Full Paper

Spectrofluorimetric Study and use of Tris (3-(2-Hydroxy acetophenone)Propyl) Amine) as a Novel Sensing Material for Preparation of Zn²⁺ Potentiometric Sensor

Farhang Mizani[*, 1] **and Morteza Hosseini**[2]

[1]*Department of Chemistry, Faculty of Science, Payame Noor University, PO Box 19395-3697 Tehran, I. R. Iran*

[2]*Department of Life Science Engineering, Faculty of New Sciences & Technologies, University of Tehran, Tehran, Iran*

* Corresponding Author, Tel.: +98-281 2224024; Fax: +98-281 2233386

E-Mail: F_mizani@pnu.ac.ir

Abstract- Spectrofluorimetric studies on the binding properties of Tris (3-(2-hydroxy-acetophenone) propyl) amine) (L) toward different heavy metal ions in acetonitryl solution revealed its selective 1:1 complexation with Zinc ion. Consequently, L was used as a suitable ionophore for the preparation of new plasticized PVC membrane-selective electrodes for the determination of Zinc ion. The sensor exhibits a Nernstian response for Zn(II) over a wide concentration range (2.0×10^{-7}-1.0×10^{-1} M) and detection limit of (9.6×10^{-8} M). The best performance was obtained with a membrane composition of PVC (30%), ortho-nitrophenyloctyl ether (o-NPOE) (64%), ionophore **(L)** (5%) and Potassium tetrakis (KTpCIPB) (1%). The sensor exhibits the advantages of fast response time (12 seconds), operational lifetime (24 weeks) and good selectivity co-efficient for Zn(II) over an alkali, alkaline earth and transition metal ions. The electrode was used as indicator electrode in potentiometric titration of Zn(II) with ethylenediaminetetraacetic acid (EDTA) and in the determination of Zn^{2+} ion in real samples.

**Keywords-** Spectrofluorimetric, Zn^{2+} Ion-selective electrode, Potentiometry, PVC membrane, Sensors

1 .INTRODUCTION

Zinc ion is an important divalent cation in biological systems and plays important roles in the human body influencing, DNA synthesis, microtubule polymerization, gene expression, apoptosis, immune system function, and the activity of enzymes such as carbonic anhydrase and matrix metalloproteinase [1]. Moreover, zinc ion is also a contributory factor in neurological disorders such as epilepsy and Alzheimer's diseases [2]. Consequently, investigation focused on detecting Zn^{2+} of low concentration in vivo has attracted increasing interest [3].

Though several analytical techniques such as UV–Vis spectroscopy [4], potentiometry [5] and flame atomic absorption spectrometry [6], inductivity coupled plasma atomic emission spectroscopy (ICPAES) [7] and fluorescence methods [8,9] have been reported for zinc ion assay in various samples. The available detection methods of Zn^{2+} are still limited due to its $3d^{10}4s^0$ electron configuration not giving any spectroscopic or magnetic signals. Among these techniques, the ion selective electrodes (ISEs) are relatively simple, fast and inexpensive. Due to the critical importance of selective Zn^{2+} ion determination, especially, in biological, industrial and water samples, there are a number of reports on the preparation of Zn^{2+} ion-selective electrodes based on a variety of ionophores [10-17].

Schiff bases (SBs) are known to form stable complexes with transition metal ions and act as ion carriers. Almost all metals form 1:1 metal complexes with SBs. The feature of SBs gives geometric and cavity control of host–guest complexation and modulation of its lipophilicity, and produces remarkable selectivity, sensitivity and stability for a specific ion. The resulting SB complexes have attracted increasing attention in the area of ionic binding due to their unique properties and reactivity. Schiff bases with N and O as donor atoms are well known to form strong complexes with transition metal ions and recently were used as ionophores in sensors for cation determination [18-21]. In this present work a Schiff base, Tris (3-(2-hydroxyacetophenone) propyl) amine) (L), Scheme 1, was used as an ionophore with N and O donor atoms for construction of a Zn(II) ion-selective electrodes.
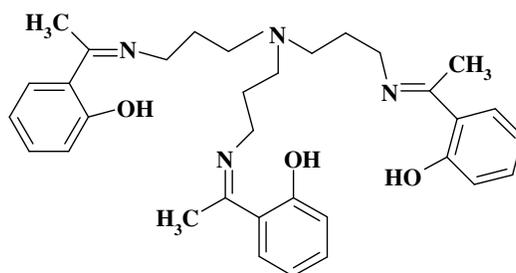
Scheme 1. Structure of ligand **(L)**

2 . EXPERIMENTAL

2.1. Reagents

Reagent grade 2-nitrophenyloctyl ether (NPOE), benzyl acetate (BA), dioctyl phthalate(DOP), dibutyl phthalate (DBP), high relative molecular weight PVC, oleic acid (OA), potassium tetrakis(*p*-chlorophenyl) borate (KTpClPB), sodium tetraphenylborate (STPB) and tetrahydrofuran (THF) were obtained from Fluka. The nitrate or chloride salts of the cations used (from Merck or Aldrich) were of the highes purity available. Doubly distilled water was used throughout.

