Applied *Nanomaterials and smart Polymers,*
ISSN: ……… eISSN: ………..
Vol. 1, No. 1

ANSP

Novel ZrO^{2+} Ion-selective Electrode Based on a Hexa Cosine Compound in PVC Matrix

Masoud Giahi[1*], Khoorshid Mehdizadeh[2], Niloofar Rafizadeh Zaeem[3]

[1]Department of Chemistry, South Tehran Branch, Islamic Azad University, Tehran, Iran

[2]Department of Chemistry, Roudsar and Amlash Branch, Islamic Azad University, Roudsar, Iran

[3]Department of Polymer Engineering, South Tehran Branch, Islamic Azad University, Tehran, Iran

ABSTRACT

A novel PVC membrane electrode that is highly selective to ZrO^{2+} ions was prepared using 4,7,13,16,21,24-hexa oxa-1,10-diazabicyclo[8,8,8]-hexacosine (HODBHC) as a suitable neutral carrier. The sensor exhibited 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 at 25 °C, and was found to be very selective, precise, and applicable within the pH range of 5.0–8.0. The sensors showed a response time of <15s and can be used for at least 3 months without any measurable divergence in potential. The limit of detection was 8.0×10^{-7} M. The electrodes possess the advantages of low resistance, very fast response time, and a relatively long lifetime. The proposed sensors showed a fairly good discriminating ability towards ZrO^{2+} ion in comparison with some hard and soft metal ions. It was used as the indicator electrode in the potentiometric determination of ZrO^{2+} ions by the standard addition method in two samples.

Keywords

Selectivity; ZrO^{2+} sensor; PVC membrane; Potentiometry, metal ions.

1. Introduction

The development of selective membrane electrodes based on neutral carriers is one of the most promising trends in ionometry [1]. Crown ethers have been considered highly selective complexing agents for many metal ions. They can be applied in the separation and determination of metal ions through molecular recognition. Generally, crown ether forms a complex with a metal ion that fits well in its cavity. The new ion-selective membrane electrodes have played a fundamental role in the development of potentiometric measurements. The advantages of ISEs ion-selective electrodes over many other methods for cation and anion detection are their easy handling, non-destructive analysis, and inexpensive sample preparation. Potentiometric sensors have been shown to be very effective tools for the analysis of a wide variety of cations and anions [2-6]. Solvent polymeric membrane-based ISEs along with the incorporation of new ion carriers have shown to be a very useful tool for chemical, clinical, and environmental analyses in process monitoring [7-12].

In this paper, we have designed a new ISE for the determination of ZrO^{2+} ion based on 4,7,13,16,21,24-hexa oxa-1,10- diazabicyclo [8,8,8]- hexa cosine (HODBHC), which demonstrated a wide working concentration range, fast response time and gave reproducible results.

2. Experimental

2.1. Materials

Reagent grade dibutyl phthalate (DBP), acetophenone (AP), 2-nitrophenyloctyl ether (2-NPOF), oleic acid (OA), sodium tetraphenylborate

---

[*] Corresponding Author Email: giahi_m@yahoo.com

(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 (all from Merck) were of the highest purity available and used without any further purification. Double distilled deionized water was used throughout the experiment.

2.2. Methods

2.2.1. 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 (uncertainties in weighting process are respectively 0.12, 0.012, 0.23 and 0.041). 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 in 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 1h before filling with the internal solution, 1.0× 10^{-3} M $ZrOCl_2$, in an acidic solution. The electrode was finally conditioned for 8h by being soaked in a 1.0× 10^{-2} M $ZrOCl_2$ in an acidic solution. The potential measurements were carried out using the following equation:

SCE /internal solution, 1.0 ×10^{-3} M $ZrOCl_2$ +1.0 ×10^{-4} 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 ×10-4 mol dm-3 HCl solution was used as an electrolyte medium. The electrode was connected to YSI TruLab 1320. “Ion being measured was” selected on a meter and calibration was done. The ion concentration was reported 180%.

3. Results and Discussion

3.1. Effect of Membrane Composition on the Electrode Response

The influences of the membrane composition, nature and the amount of plasticizer, and the 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 using 57 % DBP in the presence of 30% PVC, % ionophore and 10 % oleic acid (No. 7, Table 1) results in a good electrode performance.

