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A comparative study of Pb^{2+} selective sensors based on derivatized tetrapyrazole and calix[4]arene receptors

A.K. Jain [a], V.K. Gupta [a,*], L.P. Singh [b], J.R. Raisoni [a]

[a] *Department of Chemistry, Indian Institute of Technology, Roorkee, Uttaranchal 247667, India*
[b] *Central Building Research Institute, Roorkee, India*

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Abstract

Two neutral ionophores, 2,12-dimethyl-7,17-diphenyltetrapyrazole (**I**) and 5,11-dibromo-25,27-dipropoxycalix[4]arene (**II**) have been explored for preparing PVC based membrane sensors selective to Pb^{2+}. The addition of sodium tetraphenylborate and various plasticizers viz. DOS, TEHP, DBP, DOP and TBP has been found to substantially improve the performance (working concentration range, slope and response time) of the sensors. The best performance was obtained with the sensor having a membrane of composition (w/w) of (**I**) (1%):PVC (33%):TBP (65%):NaTPB (1%). The sensor exhibits Nernstian response in the concentration range 2.5×10^{-6} to 5.0×10^{-2} M Pb^{2+}, performs satisfactorily over wide pH range (1.6–6.0) with a fast response time (∼10 s). The sensor was found to work satisfactorily in partially non-aqueous media up to 25% (v/v) content of acetone, methanol or ethanol and could be used over a period of 5 months. Potentiometric selectivity coefficients as determined by match potential method (MPM) indicate excellent selectivity for Pb^{2+} ions. The sensors could be used successfully in the estimation of lead in Eveready battery waste and also as an indicator electrode in potentiometric titration.

Keywords: Pyrazol; Calixarene; Chemical sensors; Ion selective electrodes; Ion sensors

1. Introduction

Lead is ubiquitous in the environment and has been used recklessly until very recently. All forms of lead are toxic and adversely affect reproductive, nervous, immune, cardiovascular systems as well as developmental processes in children [1]. Several analytical techniques, such as atomic absorption spectrometry (AAS), inductive coupled plasma-atomic emission spectrometry (ICP-AES), inductive coupled plasma-mass spectrometry (ICP-MS), etc., are available for the quantification of lead. However, maintenance and operational cost of these techniques are expensive and require adequate expertise. Therefore, the analysis is often limited to laboratory level only. A reliable, low cost, quick and portable analytical technique is the need of the day and such requirements are greatly met with ion-sensors. Thus, a number of Pb^{2+} selective sensors have been reported using a variety of sensing agents in inert matrices, such as PVC, polystyrene, etc. Chalcogenide glass sensors based on $PbS–Ag_2S–As_2S_3$ membranes were used for online detection of Pb^{2+} ions in river water but deviation in response characteristics during continuous usage was observed [2]. Polyhydroxamic acid based Pb^{2+} sensors exhibited severe interference to Ni^{2+} and Hg^{2+} ions [3] whereas neutral carrier, methylene bis-di-isobutyldithio carbamate [4] and cyclic amides/oxamides [5], based Pb^{2+} sensors suffer interference from other heavy metals. A number of diverse ligands, viz. tetrabenzyl pyrophosphate [6], 9,10-anthraquinone [7] and 3,4,4a,5-tetrahydro-3-methylpyrimido-[1,6-a] benzimidazole-1(2H)thione [8] have also been used to prepare Pb^{2+} sensors. Besides this, crown ethers and calixarenes have recently been widely investigated as sensing materials to prepare Pb^{2+} sensors. Some of such reported sensors are based on the membranes of benzo-15-crown-5 [9], diazacrown ether [10], 18-crown-6 [11], lariat crown

* Corresponding author. Tel.: +91 1332 285801; fax: +91 1332 273560.
E-mail address: vinodfcy@iitr.ernet.in (V.K. Gupta).

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ethers [12,13], 1,10-dibenzyl-1,10-diaza-18-crown-6 [14], thiacrown ether [15] and calix[*n*]arenephosphine oxide derivatives [16], di- and tetrathioamide calix[4]arene [17], thiophosphorylated calix[6]arene [18], 4-*tert*-butylcalix[6]arene [19], calixarene carboxyphenyl azo derivative [20] and 4-*tert*-butylcalix[4]arene [21]. A perusal of performance characteristics of reported Pb^{2+} sensors show that they exhibit limitations in terms of selectivity, sensitivity and response time which hinders sometimes their widespread use. It is needless to say that efforts are still needed to develop a highly selective and sensitive sensor for Pb^{2+} ions with low response time and long shelf life.