The Schiff-base ligand Tris(3-(2-hydroxyacetophenone) propyl) amine) (Scheme 1) was prepared by reaction of tris(3-aminopropyl)amine with 3 equivalent of 2-hydroxyacetophenone. To a solution of 2-hydroxyacetophenone (20 mmol, 2.72 g) in ethanol (40 mL) was added tris(3-aminopropyl)amine (1.25 g, 6.67 mmol) in absolute ethanol (40 mL). After the addition of additional diethyl ether (50 mL) and cooling in an ice bath for 50 min, the yellow precipitate formed was filtered off, washed with diethylether and dried in vacuo. Yield, 78%; Anal. Calcd. for $C_{33}H_{42}N_4O_3$: C, 73.04%; H, 7.80%; N, 10.32%, Found: C, 72.12%; H, 7.44%; N, 10.74%; ^{1}H-NMR (400 MHz, CDCl$_3$, internal reference TMS): δ 2.19 (m, 6H), 3.11 (t, 6H), 3.73 (t, 6H), 11.70 (s, 3H, OH), 2.36 (s, 9H, C(CH$_3$)N), 6.68–7.92 (m, 12H, aromatic); IR (Nujol mull) cm^{-1}: 1635, 1617 (sh), 1590, 1450 (s, νC=N and νC=C). Complete condensation of all primary amino groups is confirmed by the lack of N–H stretching bands in the IR 3150–3450 cm^{-1} region and the presence of strong C=N stretching bands for ligand. This conclusion is also supported by the ^{1}H-NMR data which shows not only the absence of N–H hydrogen resonances but also the presence of C=N.

2.2. Electrode preparation

Membrane solutions were prepared by thoroughly dissolving 5 mg of ionophore (**L**), 30 mg of powdered PVC, 64 mg of plasticizer NPOE and 1mg of additive KTpClPB in 3 mL of THF.

The resulting clear mixture was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (5 mm o.d.) was dipped into the mixture for ~10 s so that a nontransparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at room temperature for ~1 h. The tube was then filled with an internal solution of 1.0×10^{-3} M zinc nitrate. The electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-3} M Zn (NO$_3$)$_2$ solution. A silver–silver chloride electrode was used as the internal reference electrode.

2.3. Apparatus

Fluorescence spectra were recorded on a Perkin-Elmer luminescence spectrometer LS-30, equipped with a Xenon lamp, a 7μL fused-silica flow cell, and a peristaltic pump. Excitation

and emission bandwidths were both set at 10 nm. In all measurements, the temperature was kept constant at 25.0±0.1 with the aid of a Huber polystate K6-3 thermostat assembly including a water bath circulating system. The vessel was located on a magnetic stirrer (~300 rpm) [22-24].

The emf measurements with the polymeric membrane electrodes were carried out with the following cell assembly:

Ag–AgCl | 3 M KCl | internal solution, 1.0×10^{-3} M $Zn(NO_3)_2$ | PVC membrane | test solution | Hg –Hg_2Cl_2, KC1 (satd.)

A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25.0 $^\circ$C. Activities were calculated according to the Debye–Hückel procedure [25].

3. RESULTS AND DISCUSSION

3.1. Preliminary studies

In preliminary experiments the complexation of **L** with a number of metal ions was investigated spectrofluorometrically in acetonitrile solution at 25.0±0.1 $^\circ$C. A 5.0×10^{-6} mol L^{-1} solution of **L** in MeCN–H2O (1:1, v/v) solution was titrated with microliter amounts of 1.0×10^{-4} M solutions of metal ions spectrofluorometrically (at λ_{ex}=395 nm), at a constant ionic strength of 0.01 M ammonium nitrate in 25.0±0.1 $^\circ$C.

The resulting fluorescence intensity–mole ratio data for K^+, Ca^{2+}, Hg^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+} and Ce^{3+} ions was studied.

Results shown that only the Zn^{2+} ion can increase the fluorescence intensity of the ligand. Other metal ions that have importance in environmental studies, i.e. Cd^{2+}, Hg^{2+}, etc., and biologically significant cations cannot enhance the intensity as a Zn^{2+} ion can. Emission intensity remains unaltered or quenches in the presence of other metal ions. Among transition metal cations, Co^{2+}, Ni^{2+}, Cu^{2+} and Cd^{2+} quench the emission, due to an electron or energy transfer between the metal cation and fluorophore known as the fluorescence quenching mechanism [26,27]. K^+, Ca^{2+} and Ce^{3+} can only increase the intensity slightly. The enhancement of fluorescence is attributed to the introduction of Zn^{2+}, and the strong complexation occurs with ligands evident from large binding constant values. As a result of that it imposes rigidity and hence decreases the non-radiative decay of the excited-state as well as increases in radiative decay. These results are presumably due to the poor complexation of alkali metals or alkaline earth metals with the chelator (ligand).

