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Novel ZrO^{2+} ion-selective electrode based on 4,7,13,16,21,24-hexa oxa-1,10- diazabicyclo[8,8,8]-hexa cosane as neutral carrier in PVC matrix

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ABSTRACT

In this work, a novel ZrO^{2+} PVC-based membrane sensor based on 4,7,13,16,21,24-hexa oxa-1,10- diazabicyclo [8,8,8]- hexa cosane (HODBHC) as a new ionophore is presented. The sensor displays a linear dynamic range between 1.0×10^{-1} and 1.0×10^{-6} M, with a near Nernstian slope of 29.9 ± 0.4 mV per decade in an acidic solution (pH=1). The limit of detection is 8.0×10^{-7} M. The electrodes possess advantages of low resistance, very fast response time, relatively long lifetimes and, especially, good selectivities relative to a wide variety of other cations. It was used as indicator electrode in potentiometric determination of ZrO^{2+} ion by standard addition method at pH 1.0 in two samples.

Keywords: Potentiometry, ZrO^{2+} sensor, PVC membrane, Ionophore.

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INTRODUCTION

The introduction of new ion-selective membrane electrodes have played a fundamental role in the development of potentiometric measurements. The advantages of ISEs over many other methods for cations and anions detections are their easy handling, non-destructive analysis and inexpensive sample preparation. Potentiometric sensors have been shown to be very effective tools for analysis of a wide variety of cations and anions[1-5]. Solvent polymeric membrane based ISEs together with the incorporation of new ion carriers have shown to be a very useful tool for chemical, clinical, and environmental analyses as process monitoring [6-11].

In this paper we reported that a new ISE for determination of ZrO^{2+} ion based on 4,7,13,16,21,24-hexa oxa-1,10- diazabicyclo [8,8,8]- hexa cosane (HODBHC) as a new ionophore, has a wide working concentration range, fast response time and gives reproducible results.

EXPERIMENTAL

1. Reagents and materials

Reagent grade dibutyl phthalate (DBP), acetophenone (AP), 2-nitrophenyloctyl ether (2-NPOF), oleic acid (OA), sodium tetraphenylborate (Na TPB), tetrahydrofuran (THF) and high relative molecular weight PVC (all from Merck) were used as received. Chloride and nitrate salts of all other cations used (all from Merck) were of the highest purity available and used without any further purification. Double distilled deionized water was used throughout.

2. Electrode preparation and potential measurements

The general procedure used to prepare the PVC membrane was to mix thoroughly 30 mg of powdered PVC, 3 mg of ionophore (HODBHC), 57 mg of plasticizer DBP and 10 mg of additive oleic acid until the PVC was wet. The mixture was then dissolved in 3 ml of dry freshly distilled THF. The resulting clear mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (5 mm o.d.) was dipped into the mixture for about 10s so that a non-transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out of the mixture and kept at room temperature for about 1 h before filling with internal solution 1.0×10^{-3} M $ZrOCl_2$, pH = 1. The electrode was finally conditioned for 8 h by soaking in a 1.0×10^{-2} M $ZrOCl_2$ solution, pH = 1.

The potential measurements were carried out with the following assembly:

SCE /internal solution, 1.0×10^{-3} M $ZrOCl_2$ $+1.0 \times 10^{-1}$ M HCl / PVC membrane /test solution / SCE

The potentiometric measurements were performed with a model 701 Orion ion analyzer pH/mV meter at 25.0 ± 0.1 °C. In all cases, a 1.0×10^{-1} mol dm^{-3} HCl solution was used as electrolyte medium.

RESULTS AND DISCUSSION

1. Effect of membrane composition on the electrode response

The influences of the membrane composition, nature and amount of plasticizer and amount of oleic acid as a lipophilic additive on the potential response of the ZrO^{2+} sensor were investigated and the results are summarized in Table 1. It is seen that, the use of 57 % DBP in the presence of 30 % PVC, 3 % ionophore and 10 % oleic acid (No. 7, Table 1) results a good electrode performance.

The potential response of the membrane at varying concentration of ZrO^{2+} ion, indicates a rectilinear range from 1.0×10^{-6} to 1.0×10^{-1} M (Fig. 1). The slope of the calibration curve was 29.9 ± 0.4 mV/decade of ZrO^{2+} concentration. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 8.0×10^{-7} M. The standard deviation of 8 replicate measurements is ± 0.4 mV. The membrane sensors prepared could be used for more than 90 days without any measurable change in potential.