The potential responses of different ion-selective electrodes based on HODBHC are shown in Fig. 1. Among different cations that were tested, the highest sensitivity was obtained for the ZrO^{2+} ion. The emf vs.–log a ($ZrO^{2+)}$ of the PVC membrane based on HODBHC, which was prepared under optimal composition, indicated a rectilinear range from 1.0×10^{-6} to 1.0×10^{-1} M. The slope of the calibrations curve was 29.9±0.4 mV per 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 was ±0.4 mV. The membrane sensors 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 [13,14], or salts of two lipophilic ions [15], could diminish membrane resistance, eliminate the diffusion potential [16], and in some cases, change the selectivity pattern of the ion-selective PVC membrane, resulting in a good performance.

Table 1.Optimization of the membrane ingredients.

No.	Composition (%)				Slope (mV/decade)	Linear range [M]
	Ionophore	**PVC**	**Plasticizer**	**Additive**		
1	-	30	67(DBP)	3(OA)	8.3	1.0×10^{-5}-1.0×10^{-2}
2	-	30	67(DBP)	3(NaTPB)	12.1	1.0×10^{-5}-1.0×10^{-2}
3	3	30	67(DBP)	-	16.1	1.0×10^{-5}-1.0×10^{-2}
4	3	30	62(DBP)	5(OA)	32.1	1.0×10^{-5}-1.0×10^{-2}
5	3	30	64(DBP)	3(OA)	21.2	1.0×10^{-6}-1.0×10^{-2}
6	3	30	60(DBP)	7(OA)	28.4	1.0×10^{-6}-1.0×10^{-2}
7	3	30	60(AP)	7(OA)	13.0	1.0×10^{-6}-1.0×10^{-2}
8	3	30	57(DBP)	10(OA)	29.9	1.0×10^{-6}-1.0×10^{-1}
9	5	30	55(AP)	10(OA)	22.5	1.0×10^{-6}-1.0×10^{-2}
10	2	30	64(2NPOE)	4(NaTPB)	24.3	1.0×10^{-6}-1.0×10^{-2}
11	3	30	62(2NPOE)	5(NaTPB)	42.1	1.0×10^{-6}-1.0×10^{-2}
12	8	30	52(DBP)	10(OA)	20.9	1.0×10^{-5}-1.0×10^{-2}

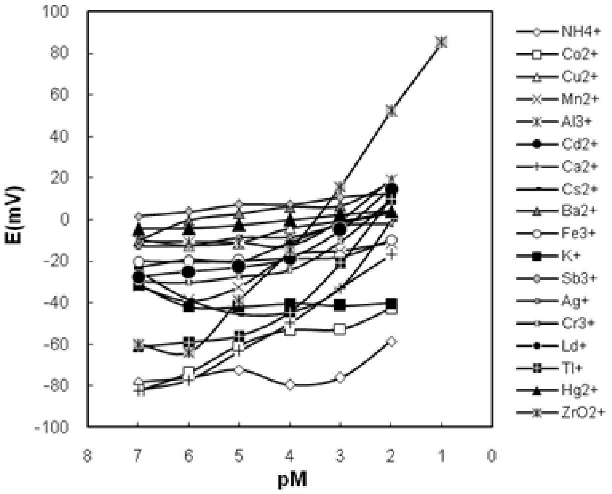

Fig1. Potential response of various metal ion-selective electrodes based on HODBHC

.

3.2. . Effect of pH

The pH dependence of the membrane electrode was studied at 1.0 ×10^{-3} mol L^{-1} ZrO^{2+} ion concentration and the results are shown in Fig. 2. The potential was found to remain constant from pH values of 3.0 to 8.0, which indicates the working pH range of the electrode. At pH values lower than 4.0, the pH of the solution also influenced the potential response. This is because the electrode becomes H+-sensitive at this pH [17]. At higher pH values, the zirconium-free ions precipitate as hydroxide in the aqueous test solutions.

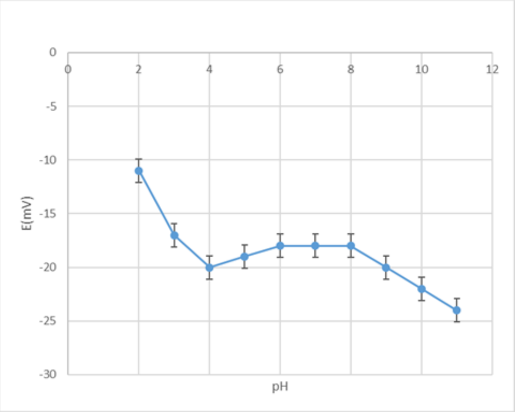

Fig2. Effect of pH of the test solution on the potential response of the ZrO^{2+} – selective electrode.

