Application of metallocomplexes as ionophores in various polymer matrices

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Abstract

In the framework of presented studies, various metallocomplexes (mainly metalloporphyrins) have been tested in plasticized aminated or carboxylated poly(vinyl chloride) (PVC) and unplasticized polyurethane instead of usually used plasticized PVC-based membranes. Such modification allows for relatively simple preparation of miniaturized planar electrodes (thanks to good adhesion of these membranes to certain substrates) or immobilization of biomolecules to prepare biosensors (thanks to functional groups of applied polymers). It was found, that the presence of functional groups of applied polymers can influence the complexing properties of tested ionophores and consequently the working parameters of ion-selective electrodes prepared with their use.

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Keywords: metalloporphyrins, anion-selective electrodes, polyurethane, functionalized poly(vinyl chloride)

1. Introduction

Ion-selective electrodes (ISEs) have proved to be valuable analytical tools allowing for fast and cheap analysis of many ionic species [1]. In case of polymer membrane-based ISEs - the group, which is the most frequently studied and has the biggest range of applications (among all ISEs), the most important component of ion-selective membrane is an ionophore. Ionophore is responsible for selective complexation of target ion, which assures the appropriate functioning of electrodes, even in samples of complex matrices. The polymer materials, which give the appropriate physical properties of membranes are usually chemically inert and do not influence the selectivity neither other working parameters of ISEs.

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However, when preparing the miniaturized ISEs or enzymatic biosensor based on ISEs, such inertness can be considered as a significant drawback. The presence of functional groups in a backbone of applied polymers can distinctly influence the properties of membranes, increasing the adhesion to various substrates (particularly important for miniaturization of ISEs in a planar variant) and allowing for biomolecule (enzymes, antibodies, aptamers, etc.) immobilization on their surface [2,3]. Unfortunately, the functional groups of applied polymers are also capable of interaction with ionophores present in a membrane phase, influencing their complexing abilities. Moreover, the working parameters of electrodes prepared with the use of polymers bearing such functionalities can be also altered in comparison with electrodes based on unmodified PVC doped with the same ionophores.

2. Experimental

The compounds: chloro 2,7,12,17-tetra-tert-butyl-5,10,15,20-tetraazaporphine aluminum(III) (AlTAP) - described as F-selective ionophore [4], chloro 5,10,15,20-tetrakis(4-t-butylphenyl)porphyrin aluminum(III) (AlBTPP) - described as F-selective ionophore [5], dichloro 5,10,15,20-tetrakis(4-t-butylphenyl)porphyrin zirconium(IV) (ZrBTPP) - described as F-selective ionophore [5], chloro 5,10,15,20-tetrakis(4-t-butylphenyl)porphyrin gallium(III) (GaTTPP) - described as F-selective ionophore [6], 5,10,15,20-tetrakis(4-t-butylphenyl)porphyrin nickel(II) (NiTTPP) - described as SCN-selective ionophore [7], dichloro 5,10,15,20-tetrakis(4-t-butylphenyl)porphyrin tin(IV) - described as salicylate-selective ionophore [8], chloro 5,10,15,20-tetrakis(4-t-butylphenyl)porphyrin manganese(III) (MnTTPP) - described as SCN-selective ionophore [9], chloro 2,3,7,8,12,13,17,18-octaethylporphyrin chromium(III) (CrOEP) - chromium complexes described as salicylate-selective ionophore [10] and chloro 2,3,7,8,12,13,17,18-octaethylporphyrin indium(III) (InOEP) - described as Cl-selective ionophore [11] were chosen as anion-selective ionophores. For preparation of polymeric ion-selective membranes carboxylated poly(vinyl chloride) (cPVC) (1.8% carboxyl basis), aminated poly(vinyl chloride) (0.79% N of product), polyurethane (PU, Tecoflex SG-80A), o-nitrophenyloctyl ether (o-NPOE), dioctylsebacate (DOS), potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTFPB) and tetrahydrofuran (THF) were used. For preparation of buffer solutions, glycine (Gly) and orthophosphoric acid were used. The ion-selective membranes based on functionalized PVC contained 1 wt.% of ionophore in a carboxylated or aminated PVC:plasticizer (1:2) polymeric matrix. The ion-selective membranes based on PU consisted of 1 wt.% of and 99 wt.% of PU. Some of the ion-selective membranes were also doped with anionic additives. All components were dissolved in 2 mL of THF and the mixture was then transferred to a glass ring (24 mm i.d) mounted on a glass slide. The solvent was allowed to evaporate overnight. Discs (5 mm o.d.) were then cut out from the parent membrane and mounted into Philips electrode bodies (ISE – 561) (Glasblaser ei, W. Moller AG, Zurich, Switzerland). The performance of the electrodes was examined by measuring the cell EMF for aqueous solutions of given anions (sodium salts) over the concentration range of 10^{-7} to 10^{-1} mol·dm^{-3} in buffer solution (0.05 M Gly/H₃PO₄ buffer, pH 3.0 was used).

