

Ph. D. thesis

Róbert Bereczki

**Development and analytical characterization of novel
synthetic ionophore based ion-selective electrodes**

Advisors:

Prof. Dr. Klára Tóth

Dr. Béla Ágai associate professor

Co-advisor:

Dr. Róbert E. Gyurcsányi associate professor

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BME

Institute of General and Analytical Chemistry
Department of Organic Chemical Technology

INTRODUCTION

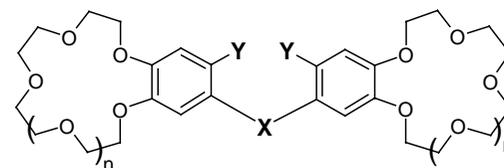
The first ion selective electrodes (ISEs) were implemented in the beginning of the 20th century. Since then ISEs became indispensable devices in the field of process control as well as clinical and environmental analysis.

Neutral ionophore based liquid membrane electrodes are one of the most important ion sensitive devices.

Although the first natural ionophores with antibiotic properties such as Valinomycin, Nonactin etc. are still successfully used in the analytical routine, the broadening of the range of the assessable analytes become possible with the advent of the synthetic ionophores. Owing to the extensive research for tailored synthesis of selective complexing agents ISEs for more than 60 different analytes have been reported.

Experimental work

Based on methods developed earlier for synthesis of potassium ionophores (*Table 1*, **1**: BME 15, **3**: BME 44) three new, bis(benzo-18-crown-6)ether type cesium selective ionophores were prepared (ligands **2**, **4**, **6**). The potentiometric performance characteristics of these molecules were evaluated and compared with that of other biscrown type cesium ionophores.



Y	X	Ionofor	
		n=1	n=2
NO ₂		1	2
NO ₂		3	4
NO ₂		5	6

Table 1

Furthermore, a new class of thiacalixmono- and biscrown ethers (*Figure 2, 7, 8, 9*) were incorporated in plasticized PVC membranes and tested as potential cesium ion selective molecules. The results unambiguously demonstrated that the ion complexing properties of these ligands are comparable to the best calixarene type ionophores reported in the literature.

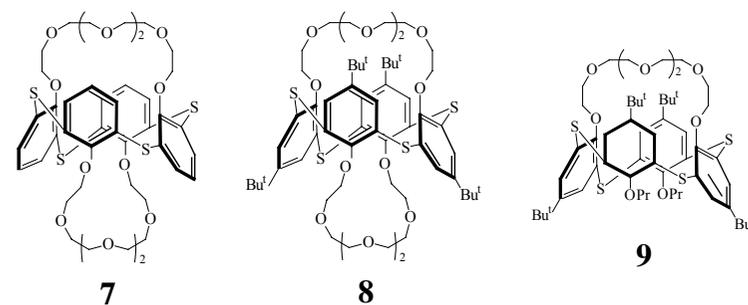


Figure 2

The selective extraction of radioactive cesium isotope from nuclear wastes has an important role in the economical reprocessing of highly radioactive nuclear. Solvent extraction seems to be the most convenient way for the separation of ^{137}Cs from solutions containing elevated concentrations of other alkali ions (3-4 M Na^+ , 1 M K^+). This justifies the efforts towards the synthesis and identification of cesium ionophores with high $\text{Cs}^+/\text{Na}^+, \text{K}^+$ selectivity.

Although the high selectivity is probably the most important goal of any ionophore design and synthesis related research, recently there is growing interest towards ionophores custom-tailored for particular applications. Regarding this research direction, we have synthesized novel ionophores with optical activity (chromoionophores) as well as ionophores appropriate for covalent immobilization.

Therefore I have synthesized ester-substitued bis(benzo-15-crown-5)ethers as potential active components for the preparation of direct fluorescent optodes. (*Figure 3, 10, 11, 12*).