It is noteworthy that because of the very short fluorescence lifetimes and low concentration conditions used, the effect of concentration quenching was negligible. Results illustrate that upon addition of **L**, the quantity of metal ions increased, and then they begin to level off and go up again at a metal/ligand ion molar ratio of 1. From such a sharp inflection point at a molar ratio of 1, it can be immediately concluded that in all cases a 1:1 $[ML]^{n+}$

complex cation is formed in MeCN–H2O (1:1, v/v) solution. The formation constants of the resulting complexes were evaluated by fitting the fluorescence intensity–metal ion molar ratio data to a 1:1 model using a nonlinear least-squares curve-fitting program, as described elsewhere [28,29]. The results are summarized in Table 1. Despite the observed different trend of fluorescence changes at such different experimental conditions, the results obtained supported the formation of the most stable $[ZnL]^{2+}$ complex in the series.

Table 1. The formation constants of $L - M^{n+}$ complexes

Cation	Log K_f	Cation	Log K_f
Zn^{2+}	**5.92 ± 0.12**	Pb^{2+}	2.56 ± 0.17
Ce^{3+}	3.35 ± 0.15	Al^{3+}	2.45 ± 0.13
Cr^{3+}	3.12 ± 0.13	Cs^+	2.21 ± 0.15
Cu^{2+}	3.06 ± 0.19	Co^{2+}	<2.0
Hg^{2+}	2.89 ± 0.17	Ni^{2+}	<2.0
Ag^+	2.71 ± 0.09	Cd^{2+}	<2.0

According to these preliminary results and considering the high lipophilic character of the complex $[ZnL]^{2+}$, we expected **L** to act as a suitable ionophore for Zinc ion in a PVC membrane electrode. In preliminary experiments, it was found that, while the use of an ionophore-free PVC membrane resulted in no measurable response with respect to Zn^{2+} ion, the addition of **L** shows a Nernstian response for the cation over a wide concentration range of 1.0×10^{-6} to 1.0×10^{-1} M (Fig. 1).

Meanwhile, the ligand **L** was also used as a neutral ionophore to prepare membrane electrodes for a variety of ions including K^+, Ca^{2+}, Hg^{2+}, Cd^{2+}, Co^{2+}, Zn^{2+}, Cu^{2+} and Ce^{3+}, the potential responses of which are also shown in Fig. 1. Except for the Zn^{2+} ion-selective electrode, in all other cases the slope of the corresponding potential–pM plots was much lower than the Nernstian slopes of 59, 29.5 and 19.5 mV per decade expected for mono-, bi- and trivalent cations, respectively. Therefore, Zinc ion with the most sensitive Nernstian response over a wide concentration range seems to be suitably determined with the PVC membrane electrode based on the neutral ionophore **L**.

This is a further indication of the highly selective behavior of the ionophore for Zn^{2+} over the other cationic species considered.
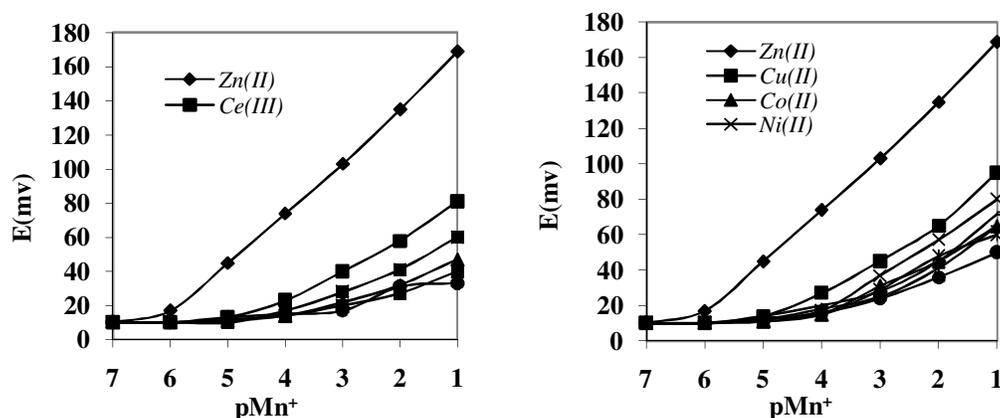
Fig. 1. The potential responses of various ion-selective electrodes based on **L**

3.2. Optimization of potentiometric response of the PME

It is well known that the sensitivity, and the linearity of the ion-selective electrodes not only depend on the nature of ionophore used but also significantly on the membrane composition and the properties of plasticizers used [30-36]. Thus, the effects of membrane composition and the nature and the amount of plasticizer and additive on the potential response of the Zn^{2+} ion-selective electrode were investigated and the results are summarized in Table 2. The nature of plasticizer is known to influence both the dielectric constant of the membrane and the mobility of the ionophore and its cation complex [37,38].

