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Screening highly selective ionophores for heavy metal ion-selective electrodes and potentiometric sensors

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ABSTRACT

Screening highly selective ionophores from a large amount of ionophores is the principle and most realizable method to discover new ionophores used in ion-selective electrodes (ISEs). In this paper a screening method is described for ionophore-based polymeric membrane heavy metal ion-selective electrodes (IBPMHM ISEs) to determine heavy metal ions (Cu^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Ag^+). The protocol uses the averaged negative logarithmic potential selectivity coefficients ($\overline{pK_5}$) of five major interfering ions as screening parameters. The specified five major interfering ion group (Group A) can enhance the screening ability of the parameter $\overline{pK_5}$. The molecular categories of preferred ionophores ($\overline{pK_5}$>2.00) for these ISEs were as follows: Schiff bases for Cu^{2+}-ISE; Schiff bases and macrocycles for Zn^{2+}-ISE; calixarenes, crown ethers and macrocycles for Ag^+-ISE; calixarenes, Schiff bases and crown ethers for Pb^{2+}-ISE, and another group for both Cd^{2+}- and Hg^{2+}-ISEs. Strong interaction between the donor atoms of ionophores and the heavy metal ions follows the hard soft acids and bases rule (HSAB). This approach efficiently screens the best ionophores for these IBPMHM ISEs, and provides a new route to explore new ionophores for other ionophore-based ISEs and potentiometric sensors.

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1. Introduction

Heavy metal ions are highly toxic industrial pollutants, whose maximum allowed concentration in drinking water is in the ppb range (e.g. 5ppb for Cd^{2+} and 50 ppb for Ni^{2+}) [1]. Excessive disposal of them can cause severe damages on the environment and human health [2,3]. Much attention has been paid to analytical methods for sensitive and selective detection of heavy metals in environmental and waste samples, which has become a priority in environmental monitoring and the related industrial processes such as metallurgical, galvanizing and electroplating industries [4].

The importance of determining heavy metal at low concentration has been demonstrated through the toxicity of nanoparticles when they are used for the treatment of human health and disease. Nanotechnology is a newly developing scientific field that has potentially widespread applications in medicine such as chronic disease therapy, cancer treatment, drug delivery system etc. [5] However, the emerging of nanotoxicology in health and disease has

received much attention. Johnson et al. [6]. reported that the release of Zn^{2+}ions from ZnO nanoparticles triggers the production of excessive intracellular reactive oxygen species, resulting in autophagic death. Recently, it was found experimentally that Cd-based nanoparticle can induce significant toxic effects on the fertility and gestation of mice [7]. Many research results demonstrated that nanomaterials interact with biological systems after entering the human body and give rise to various cytotoxic effects during the processes of absorption, distribution, metabolism and excretion [5]. It is urgent and necessary to explore adequate risk assessment of nanomaterials and investigate the cellular mechanisms of nanoparticle actions and their effect on cell properties. Therefore, a new subject has been developed for analytical chemists to real-time analysize and monitore the content or concentration of heavy metal in vivo after nanomaterials enter the human or biological body.

There are several methods to determine heavy metal ions at low concentration, including spectroscopic methods such as atomic absorption spectrometry (AAS) [8] and inductively coupled plasma-optical mass spectrometry (ICP-MS) [9][9], and electrochemical methods as voltammetry and potentiometry using ISEs [10]. The spectroscopic methods require highly trained staff, expensive

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instrumental and operational costs, preliminary sample treatment which could increase significantly the risk of contamination of the samples, as well as complicated instrument setup. All these make it difficult to employ these techniques to in-field on real-time measurements [11][11]. The continual rise of heavy metal and ion usage in industrial processes makes ion-selective sensors vital for the proper sensing and quantification of potential sensors [12]. Compared to other methods, direct potentiometry using ISEs offers many advantages such as low cost, simplicity, wide linear dynamic range for an analyzed ion (up to more than 6 orders of concentration), and low detection limits, which are in the nano-molar concentration range with polymeric membrane ISEs [13,14] or in the sub-nano-molar concentrations with ion-selective internal solid contact sensors [15–17], without any sample accumulation steps or electrical signal amplification. In addition, portably analytical instruments can be realized easily for application to real-time on-site analysis because a reduction in sample or sensor size will not have an effect on the sensor output signal [18]. During the last four decades, a lot of IBPMHM ISEs or potentiometric sensors have been reported, including coated wire (carbon or graphite) electrodes and internal solid contact sensors. A review on the membrane sensor preparation for each of the six heavy metal ions, the effect of pH, the degradation kinetics, and the type of biological or environmental samples *etc.* on the analysis will be in another paper. Although more than thirty kinds of ionophores have been presented for each IBPMHM ISEs, very few ionophores/ IBPMHM ISEs can meet the desirable selectivity and response for a heavy metal ion in complicated samples.

