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Bis-Substituted Benzo-15-crown-5 Ethers as Ion Carriers in Potassium Ion-Selective Electrodes

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Abstract. Lipophilic bis-substituted ester and ether derivatives of benzo-15-crown-5 have been synthesised. The correlation between the structure and potentiometric ion-selectivity has been studied in PVC membrane ion-selective electrodes. An ion-selective potassium sensitive electrode based on 4′,5′-bis (biphenyloxymethyl)benzo-15-crown-5 exhibited the best electrode properties. The detection limit was $\log a_K = -5.4$; $\log K^{pot}_{K,Na} = -3.5$. The effect of the lipophilicity of neutral carriers upon electrode performance has been also discussed.

Key words: Crown ethers, substitution, lipophilicity, potassium selective electrodes, selectivity.

1. Introduction

It has previously been observed that introduction of lipophilic substituents into the benzocrown ether ring has an unpredictable influence on the selectivity of the corresponding ion-selective electrodes [1–4]. Systematic studies of benzo-15-crown-5 derivatives have shown that an increase in lipophilicity increases the selectivity towards potassium of an electrode based on these carriers [5, 6]. This phenomenon was rationalized by an assumption that the complexes formed between the ligand and sodium had a 1:1 stoichiometry and those with potassium had a 2:1 stoichiometry. The main factor was thought to be the lipophilicity of the substituents rather than that of the parent ligands or the nature of the respective cations. This increases the partition of a potassium complex from water to the electrode membrane with respect to the sodium complex.

In previously reported examples substituted crown ethers with one substituent in the benzene ring were used. The synthesis of bis-substituted derivatives is more difficult as compared with the respective mono-derivatives. The introduction of two substituents may, to some extent, be more effective in increasing the lipophilicity of the crown ether as compared with the mono-derivatives. A very easily available starting material which enables the facile synthesis of bis-derivatives is 4′,5′-bis(bromomethyl)benzo-15-crown-5 [6, 7]. Such a compound, possessing two reactive bromomethyl groups, is very susceptible towards nucleophilic substitition. Two sets of benzo-15-crown-5 derivatives: the bis-esters and bis-ethers with aliphatic and aromatic substituents were prepared and studied as ionophores in ion-selective electrodes.

2. Experimental

2.1. SYNTHETIC PROCEDURES

^{1}H NMR spectra were recorded on a TESLA apparatus at frequencies of 60, 80, or 100 MHz in $CDCl_3$ with TMS as internal standard. IR spectra were recorded on a SPECORD M 80 spectrophotometer in Nujol mulls or films. Mass spectra were recorded on a VARIAN MAT 711 apparatus using the FD technique to establish molecular weights and the purity of the final products. The homogeneity of all products has been checked using thin layer chromatography (Kieselgel 60, MERCK, aluminium foil) in a chloroform–acetone–99.8% ethanol (3:1:1) solvent system and iodine vapour to detect the spots. Melting points were measured on a BOETIUS apparatus and are uncorrected.

The sodium salts of the carboxylic acids used in the synthesis of esters were prepared by heating equivalent amounts of the respective carboxylic acid and sodium hydroxide in water. The crude products were recrystallized from water. Ferrocenecarboxylic acid was obtained from acetylferrocene by the haloform reaction analogous to the procedure described by Kasahara *et al.* [8].

2.2. SYNTHESIS OF FERROCENECARBOXYLIC ACID

To a stirred and ice cooled solution of sodium hypobromite (obtained from 23 g of NaOH, 140 mL of water and 26 g of bromine) 70 mL of dioxane was added. To this mixture was added portionwise 5.9 g (0.026 mole) of acetylferrocene [9]. Stirring was continued for an additional hour at 5°C. The mixture was filtered and the filtrate was extracted twice with methylene chloride. The aqueous layer was then heated to 80°C to remove excess of the organic solvent. The solution was then cooled and acidified to afford ferrocenecarboxylic acid which was purified via the potassium salt. Yield 2.45 g (41%) of a product melting at 209–210°C with decomposition. This compound was identical with an authentic sample.

