



A calixarene-based ion-selective electrode for thallium(I) detection



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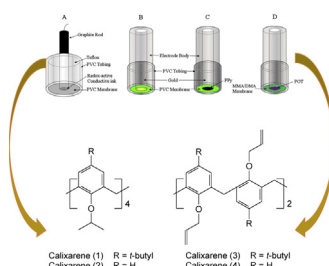
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HIGHLIGHTS

- Tuning of metal binding cavities in thallium(I) calixarene ionophores.
- Novel calixarene-based ionophores with improved selectivity for thallium(I).
- Sandwich membrane characterization of thallium(I) binding in novel calixarenes.
- Improved selectivity and sensitivity with novel thallium(I) calixarene ionophores.
- Solid contact ion-selective electrodes for novel thallium(I) calixarene ionophores.

GRAPHICAL ABSTRACT



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ABSTRACT

Three new calixarene Tl^+ ionophores have been utilized in Tl^+ ion-selective electrodes (ISEs) yielding Nernstian response in the concentration range of 10^{-2} – 10^{-6} M $TlNO_3$ with a non-optimized filling solution in a conventional liquid contact ISE configuration. The complex formation constants ($\log \beta_{11}$) for two of the calixarene derivatives with thallium(I) (i.e. 6.44 and 5.85) were measured using the sandwich membrane technique, with the other ionophore immeasurable due to eventual precipitation of the ionophore during these long-term experiments. Furthermore, the unbiased selectivity coefficients for these ionophores displayed excellent selectivity against Zn^{2+} , Ca^{2+} , Ba^{2+} , Cu^{2+} , Cd^{2+} and Al^{3+} with moderate selectivity against Pb^{2+} , Li^+ , Na^+ , H^+ , K^+ , NH_4^+ and Cs^+ , noting that silver was the only significant interferent with these calixarene-based ionophores. When optimizing the filling solution in a liquid contact ISE, it was possible to achieve a lower limit of detection of approximately 8 nM according to the IUPAC definition. Last, the new ionophores were also evaluated in four solid-contact (SC) designs leading to Nernstian response, with the best response noted with a SC electrode utilizing a gold substrate, a poly(3-octylthiophene) (POT) ion-to-electron transducer and a poly(methyl methacrylate)–poly(decyl methacrylate) (PMMA–PDMA) co-polymer membrane. This electrode exhibited a slope of 58.4 mV decade⁻¹ and a lower detection limit of 30.2 nM. Due to the presence of an undesirable water layer and/or leaching of redox mediator from the graphite redox buffered SC, a coated wire electrode on gold and graphite redox buffered SC yielded grossly inferior detection limits against the polypyrrole/PVC

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SC and POT/PMMA–PDMA SC ISEs that did not display signs of a water layer or leaching of SC ingredients into the membrane.

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1. Introduction

The analysis of heavy metals in the environment is extremely important due to their toxicity and harmful nature to both plants and animals. Thallium is often overlooked as a potential threat to human health due to its limited use in modern society. However, thallium still has the potential to cause adverse health effects especially in the areas of zinc and lead smelting, coal burning, and may also feature in homicide cases. As thallium is odourless and tasteless, it has been successfully used as a poison, but has now been banned in many western countries. In spite of its limited use, both intentional and unintentional poisonings still occur today and, since chronic thallium uptake mimics other diseases, it is often diagnosed too late [1,2]. Accordingly, an inexpensive and quick analytical method for the determination of thallium in clinical and environmental samples employing an ion-selective electrode (ISE) is highly desirable.

Since thallium possesses the properties of both hard metals and soft/heavy metals, ionophores have ranged from crown-ethers, typical alkali ion ligands [3] to thia substituted macrocycles [4], which are known for their heavy metal affiliation [4–9]. The compounds based on crown-ethers usually suffered from alkali and alkaline earth interferences, and could not be used in many practical applications in the presence of relatively high concentrations of these ions [3,5]. Improved selectivities for the alkali and alkaline earth ions were observed with a range of thia-substituted compounds [4,10]; however, these compounds suffered from interferences by heavy metals, with most showing poor selectivity against silver. Other compounds such as calix[4]pyrrole, indeno-pyran and a quinoline-carbonitrile compounds have also been reported and showed good to moderate selectivity for most ions with the calix[4]pyrrole only suffering from a silver interference and the quinoline-carbonitrile suffering from a caesium interference [8,9,11].

