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Review

Lead(II)-selective ionophores for ion-selective electrodes: A review

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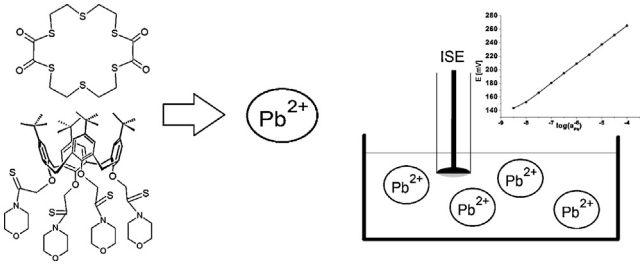
HIGHLIGHTS

- Description and comparison of the newest synthesized lead(II)-selective ionophores.
- A need of determination unbiased (true) selectivity coefficients.
- Lead as a pollutant.
- Synergistic collaboration between synthetic organic chemists and electrochemists.
- Further search for highly selective lead(II) ionophores for environmental analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

In potentiometry, high selectivity of the ion-selective membranes must be assured in order to reliably measure various analytes in clinical, industrial and environmental samples. Due to the toxic nature of lead(II) it is important to monitor Pb^{2+} distribution in natural waters. This may be achieved by implementation of ion-selective electrodes (ISEs) with high selectivity towards lead(II) and low detection limit. A great number of Pb^{2+}-ionophores were synthesized and studied. In this work lead(II)-selective ionophores, starting from late 90s, are gathered and discussed. This work gives a comprehensive description and discussion on the novel and available lead(II)-selective ionophores for ISEs.

Contents

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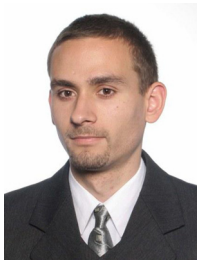

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1. Introduction

Ion-selective electrodes (ISEs) are commonly used in clinical, industrial and environmental analysis. The relatively low cost and low maintenance make this modest design of chemical sensors advantageous over other analytical techniques. More importantly, measurements with ISEs are done in potentiometric mode leaving the measured sample intact in means of chemical composition, thus further analysis on the same sample by other methods is possible [1,2]. ISEs are suitable for reliable monitoring of pollutants in natural waters if requirements of high selectivity and low detection limit are fulfilled. Taking into consideration toxic properties of lead and rigorous regulations of its distribution, ISEs become a valuable tool for determination of this component [3]. Despite the immense effort, which is done towards obtaining ISEs devoted for determination of the ionized lead at low concentrations in environmental samples, there is no industrially available ISE for determination of trace concentrations of Pb^{2+} [4–6].

Looking back, the first design of lead-selective electrodes was a solid-state electrode based on sparingly soluble salts, from which sulphide salts were the most common. Typically, to increase conductivity and binding properties of heterogeneous solid-state membranes, these consisted of two components, e.g. PbS and Ag_2S. Unfortunately, these kinds of membranes suffer from severe interferences from the presence of cations such as: Hg_2^{2+}, Hg^{2+}, Ag^+ and Cu^{2+} [2]. However recently, it was shown that Cu^{2+} does not necessarily interfere with Pb^{2+} determination using PbS/Ag_2S solid state electrode if both analytes are at low and similar concentrations. Authors explained that most probably that behaviour may be attributed to insufficient driving force of copper ions to provoke metathesis of Pb^{2+}-ISE membrane and to ignite nucleation of CuS. Furthermore, if this actually occurs, the conventional interpretation of selectivity in this case is not valid [7].

The development of carrier based ion-selective electrodes offered a possibility of improving the selectivity towards Pb^{2+} over various interfering cations and lowering of the detection limit. Decades passed since the development of the first plastic membrane with ionophore for ionized lead [8]. Since then a great number of lead ionophores were synthesized and investigated in ion-selective electrodes [1,2]. The main groups of these compounds recognized as lead selective ionophores are crown ethers, calixarenes, amides, and thioamides.

Due to environmental restrictions towards distributions of selected heavy metals like Pb^{2+}, the research in the field of synthesis and characterisation of compounds as novel lead(II)-selective ionophores is vibrant. After the concise description of ionophores up to late 1990s [1,2] the present study is focused on the newest lead(II) ionophores. All compounds synthesized as for use in Pb^{2+}-ISEs within recent years will be discussed in this report.

2. The selectivity coefficient

The selectivity is the most important parameter of each ISE. It describes the ability of the electrode to discriminate other ions (interfering ions) in the presence of the primary ion. If primary ion (I) and interfering ion (J) have the same charge and form strong