The selectivity is the most important parameter of each ISE and potentiometric ion sensor. A majority of present work in ionophore-based sensors focuses on developing novel ionophore/selectivity [19][19]. One approach to explore new ionophores with higher selectivities is the theoretical calculation based on the interactions between a given ionophore and ions in solution. However, it is very difficult to rationally plan new ionophores only by computations [20]. Another method, which is obviously the most realizable, is directly screening parent ionophores with higher selectivity from a variety of ionophores in literature, and modifying the structures of parent ionophores. However, no effective screening method has been developed until now because of: (1) the serious interfering ions or interference contents vary with different ionophores; (2) no sufficient data of potential selectivity coefficients ($K_{i,j}^{pot}$) for a given metal ion ISE. The interfering ions of an ionophore vary with works when different ionophore-based polymeric membrane ISEs are studied, resulting in a very difficult issue for establishing the kinds of the interfering ions. Herein, we report a screening method ($\overline{pK_5}$ method) by using

the averaged negative logarithmic potential selectivity coefficient ($\overline{pK_5}$) of an ISE for five major interfering ions, which offers a new path to screen the ionophores of IBPMHM ISEs and potentiometric ion sensors.

2. Screening method

2.1. Screening parameter($\overline{pK_5}$)

In this study, five kinds of interfering ions are taken. The averaged negative logarithmic potential selectivity coefficients ($\overline{pK_5}$) of five kinds of interfering ions are used as screening parameters. The values of $\overline{pK_5}$ are calculated by the following equation:

$$\overline{pK_5} = \frac{1}{5}\sum_{j=1}^{5}(-\log K_{i,j}^{pot}) \qquad (1)$$

The larger the value of $\overline{pK_5}$ is, the higher is the selectivity of the ionophore. In general, the selectivity of an ionophore with $\overline{pK_5} \geq 2.00$ is counted as relatively good. Five kinds of interfering ions (called major interfering ions) used are listed in Table 1 (group A).

2.2. Evaluating the percentage for the numbers of the ionophores under a specific condition

The percentage for the numbers of the ionophores under a specific condition was expressed in Eq.(2):

$$P_i(\%) = \frac{n_i \times 100}{n_{total}} \qquad (2)$$

Where n_i is the number of ionophores in a given condition such as a given value of $\overline{pK_5}$ or a given deviation range (Δ) for $\overline{pK_5}$, and n_{total} is the total number of the ionophores.

2.3. Procedures

2.3.1. Procedures of establishing a major interfering ion group

It is necessary to establish a major interfering ion group for a given ISE before screening. A major interfering ion group is composed of five major interfering sub-groups with close sum values of the percentage of interference appearance (PIA). Each sub-group is consisted of 2–4 interfering ions with small PIA values (PIA <50%) or a single interfering ion (PIA >50%). The steps to determine the major interfering ion group were as follows: (1) collecting as much K_{ij} of different ionophores, and listing all involved interfering ions; (2) calculating the PIA value of indiviual

Table 1
Two major interfering ion groups (Group A and Group B) for the heavy metal ISEs.

