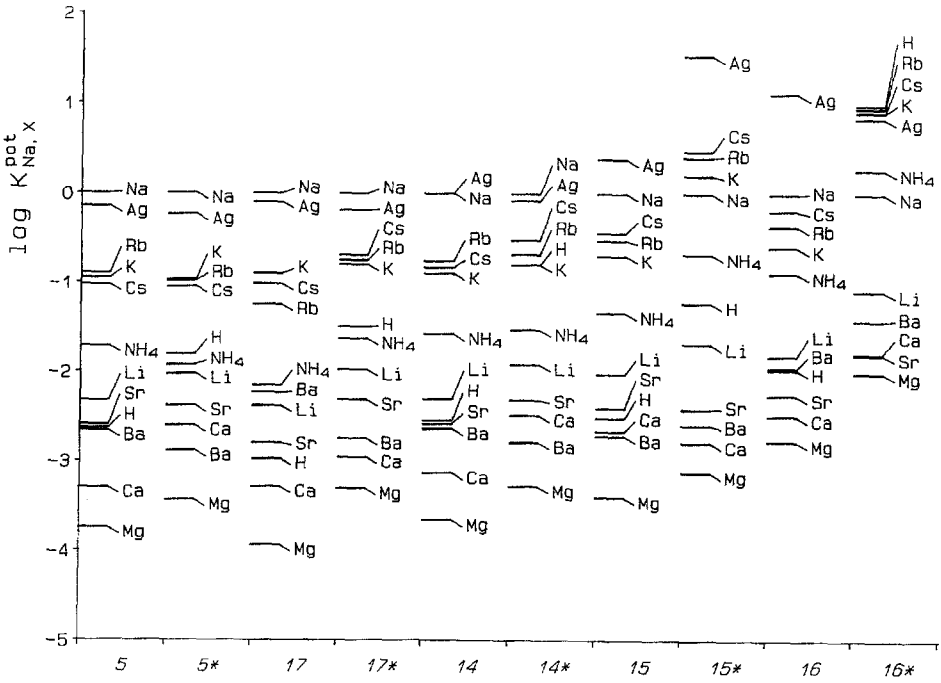


Figure 1. Selectivities of membrane electrodes. Influence of location of the lipophilic alkyl substituent. * denotes membrane electrode without lipophilic salt.

crown-4. The higher effect was observed for alkyl residues with 8–12 carbon atoms. However, the location of the substituent in a vicinal position to the macroring suppress the sodium selectivity. The last effect could be ascribed to the influence of the substituent on the conformation of the crown ethers which, in turn, cause changes in the stabilities and structures of their sodium and potassium complexes.

The influence of the location of the lipophilic substituents is best reflected when comparing electrodes with and without KTClPB (see Figure 1). The addition of a lipophilic salt to the membrane does not significantly affect the selectivity log $K^{pot}_{Na,K}$ for monosubstituted 4′-*n*-alkylbenzo-12-crown-4, however, as in all other cases it is beneficial for their potential stability. In the case of 4′-monoderivatives with secondary alkyl substituents and 4′,5′-dialkyl derivatives of benzo-12-crown-4 only a slight sodium selectivity increase is observed in the presence of KTClPB (difference approximately 0.1 in the logarithmic scale). Membranes with sterically overcrowded 3′,5′-disubstituted derivatives of benzo-12-crown-4 and 3′,4′,6′-trisubstituted derivatives of benzo-12-crown-4 are more selective for potassium. Addition of potassium tetrakis(chlorophenyl)borate to the membranes make them sodium selective. The log $K^{pot}_{Na,K}$ changes at least by 0.5 for the disubstituted, and over 1 in the case of trisubstituted derivatives. Generally the influence of lipophilic salt on the selectivity of ion-selective electrodes is uncertain. In the case of crown

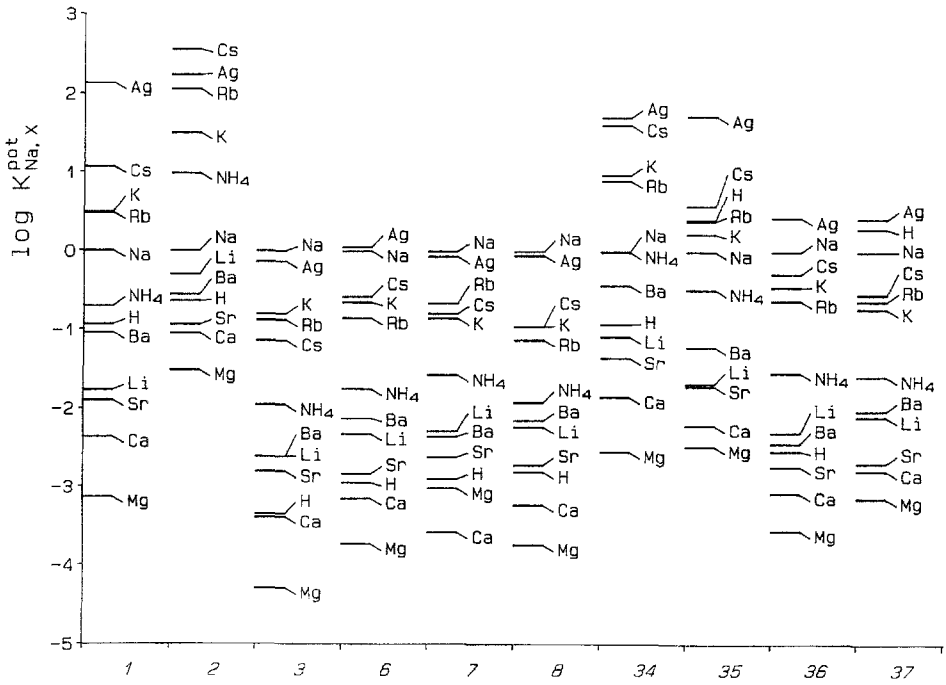


Figure 2. Selectivities of membrane electrodes. Influence of polar groups.

ether derivatives with branched alkyl residues in vicinal positions to the macroring the influence of potassium tetrakis(chlorophenyl) borate is significant. It diminishes their selectivity towards potassium. The possible explanation of this phenomenon lies in the assumption that the large (chlorophenyl)borate anion prefers formation of ionic pairs with crown ether complexed potassium (cf. structures of benzo–12-crown–4 with sodium and potassium iodides [12]).

Polar acetyl as well as hydroxyethyl derivatives of benzo-12-crown-4 are not sodium selective (Figure 2). The increase in the length of the alkyl chain successively compensates the influence of the carbonyl and hydroxyl groups. The effect of the nitro group also inhibits sodium selectivity. The effect of a nitro or amino group is limited by the simultaneous introduction of an alkyl chain into the aromatic moiety of the crown ether.

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