2.3. SYNTHESIS OF BIS-ESTERS **1–9**

A mixture of 1 mmole of 4′,5′-bis(bromomethyl)benzo-15-crown-5 and 4 mmoles of the sodium salt of the respective carboxylic acid was heated in 2 mL of dry dimethylformamide (DMF) at 100°C for 2 h. The solvent was removed under reduced pressure, the residue was mixed with 25 mL of water and extracted twice with chloroform. The combined extracts were dried with anhydrous magnesium sulfate, the solvent was removed and the crude material thus obtained was purified by crystallization from the appropriate solvent or by column chromatography on silica gel or on alumina as described at the bottom of Table I.

2.4. SYNTHESIS OF 4′, 5′-BIS(ETHOXYMETHYL)BENZO-15-CROWN-5, **11**

To a solution obtained from 230 mg (10 mmole) of sodium metal and 15 mL of absolute ethanol was added 454 mg (1 mmole) of bis(bromomethyl)benzo-15-crown-5. The mixture was boiled for 1 h. The solvent was removed under reduced pressure, water (25 mL) was added and the product was extracted with chloroform.

Table I. Properties and spectral characteristic of bis-esters.

Compound No	M.p. °C	Yield %	IR bands cm^{-1}	^1H NMR δ [ppm]	m/z	Remarks
1	98–98.5	55	C=O 1715	1.9 (6H, s, CH_3); 3.55–4.17 (16H, m, CH_2CH_2O); 4.93 (4H, s, CH_2OCO); 6.73 (2H, s, aromatic)	412	I
2	75.5–76.5	62	C=O 1725	0.85–1.83 (16H, m, CH_2); 2.19 (6H, t, CH_3); 3.55–4.15 (16H, m, CH_2CH_2O); 4.93 (4H, s, CH_2OCO); 6.73 (2H, s, aromatic)	524	II
3	71–73	56	C=O 1720	0.89–1.97 (40H, m, CH_2); 2.22 (6H, t, CH_3); 3.55–4.15 (16H, m, CH_2CH_2O); 4.95 (4H, s, CH_2OCO); 6.77 (2H, s, aromatic)	692	I
4	84–85	51	C=O 1720	0.78–1.78 (64H, m, CH_2); 2.34 (6H, t, CH_3); 3.63–4.26 (16H, m, CH_2CH_2O); 5.08 (4H, s, CH_2OCO); 6.89 (2H, s, aromatic)	860	III
5	130–131	82	C=O 1710	3.37–4.20 (16H, m, CH_2CH_2O); 5.28 (4H, s, CH_2OCO); 6.83–8.02 (12H, m, aromatic)	536	III
6	60–62	74	C=O 1720	3.46–4.13 (20H, m, CH_2CH_2O, CH_2Ph); 5.01 (4H, s, CH_2OCO); 6.73 (2H, s, aromatic); 7.21 (10H, m, aromatic)	564	III
7	63–65	61	C=O 1730	3.30–4.07 (16H, m, CH_2CH_2O); 4.43 (4H, s, $COCH_2O$); 4.98 (4H, s, CH_2OCO); 6.50–7.20 (12H, m, aromatic)	596	III
8	138–139	15	C=O 1730	3.47–4.13 (16H, m, CH_2CH_2O); 5.27 (4H, s, CH_2OCO); 6.80 (2H, s, aromatic); 7.80–9.10 (8H, m, pyridine unit)	538	III
9	oil	41	C=O 1710	3.75–4.25 (16H, m, CH_2CH_2O); 4.12 (10H, s, C_5H_5); 4.37 and 4.75 (8H, 2t, C_5H_4CO); 5.35 (4H, s, CH_2OCO); 7.02 (2H, s, aromatic)	752	IV
10*	oil	30	C=O 1710 O—H 3430 assoc.	3.75–4.35 (16H, m, CH_2CH_2O); 4.07 (5H, s, C_5H_5); 4.40 (2H, t, C_5H_4CO); 4.80 (2H, C_5H_4CO and 2H, $C\underline{H}_2OH$, m); 5.32 (2H, s, CH_2OCO); 7.01 and 7.05 (2H, 2s, aromatic)	540	IV