As it is seen from Table 2, among the three different plasticizers used, NPOE is found to be the most effective solvent mediator in preparing the Zn^{2+} ion-selective electrode.

As it was expected, the amount of ionophore **L** was also found to affect the PVC membrane sensitivity. The calibration slope increased with ionophore content up to a value of 5%. However, further increase in the amount of **L** resulted in diminished calibration slope of the electrode, presumably due to some inhomogenities and possible saturation of the membrane [39].

The sensitivity of the PVC membrane is quite low in the absence of a proper lipophilic additive [40,41]. Meanwhile, it was found that, maximum membrane selectivity towards Zn^{2+} ion can be obtained in the presence of 1% KTpClPB as a suitable additive. As it is seen from Table 2, membrane number 8 with PVC: NPOE: KTpClPB: **L** percent ratio of 30:64:1:5 resulted in the Nernstian behavior of the membrane electrode over a very wide concentration range for the PME.

3.3. Effect of Internal Solution

The influence of the concentration of the internal solution on the potential response of the PME was investigated. The $Zn(NO_3)_2$ concentrations were changed from 1.0×10^{-4} M to

1.0×10^{-2} M and the emf-pZn(II) plots were obtained. It was found that the concentration of the internal solution has a negligible effect on the potential response of the electrode, except for on expected change in intercept of the resulting plot. A 1.0×10^{-3} M concentration of the references solution is quite appropriate for a smooth functioning of the polymeric membrane system. It should be noted that a change in concentration of the internal solution is expected to change the potential difference on the internal solution/membrane interface and, consequently, the overall emf of the cell assembly.

Table 2. Optimization of membrane ingredients of the Zn^{2+} ion-selective electrode based on **L**

Sensor No.	Composition (%wt.)				Slope (mV per decade)	Concentration range (M)
	L	**additive**	**Plasticizer**	**PVC**		
1	0	0	BA, 69	31	5.5 ± 0.4	9.2×10^{-3} - 3.0×10^{-2}
2	1.0	0	BA, 68	31	10.4 ± 0.5	5.6×10^{-5} - 3.5×10^{-2}
3	2.0	0	BA, 67	31	14.1 ± 0.3	2.5×10^{-5} - 1.0×10^{-1}
4	4.0	0	BA, 66	30	15.7 ± 0.4	1.0×10^{-5} - 1.0×10^{-1}
5	6.0	0	BA, 64	30	14.4 ± 0.4	1.9×10^{-5} - 1.0×10^{-1}
6	4.0	1.0, KTpCIPB	BA, 65	30	18.0 ± 0.7	1.0×10^{-6} - 1.0×10^{-1}
7	4.0	1.5, KTpCIPB	BA, 63.5	30	23.6 ± 0.3	4.0×10^{-6} - 1.0×10^{-1}
8	**5.0**	**1.0, KTpCIPB**	**NPOE, 64**	**30**	**29.8 ± 0.2**	**2.0×10^{-7} - 1.0×10^{-1}**
9	4.0	2.0, KTpCIPB	DBP, 64	30	16.4 ± 0.6	7.5×10^{-6} - 1.0×10^{-1}
10	4.0	2.0, KTpCIPB	DOP, 64	30	$21..2 \pm 0.5$	3.7×10^{-6} - 1.0×10^{-1}

### 3.4. Response Characteristics of the Membrane Electrode

Optimum conditioning time for the PME 1.0×10^{-2} M $Zn(NO_3)_2$ solution was found to be 24 h. They then generate stable potentials when placed in contact with Zn^{2+} solutions.

The critical response characteristics of the proposed electrodes were assessed according to IUPAC recommendation [42]. The emf response of the polymeric membrane electrode (Fig. 2) indicates their Nernstian behavior over a wide concentrations range. The slopes and linear ranges of the resulting emf-p Zn^{2+} graphs are given in Table 3. The limits of detection, defined as the calibration of Zinc ion obtained when the linear regions of the calibration graphs are extrapolated to the baseline potentials, are also included in Table 3.

For analytical applications, the response time of a membrane sensor is an important factor. The static response time of the electrode tested by measuring the average time required to achieve a potential within ±1 mV of the final steady state potential upon

successive immersion of a series of Zn^{2+} ions, each having a tenfold difference in concentrations, was within <13 s for Zn^{2+} concentrations<10×10^{-3} M (Fig. 3).

