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Fluoride sensing by polymeric membranes based on organoboron Lewis acid receptors

Martyna Jańczyk[1], Agnieszka Adamczyk-Woźniak[2], Andrzej Sporzyński[2], Wojciech Wróblewski[1]
[1] Warsaw University of Technology, Department of Microbioanalytics, Noakowskiego 3, Warszawa 00-664, Poland, mjanczyk@ch.pw.edu.pl
[2] Warsaw University of Technology, Department of Physical Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland

Abstract

Intensive research is focused on organoboron receptors characterized by strong and selective interactions of three-coordinate boron center ("hard" Lewis acid) with fluoride ions ("hard" Lewis base). In this work, newly syntesized 4-octyloxyphenylboronic acid (OPBA) and pinacol ester of 2,4,6-trifluorophenylboronic acid (PE-PBA) were proposed as fluoride-selective ionophores in polymer membranes. The membranes containing OPBA showed enhanced selectivity, but the slopes of the fluoride responses in acidic conditions were super-Nernstian. In contrary, theoretical behavior was noticed in the case of membranes doped with the pinacol ester derivative. A response mechanism of the polymer membrane electrodes based on organoboron receptors was proposed on the basis of potentiometric and 19F NMR studies.

Key words: organoboron receptor, 4-octyloxyphenylboronic acid (OPBA), pinacol ester of 2,4,6-trifluorophenylboronic acid (PE-PBA), determination of fluoride

Introduction

Quantitative analysis of fluoride is important in environmental protection, medicine and biology. Originally, fluoride anions were determined by titration with thorium nitrate. Other recently reported methods were based on potentiometry [1], fluorimetry [2] and colorimetry [3]. Direct potentiometric methods, commonly applying the crystalline fluoride-selective electrode, are suitable for continuous monitoring and replace the expensive and time-consuming instrumental methods. Polymer membrane electrodes with fluoride-selective ionophores are also developed. The reported high affinity of boronic acids towards fluoride ions [4] provides the possibility of their application as receptors in polymeric selective layers.

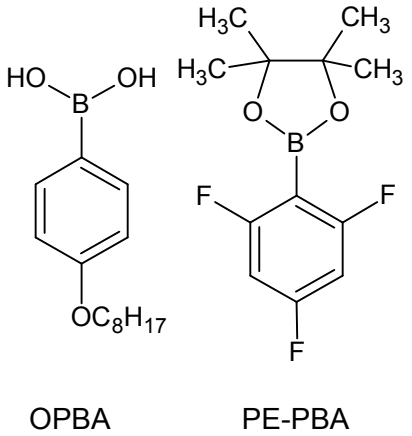

Fig. 1. The structures of organoboron compounds

Results and Discussion

Potentiometric detection of fluoride ions by polymer membranes containing organoboron compounds – 4-octyloxyphenylboronic acid (OPBA) and pinacol ester of 2,4,6-trifluoro-phenylboronic acid (PE-PBA) (Fig. 1) – was presented in this paper.

Increased fluoride selectivity was determined for PVC/DOS membranes containing OPBA (Fig. 2); however, the values of fluoride response slopes were super-Nernstian (Fig. 3). This could be explained by the variation of the stoichiometry of the OPBA-F- complex formed in the membrane phase (from 1:1 to 1:3) during the electrode calibration at higher fluoride concentrations.

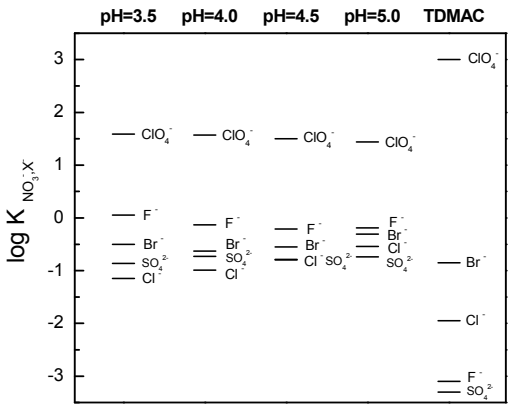

Fig. 2. The selectivity patterns of PVC/DOS membranes doped with OPBA determined over the pH range 3.5-5.0

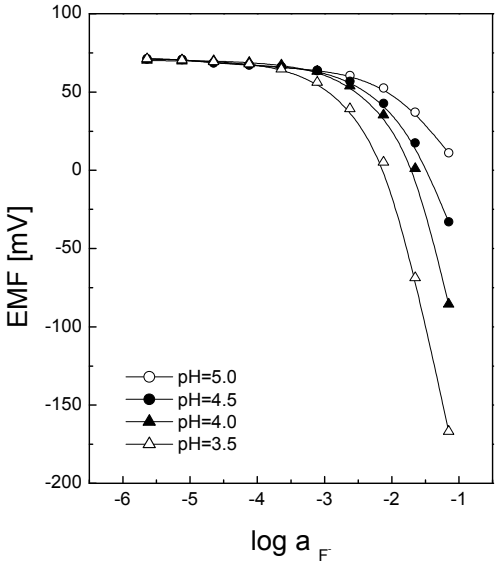

Fig. 3. The fluoride responses of ion-selective electrodes based on OPBA, measured in acetate buffer solution at various pH

Such changes lead to the decrease of the concentration of the free primary anion in the membrane and thus to its non-theoretical behavior. This mechanism was supported by the 19F NMR experiments, proving that the fluoride complexation proceeds more effectively in acidic environment leading to the various phenylboronic acid-fluoride adducts with predominant PhBF3- species. The PVC membranes based on pinacol ester of phenylboronic acid were characterized by theoretical responses due to the strengthened B–O bond, favoring the formation of anionic single fluoride adduct in the membrane phase (Fig. 4).

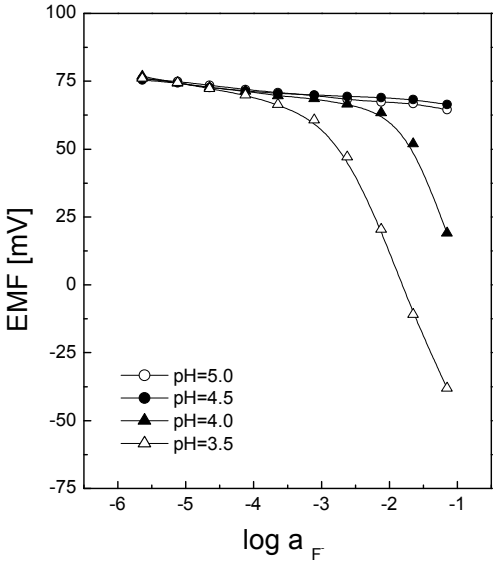

Fig. 4. The fluoride responses of ion-selective electrodes based on PE-PBA, measured in acetate buffer solution at various pH

Concluding, boronic acid derivatives could not be used as effective fluoride ion receptors. Therefore, further research is focused on the synthesis of novel organoboron Lewis acid receptors and their application as ionophores in polymer membrane electrodes.

Acknowledgements

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