Isolation, method I: twofold crystallization from *n*-heptane; Method II: twofold crystallization from *n*-hexane; method III: extraction of the crude product with hot *n*-heptane and column chromatography on silicagel. Eluent benzene/chloroform. Method IV: column chromatography on alumina. Eluent *n*-hexane/chloroform.

*Monoester.

The organic layer was washed with water and dried. The residue, obtained after evaporation of the solvent was extracted several times with boiling heptane. After chromatography (alumina; hexane/chloroform) and crystallization from *n*-heptane 263 mg (68%) of product **11** were obtained as bright plates melting at 70–71°C.

2.5. SYNTHESIS OF ALIPHATIC BIS-ETHER 12

A mixture of 375 mg (2 mmole) of 1-dodecanol and 46 mg (2 mmole) of metallic sodium was gently and carefully heated until dissolved. After cooling 454 mg (1 mmole) of bis(bromomethyl)benzo-15-crown-5 and 2 mL of dry DMF were added and the mixture was heated at 70°C for 4 h. The solvent was removed under reduced pressure and the residue was mixed with water (25 mL) and extracted with chloroform. The combined extracts were dried with anhydrous magnesium sulfate, the solvent was removed and the crude material was purified by column chromatography (support: alumina; eluent: hexane-chloroform mixture of increasing polarity). Yield 226 mg (34%) of product **12** melting at 59–61°C.

2.6. SYNTHESIS OF BIS-ARYL ETHERS 13–17

A mixture of 1 mmole of 4′,5′-bis(bromomethyl)benzo-15-crown-5, 4 mmoles of the respective phenol, 4.5 mmoles of anhydrous potassium carbonate and 5 mL of DMF was stirred overnight at room temperature. The solvent was then removed under reduced pressure and the residue was mixed with chloroform. The organic layer was washed with 10% sodium hydroxide solution to remove an excess of phenol. Then the solution was washed with water and dried. The crude product was purified using column chromatography (alumina; hexane/chloroform). The properties of all the bis-ethers obtained are shown in Table II.

2.7. SYNTHESIS OF BIS(2-NAPHTHYL)THIOETHER 18

To a solution of 58 mg of sodium in 100 mL of absolute ethanol was added 320 mg (2 mmole) of 2-thionaphthol and the mixture was boiled until dissolution. Then 454 mg (1 mmole) of bis(bromomethyl)benzo-15-crown-5 was added and boiling was continued for another 2 h. The solvent was then removed and the residue was extracted with boiling chloroform. The combined extracts were washed twice with water and dried with magnesium sulfate. The product obtained after evaporation of the solvent was crystallized twice from ethanol. Yield 448 mg (73%) of slightly pink crystals melting at 115–116°C.

