DOCTORAL THESIS

Design of chemical sensors based on calixarene and fluorescein octadecyl ether octadecyl ester: from ion selective electrode to fluorescent optode

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Design of Chemical Sensors Based on Calixarene and Fluorescein Octadecyl Ether Octadecyl Ester – From Ion Selective Electrode to Fluorescent Optode

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Abstract

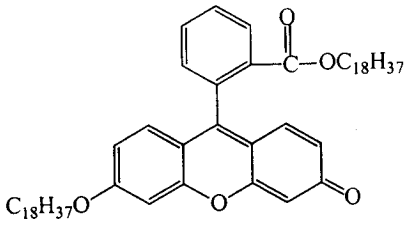
This thesis describes the design of chemical sensors based on calixarenes and fluorescein octadecyl ether octadecyl ester (FODEE) (**I**). An ion-selective electrode (ISE) for the determination of mono-carboxylic acids was developed *via in situ* generation of the corresponding amines. The sensing membrane contained calix[6]arene hexaester ionophore in poly vinyl chloride (PVC) matrix. It exhibited Nernstian responses to mono-carboxylic acids in concentration range of 10^{-2} to 10^{-5} mol dm^{-3}, after the carboxylic acids were converted into their corresponding amines.

A fluorescent indicator is required, in order to convert the ion-selective electrode system into an ion-selective fluorescent optode system based on the same neutral ionophore. FODEE was selected because it exhibited high lipophilicity and its fluorescence intensity in PVC matrix could be attenuated by incorporating potassium tetrakis (4-chlorophenyl) borate (KT*p*ClPB) in the membrane. A fluorescent amine-selective optode was then developed by immobilizing calix[6]arene hexaester, FODEE and KT*p*ClPB in PVC matrix. It was proposed that HT*p*ClPB, being the major specie of the lipophilic borate in plain acidic buffer solution, would form an ion pair (**II**) with the zwitterion of FODEE and quenched the fluorescence light emitted from FODEE in PVC matrix. When the sensing membrane was put in contact with amine in acidic buffer solution, the positively charged guest-host complex formed between calixarene and alkylammonium ion (**III**) would hold the $TpClPB^-$ anion in its vicinity, released HT*p*ClPB from the ion pair and caused fluorescence recovery effect on the sensing membrane. In this way, KT*p*ClPB not only provided anionic sites for the amine-selective fluorescent optode system but also played the role of fluorescence signal transducer. This

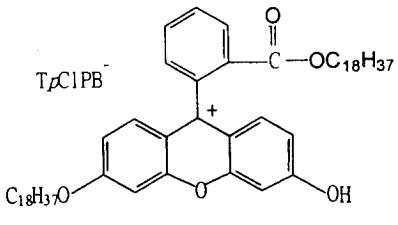
fluorescent amine-selective optode measured 1-octamine in concentration range of 10^{-2} to 10^{-6} mol dm^{-3} pH 5.0 lithium acetate buffer.

To demonstrate that it is a general design of cation-selective optode based on FODEE, a sodium-selective optode was constructed by immobilizing calix[4]arene tetraester, FODEE and KT*p*ClPB in PVC matrix. It operated on the same principle for amine-selective optode and measured sodium ion in magnesium acetate buffer in concentration range of 10^{-1} to 10^{-6} mol dm^{-3}. Practical use of this sensor was demonstrated by real sample analysis in water samples of complex context.

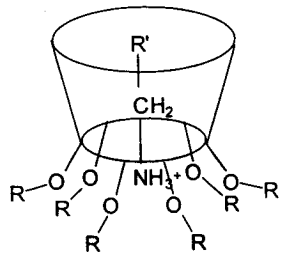
During the study of fluorescence properties of FODEE in PVC matrix, a pH sensing membrane, a fluorescent optode for phenol and a chemical probe for mercury (II) were also constructed.



(I) Neutral form of FODEE



(II) Proposed ion pair HT*p*ClPB/FODEE



(III) Positively charged guest-host complex

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