3. Results and discussion

All of the prepared electrodes based on aminated PVC membranes shown anionic response (see table 1). However, the chemical nature of primary amine groups influenced the working parameters of electrodes with membranes doped with of examined metallocomplexes. When comparing the calibration curves of electrodes with membranes formulated with unmodified PCV (with no additives) with electrodes with membranes formulated with aminated PCV, one can observe shifting of selectivity in favor of more lipophilic anions for aPVC-based electrodes (however, still distinct from Hofmeister series). The amine groups present in a backbone of aPVC can undergo protonation (pH 3.0 was applied),
Table 1. The influence of a membrane material on complexing ability of tested metallocomplexes.

<table>
<thead>
<tr>
<th>Ionophore</th>
<th>Membrane</th>
<th>AITAP</th>
<th>AlBTPP</th>
<th>GaTPP</th>
<th>ZrBTPP</th>
<th>InOEP</th>
<th>MnTPP</th>
<th>CrOEP</th>
<th>SnTPP</th>
<th>NiTPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>aPVC</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>h</td>
</tr>
<tr>
<td>cPVC</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

'+' - ionophore works, '-' - ionophore does not work (no response), 'h' - ionophore does not work (selectivity pattern according to Hofmeister series)

by becoming the anion-exchanger. For NiTPP the influence of aPVC was so pronounced, that the NiTPP-based electrode exhibited selectivity corresponding to Hofmeister series. The effect of amine groups on ionophores could be neutralized by addition of anionic sites to the membranes. Fig.1. shows the influence of KTFPB addition to the aPVC-base membranes doped with AlBTPP, AITAP or ZrBTPP on selectivity of electrodes prepared with the use of these ionophores. As it is easy to observe, the higher the KTFPB concentration (up to some limit), the smaller is the influence of lipophilic anions on electrodes' response.

![Fig. 1. Potentiometric selectivity coefficients of electrodes based on aPVC doped with AlBTPP, AITAP, ZrBTPP and KTFPB (mol.% according to ionophore).](image)

In contrary to membranes prepared from aminated PVC, only few ionophores (among tested) exhibited useful properties in carboxylated PVC membranes. In case of electrodes with cPVC membranes doped with GaTPP, ZrBTPP, InOEP, GaTPP or NiTPP no anionic response was observed. These electrodes shown only cationic response for high concentration (usually over $10^{-7}$ M) of salts used for calibrations (response towards sodium cation). The carboxylic groups present in the polymer structure can function as anionic additives, in some cases suppressing (due to their big amount) the complexing ability of...
ionophores, but in other improving the working parameters of electrodes such as selectivity or detection limit (in comparison with unmodified PVC). Moreover, the carboxylic anion is also capable of direct interaction with metallic centers of ionophores, which can be also reflected as a complete lack of anion response. The compounds based on Al$^{3+}$, Mn$^{3+}$ and Cr$^{3+}$ can be successfully used as ionophores in cPVC-based membranes. While for CrOEP and MnTPP, the replacement of PVC with cPVC reflected as only tiny shift in selectivity, in the case of AlTAP and AlBTPP (F-selective ionophores) the effect of such replacement was more distinct. The selectivity coefficients ($K_{F,Y}$) against the most lipophilic anions such as thiocyanate and perchlorate were lower about one order of magnitude when polymer was changed from PVC to cPVC.

The experiments carried out for unplasticized PU-based membranes revealed that anion response of some of the tested ionophores is blocked in such membranes. However, among others Al$^{3+}$-complexes could be successfully used as ionophores in such membranes.

Acknowledgements

This work has been financially supported by Warsaw University of Technology

References