2.8. MEASUREMENTS

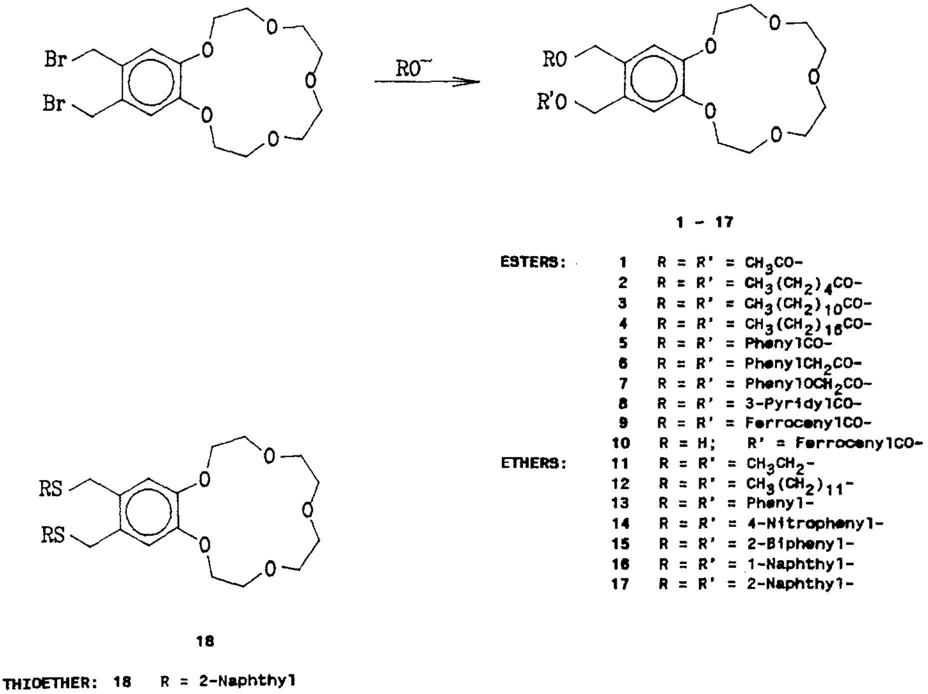
Poly(vinyl chloride) membranes were prepared conventionally [10]. A typical composition (w/w) of a membrane was as follows: 2% of the respective ionophore, 34% of poly(vinyl chloride) (POLANVIL S-70 or HOSTALIT PVC – HOECHST SLP-1109) and 64% of *o*-nitrophenyl octyl ether. All these components were dissolved in 2 mL of tetrahydrofuran and the solution was poured into a glass ring located on a glass plate. The average thickness of the membranes obtained was

Table II. Properties and spectral characteristics of aliphatic and aromatic bis-ethers.

Compound No	M.p. °C	Yield %	IR bands [cm^{-1}]	^1H NMR δ [ppm]	m/z
11	70–71	68	–	1.23 (6H, t, $CH_2C\underline{H}_3$); 3.53 (4H, q, $C\underline{H}_2CH_3$); 3.68–4.34 (16H, m, CH_2CH_2O); 4.49 (4H, s, CH_2O); 6.94 (2H, s, aromatic	384
12	59–61	34	–	0.75–1.78 (44H, m, CH_2); 3.48 (6H, t, CH_3); 3.66–4.30 (16H, m, CH_2CH_2O); 4.48 (4H, s, CH_2O); 6.93 (2H, s, aromatic)	664
13	135–137	70	–	3.64–4.33 (16H, m, CH_2CH_2O); 5.04 (4H, s, CH_2O); 6.83–7.43 (12H, m, aromatic)	480
14	207–209	65	NO_2 1510, 1335	in DMSO-d_6 3.15–4.28 (16H, m, CH_2CH_2O); 5.23 (4H, s, OCH_2); 7.08–8.2 (10H, m, aromatic)	570
15	136–137	47	–	3.33–3.87 (16H, m, CH_2CH_2O); 4.77 (4H, s, CH_2O); 6.53–7.52 (20H, m, aromatic)	632
16	164–166	59	–	3.55–4.40 (16H, m, CH_2CH_2O); 5.31 (4H, s, CH_2O); 6.69–8.50 (16H, m, aromatic)	580
17	148–148.5	69	–	3.49–4.33 (16H, m, CH_2CH_2O); 5.23 (4H, s, CH_2O); 6.88–8.09 (16H, m, aromatic)	580
18	115–116	73	–	3.38–4.11 (16H, m, CH_2CH_2O); 4.28 (4H, s, CH_2S); 6.68 (2H, s, aromatic); 6.93–7.9 (14H, m, naphthyl)	612

0.18 mm. The discs were cut out and incorporated into an Ag/AgCl electrode body using a standard procedure. The internal diameter of the membrane was about 2 mm. The electrode was conditioned in a 10^{-3} mol dm^{-3} KCl solution for 24 h before measurements.