The primary requirement for a material to be used as electroactive substance (sensing material) in the preparation of ion sensor is high affinity to a particular ion for which the sensor is designed. The availability of such materials is limited. Nevertheless with the synthesis of a variety of newer materials, the possibility of having a selective material for a specific ion is opening up. A survey of literature reveals that tetrapyrazole macrocycles have shown excellent selectivity for Hg^{2+} and Pb^{2+} over alkali and transition metal ions in solvent extraction studies [22,23]. Further, it has been shown that calix[4]arene derivative which exists in cone conformation binds Pb^{2+} selectively [24–26]. Therefore, there exists a good possibility for tetrapyrazole macrocycles and calix[4]arene derivatives to be used as Pb^{2+} selective ionophore for preparing membranes to determine lead ions. Thus, studies on the preparation of PVC based membranes of 2,12-dimethyl-7,17-diphenyltetrapyrazole (**I**) and 5,11-dibromo-25,27-dipropoxycalix[4]arene (**II**) and their utilization as Pb^{2+} selective sensors were undertaken. The results, reported in the present communication, show that these membranes exhibit high selectivity towards lead ions over large number of cations and could, therefore, be used as a selective sensor for its quantification.

2. Experimental

2.1. Reagents

The 2,12-dimethyl-7,17-diphenyltetrapyrazole (**I**) prepared by the method [27] was received as gift from Professor S. Radi. 5,11-dibromo-25,27-dipropoxycalix[4]arene (**II**) (Fig. 1) was obtained from Acros Organics, USA. Bis(2-ethylhexyl)sebacate (DOS) and high molecular weight polyvinyl chloride (PVC), Aldrich, USA; sodium tetraphenylborate (NaTPB) and tri-*n*-butylphosphate (TBP), BDH, England; dibutylphthalate (DBP) and dioctylphthalate (DOP), Reidel, India; tris(2-ethylhexyl) phosphate (TEHP), E. Merck, Germany were used as obtained. Analytical reagent-grade tetrahydrofuran (THF), nitric acid and sodium hydroxide were obtained from Ranbaxy, India. Solutions of metal (nitrates) were prepared in double distilled water and standardized by the reported methods where ever necessary. Working solutions of different concentrations were prepared by diluting 0.1 M stock solutions.

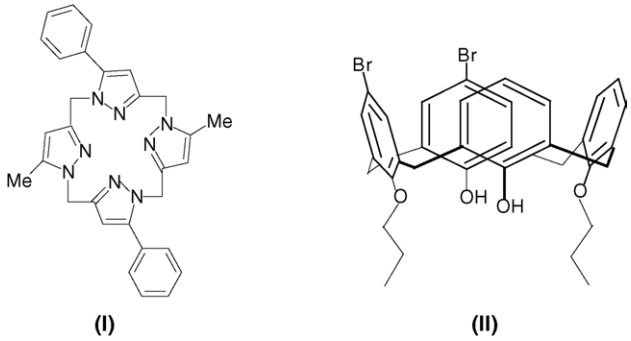

Fig. 1. Structures of 2,12-dimethyl-7,17-diphenyltetrapyrazole (**I**) and 5,11-dibromo-25,27-dipropoxycalix[4]arene (**II**).

2.2. Preparation of membranes

The PVC based membranes were prepared by dissolving different amounts of (**I**) or (**II**), anion excluder NaTPB, solvent mediators (DOS, TEHP, DBP, TBP and DOP) and PVC in THF (10 ml). The components were added in terms of weight percentages with total amount of all being 190 mg. After complete dissolution of all the components, the homogeneous mixture was concentrated by evaporating THF and it was then poured into polyacrylates rings placed on a smooth glass plate. To obtain membranes with reproducible characteristics, the solvent evaporation was carefully controlled otherwise morphology and thickness of the membranes shows significant variation which ultimately affected the sensor response. The transparent membranes of 0.4 mm thickness were removed carefully from the glass plate. A 5 mm diameter piece was cut out and glued to one end of a "Pyrex" glass tube. The membranes thus prepared were equilibrated for 2 days in 0.1 M Pb^{2+} solution. It is known that the sensitivity, linearity, and selectivity obtained for a given ionophore depend significantly on the membrane composition and nature of plasticizer used [28,29]. Thus, several membranes of varying compositions were prepared and investigated. The membranes, which gave reproducible results and best performance characteristics, were selected for detailed studies. The optimum composition of membranes performing best is given in Tables 1 and 2 wherein the amount of ionophore in the best performing systems was found to be 1.9 mg/190 mg of the total weight of the membrane.

2.3. Potential measurements

The potential measurements were carried out at $25 \pm 0.1\,^{\circ}C$ with a digital potentiometer (Model 5652 A, ECIL, India) and Century Microvoltmeter (Model CVM 301, India) by setting up the following cell assembly, employing