SELECTIVE OPTODE MEMBRANES FOR HEAVY METAL ION DETECTION.

Niels J. van der Veen, Richard J.M. Egberink, Johan F.J. Engbersen and David N. Reinhoudt

Department of Supramolecular Chemistry and Technology, MESA Research Institute, University of Twente, P.O. Box 217, 7500AE, Enschede, The Netherlands

0. Abstract

Optode membranes for Lead(II) based on an ion-exchange mechanism and neutral ionophores show that the calix[4]arene ionophores developed for CHEMFETS can be used in optical sensing schemes. To achieve pH independent sensor response, chromoionophores have been developed based on these neutral ionophores, which show a optical response to the complexation of metal ions.

Keywords: optode membrane, chromoionophores, heavy metal ions

1. Introduction

The monitoring of heavy metal concentrations in surface water, harbor sludge, ground or waste water will be crucial in solving environmental problems related to these pollutants. Ionophores selective for several heavy metal ions have been used in chemically modified field effect transistors (CHEMFETs)[1], which involve the transduction of the supramolecular recognition of the ions by the selector molecules into an electrical signal. In principle, these ionophores can also be applied in optode membranes. The use of optical transduction has a number of advantages, such as the absence of a reference electrode, the insensitivity to electric or magnetic fields, the possible variation of transduction schemes and the possibility of remote sensing using fiber optics.

A well studied optical transduction scheme was developed by Simon *et al.* It involves the use of pH dyes by an ion exchange process, which changes the absorption spectrum of the optode membrane. The method has been used to develop optode membranes for detection of metal ions such as lead(II)[2] and silver(I).[3] The principle disadvantages of these optode membranes is that the response is intrinsically pH dependent and that plasticized PVC is used, which limits the durability because of leaching of the plasticizer. We therefore work on the development of optode membranes based on polysiloxanes, which are intrinsically elastomeric and therefore do not need plasticizers. The membrane processing with these polymers is compatible with IC technology.[4] This would make it possible to photochemically bind the optode membrane to a silica waveguide and so integrate membrane and optics in a device. For pH independent optode membranes a different transduction scheme should be employed. We present the synthetic strategy for preparation of selective heavy metal ion chromoionophores which could be used in such a scheme.

A. Berg et al. (eds.), *Sensor Technology in the Netherlands: State of the Art*

2. Application of calix[4]arene receptors in ion exchange optode membranes

The metal ion receptors developed for use in CHEMFETs can be used in ion exchange optode membranes involving pH dyes. These liquid polymer membranes contain ionophores, a pH dye and lipophilized anionic sites. When the membrane is exposed to an analyte solution, the complexation of ions by the receptor causes an influx of positive charge into the membrane. This triggers deprotonation of the pH dye, which is accompanied by a change in absorption spectrum. The two equilibria involved, ion complexation-decomplexation by the receptor and pH dye protonation-deprotonation, compete and result in a reversible color response of the membrane. This mechanism is illustrated in figure 1.

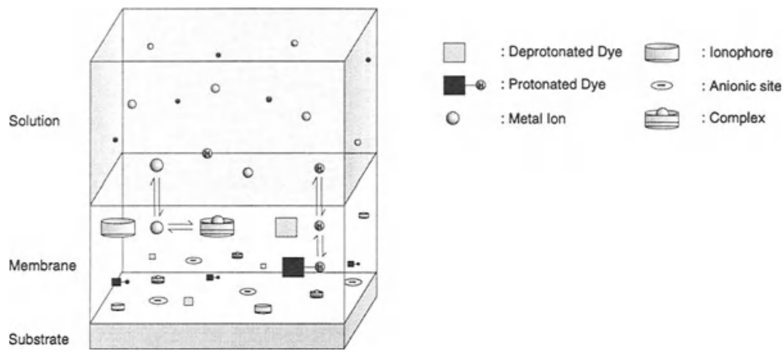

Figure 1: *Mechanism of response of an optode membrane containing a pH dye*

In figure 2, the response of a DOS-plasticized PVC membrane containing a calix[4]arene based Pb(II) receptor is demonstrated. As the concentrations of Pb(II) get higher, the absorption spectrum of the membrane shifts from the spectrum dominated by the protonated pH dye to the spectrum dominated by the deprotonated dye. The response is reversible.

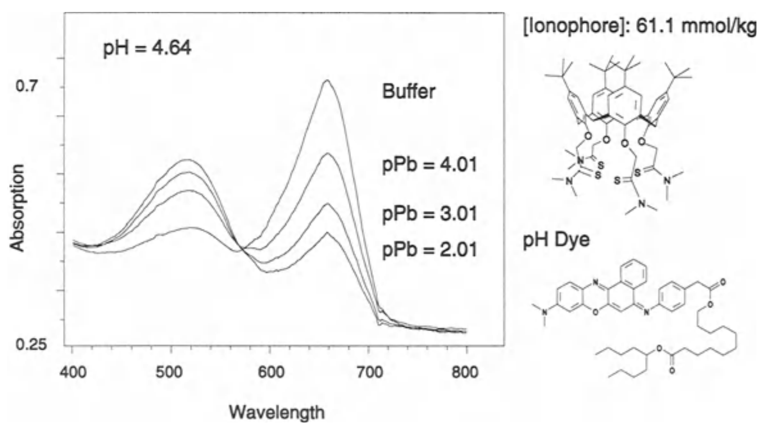

Figure 2: *Response of a Lead selective plasticized PVC optode membrane based on ion-exchange.*

3. Chromoionophores derived from selective heavy metal ion receptors

Optode membrane response should preferably be pH insensitive. This cannot be achieved when the transduction involves pH dyes. An improved transduction scheme requires chromoionophores which couple the recognition event directly to a color change. The synthetic strategy for making selective chromoionophores is to couple chromophores to known receptors. Therefore, chromoionophores **2** and **4** in figure 3 are currently being synthesized as derivatives of the Pb(II) and Cd(II) ionophores **1** and **3**, respectively. Recent results will be reported.