All solutions used were prepared from analytical grade reagents and from quartz apparatus double distilled water. The slope and the detection limit of the electrodes were determined according to IUPAC [11]. The selectivity coefficients log $K^{pot}_{K,M}$ were determined by the separate solution method (SSM) recommended by IUPAC [11] at a 10^{-1} mol dm^{-3} concentration level of the corresponding metal chlorides. The theoretical slope value 59.16 mV decade^{-1} was used [4] for calculations. The



1 - 17

ESTERS:
1 R = R' = CH_3CO-
2 R = R' = $CH_3(CH_2)_4CO$-
3 R = R' = $CH_3(CH_2)_{10}CO$-
4 R = R' = $CH_3(CH_2)_{16}CO$-
5 R = R' = PhenylCO-
6 R = R' = PhenylCH_2CO-
7 R = R' = PhenylOCH_2CO-
8 R = R' = 3-PyridylCO-
9 R = R' = FerrocenylCO-
10 R = H; R' = FerrocenylCO-

ETHERS:
11 R = R' = CH_3CH_2-
12 R = R' = $CH_3(CH_2)_{11}$-
13 R = R' = Phenyl-
14 R = R' = 4-Nitrophenyl-
15 R = R' = 2-Biphenyl-
16 R = R' = 1-Naphthyl-
17 R = R' = 2-Naphthyl-

18

THIOETHER: 18 R = 2-Naphthyl

Fig. 1. The bisethers studied in this paper.

Table III. Selectivity of ion-selective electrodes based on compounds **1–18**, $-\log K^{pot}_{K,M}$.

No\M	Li^+	Na^+	NH_4^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	log *P*
1	0.2	1.4	0.7	0.2	1.2	1.4	1.8	1.0	1.6	1.6
2	3.1	2.7	1.6	0.4	2.7	4.1	3.4	3.0	3.2	5.6
3	3.2	2.9	1.8	0.4	2.5	4.2	3.7	3.2	3.4	11.6
4	3.0	2.5	1.6	0.8	2.3	3.5	3.4	3.0	3.4	17.6
5	3.3	2.95	1.7	0.7	2.4	4.1	3.8	3.1	3.9	4.9
6	3.3	2.9	1.7	0.5	2.9	4.3	3.6	3.2	3.5	5.9
7	3.2	2.9	1.8	0.7	2.5	4.1	3.7	3.1	3.8	4.8
8	−0.3	1.1	0.6	0.2	1.0	0.9	1.8	0.6	1.5	1.9
9	2.9	2.7	1.7	1.0	2.4	3.9	3.6	3.1	3.3	5.5
10	2.4	2.5	1.4	1.1	2.2	3.4	3.2	2.7	2.9	2.7
11	0.5	1.6	1.0	0.2	1.4	1.2	2.5	1.9	1.8	3.0
12	2.9	2.6	1.6	0.5	2.2	4.0	3.5	3.3	3.3	13.0
13	3.4	2.9	1.7	0.8	2.7	4.3	3.4	3.4	3.3	6.0
14	1.3	1.9	1.3	0.9	2.0	2.6	2.7	2.1	2.4	5.4
15	3.4	3.0	1.9	0.9	2.7	4.3	3.8	3.2	3.4	9.9
16	2.2	2.5	1.6	0.6	1.7	3.0	2.9	2.4	2.6	8.6
17	3.0	2.6	1.5	0.3	2.6	4.3	3.7	3.2	3.3	8.6
18	3.2	2.8	1.7	0.9	2.5	4.3	3.7	3.2	3.2	10.0

following cell with a double junction was used for all measurements:

$$\text{Ag, AgCl} \mid 1\ \text{mol dm}^{-3}\ \text{KCl} \mid 10^{-1}\ \text{mol dm}^{-3}\ \text{LiOAc} \mid \text{studied solution} \parallel \text{membrane} \parallel 10^{-3}\ \text{mol dm}^{-3}\ \text{KCl} \mid \text{AgCl, Ag}$$

The fixed interference method (FIM) employing solutions of fixed concentration (10^{-1} mol dm^{-3}) of sodium cation and varying amount of potassium cation (10^{-6}–10^{-1} mol dm^{-3}) was also used to evaluate the $K^{\mathrm{pot}}_{\mathrm{K,Na}}$ selectivity coefficient (Table IV).