Furthermore, the prepared electrode could be used frequently for at 4 months, without any measurable divergence.
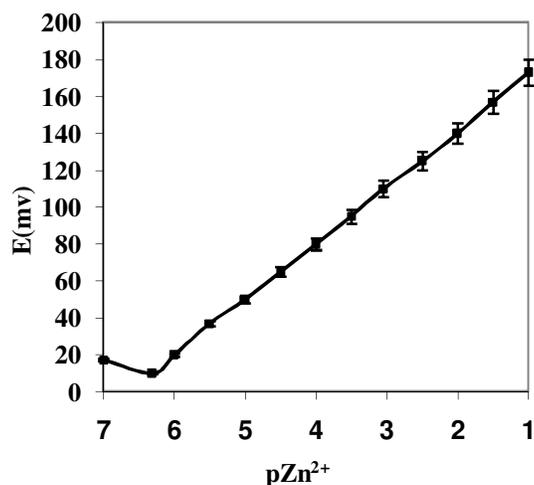
Fig. 2. Calibration curve of Zn^{2+} Ion selective electrode; Linearity range: 2.0×10^{-7}-1.0×10^{-1} M
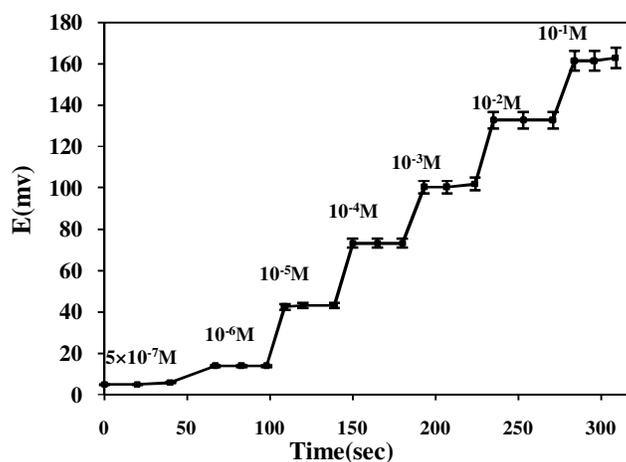
**Fig. 3.** Dynamic response time of the proposed sensor for step changes in the concentration of Zn^{2+}

3.5. Effect of pH of the Test Solution

The influences of the pH of the test solution on the potential response of the electrode in the presence of 1.0×10^{-3} M Zn^{2+} ion are shown in (Fig. 4). The results are depicted as can be seen; the potential remains fairly constant in the pH range of 3.0-7.5 (the pH of the solutions

was adjusted by either HCl or NaOH solutions). As can be seen, the potential remains constant from to beyond which it changes considerably. At higher pH values hydroxy complexes of Zn^{2+} can be formed on the other hand, at lower pH values the decrease in potential is due to the protonations of ionophore.

Table 3. Response characteristics of the copper ion-selective electrodes

	Slope (mV decade^{-1})	Linear Range (M)	LOD (M)	Response Time (s)
Zn(II) ISE	29.8±0.2	2.0×10^{-7}-1.0×10^{-1}	9.6×10^{-8}	<13
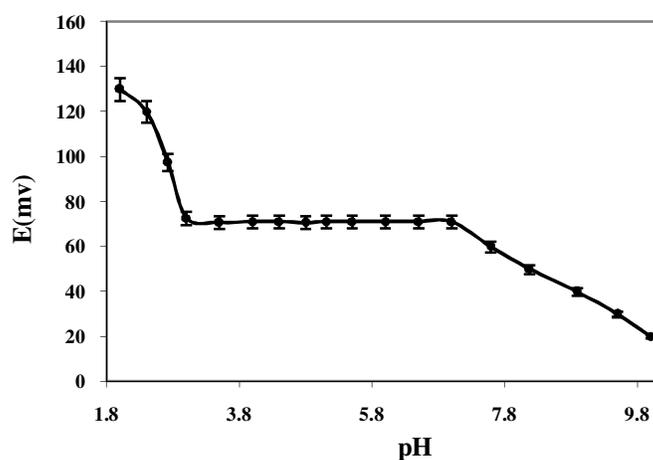
Fig. 4. Influences of pH of the test solution on the potential response of electrode in the presence of 1.0×10^{-3} M Zn^{2+}

3.6. Selectivity Coefficients

The influence of interfering ions on the potential response behavior of the ion selective membrane electrodes is usually described in terms of the selectivity coefficient [43-46].

Potentiometric selectivity coefficient, $K_{Zn,B}^{pot}$, describing the preference by the membrane for an interfering ion relative to Zn^{2+}, were determined by separated solutions method [44] To determine the selectivity coefficients by the separated solution method, [46-49] the emf-pM^{n+} plots were obtained for the Zn^{2+} and the interfering ion (over a pM^{n+} range of 2-6), separately, using the proposed electrode system. Then by using a pair of values of primary (a_A) and interfering (a_B) ion concentrations at which the electrode takes the same potential in separate solutions (isopotential concentrations) and equation $K_{Zn,B}^{pot} = a_A \Big/ a_B^{2/z}$ (where z is the charge of interfering ion), the selectivity coefficient $K_{Zn,B}^{pot}$ was determined.

