

Characterization of a New Zn²⁺-Selective Electrode Based on Schiff-base as Ionophore

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Received: 9 June 2012 / Accepted: 27 June 2012 / Published: 1 August 2012

A new Zn²⁺-selective electrode based on Schiff-base as ionophore was prepared. Potentiometric responses revealed that this new electrode has good selectivity to Zn²⁺ relative to a wide variety of other cations. The effect of plasticizers and ion-exchanger on the performance of electrode was also studied. With the optimal membrane compositions, the electrode based on this new ionophore reveals a good Nernstian behavior over a wide concentration ranges of 1.0×10^{-6} — 1.0×10^{-3} M with a detection limit of 7.4×10^{-7} M Zn²⁺. The electrode possesses advantages of low resistance, very fast response time and long lifetime. The potentiometric responses are independent of the pH of the test solution in the pH range 3.4–5.8. The electrode can be used as indicator electrode for the potentiometric titration of Zn²⁺ in spiked water.

Keywords: Ion-selective electrode, Zn²⁺, Schiff-base

1. INTRODUCTION

Zinc is widely used in galvanising of steel, batteries, brass metallurgy, die casting and chemical compounds for a broad range of industries [1]. It is the second most abundant transition metal ion in the human body and plays significant role in many biological processes such as brain function and pathology, immune function, gene transcription. However, a major problem is the subsequent pollution and harm to the environment and humans because of its frequent use [2]. Excessive Zn²⁺ intake can lead to many diseases such as fever, nausea, anaemia and renal failure. As a consequence, the quantification of Zn²⁺ is of great interest to many different areas.

Ion-selective electrodes (ISEs) are powerful tools to monitor metal ions because of their good property such as high selectivity, good precision, low cost and simplicity [3]. Ionophore is the key composition of membrane and it decides the potentiometric property of the ISEs. So the synthesis of new ionophores is important for the construction of ISEs, and many groups are focus on this area [4-5].

However, it is a pity that only a few of Zn^{2+} -ISEs have been reported compared to Cu^{2+} [6], Hg^{2+} [7], Ag^+ [8], et al. Thus, it is still an urgent work to develop new highly Zn^{2+} -selective ISEs [9-13]. In this work, a new Zn^{2+} -selective electrode based on a new Schiff-base was characterized, and study shows that this new ISE has good selectivity and sensitivity towards Zn^{2+} .

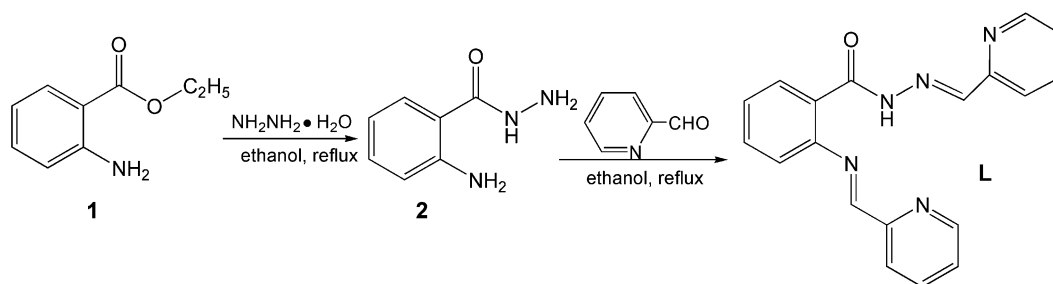
2. EXPERIMENTAL

2.1. Reagents and instrumentation

2-nitrophenyl octyl ether (*o*-NPOE), bis (2-ethylhexyl) sebacate (DOS), dibutylphthalate (DBP), dioctyl phthalate (DOP), sodium tetrakis [3, 5-bis (trifluoromethyl)phenyl]borate (NaTFPB) and poly (vinyl chloride) (PVC) were purchased from Sigma-Aldrich. All other reagents used were purchased from Sinopharm Chemical Reagent and of analytical grade purity or better. Deionized water with specific resistance of 18.2 M Ω cm was obtained by a Pall Cascada laboratory water system.