A range of calixarene molecules have also been reported showing good to moderate selectivity for thallium(I) over other ions [12–14]. However, the calixarene molecules discussed in the literature still suffer from significant interferences from at least one ion, whether it is a hard alkali metal ion or a soft heavy metal ion. The binding sites of the reported calixarenes have been shown

to be the aromatic cavity. If the size of the cavity could be tailored to accept only one ion, the selectivity could be improved over previously studied molecules.

A novel and promising way of modifying calixarenes is by attaching bridging chains to either the lower or upper rim. The bridging chains can be either intramolecular or intermolecular, and consist of a range of chemical moieties [15–19]. The bridging units can be as simple as crown ethers or complexes like porphyrins connected to the phenolic protons at different locations, and can bridge more than two calixarenes [18,20,21]. Apart from helping to lock the calixarene into a set conformation, bridging units also offer the potential of a set of very precise and well-organized binding sites. The cavity can be tailored to suit the size of the guest ion by altering the length of the bridge [15,16].

The calixarenes synthesized in this work (see Fig. 1) are expected to allow π -electrons of the aromatic units to interact with Tl^+ as reported with other calixarenes, and should enhance the selectivity by only allowing ions of a particular size to interact. Similar calixarenes reported by Kimura et al. [13] showed good thallium(I) selectivity over most ions in a Tl^+ ISE; however, these calixarenes suffered from silver interferences. The calixarenes reported herein were designed with a view of enhancing the selectivity by reducing the size of the aromatic cavity by pinching the aromatic units together, so that two are parallel instead of possessing an angle as found in symmetrical cone conformations. Accordingly, this should allow an enhanced discrimination of Tl^+ over interfering ions, and this was the central hypothesis of the present research.

In this research, four synthetic calixarene ionophores for Tl^+ have been evaluated in terms of their lower limits of detection, Nernstian response attributes and selectivities for Tl^+ over common interferences. Furthermore, the complex formation constants in polymeric membranes have been evaluated using the well-known sandwich membrane technique, and the detection limits of ISE membranes have been lowered using either optimized filling solutions in liquid contact ISEs and/or solid-contact ISEs using either plasticized PVC membranes or hydrophobic and unplasticized poly(methyl methacrylate) (PMMA)/poly(decyl methacrylate) (PDMA) co-polymer membranes.

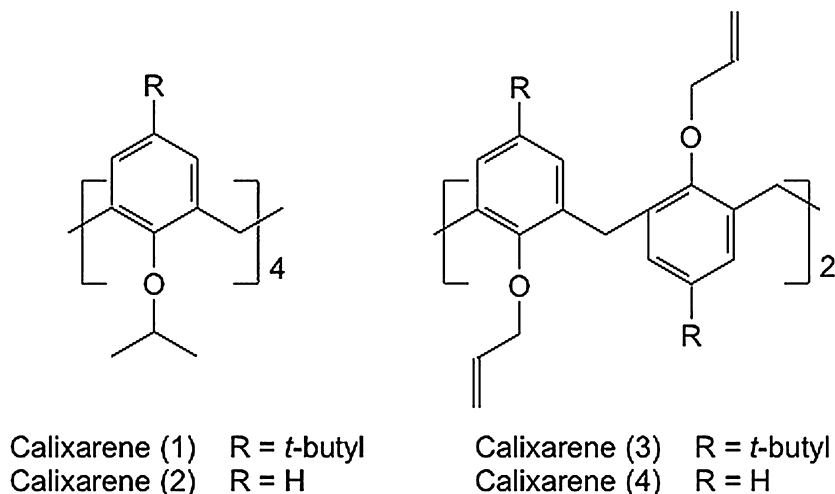


Fig. 1. Structures of the synthesized thallium calixarene ionophores.

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