The resulting values are listed in Table 4. It is interesting to note that there is a satisfactory agreement between the trends observed for the selectivity coefficients reported in Table 4 with the data shown in Fig. 1.

The selectivity coefficient patterns presented in Table 4 clearly indicate that the electrodes are highly selective to Zn^{2+} over other cations tested, the selectivity coefficient are on the order of 10^{-3} or lower (except Ce^{3+} and Cu^{2+}), which seems to indicate that these cations have negligible impact on the functionality of the Zn^{2+}.

Table 4. Selectivity coefficients of various interfering cations for the Zn^{2+} sensor, calculated by SSM

Cation	$K^{pot}_{Zn,B}$	Cation	$K^{pot}_{Zn,B}$
Ag^+	3.5×10^{-4}	Hg^{2+}	4.0×10^{-3}
Tl^+	1.9×10^{-4}	Co^{2+}	3.8×10^{-3}
Pb^{2+}	4.3×10^{-5}	Cd^{2+}	2.9×10^{-3}
Mg^{2+}	4.2×10^{-5}	Al^{3+}	1.1×10^{-4}
Na^+	6.7×10^{-3}	Ca^{2+}	4.4×10^{-5}
Cu^{2+}	8.1×10^{-2}	Cr^{3+}	5.7×10^{-4}
K^+	5.1×10^{-5}	La^{3+}	6.7×10^{-5}
Cs^+	9.7×10^{-4}	Ce^{3+}	5.5×10^{-2}
Bi^{3+}	7.4×10^{-4}	Ni^{2+}	7.8×10^{-4}

3.7. Comparison with the pervious works

In Table 5 linear dynamic range, slope and detection limit of different Zn^{2+} ion-selective electrodes based on different ionophores are compared with those of this work. The data show that the proposed sensor is comparable and has a lower limit of detection, a wide dynamic range of application when compared with other sensors [10–17,32].

3.8. Analytical Applications of the Sensor

The optimized Zn^{2+} selective electrode was found to work well under laboratory conditions. To assess the applicability of the proposed electrode to real samples, an attempt was made to determine zinc content of synthetic solutions and electroplating industrial waste water samples.

For synthetic solution, two solutions of Zn^{2+} in the presence of different concentration of other ions were prepared. In the case of electroplating waste water, 1.0 mL of each sample was taken and diluted to 50.0 mL by acetic acid/sodium acetate buffer (pH 4.0) and distilled water. The zinc content of the sample solutions was determined by the proposed zinc

selective electrode using the calibration method. The results are summarized in Table 6. As it is seen from Table 6, the results determined with the proposed electrode are in good agreement with those obtained by inductivity coupled plasma atomic emission spectroscopy (ICP-AES) method.

Table 5. Comparison of the characteristics of the proposed sensor with those of the previously reported Zn^{2+} sensor

Ionophore	L.O.D (M)	Dynamic range (M)	Slope (mV decade^{-1})	Ref.
N,N-Bis(acetylacetone)ethylenediimine	8.9×10^{-7}	1.0×10^{-6}-1.0×10^{-1}	30	11
DBDA15C4	3.0×10^{-5}	5.0×10^{-5}-1.0×10^{-1}	22	12
Bzo2Me2Ph2(16)hexaeneN4	2.24×10^{-6}	2.8×10^{-6}-1.0×10^{-1}	28.5	13
5,10,15,20-Tertraphenyl-21H,23H-porphine	-	6.2×10^{-6}-1.0×10^{-1}	29	14
1,13-diaza-2,3;11,12;15,18-tribenzo-4,7,10-trioxacyclononaoctane-14,19-dione	5.0×10^{-5}	9.0×10^{-5}-1.0×10^{-1}	30	15
Thiazolidin-4-one	8.5×10^{-7}	1.0×10^{-6}-1.0×10^{-2}	29.3	16
N,N′-phenylenebis (salicylideaminato)	2.6×10^{-7}	5.0×10^{-7}-1.0×10^{-1}	29.4	17
N,N-bis (2hydroxy -4-etoxybenzaldehyde)-2,6-di amino pyridine	7.9×10^{-8}	1.0×10^{-7}-1.0×10^{-1}	29.5	32
Tris(3-(2-hydroxy-acetophenone)propyl)amine)	9.6×10^{-8}	2.0×10^{-7}-1.0×10^{-1}	29.8±0.2	**This work**

The other analytical application of Zn^{2+} sensor based on L was tested by the potentiometric titration of Zn^{2+} with EDTA solution. A 50 mL (10^{-3} M) of testing solution was titrated with 10^{-2} M EDTA solution. With the addition of EDTA solution into the testing solution, the Zn^{2+} concentration and the output voltage were decreased because of the formation of Zn-EDTA complex. Results exhibit that the end point represent the stochiometric formulation of Zn-EDTA complex and it also suggests that the almost all of the Zinc ions are used up in the formation of Zn-EDTA complex and so after the equivalent point, the potential response was found to almost be constant. It is therefore suggested that the proposed sensor based on L can successfully be used as an indicator electrode for the determination of Zn^{2+} by potentiometric titration.