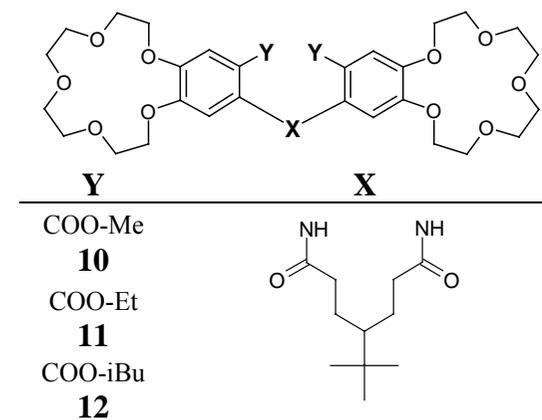


Figure 3

Further on I have synthesized a potassium ion selective biscrown ether (*Figure 1, 5*) that can be copolymerized with different monomers such as acrylates and vinylchloride

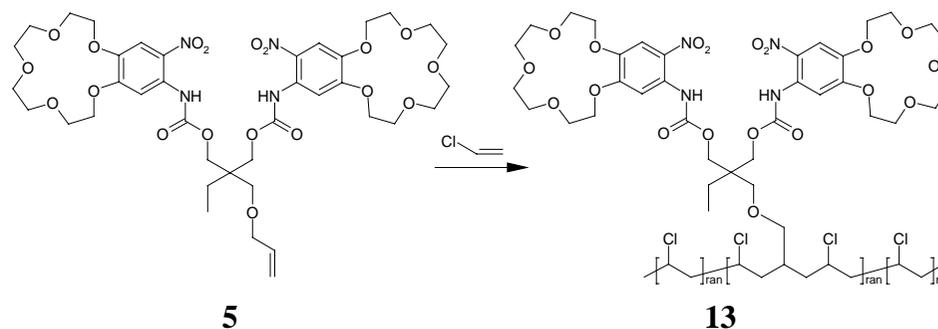


Figure 4

The successful copolymerization of the alkenyl group bearing potassium ionophores led to synthesis of the first ionophore covalently attached to an inert PVC backbone (*Figure 4, 13*). Characteristic properties such as ion selectivity, complex stability, diffusion coefficient etc. of the novel ionophores were determined and compared with the relevant mobile ionophores. The synthesis method developed can represent a feasible alternative for the preparation of novel covalently linked ionophores and by that can contribute to the development of ISEs with low detection limit.

Results

1. I have synthesized three new bis(benzo-18-crown-6)ether based cesium selective ionophores, one of which is suitable for covalent grafting to polymer backbones by its copolymerization with vinyl or acryl type monomers. After incorporation in solvent polymeric membranes, the potentiometric performance characteristics of the ionophores were determined. The structural properties of the biscrownethers determining the exquisite selectivity of potassium selective ionophores were found to not improve significantly the selectivity of the similar structure cesium ionophores.

2. I have studied the potentiometric performance characteristics of novel thiacalixmono- and biscrownether type compounds. I have determined that each of the studied molecules possessed excellent cesium selectivity. After optimization of the composition of the ion selective membranes, I could conclude that the monocrown type compound proved to be has the best cesium selectivity. The selectivity data were correlating closely with the ratio of the relevant complex formation constants

3. I have successfully synthesized different ester group bearing potassium selective bis(benzo-15-crown-5)ether ionophores. The potassium selectivity of the novel ionophores was determined after their incorporation in PVC based solvent polymeric membranes. Although the selectivity of the ionophores was somewhat smaller than that of the best biscrown ether type ionophore (BME 44) the optical properties of compounds make them suitable candidates as active components in fluorescent direct optodes

4. I have successfully synthesized an alkenyl group bearing potassium ionophore derivative, which is suitable for copolymerization with different vinyl and acrylic type monomers. After incorporation in PVC based solvent polymeric membranes, the potentiometric performance characteristics of the ionophore were determined and it proved to be similar with that of the BME-44.

