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Strontium PVC-membrane sensor based on 2-[(2-mercaptophenylimino)methyl]phenol

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Abstract

The 2-[(2-mercaptophenylimino)methyl]phenol (MPMP) was used as an excellent ionophore in the construction of a Sr^{2+} PVC-based membrane sensor. The best performance was obtained with a membrane composition of 30% poly(vinyl chloride), 62% nitrobenzen (NB), 5.5% MPMP and 2.5% sodium tetraphenyl borate (NaTBP). This sensor demonstrates a good selectivity and sensitivity towards the strontium ion for many cations, including alkali, alkaline earth, transition and heavy metal ions. The sensor revealed a great enhancement in selectivity coefficients for strontium ions in comparison with the previously reported strontium sensors. The proposed sensor exhibits a Nernstian behavior (with a slope of 29.6 ± 0.3 mV per decade) for the concentration range of (1.0×10^{-6}–1.0×10^{-1} M) with a detection limit of 5.5×10^{-7} M (48.2 ng/mL). It illustrates a relatively fast response time in the whole concentration range (<10 s) and it can be used for at least 10 weeks in a pH range of 2.8–9.6. The developed sensor was successfully used as an indicator electrode in the Sr(II) titration with EDTA and the Sr^{2+} ion recovery from binary mixtures.

Keywords: 2-[(2-mercaptophenylimino)methyl]phenol; Strontium sensor; Potentiometry; PVC

1. Introduction

Strontium is an important alkaline earth metal which is used in the production of glasses for color television sets. In addition, it is used in zinc refining and in tin and lead alloys for the hardness and durability increase [1]. Therefore, the determination of strontium is important and several instrumental methods are used in order to determine Sr such as atomic absorption spectrometry [2–4], flame photometry [5], ICP-AES [6,7], etc. In spite of providing an accurate determination, these methods are not appropriate because they demand high cost and sample pretreatment.

Potentiometric determination by ion-selective electrodes (ISEs) offers a simple, low cost and fast analysis procedure without any special equipment. Moreover, this method is non-destructive, without any sample pretreatment requirement.

Several electrodes based on neutral carriers and inorganic ion exchangers as selective part of the membrane are reported. However, these electrodes exhibit a significant interference with other alkaline earth metals, high response time, functioning for a limited pH range [8–16]. An essential characteristic for a material to be employed as a membrane selective part is its high specificity for a particular ion. Calixarenes have emerged as selective materials for alkali and alkaline earth metals. It is documented that ester derivatives of calixarenes [17–21] tend to show a better selectivity than the parent calixarene due to the change in cavity size, conformation and increased number of binding sites. There have been some reports of ion-selective strontium electrodes in the literature [22–25].

Recently, several studies concerning the selective and sensitive PVC-membrane ion-selective electrodes have been reported for some ions [26–36]. In this paper, a highly strontium (II)-selective sensor is described, based on the 2-[(2-mercaptophenylimino)methyl]phenol (MPMP), as a novel neutral ionophore (Fig. 1).

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2. Experimental

2.1. Reagents

The Aldrich and the Merck Chemical Co. were the providers for the nitrate and chloride salts of all cations. Furthermore, the Merck Chemical Co. supplied the following reagents; reagent-grade dibutyl phthalate (DBP), nitrobenzene (NB), benzyl acetate (BA), tetrahydrofuran (THF), sodium tetraphenyl borate (NaTPB) and high relative molecular weight PVC.

All reagents were used without any modification. As far as the nitrate and chloride salts of all employed cations are concerned, they were of the highest available purity and were P2O5-vacuum dried. During the experiments, triply distilled deionized water was used.