Table 6. Comparison of results from the determination of the Zn^{2+} in synthetic and real samples by the proposed method and that of ICP

Sample	Zn^{2+} content (M)[a]	
	ISE	**ICP**
Synthetic solution		
Sample 1	$5.5(\pm0.08)\times10^{-5}$	$6.6(\pm0.03)\times10^{-5}$
Sample 2	$2.3(\pm0.04)\times10^{-6}$	$2.0(\pm0.05)\times10^{-6}$
Electroplating industrial Wastewater		
Sample 1	$7.9(\pm0.04)\times10^{-4}$	$6.3(\pm0.02)\times10^{-4}$
Sample 2	$3.2(\pm0.07)\times10^{-4}$	$3.4(\pm0.05)\times10^{-4}$

[a] Average of three determinations ± S.D

4. CONCLUSIONS

The membrane assembly prepared using Tris(3-(2-hydroxyacetophenone) propyl) amine) **(L)** as membrane ingredient with plasticizers (NPOE) and anion excluder (KTpCIPB) exhibited linearity over a wide concentration range (2.0×10^{-7}-1.0×10^{-1}M) with Nernstian slope (29.8 ± 0.2 mV/decade of activity), fast response time (13s) and selectivity (of the order of 10^{-3} and 10^{-4}) over a number of cations. The Zinc ion-selective electrode can be employed as an indicator electrode in potentiometric titration and the determination of Zinc ions in real samples.

REFERENCES

[1] J. M. Berg, and Y. Shi, Science 271 (1996) 1081.

[2] J. H. Weiss, S. L. Sensi, and J. Y. Koh, Trends Pharmacol. Sci. 21 (2000) 395.

[3] T. Budde, A. Minta, J. A. White, and A. R. Kay, Neuroscience 79 (1997) 347.

[4] P. Kaur, S. Kaur, A. Mahajan, and K. Singh, Inorg. Chem. Commun. 11 (2008) 626.

[5] N. R. Gupta, S. Mittal, S. Kumar, and S. K. A. Kumar, Mater. Sci. Eng. C 28 (2008) 1025.

[6] Q. Li, X. H. Zhao, Q. Z. Lv, and G. G. Liu, Sep. Purif. Technol. 55 (2007) 76.

[7] P. Wilhartitz, S. Dreer, R. Krismer, and O. Bobleter, Microchim. Acta 125 (1997) 45.

[8]   M. Hosseini, Z. Vaezi, M. R. Ganjali, F. Faridbod, S. Dehghan Abkenar, K. Alizadeh, and   M. Salavati-Niasari, Spectrochim. Acta Part A 75 (2010) 978.

[9]   Q. J. Ma, X. B. Zhang, Y. Zhao, C. Y. Li, Z. X. Han, G. L. Shen, and R. Q. Yu, Spectrochim. Acta A 71 (2009) 1683.

[10]   R. Dumkiewicz, C. Wardak, and S. Zareba, Analyst 125 (2000) 527.

[11]   V. K. Gupta, S. Agarwal, A. Jakob and H. Lang, Sens. Actuators B 114 (2006) 812.

[12]   A. R. Fakari, M. Alaghemand, and M. Shamsipur, Anal. Lett. 33 (2000) 2169.

[13]   A. K. Singh, A. K. Jain, P. Saxen, and S. Mehta, Electroanalysis 18 (2006) 1186.

[14]   V. K. Gupta, A. K. Jain, R. Mangla, and P. Kumar, Electroanalysis 13 (2001) 1036.

[15]   M. Shamsipur, S. Rouhani, M. R. Ganjali, H. Sharghi, and H. Eshghi, Sens. Actuators B 59 (1999) 30.

[16]   M. R. Ganjali, H. A. Zamani, P. Norouzi, M. Adib, M. Rezapour, and M. Aceedy, Bull. Kor. Chem. Soc. 26 (2005) 579.

[17]   M. Hosseini, S. Dehghan Abkenar, M.R. Ganjali and F. Faridbod, Mater. Sci. Eng. C 31 (2011) 428.

[18]   M. Hosseini, M. R. Ganjali, B. Veismohammadi, S. Riahi, P. Norouzi, M. Salavati-Niasari and S. D. Abkenar, Anal. Lett. 42 (2009) 1029.

[19]   M. Hosseini, H. B. Sadeghi, M. Rahimi, M. Salavati-Niasari, S. D. Abkenar, K. Alizadeh, and M. R. Ganjali, Electroanalysis 21 (2009) 859.