3.3. 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) [18]. MPM is a recently recommended procedure by IUPAC, which eliminates the limitations of the corresponding methods based on the Nicolsky-Eisenman equation for the determination of potentiometric 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+} and Lu^{3+}. The proposed supported liquid membrane electrode seems to be reasonably selective towards $ZrOCl_2$.

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}

3.4. Response Time

Dynamic response time is an important factor for an ion-selective electrode [19]. In this study, the practical response time was recorded by changing the solution with different ZrO^{2+} concentrations from 1.0×10^{-5} to 5.0×10^{-3} M. The actual potential versus time traces is shown in Fig.3. As can be seen, the electrode reaches the equilibrium response in a short time of about 10s.

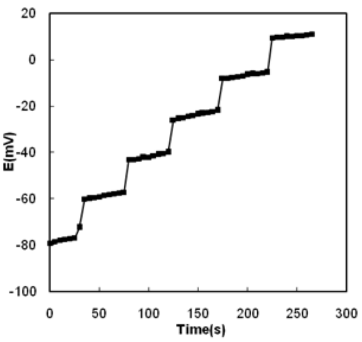

Fig3. Dynamic response time of the electrode for step change in concentration of ZrO2+: a)1.0 × 10^{-5} M, b) 5.0 × 10^{-5} M, c) 1.0 × 10^{4} M, d) 5.0 × 10^{-4} M, e) 1.0× 10^{-3} M, f) 5.0× 10^{-3} M

3.5. Reversibility of the Electrode Response

To evaluate the reversibility of the electrode, a similar procedure with the opposite direction was adopted. The measurements were performed in the sequence of high-to-low sample concentrations and the results are shown in Fig. 4. It was concluded that the potentiometric responses of the sensor were reversible and had no memory effect, the time needed to reach equilibrium values was the same as low-to-high sample concentration [13].

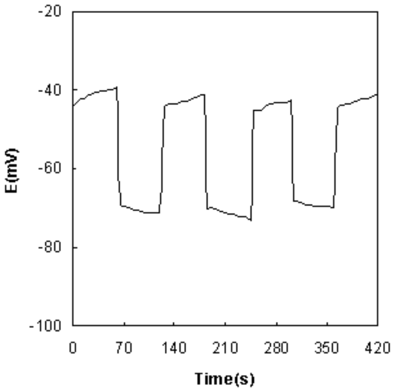

Fig. 4.

Fig4. Dynamic response characteristics of the ZrO^{2+}- electrode for several high-to-low sample cycles.

3.6. Analytical Application

The proposed electrode was successfully applied to the determination of $ZrOCl_2$ in making the sample by standard addition. In this method, the potential of 10 ml ZrO^{2+} solution with pH = 4 was measured as a testing sample (E_u). Then 0.1 ml of 5.0×10^{-2} M, $ZrOCl_2$ standard solution with pH = 4 was added to the testing solution and the equilibrium potential of Es was obtained. From the potential change of ΔE ($E_u - E_s$), one can calculate the concentration of the testing sample using the equation given below;

$$Cx= \frac{C_s \times V_s}{(V_x + V_s)\, 10^{\Delta E/S} - V_x} \quad \text{(Eq.1)}$$

where C_x is the $ZrOCl_2$ concentration of making sample , Cs 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 [20]. In the determination of ZrO^{2+} in aqueous solutions, the electrode showed promising results. The reproducibility was good and the relative standard deviation of the determinations was less than 2% (Table 3).

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

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

4. Conclusions

The results obtained in the present work demonstrate that 4,7,13,16,21,24-hexa oxa-1,10-diazabicyclo [8,8,8]- hexa cosine as an ionophore can be used in the development of a PVC based ion-selective electrode. The main advantages of this sensor are its simplicity of preparation, short conditioning time, wide dynamic range, Nernstian behavior, low detection limit, low cost, and good selectivity. The proposed sensors showed a fairly good discriminating ability towards ZrO^{2+} ion in comparison to some hard and soft metal ions. This electrode could be used for the determination of ZrO^{2+} ion by standard addition method in two samples.

References

[1] Petrukhin OM, Avdeeva EN, Zhukov AF, Polosuchina IB, Krylova SA, Rogatinskaya SL, Bodrin GV, Nesterova NP, Polikarpov YM, Kabachnik MI. Bidentate organophosphorus compounds as ionophores for calcium-and uranyl-selective electrodes. Analyst. 1991;116(7):715-9.

[2] Mousavi MF, Sahari S, Alizadeh N, Shamsipur M. Lead ion-selective membrane electrode based on 1, 10-dibenzyl-1, 10-diaza-18-crown-6. Analytica chimica acta. 2000 Jun 1;414(1-2):189-94.

