Zn²⁺ PVC-based Membrane Sensor Based on 3-[(2-Furylmethylene)amino]-2-thioxo-1,3-thiazolidin-4-one

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The 3-[(2-furylmethylene)amino]-2-thioxo-1,3-thiazolidin-4-one (FTT) was used as an excellent ionophore in construction of a Zn²⁺ PVC-based membrane sensor. The best performance was obtained with a membrane composition of 30% poly(vinyl chloride), 62% nitrobenzen (NB), 3% FTT and 5% sodium tetraphenyl borate (TBP). This membrane sensor shows very good selectivity and sensitivity towards Zn²⁺ over a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. The membrane sensor revealed a great enhancement in selectivity coefficients for Zn²⁺ ions, in comparison to the previously reported Zn²⁺ membrane sensors. Theoretical studies also showed the selective interaction of TFF and Zn²⁺ ions. The proposed membrane sensor exhibits a Nernstian behavior (with slope of 29.3 ± 0.3 mV per decade) over a wide concentration range $(1.0 \times 10^{-6}\text{-}1.0 \times 10^{-2})$ with a detection limit of 8.5×10^{-7} M (52 ng mL⁻¹). It shows relatively fast response time, in the whole concentration range (< 20 s), and can be used for at least 10 weeks in a pH range of 3.0-7.0. The proposed membrane sensor was successfully used in direct determination of Zn²⁺ ions in wastewater of industrial zinc electroplating companies, and also as an indicator electrode in titration with EDTA.

Key Words : 3-[(2-Furylmethylene)amino]-2-thioxo-1,3-thiazolidin-4-one, Zn²⁺ membrane sensor, Potentiometry, PVC

Introduction

Zinc is one of the transition metals, which is used in paint, electroplating, pharmaceutical and chemical industries, and thus occurs widely in the environment. Zinc is a toxic elements, and its monitoring in biological, food, and in environmental sample is very important.

During the last decade, there has been a renewed resurgence in developing potentiometric membrane electrodes as devices for rapid, accurate, low cost and non destructive analysis of different samples with small volume samples.

In recent years, a number of Zn²⁺ membrane sensors based on different ion carriers have been reported in the literature.[1-9] The main problem of these sensors is relatively low affinity for Zn²⁺ with respect to other metal ions such as Na⁺, Mg²⁺, Co²⁺, etc. In this work we wish to introduce a highly selective Zn²⁺ membrane sensor based on 3-[(2-furylmethyl-ene)amino]-2-thioxo-1,3-thiazolidin-4-one (Fig. 1) for monitoring of Zn²⁺ in industrial samples.

Experimental Section

Reagents. Reagent grade dibutyl phthalate (DBP), nitrobenzene (NB), benzyl acetate (BA), sodium tetraphenyl borate (NaTPB), 2-furancarbaldehyde, acetic acid, ethanol, high relative molecular weight (PVC) and tetrahydrofuran (THF) were purchased from Merck or Aldrich, and used as received. The chloride and nitrate salts of all the cations used (all from Merck or Aldrich) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. Triply distilled de-ionized water was used throughout.

Synthesis of the ionophore. The procedure for the preparation of 3-[(2-furylmethylene)amino]-2-hioxo-1,3-thiazolidin-4-oneis as follows. A mixture of 2-furancarbaldehyde (0.01 mol, 0.96 g), N-aminorhodanine (0.01 mol, 1.48 g) and a catalytic amount of acetic acid was refluxed in absolute ethanol (20 mL) for 1 h. The reaction mixture was then cooled to the room temperature and the yellow microcrystals of the product were filtered, washed with ethanol, and dried under the reduced pressure.

C, 2.2 g, yield 98%. m.p. 119-121. IR (KBr) (v_{max}/cm⁻¹): 1736 (C=O), 1608, 1470, 1312, 1225, 1018, 881, 765. MS, m/z (%): 226 (M⁺, 59). Anal. Calcd. for $C_8H_6N_2O_2S_2$ (226.28): C, 42.46; H, 2.67; N, 12.38. Found: C, 42.5; H,
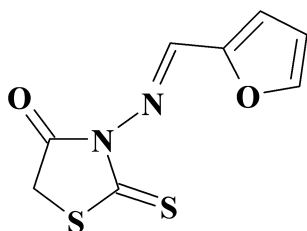

Figure 1. Structure of FTT.