[20]   M. R. Ganjali, A. Ghesmi, M. Hosseini, M. R. Pourjavid, M. Rezapour, M. Shamsipur, and M. Salavati-Niasari, Sens. Actuators B 105 (2005) 334.

[21]   M. R. Ganjali, J. Ravanshad, M. Hosseini, M. Salavati-Niasari, M. R. Pourjavid and M.R. Baezzat, Electroanalysis 16 (2004) 1771.

[22]   M. Hosseini, Z. Vaezi, M. R. Ganjali, F. Faridbod, S. D. Abkenar, K. Alizadeh, M. Salavati-Niasari, Spectrochim. Acta A 75 (2010) 978.

[23]   M. Shamsipur, A. Soleymanpour, M. Akhond, H. Sharghi and A.R. Massah, Talanta 58 (2002) 237.

[24]   M. Shamsipur, M. Hosseini, K. Alizadeh, M. F. Mousavi, A. Garau, V. Lippolis, and A. Yari, Anal. Chem. 77 (2005) 276.

[25]   S. Kamata, A. Bhale, Y. Fukunaga, and A. Murata, Anal. Chem. 60 (1988) 2464.

[26]   S. Banthia, and A. Samanta, J. Phys. Chem. B 106 (2002) 5572.

[27]   M. Shamsipur, K. Alizadeh, M. Hosseini, C. Caltagirone and V. Lippolis, Sens. Actuators B 113 (2006) 892.

[28]   S. Banthia and A. Samanta, J. Phys. Chem. B 110 (2006) 6437.

[29]   P. Roy, K. Dhara, M. Manassero, and P. Banerjee, Inorg. Chim. Acta 362 (2009) 2927.

[30]   F. Mizani, M. Majdi, and S. Taghvaei-Ganjali, Anal. Bioanal. Electrochem. 4 (2012) 529.

[31]   F. Mizani, M. Shamsipur, M. R. Yaftian, and D. Matt, Anal. Sci. 29 (2013) 361.

[32] F. Mizani, and M. Ziaeiha, Int. J. Electrochem. Sci. 7 (2012) 7770.

[33] H. A. Zamani, A. Imani, A. Arvinfar, F. Rahimi, M. R. Ganjali, F. Faridbod and S. Meghdadi, Mater. Sci. Eng. C 31 (2011) 588.

[34] F. Mizani, M.R. Ganjali, F. Faridbod and S. Esmaeilnia, Int. J. Electrochem. Sci., 8 (2013) 10473.

[35] F. Faridbod, F. Mizani, M. R. Ganjali, and, P. Norouzi, Int. J. Electrochem. Sci. 7 (2013) 7643.

[36] M. Javanbakht, S. E. Fard, A. Mohammadi, M. Abdouss, M. R. Ganjali, P. Norouzi and L. Safaraliee, Anal. Chim. Acta 612 (2008) 65.

[37] D. Ammann, E. Pretsch, W. Simon, E. Lindner, A. Bezegh, and E. Poungor, Anal. Chim. Acta 171 (1985) 119.

[38] X. Yang, N. Kumar, H. Chi, D. D. Hibbert, and P. N. W. Alexander, Electroanalysis 9 (1997) 549.

[39] D. Ammann, E. Pretsch, W. Simon, E. Lindner, A. Bezegh, and E. Poungor, Anal. Chim. Acta 171 (1985) 119.

[40] F. Faridbod, M. R. Ganjali, B. Larijani, P. Norouzi, S. Riahi and F. S. Mirnaghi, Sensors 7 (2007) 3119.

[41] R. Eugster, T. M. Gehring, W. E. Morf, U. E. Spichiger, and W. Simon, Anal. Chem. 63 (1991) 2285.

[42] IUPAC Analytical Chemistry Division Commission on Analytical Nomenclature, Pure Appl. Chem. 48 (1976) 127.

[43] Y. Umezawa, K. Umezawa, and H. Sato, Pure Appl. Chem. 62 (1995) 427.

[44] H. A. Zamani, M. R. Ganjali, P. Norouzi and M. Adib, Mater. Sci. Eng. C 28 (2008) 157.

[45] H. A. Zamani, M. R. Ganjali and M. Adib, Sensor Lett. 4 (2006) 345.

[46] IUPAC Analytical Chemistry Division Commission on Analytical Nomenclature, J. Pure Appl. Chem. 67 (1995) 507.

[47] G. G. Guilbault, R.A. Durst, M. S. Frant, H. Freiser, E. H. Hansen, T. S. Light, E. Pungor, G. Rechnitz, N. M. Rice, T. J. Rohm, W. Simon, and J. D. R. Thomas, Pure Appl. Chem. 48 (1976) 127.

[48] R. P. Buck, and E. Lindner, Pure Appl. Chem. 66 (1994) 2527.

[49] C. Macca, Electroanalysis 15 (2003) 997.