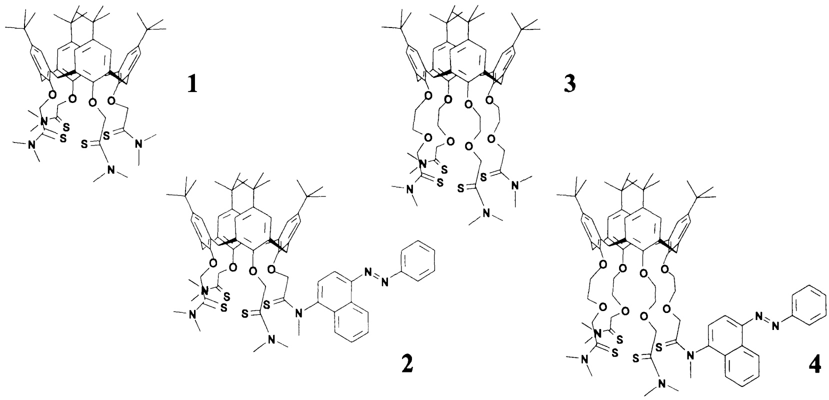

Figure 3: *Chromoionophores for selective recognition of lead and cadmium ions*

The molecule depicted in figure 4 is a compound *en route* to a chromoionophore selective for Lead(II) ions. The dye functionalities are conjugated with the amide carbonyl groups, which are responsible for the complexation of metal ions. These amide groups will later be transformed to thio-amide groups to obtain selectivity for heavy metal ions. The molecule has no acidic or basic sites, which should make its response to changes in pH small. In figure 5 the response is shown of this chromoionophore to complexation of Sodium ions. It can be seen that by coupling of chromophores to the metal complexing amide-moieties transduction of the complexation in an optical signal is indeed possible. The spectral changes upon complexation of the metal ion are clear.

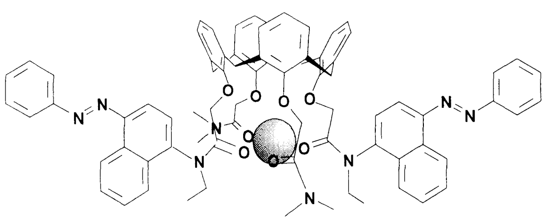

Figure 4: *Chromoionophore for optical transduction of selective recognition of metal ions.*

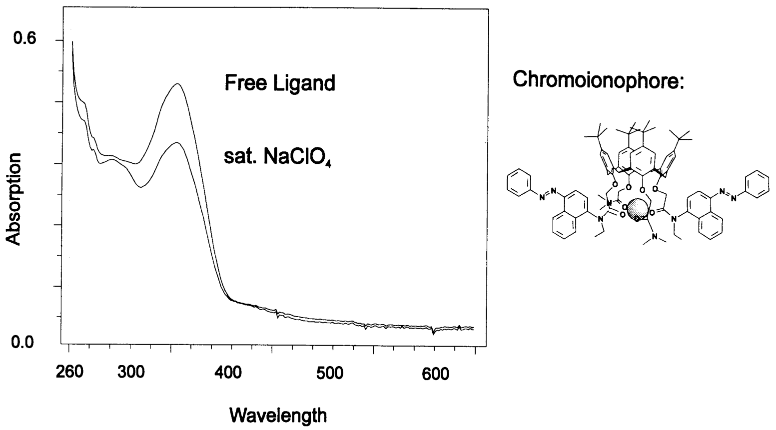

Figure 5: *Optical transduction of the complexation of Sodium ions by a chromoionophore.*

4. Conclusions

It has been shown that calix[4]arene neutral ionophores can be used in optical transduction schemes. Also, chromoionophores based on integration of a dye functionality into the chemical structure of these ionophores respond to complexation of metal ions by changing their spectral characteristics.

5. Acknowledgment

We thank the Technology Foundation (STW) and the Netherlands Organization for Scientific Research (NWO) for financial support.

6. References

1 P.L.H.M. Cobben, R.J.M. Egberink, J.G. Bomer, P. Bergveld, W. Verboom and D.N. Reinhoudt, *J. Am. Chem. Soc.* **114** (1992) 10573.
2 M. Lerchi, E. Bakker, B. Rusterholz and W. Simon, *Anal. Chem.* **64** (1992) 1534-1540.
3 M. Lerchi, F. Orsini, Z. Cimerman, E. Pretsch, D.A. Chowdhury and S. Kamata, *Anal. Chem.* **68** (1996) 3210-3214.
4 R.J.W. Lugtenberg, M.M.G. Antonisse, R.J.M. Egberink, J.F.J. Engbersen, D.N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2*, (1996) 1937-1941.