It should be noted that the presence of lipophilic and immobilized ionic additives [12,13], or salt of two lipophilic ions [14], could diminish membrane resistance, eliminate the diffusion potential [15], and in some cases, change the selectivity pattern of the ion-selective PVC membrane, resulting in a good working performance.

2. Potentiometric selectivity

The selectivity coefficients of the proposed membrane selective electrode were determined against a number of interfering ions by using matched potential method (MPM) [15]. MPM is a recently recommended procedure by IUPAC, which gets rid of the limitations of the corresponding methods based on the Nicolski-Eisenman equation for the determination of ptentiometric selectivity coefficients. These limitations include non–Nernstian behavior of interfering ions and inequality of charges of primary and interfering ions. The obtained results for the $K^{pot}_{zrO^{2+},M}$ of ZrO^{2+} electrode are summarized in Table 2. There was no significant interference from most of the tested substances, with the exception of Gd^{3+}, Lu^{3+}. The proposed supported liquid membrane electrode seems to be reasonably selective towards $ZrOCl_2$.

3. Response time

Dynamic response time is an important factor for an ion-selective electrode [16]. In this study, the practical response time was recorded by changing solution with different ZrO^{2+} concentration from 1.0×10^{-5} to 5.0×10^{-3} M. The actual potential versus time traces is shown in Fig.2. As can be seen, the electrode reaches the equilibrium response in a short time of about 10s.

4. Reversibility of the electrode response

To evaluate the reversibility of the electrode, a similar procedure with opposite direction was adopted. The measurements were performed in the sequence of high-to-low sample concentrations and the results are shown in Fig. 3. It shows that the potentiometric responses of the sensor was reversible and had no memory effect, the time needed to reach equilibrium values were the same as low-to-high sample concentration [12].

CONCLUSION

The membrane sensor incorporating BTD as the electroactive phase can be used to determine Cr(III) in the wide concentration range. The sensor exhibited good reproducibility over a useful lifetime about 2 months.

This electrode is supervior to the existing electrodes with regard to the slope, pH range, response time and selectivity over a number of cation (Table 2). The present electrode permits the direct measurement of Cr(III) in real samples without prior separation steps, thus considerably simplifying the determination procedure with respect to the other analytical methods used.

ANALYTICAL APPLICATION

The proposed electrode was successfully applied to the determination of $ZrOCl_2$ in making sample by standard addition. In this method, the potential of 10 ml ZrO^{2+} solution with pH = 1 was measured as testing sample (E_u). Then 0.1 ml of 5.0×10^{-2} M, $ZrOCl_2$ standard solution with pH = 1 was added into the testing solution and the equilibrium potential of E_s was obtained. From the potential change of ΔE ($E_u - E_s$) one can determine the concentration of the testing sample using the equation given below:

$$C_x = \frac{C_s \times V_s}{(V_x + V_s)\,10^{\Delta E / S} - V_x}$$

Here C_x is $ZrOCl_2$ concentration of making sample, C_s the concentration of the standard, V_x and V_s the corresponding volumes, S the slope of the electrode response, and ΔE the change in potential [17]. In the determination of ZrO^{2+} in aqueous solutions, the electrode showed almost identical behavior. The reproducibility was good and the relative standard deviation of the determinations was less than 2% (Table 3).

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Table 1. Optimization of the membrane ingredients

No.	Composition(%)				Slope (mV/decade)	Linear range [M]
	Ionophore	PVC	Plasticizer	Additive		
1	-	35	60(DBP)	5(OA)	8.3	1.0×10^{-6}-1.0×10^{-3}
2	3	30	67(DBP)	-	18.7	1.0×10^{-6}-1.0×10^{-3}
3	3	30	62(DBP)	5(OA)	32.1	1.0×10^{-5}-1.0×10^{-2}
4	3	30	64(DBP)	3(OA)	21.2	1.0×10^{-6}-1.0×10^{-2}
5	3	30	60(DBP)	7(OA)	28.4	1.0×10^{-6}-1.0×10^{-2}
6	3	30	60(AP)	7(OA)	13.0	1.0×10^{-6}-1.0×10^{-2}
7	3	30	57(DBP)	10(OA)	29.9	1.0×10^{-6}-1.0×10^{-1}
8	5	30	55(AP)	10(OA)	22.7	1.0×10^{-6}-1.0×10^{-2}
9	2	30	64(2NPOE)	4(NaTPB)	24.3	1.0×10^{-6}-1.0×10^{-2}
10	3	30	62(2NPOE)	5(NaTPB)	42.1	1.0×10^{-6}-1.0×10^{-2}

Table 2. Selectivity coefficient ($K^{pot}_{zro^{2+},M}$) of various interfering ions