The activity of cations was calculated from the Debye–Hückel equation [12]. All measurements were made at 25 ± 1°C using a N517 (MERA ELWRO) pH meter allowing readings to ± 0.1 mV. Lipophilicity ($\log P$) values were calculated according to Hansch *et al.* [13, 14].

The synthesised compounds are shown in Figure 1 and their properties are summarized in Tables I and II. The relationship between the lipophilicities and the selectivities of the electrodes are shown in Table III.

3. Results and Discussion

The 4′,5′-bis(bromomethyl)benzo-15-crown-5 is as reactive as expected for bromomethyl derivatives of aromatic systems. The nucleophilic reactions performed with the use of this material gave the expected compounds with rather good yields. In the case of good nucleophiles like the carboxylate anion or the phenolate anion the yields are high and the reaction may be performed under mild conditions. The main products are always the bis-derivatives. When the reaction is hindered due to a specific structure or to low nucleophilicity of the nucleophile the yield decreases. As an example the formation of significant amounts of monoester **10** having a hydroxymethyl group joined to the benzene nucleus was observed during the reaction of bis(bromomethyl)crown derivative with sodium ferrocene-carboxylate. The side product was formed during the nucleophilic attack of hydroxide ion on the product or on the respective intermediate. A similar reaction course was observed also in other cases, but the yields of the respective monoesters are much lower. Similarly the yields of aliphatic bis-ethers depend on the nature of the alkoxide ion. Thus the bis-ethoxy derivative **11** was obtained in much higher yield than the dodecyloxy compounds **12**. On the other hand the yields of aryloxyderivatives **13–17** as well as the bis-thioether **18** are quite good.

The selectivity coefficients of electrodes based on benzo-15-crown-5 derivatives are presented in Table III. The selectivity towards potassium over sodium changes with the struture of the ionophores. The preliminary inspection of the results indicates that, the higher the lipophilicity, the better the selectivity $\log K^{\mathrm{pot}}_{\mathrm{K,Na}}$ of the ionophore based electrode. But more exact examination reveals many deviations.

To explain the properties of ion-selective electrodes as a function of the structure of the respective ionophores it is necessary to assume that all compounds possess two active sites: the first formed by the polyoxyethylene macrocycle and the second, composed of the electron donating sulfur, oxygen or nitrogen atoms of the benzene substituents.

Both of these sites contribute to the observed selectivity. As the electron density of the macrocyclic oxygen atoms can be assumed to be constant, the changes in lipophilicity of the whole molecule and the contribution of the second complexing center are the main donating factors changing the selectivity. The decrease in susceptibility of complex formation within the second active site and increase in lipophilicity causes an increase of potassium selectivity. So a rise in lipophilicity with an unchanged second electron donor center (small increase in electron densities as a result of $+I$ effect may be neglected) causes an increase in selectivity. Comparison of **1**, **2** and **3** with increasing lipophilicities ($\log P$ equals 1.6; 5.6 and 11.6, respectively) and a parallel increase of selectivities ($\log K^{\mathrm{pot}}_{\mathrm{K,Na}}$ equals -1.4; -2.7 and -2.9, resp.) may serve as examples. Compound **2** possesses slightly better properties as compared with 4′-hexanoyloxymethylbenzo-15-crown-5 [15]. On the other hand the susceptibility of the second electron rich site to complex cations may decrease as a result of an electron withdrawing action (mesomeric and inductive effects) of the benzene ring in benzoyl derivative **5**. The bis benzoyl derivative **5**, although less lipophilic ($\log P = 4.9$) than compound **2**, recognizes potassium better in a mixture with sodium ($\log K^{\mathrm{pot}}_{\mathrm{K,Na}} = -2.95$). Similarly ionophore **12** with $\log P = 13.0$ is less selective as compared with **13** ($\log P = 6.0$). The respective K/Na selectivities are -2.6 and -2.9 on the logarithmic scale. In compound **13** the electron density on the ether oxygen atoms of the second site is lowered primarily by the mesomeric effect of the aryloxy groups. Substitution of the oxygen atoms in **17** for sulfur atoms (compound **18**) also increases the selectivity. This may be rationalized by assumption of the lower susceptibility of a soft sulfur atom to form complexes with hard sodium or potassium cations in agreement with the Pearson HSAB concept [16]. Because of the large distance between substituent and the macrocycle the direct influence of the substituent on the electronic density inside the macrocyclic cavity may be neglected.