5. The alkenyl group bearing ionophore was successfully copolymerized with methylmetacrylate/n-butylacrylate and the resulted covalently immobilized ionophore could be further used for the preparation of so-called self-plasticized membranes. Comparing the potentiometric performance characteristics of these and mobile ionophore (incorporated in PVC membranes) containing membranes, it could be concluded that the immobile ionophores performance is somewhat lower.

6. I have successfully prepared the first ionophore based on the direct copolymerization of the vinyl-chloride monomer and a suitable ionophore. The resulted potassium selective copolymer was characterized with gel permeation chromatography and the ionophore content of the copolymer was determined by spectrophotometry using standard addition technique. I have studied the ion transport properties of ISEs based on this membranes with chronoamperometry and hyperspectral imaging. With the exception of the selectivity, which was somewhat lower, the other potentiometric performance characteristics closely matched that of the BME 44 membranes used as reference.

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Papers

1. Agai B, **Bereczki R**, Bitter I, *et al.* Synthesis of bis(benzo-18-crown-6) ionophores and their application in developing Cs⁺-selective ligand membrane electrodes. *Magyar Kemiai Folyoirat* **1999**; 105(7): 256-263.
2. **Bereczki R**, Agai B, Bitter I, Toke L, Toth K. Bis(benzo-18-crown-6) derivatives: Synthesis and ion-sensing properties in plasticized PVC membranes. *Journal of Inclusion Phenomena and Macrocyclic Chemistry* **2003**; 45(1-2): 45-50.
3. **Bereczki R**, Agai B, Bitter I. Synthesis and alkali cation extraction ability of new mono and bis(benzocrown ether)s with terminal alkenyl groups. *Journal of Inclusion Phenomena and Macrocyclic Chemistry* **2003**; 47(1-2): 53-58.
4. **Bereczki R**, Gyurcsanyi ER, Agai B, Toth K. Synthesis and characterization of covalently immobilized bis-crown ether based potassium ionophore. *Analyst* **2005**; 130(1): 63-70.

Submitted papers

- 1 **Bereczki R**, Takacs B, Langmaier J, et al.
How to Assess the Limits of Ion-Selective Electrodes: Simple Method for the Determination of the Unbiased Span, Response Range and Selectivity Coefficients of Neutral Carrier-Based Cation Selective Electrodes.
Analytical Chemistry **Beküldve**.
- 2 **Bereczki R**, Csokai V, Grun A, Bitter I, Toth K.
Crown bridged thiacalix[4]arenes as cesium-selective ionophores in solvent polymeric membrane electrodes.
Analytica Chimica Acta **Beküldve**.

Lectures on scientific conferences:

- 1 **Bereczki R.**, Ágai B., Tóth K., Bitter I., Tóke L.: Új cézium ionszelektív koronaéterek szintézise és elektroanalitikai vizsgálata
Vegyészkonferencia, Eger, Magyarország, **1999**. június 22-24.
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XXV. Kémiai Előadói Napok, Szeged, Magyarország, **2002**. október 28-30.

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VIII. Vegyészkonferencia, Kolozsvár, Románia, **2002.** november 15-17.

4 **Bereczki R.**, Gyurcsányi E.R., Ágai B., Tóth K.: PVC-mátrixban kovalensen immobilizált kálium-ionofór szintézise és vizsgálata
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Analitikai Vegyészkonferencia, Balatonföldvár, Magyarország, **2003.** június 30-július 2.

Posters on scientific conferences

1. **R. Bereczki**, B. Ágai, I. Bitter, K. Tóth: New mono- and bis(crown ether)s with different alkenyl group: Extraction data and potentiometric selectivity properties in plasticized PVC membranes
Mátrafüred'02, International Conference on Electrochemical Sensors, Mátrafüred, 13-18. October **2002.** (Hungary).

2. **Bereczki Róbert**, Ágai Béla, Bitter István és Tóth Klára: Kovalens immobilizálásra alkalmas makrociklusok szintézise, kopolimerizációja és vizsgálata
Vegyészkonferencia 2003, Hajdúszoboszló, Magyarország, **2003.** június 26-28.