Melting points were taken on a WRS-1B digital melting-point apparatus and were uncorrected. Infrared (IR) spectra were recorded on KBr pellets using Perkin–Elmer 1430 spectrometer. Nuclear magnetic resonance (NMR) spectra were measured with a Bruker WM-300 instrument and chemical shift were given in ppm from tetramethylsilane (TMS). Mass (MS) spectra were recorded on a Thermo TSQ Quantum Access Agilent 1100. Elemental analyses were performed with a Vario Elementar(III).

The synthesis route was shown in Scheme 1.



Scheme 1. Synthesis route of **L**.

2.2. Synthesis of Schiff-base **L**

2.2.1. Synthesis of compound **2**

Synthesis of compound **2**: Compound **2** was synthesized as reported procedure with some modification [14]. Under N_2 atmosphere, ethyl 2-aminobenzoate (1.0 mM, 0.165 g) and hydrazine hydrate (12.0 mM, 0.6 mL) were mixed in 30 mL absolute ethanol. The mixture was refluxed for 6 h. After the reaction was finished, the solvent was removed under reduced pressure, and then 50 mL petroleum ether was added to the oily residue, and the precipitate so produced was filtered and used directly. Yields: 87.2%. M.p.: 152.0-153.1 °C. MS: m/z 152.09 $[\text{M}+\text{H}]^+$.

2.2.2. Synthesis of compound **L**

Under N₂ atmosphere, 20 mL absolute ethanol containing **2** (1.52 g, 0.01 M) was added dropwise to 20 mL 2-pyridinecarboxaldehyde (2 μL, 0.02 M) absolute ethanol solution. The mixture was refluxed for 4 h and then cooled to room temperature. The precipitate so obtained was filtered and washed by water and ethanol in turn and dried in vacuum. The crude product was purified by recrystallization from absolute ethanol to give compound **L** as dark yellow solids. Yields: 90%. M.p.: 201.2-203.0 °C. MS: *m/z* 329.06 [M]⁺. IR (KBr tablet, cm⁻¹): 3313.1 (s, 1H), 2912.0 (Ar-H), 1681.6 (C=N); ¹H NMR (δ: ppm, CDCl₃): 9.04 (s, 1H, NH), 8.63 (d, 1H, *J* = 5.00), 8.61 (d, 1H, *J* = 5.00), 8.04 (d, 1H, *J* = 8.00), 8.00 (d, 1H, *J* = 8.00), 7.73 (t, 1H, *J* = 7.50), 7.60 (t, 1H, *J* = 7.75), 7.28 (t, 3H, *J* = 7.00), 7.20 (t, 1H, *J* = 6.25), 6.86 (t, 1H, *J* = 7.50), 6.70 (d, 1H, *J* = 8.50), 6.37 (s, 1H), 5.83 (s, 1H). ¹³C NMR (δ: ppm, CDCl₃): 161.33, 157.64, 153.91, 150.27, 149.97, 149.53, 145.24, 137.01, 136.45, 134.29, 129.13, 124.28, 123.45, 121.24, 120.74, 119.82, 116.15, 115.35. MS: *m/z* 329.06 (M⁺).

Anal. Calcd. for C₁₉H₁₅ON₅ (329.3): C, 69.29; H, 4.59; N, 21.26. Found: C, 69.24; H, 4.63; N, 21.20.

2.3. Membrane preparation

The membrane components (totaling 250 mg) were dissolved in 3.0 mL of THF and shaken vigorously for at least 2 h, and then poured into a glass ring (30 mm i.d.) fixed on a glass plate. The solvent was allowed to evaporate overnight at room temperature to give a transparent membrane of 180 μm thickness. For each ISE, a disk of 7 mm diameter was punched from the membranes and glued to a plasticized PVC tube (i.d. 6 mm, o.d. 9 mm) with THF/PVC slurry. Electrodes were conditioned with 1.0×10⁻³ M Zn(NO₃)₂ overnight.