M^{n+}	$K^{pot}_{zro^{2+},M}$
	MPM
Li^{+}	1.6×10^{-2}
Cs^{+}	4.6×10^{-2}
NH_4^{+}	4.0×10^{-3}
Cd^{2+}	5.4×10^{-3}
Sr^{2+}	2.1×10^{-3}
Ce^{3+}	3.5×10^{-3}
Mn^{2+}	1.3×10^{-3}
Al^{3+}	2.2×10^{-3}
Mg^{2+}	3.2×10^{-2}
Lu^{3+}	1.1×10^{-1}
Gd^{3+}	7.9×10^{-1}

Table 3. Determination of ZrO^{2+} in aqueous solutions with a ZrO^{2+}-selective membrane electrode

Sample	Concentration of ZrO^{2+} (mol. l^{-1})	Recovery (%) by standard addition method	R.S.D (%)
I	5.0×10^{-4}	98.2	1.7 (n = 5)
II	5.0×10^{-3}	98.5	1.8 (n = 5)

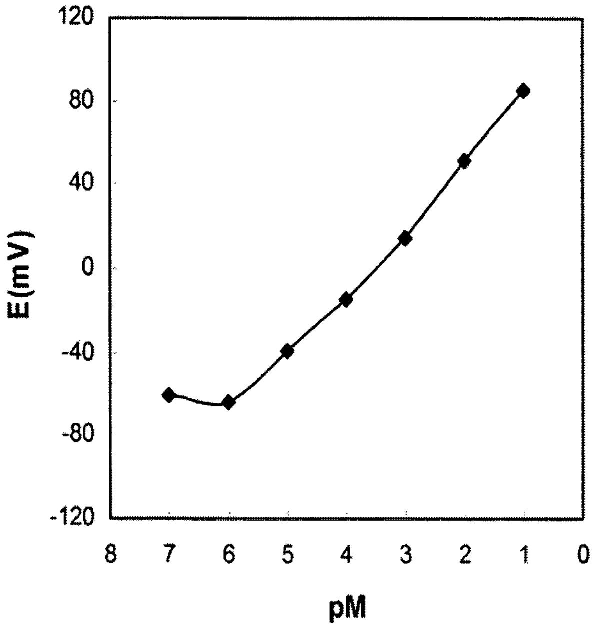

Fig. 1. Calibration curve of the proposed ZrO^{2+} sensor.

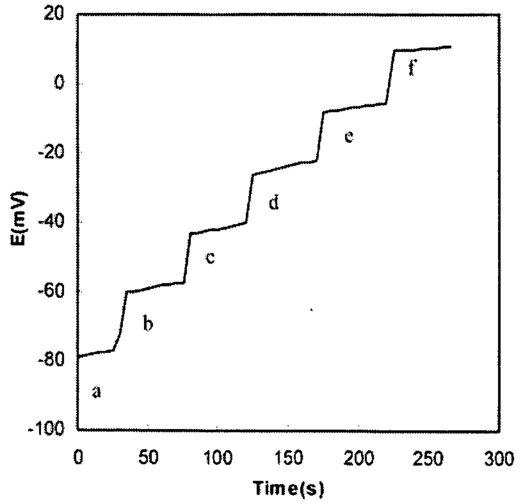

Fig. 2. Dynamic response time of the electrode for step change in concentration of ZrO^{2+}:
a) 1.0×10^{-5} M, b) 5.0×10^{-5} M, c) 1.0×10^{-4} M, d) 5.0×10^{-4} M, e) 1.0×10^{-3} M, f) 5.0×10^{-3} M

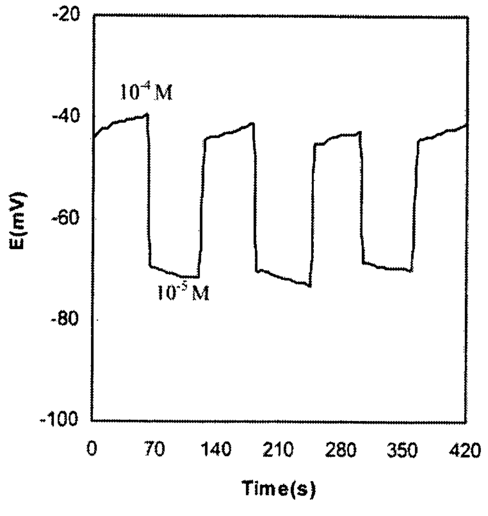

Fig. 3. Dynamic response characteristics of the ZrO^{2+}- electrode for several high-to-low sample cycles.

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