ISE	Major interfering ions	
	(Group A)	(Group B)
Pb^{2+}−ISE	$Ag^+(Ni^{2+})$ (0.67) [a], $Cu^{2+}(Co^{2+},Cr^{3+})$ (0.60), $Hg^{2+}(Ca^{2+})$ (0.61), $K^+(Zn^{2+},Fe^{3+})$ (0.63), $Na^+(Cd^{2+},Mg^{2+},Mn^{2+})$ (0.83)	$Ag^+(0.49)$, $Cu^{2+}(0.44)$, $Hg^{2+}(Zn^{2+},Co^{2+})(1.11)$, $Cd^{2+}(Ni^{2+})(0.48)$, $K^+(Na^+,Ca^{2+},Mg^{2+})$ (1.10)
Cu^{2+}−ISE	$Pb^{2+}(Fe^{3+})(0.78)$,$Cd^{2+}(Hg^{2+},Mg^{2+})(0.78)$,$Zn^{2+}(Ag^+,Mn^{2+})$ (0.78), $Co^{2+}(Ca^{2+},Cr^{3+})$ (0.73), $Na^+(K^+,Ni^{2+})$ (0.91)	$Pb^{2+}(0.54)$,$Cd^{2+}(Hg^{2+},Fe^{3+})(0.85)$,$Zn^{2+}(Ag^+,Cr^{3+})(0.79)$, $Co^{2+}(Ni^{2+},Mn^{2+})(0.40)$,$Na^+(K^+,Ca^{2+},Mg^{2+})(1.00)$
Hg^{2+}−ISE	$Ag^+(0.88)$,$Pb^{2+}(Zn^{2+},Cr^{3+})(0.53)$,$Cu^{2+}(Cd^{2+},Co^{2+},Mn^{2+})(0.49)$, $Na^+(Ca^{2+},Mg^{2+})$ (0.63),$K^+(Fe^{3+},Ni^{2+})$ (0.67)	$Ag^+(0.88)$, $Pb^{2+}(Cr^{3+},Fe^{3+})(0.51)$,$Cd^{2+}(Zn^{2+})(0.31)$, $Cu^{2+}(Co^{2+},Ni^{2+})(0.43)$,$Na^+(K^+,Ca^{2+},Mg^{2+})(1.00)$
Ag^+−ISE	Hg^{2+} (0.66), $Pb^{2+}(Zn^{2+})$ (0.24), $Cu^{2+}(Cd^{2+},Co^{2+},Ni^{2+})$ (0.22), $Na^+(Ca^{2+},Fe^{3+})$ (0.30),$K^+(Mg^{2+},Cr^{3+})$ (0.25)	$Hg^{2+}(0.66)$, $Pb^{2+}(Zn^{2+})(0.24)$,$Cu^{2+}(Cd^{2+})(0.19)$, $Fe^{3+}(Co^{2+},Ni^{2+})(0.17)$, $K^+(Na^+,Ca^{2+},Mg^{2+})(0.47)$
Cd^{2+}−ISE	$Cu^{2+}(Cr^{3+})$ (0.88), $Hg^{2+}(Ag^+,Mn^{2+})$ (0.91), $Pb^{2+}(Fe^{3+})$ (0.85), $Zn^{2+}(Co^{2+},Ni^{2+})$ (0.94), K^+ (Na^+,Ca^{2+},Mg^{2+}) (0.97)	$Cu^{2+}(Cr^{3+})(0.88)$,$Hg^{2+}(Ag^+)(0.73)$,$Pb^{2+}(Fe^{3+})(0.85)$, $Zn^{2+}(Co^{2+},Ni^{2+})(0.94)$, $K^+(Na^+,Ca^{2+},Mg^{2+})(0.97)$
Zn^{2+}−ISE	$Cu^{2+}(Hg^{2+},Mn^{2+})(1.18)$,$Cd^{2+}(Pb^{2+})(1.03)$,$Co^{2+}(Ag^+,Fe^{3+})$ (1.26), $Ni^{2+}(Ca^{2+},Cr^{3+})$ (1.23), $Na^+(K^+,Mg^{2+})$ (1.24)	$Cu^{2+}(0.68)$,$Cd^{2+}(Cr^{3+},Pb^{2+})(1.32)$,$Hg^{2+}(Ag^+)(0.68)$, $Co^{2+}(Ni^{2+},Fe^{3+})(1.44)$, $Na^+(K^+,Ca^{2+},Mg^{2+})(1.68)$

[a] The number given in a paranthesis denotes the apparent value of PIA for an interfering ion sun-group.