2.4. Potential measurements

Activity coefficients were calculated according to the Debye–Hückel approximation and EMF values were corrected for liquid-junction potentials with the Henderson equation. Membrane potentials were measured with a Model PXSJ-216 digital ion analyzer (Shanghai Instruments) in magnetically stirred solution at room temperature in the galvanic cell: SCE|sample solution|ISE membrane|inner solution (1.0×10⁻³ M Zn²⁺)|AgCl/Ag.

2.5. Selectivity measurements

The electrodes were conditioned in 1.0×10⁻³ M NaCl solution overnight for selectivity measurement. The sequence of the sample ions was: Li⁺, H⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, Cu²⁺, Cd²⁺, Pb²⁺, Hg²⁺ and Ag⁺. For detection of Hg²⁺, solutions were adjusted to pH=4 using 0.1 M HNO₃ to avoid precipitation. All the measurements were done in triplicate. The selectivity coefficients were calculated from the emf values according to the separate solution method assuming theoretical slopes.

3. RESULTS AND DISCUSSION

3.1. Influence of membrane composition

The compositions of membranes have great effect on the characteristics of ISEs [15]. Therefore, membranes with different compositions have been prepared and their potentiometric response characteristics were evaluated, and the amounts of ion-exchanger and the polarity of various plasticizers on the potentiometric response of Zn^{2+} -ISE were discussed in detail.

Table 1. Potentiometric responses of Zn^{2+} -ISEs based on ionophore **L** with different amounts of ionexchanger.

Electrode No.	Compositions of membrane w%				Liner range, M	Detection limits, M	Slope mV/dec.
	PVC	Plasticizer	Additive	L			
L₁	32.83	65.70, <i>o</i> -NPOE	1.36	1.01	3.0×10^{-6} – 1.0×10^{-4}	1.3×10^{-6}	25.6
L₂	32.81	65.50, <i>o</i> -NPOE	1.70	1.00	1.0×10^{-6} – 1.0×10^{-4}	9.8×10^{-7}	23.4
L₃	32.14	64.27, <i>o</i> -NPOE	2.62	0.97	1.0×10^{-6} – 1.0×10^{-3}	7.4×10^{-7}	30.1

As we all known, lipophilic anionic additives (NaTFPB) can act as a charge compensating counter ion in the membrane and thus facilitate the process of ion charge transduction [15]. Accordingly, the effects of the amount of NaTFPB in Zn^{2+} -selective membranes on the electrode characteristics were investigated. The amount of NaTFPB was altered while maintaining the same amounts of other membrane compositions (Table 1). The results show that the electrode based on ionophore **L** and NaTFPB in a mole ratio of 4:1 present the best potential responses. Thus, according to the reported results [16], compound **L** coordinate with Zn^{2+} in a mole ratio of 1:1 in membrane phase.

Table 2. Potentiometric responses of Zn^{2+} -ISEs based on ionophore **L** with different plasticizers.

Electrode No.	Compositions of membrane w%				Liner range, M	Detection limits, M	Slope mV/dec.
	PVC	Plasticizers	Additive	L			
L₃	32.14	64.27, <i>o</i> -NPOE	2.62	0.97	1.0×10^{-6} – 1.0×10^{-3}	7.4×10^{-7}	30.1
L₄	32.14	64.27, DBP	2.62	0.97	3.0×10^{-6} – 1.0×10^{-4}	1.2×10^{-6}	27.8
L₅	32.14	64.27, DOP	2.62	0.97	1.0×10^{-5} – 1.0×10^{-3}	6.8×10^{-6}	22.8
L₆	32.14	64.27, DOS	2.62	0.97	6.0×10^{-6} – 1.0×10^{-3}	2.0×10^{-6}	26.0