[3] Mousavi MF, Alizadeh N, Shamsipur M, Zohari N. A new PVC-based 1, 10-dibenzyl-1, 10-diaza-18-crown-6 selective electrode for detecting nickel (II) ion. Sensors and Actuators B: Chemical. 2000 Jul 25;66(1-3):98-100.

[4] Rahmani A, Barzegar M, Shamsipur M, Sharghi H, Mousavi MF. New potentiometric membrane sensors responsive to Pb (II) based on some recently synthesized 9, 10-anthraquinone derivatives.

[5] Aghaie H, Giahi M, Monajjemi M, Arvand M, Nafissi GH, Aghaie M. Tin (II)-selective membrane potentiometric sensor using a crown ether as neutral carrier. Sensors and Actuators B: Chemical. 2005 Jun 29;107(2):756-61.

[6] Gupta VK, Chandra S, Chauhan DK, Mangla R. Membranes of 5, 10, 15, 20-tetrakis (4-methoxyphenyl) porphyrinatocobalt (TMOPP-Co)(I) as MoO42--selective sensors. Sensors. 2002 May 12;2(5):164-73.

[7] Li ZQ, Wu ZY, Yuan R, Ying M, Shen GL, Yu RQ. Thiocyanate-selective PVC membrane electrodes based on Mn (II) complex of N, N'-bis-(4-phenylazosalicylidene) o-phenylene diamine as a neutral carrier. Electrochimica Acta. 1999 Jan 1;44(15):2543-8.

[8] Rouhollahi A, Shamsipur M. Triiodide PVC membrane electrode based on a charge-transfer complex of iodine with 2, 4, 6, 8-tetraphenyl-2, 4, 6, 8-tetraazabicyclo [3.3. 0] octane. Analytical chemistry. 1999 Apr 1;71(7):1350-3.

[9] Badr IH, Diaz M, Hawthorne MF, Bachas LG. Mercuracarborand “anti-crown ether”-based chloride-sensitive liquid/polymeric membrane electrodes. Analytical chemistry. 1999 Apr 1;71(7):1371-7.

[10] Fathi MR, Darviche F, Ganjali MR. Lead-selective membrane potentiometric sensor based on a recently synthesized dimethyl benzo tetrathia fulvalene.

[11] Oesch U, Ammann D, Simon W. Ion-selective membrane electrodes for clinical use. Clinical Chemistry. 1986 Aug 1;32(8):1448-59.

[12] Moody GJ, Saad BB, Thomas JD. Sel. Electrode Rev. 1988. V. 10.. 1988;10:71.

[13] Grygolowicz-Pawlak E, Plachecka K, Brzozka Z, Malinowska E. Further studies on the role of redox-active monolayer as intermediate phase of solid-state sensors. Sensors and Actuators B: Chemical. 2007 Apr 10;123(1):480-7. [14] M. Huser, P.M. Gehrig, W.E. Morf, W. Simon, E. Lindner, J. Jeney, K. Toth and E. Pungor, Anal. Chim. Acta 63 (1991) 1380.

[15] Ammann D, Pretsch E, Simon W, Lindner E, Bezegh A, Pungor E. Lipophilic salts as membrane additives and their influence on the properties of macro-and micro-electrodes based on neutral carriers. Analytica chimica acta. 1985 May 1;171:119-29.

[16] Mikhelson KN, Lewenstam A, Didina SE. Contribution of the diffusion potential to the membrane potential and to the ion-selective electrode response. Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis. 1999 Jul;11(10-11):793-8.

[17] Gutknecht J, Schneider H, Stroka J. Cryptate formation in nonaqueous solvents: new aspects in single-ion thermodynamics. Inorganic Chemistry. 1978 Dec 1;17(12):3326-9.

[18] Gadzekpo VP, Christian GD. Determination of selectivity coefficients of ion-selective electrodes by a matched-potential method. Analytica Chimica Acta. 1984 Jan 1;164:279-82.

[19] Matysik S, Matysik FM, Mattusch J, Einicke WD. Application of Zeolite-Polydimethylsiloxane Electrodes to Potentiometric Studies of Cationic Species. Electroanalysis: An International Journal Devoted to Fundamental and Practical Aspects of Electroanalysis. 1998 Feb;10(2):98-102.

[20] Buck RP, Lindner E. Recommendations for nomenclature of ionselective electrodes (IUPAC Recommendations 1994). Pure and Applied Chemistry. 1994 Jan 1;66(12):2527-36.