2.2. Electrode preparation

For the PVC membrane preparation, 30 mg of PVC, 5.5 mg of MPMP, 2.5 mg of NaTPB and 62 mg of NB were blended completely. Afterwards, the blend was dissolved in 3 mL of dry freshly distilled THF. The resulting clear mixture was evaporated slowly, until an oily concentrated mixture was obtained. A Pyrex tube (5 mm i.d.) was dipped into the mixture for about 5 s, so that a transparent membrane of about 0.3 mm in thickness was formed. The tube was, then, pulled out from the mixture, kept at room temperature for about 2 h [30–40] and filled with an internal filling solution (1.0×10^{-3} M $SrCl_2$). Finally, the electrode was conditioned for 24 h by soaking in a 1.0×10^{-3} M strontium nitrate solution. As an internal reference electrode, a silver–silver chloride electrode was used.

2.3. The (Electro Motive Force) EMF measurements

The following assembly was used for all emf measurements performance:

Ag–AgCl | internal solution, 1.0×10^{-3} M $SrCl_2$ | PVC membrane | sample solution | Hg–Hg_2Cl_2, KC1 (satd.).

A Corning ion analyzer with a 250 pH/mV meter was used for the potential measurements at 25.0 °C. Activities were calculated according to the Debye–Hückel procedure [41].

2.4. Procedure of conductance study

Conductivity measurements were carried out with a Metrohm 660 conductivity meter. A dip-type conductivity cell made of platinum black with a cell constant of $0.83\ \mathrm{cm}^{-1}$ was used. In all measurements, the cell was thermostated at the desired temperature of 25.0, using a Phywe immersion thermostat. In typical experiments, 25 ml of a cation's nitrate solution (1.0×10^{-4} M) were placed in water-jacketed cell equipped with a magnetic stirrer and connected to the thermostat that was circulating water at the desired temperature. In order to keep the electrolyte concentration constant during the titration, we assured that both the starting solution and the titrant had the same cation concentration. Then, a known amount of the MPMP (1.0×10^{-2} M) solution was added in a stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition. Addition of the MPMP was continued until the desired MPMP-to-cation mole ratio was achieved. The 1:1 binding of the cations with MPMP can be expressed by the following equilibrium:

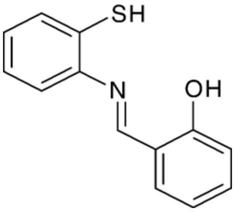

Fig. 1. The MPMP structure.

$$M^{n+} + L \xrightleftharpoons{Kf} ML^{n+} \tag{1}$$

The corresponding equilibrium constant, K_f, is given by

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} \times \frac{f_{(ML^{n+})}}{f_{(M^{n+})}f_{(L)}} \tag{2}$$

Here $[ML^{n+}]$, $[M^{n+}]$, $[L]$ and f represent the equilibrium molar concentration of complexes, free cation, free MPMP and the activity coefficient of the species indicated, respectively. Under the dilute conditions we used, the activity coefficient of the unchanged ligand can be reasonably assumed to be unity [42]. The use of Debye–Hückel limiting law of 1:1 electrolytes [43] leads to the conclusion that $f_{(M^{n+})} \approx f_{(ML^{n+})}$, so the activity coefficient in Eq. (2) is canceled out, and therefore the complex formation constant in term of the molar conductance can be expressed as [44]:

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{(\Lambda_M - \Lambda_{\mathrm{obs}})}{(\Lambda_{\mathrm{obs}} - \Lambda_{ML})[L]} \tag{3}$$

where

$$K_f = C_L - \frac{C_M(\Lambda_M - \Lambda_{\mathrm{obs}})}{(\Lambda_{\mathrm{obs}} - \Lambda_{ML})} \tag{4}$$

Here Λ_M is the molar conductance of the cation before addition of MPMP, Λ_{ML} is the molar conductance of the complexes, Λ_{obs} the molar conductance of the solution during titration, C_L the analytical concentration of the MPMP added, and C_M the analytical concentration of the cation salt. The complex formation constant, K_f, and the molar conductance of complex, Λ_{ML}, were obtained by computer fitting of Eqs. (3) and (4) to the molar conductance-mole ratio data using a nonlinear least-squares program KINFIT [45].

3. Results and discussions

3.1. Complexation of MPMP with some metal ions in acetonitrile

In primary experiments, interaction of MPMP with a number of metal ions was investigated in acetonitrile solution by