The effect of plasticizers on Zn^{2+} -selective electrodes based on the newly synthesized Schiff-base is shown in Table 2. It is clear that *o*-NPOE is more effective plasticizer than others in preparing the Zn^{2+} -ISEs, which can be explained by the fact that *o*-NPOE plasticized PVC membranes have much higher dielectric constants than DOS, DBP and DOP based membranes. In addition, *o*-NPOE plasticized the membranes dissolve the ion association complexes and adjust both permittivity and ion

exchanger sites mobility to give highest possible selectivity and sensitivity. With the best membrane compositions (PVC:NPOE:Additive:L=32.70:65.39:0.92:0.99 (w:w), total: 250 mg, sensor No. L₃), this Zn²⁺-ISE show a good Nernstian response over a wide concentration range of 1.0×10⁻⁶—1.0×10⁻³ M with a detection of 7.4×10⁻⁷ M Zn²⁺ (Fig.1).

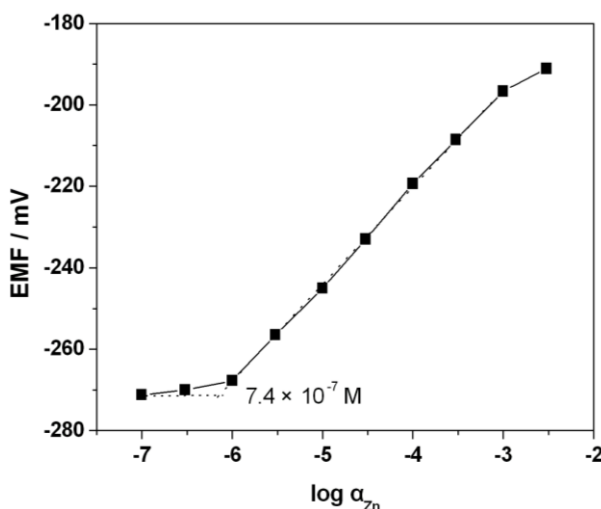


Figure 1. Potentiometric responses of Zn²⁺-selective electrode based on ionophore L (sensor No. L₃).

3.2. Potentiometric selectivity of Zinc electrodes

The influence of interfering ions on the response behavior of the ISE is usually described in terms of selectivity coefficients. The selectivity coefficients, log K_{AgJ}^{pot}, of Zn²⁺-ISE were determined by using Bakker’s method to eliminate the influence of the inherent sensitivity limit on the response toward discriminated ions [17]. Table 3 shows the selectivity coefficients of Zn²⁺-ISE based on L (sensor No. L₃). It can be seen that the electrode based on L gives the best selectivity and sensitivity toward Zn²⁺ than other cations.

Table 3. Potentiometric selectivity coefficients, log K_{AgJ}^{pot}, obtained with membrane based on ionophore L (sensor No. L₃).

Ion J	log K _{AgJ} ^{pot}	Ion J	log K _{AgJ} ^{pot}
Zn ²⁺	0 (30.11)	Ca ²⁺	-5.0 (19.45)
Li ⁺	-5.2 (30.58)	Cu ²⁺	-3.6 (28.29)
H ⁺	-3.2 (51.98)	Cd ²⁺	-4.8 (20.45)
Na ⁺	-4.0 (48.34)	Pb ²⁺	-4.2 (29.47)
K ⁺	-3.6 (55.67)	Ag ⁺	-3.5 (56.06)
Mg ²⁺	-6.3 (17.19)	Hg ²⁺	-2.4 (47.70)

3.3. Effect of pH

The influence of the pH on the response of Zn^{2+} -ISE based on ionophore **L** (sensor No. **L**₃) was studied. The pH effect is illustrated in Fig.1 by varying the pH test solutions with 0.1 M HNO_3 and 0.1 M NaOH for 1.0×10^{-3} M and 1.0×10^{-4} M $\text{Zn}(\text{NO}_3)_2$, respectively. It is clear from Fig.2 that the operational pH range was 3.4-5.8 for the electrode based on ionophore **L**. At higher pH, Zn^{2+} will form precipitate with OH^- , thus cause the potential reduction. However, when the pH was low, the concentration of H^+ shows obvious disturbance on the potentiometric response of Zn^{2+} -ISE.