It is interesting that the influence of the lipophilicity changes affects the selectivities of the electrodes towards nearly all the cations studied, which suggests a general nature of this phenomenon. An especially high influence is observed for electrode response for potassium over magnesium. Also significant changes in selectivity are observed for esters of pyridine-3-carboxylic acid. Two factors may be responsible for this behavior: the decrease of lipophilicity of compound **8** as compared to compounds **2–7** or distortion of the lipophilicity–selectivity relationship as a consequence of a created second unit of the molecule possessing chelating properties. This factor may also add to the observed slight deviations from the general rule.

Notice that compound **8** is a good carrier for a lithium ion-selective electrode.

Some exceptions to the generalized rules have to be outlined. Compound **4** is highly lipophilic, but its selectivity is poorer as compared with the other compounds. This is probably caused by partial crystallization in the membrane, which decreases the concentration of the ionophore. Additionally this compound has the highest molecular weight. It is worth adding that a very high lipophilicity may be disadvantageous in application to ion-selective electrodes due to some kinetic limitations [17]. Compound **14** also partially crystallizes in the membrane.

The best ionophores for potassium ion determination are compound **5** from the group of esters and compound **15** from the group of ethers. Their properties are:

Table IV. Comparison of selectivities ($-\log K^{\mathrm{pot}}_{\mathrm{K,M}}$) for POLANVIL S-70 and HOSTALIT PVC membranes containing ionophore **15**

M	POLANVIL S-70	HOSTALIT PVC
Li^+	3.4	3.5
Na^+	3.0	3.3*; 3.5**
NH_4^+	1.9	2.0
Rb^+	0.9	0.9
Cs^+	2.7	2.8
Mg^{2+}	4.3	4.3
Ca^{2+}	3.8	3.7
Sr^{2+}	3.2	3.1
Ba^{2+}	3.4	3.3

* – Separate solutions method (SSM).

** – Fixed interference method (FIM).

The detection limits [$-\log a_{\mathrm{K}}$] for Polanvil and Hostalit electrodes are 4.8 and 5.4; the linear responses [$-\log a_{\mathrm{K}}$] are 1–4, 4 and 1–5.1; and the slopes [mV decade^{-1}] are 56 and 58, respectively.

selectivity coefficient −2.95 and −3.0 respectively; for both ionophores the detection limit is 1.6×10^{-5} mol dm^{-3}, the linear response between 3.2×10^{-5}–10^{-1} mol dm^{-3} and slope 56 mV decade^{-1}. With the exception of **1**, **8** and **11** the slopes range from 50 to 58 mV decade^{-1} for the residual electrodes.

The best ionophore from the aromatic ether group **15** was studied by modifying the composition of the membrane. The best results were obtained when the POLANVIL S-70 poly(vinyl chloride) was replaced by a similar product obtained from HOECHST. A comparison of both electrodes is presented in Table IV. A sensor based on compound **15** and the HOECHST HOSTALIT PVC exhibits performance characteristics sufficient for biological applications and it is comparable to those of other good potassium selective ion-selective electrodes.

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