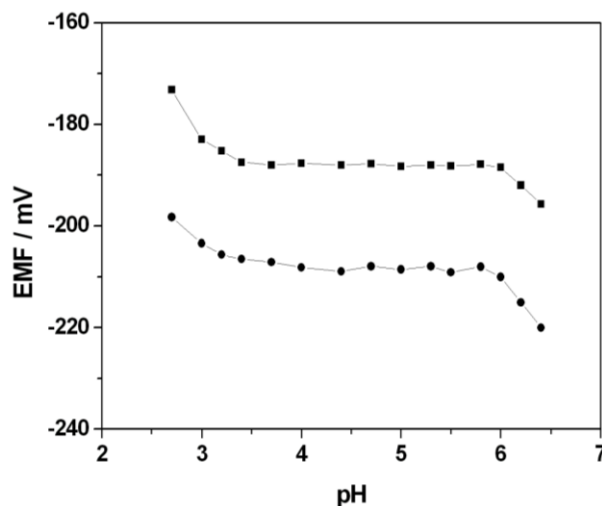


Figure 2 pH effect on the potentiometric responses of Zn^{2+} -selective electrode. (■) 1.0×10^{-3} M Zn^{2+} ; (●) 1.0×10^{-4} M Zn^{2+} (sensor No. **L**₃).

3.4. Dynamic response of Zn^{2+} -ISE based on **L**

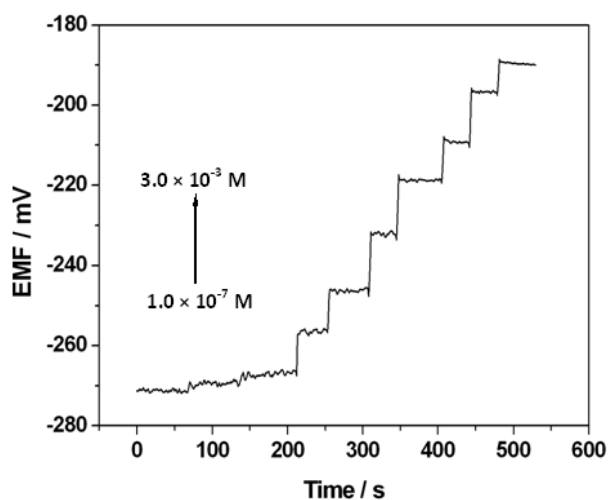


Figure 3. Dynamic response curves of Zn^{2+} -selective electrode based on ionophore **L** (sensor No. **L**₃).

For analytical purposes, response time is one of the most important factors that are taken into account. In this work, the practical response time was recorded by immediate and successive changing of Zn^{2+} concentration from 1.0×10^{-6} - 1.0×10^{-3} M and the results are shown in Fig. 3. As it can be seen, in the whole concentration range, the Zn^{2+} -ISE based on ionophore **L** (sensor No. **L**₃) need a very short time to reach equilibrium response. Lifetime studies show that this new electrode can be used for at least two months without obvious potential change.

3.5. Analytical application

The study suggested that this newly characterized Zn^{2+} -ISE (sensor No. **L**₃) could work well under the laboratory conditions. It was effectively applied as indicator electrode to the potentiometric titration of a spiked 1.0×10^{-4} M $Zn(NO_3)_2$ solution with 0.01 M EDTA as titration reagent. The results demonstrate that the Zn^{2+} amount in this solution can be determined with good accuracy.

4. CONCLUSIONS

A Zn^{2+} -ISE based on a newly synthesized Schiff-base as ionophore was prepared. The results show that this sensor showed a wide linear range of 1.0×10^{-6} - 1.0×10^{-3} M with a detection limit of 7.4×10^{-7} M Zn^{2+} .

ACKNOWLEDGEMENTS

This work was financially supported by the Research and Training Foundation of Hainan Medical University (No. HY2010-004), the Natural Science Foundation of Hainan Province (No. 812188) and Hainan Provincial Department of Education Subject (Hjkj2012-33 and Hj2010-20).

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