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2.7; N, 12.3%. ^{1}H NMR (250.1 MHz, DMSO-d_6 solution): δ 4.33 (2H, s, CH_2), 6.79 (1H, dd, J = 3.5 Hz and J = 1.8 Hz, CH), 7.36 (1 H, d, J = 3.5 Hz, CH), 8.04 (1H, d, J = 1.8 Hz, CH), 8.55 (1 H, s, N=CH). ^{13}C NMR (62.5 MHz, DMSO-d_6 solution): δ 46.65 (CH_2), 108.28, 113.65, 143.21, and 148.23 (4 CH), 154.25 (C), 167.32 (C=O), 178.45 (C=S).

Electrode preparation. The general procedure to prepare the PVC membrane was thoroughly mixing 30 mg the powdered PVC, and 62 mg plasticizer NB in 10 mL of THF. To this mixture was added, 5 mg NaTPB and 3 mg ionophore TFF and the solution was mixed well. The resulting mixture was transferred into a glass dish of 2 cm in diameter. The THF content of the mixture was evaporated slowly, until an oily concentrated mixture was obtained. A Pyrex tube (3-5 mm o.d.) was dipped into the mixture for about 10 s, so that a non-transparent membrane of about 0.3 mm thickness was formed.[10-13] The tube was then pulled out of the solution and kept at room temperature for 12 h. The tube was filled with an internal filling solution (1.0×10^{-3} M $ZnCl_2$). The electrode was finally conditioned for 36 h by soaking in a 1.0×10^{-3} M Zn^{2+} nitrate solution. A silver/ silver chloride coated wire was used as an internal reference electrode.

EMF measurements. All emf measurements were carried out with the following assembly:

Ag–AgCl | 1.0×10^{-3} M $ZnCl_2$ | PVC membrane:

test solution | Hg–Hg_2Cl_2, KCl (satd).
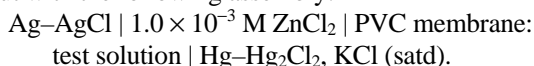
A Corning ion analyser 250 pH/mV meter was used for the potential measurements at 25.0 °C. Activities were calculated according to the Debye–Huckel procedure.[14]

Results and Discussion

Many experimental and theoretical investigations have been carried out for a better understanding of the fundamental interactions between metal ions and neutral molecules, and their relationship to molecular recognition. Computational models, capable of reliably predicting ligand selectivity in a variety of cations, have been shown to be valuable tools for the advancement of practical works.[15-18] In order to have a clear picture of the selectivity of (FTT) for various metal ions, in this work, we investigated its binding to Li^+, K^+, Ca^{2+}, La^{3+}, Sr^{2+}, Be^{2+}, Cs^+, Cd^{2+}, and Zn^{2+} ions by using ab initio theoretical calculations. The influence of the nature, size and charge of metal ions on the complexation reaction with the neutral ligand is explained on the basis of the calculation of gas – phase binding energies.

The molecular structures of the uncomplexed FTT and its complexes with Zn^{2+} and other metal ions were optimized using the lanl2mb basis set for all atoms at restricted Hartree Fock (RHF) level. No molecular symmetry constraint was applied. Rather, full optimization of all bond lengths, angles and torsion angles was carried out using the Gaussian 98 program.[19] The binding energy (DE) was calculated with the enlarged basis sets using equation (1):

$$\Delta E = E_{complex} - (E_{ligand} + E_{cation}) \qquad (1)$$

Table 1. Binding energy of complexes of the different metal ions with FTT

| Metal ion	Total energy of Metal ion/Hartree	Total energy of the complex/Hartree	Binding energy (ΔE)[a]/kcalmol^{-1}
Zn^{2+}	−62.6454	−640.6321	−269.4
Cd^{2+}	−45.7232	−623.6654	−239.4
Ca^{2+}	−35.6124	−613.4141	−147.5
La^{3+}	−29.5441	−607.5722	−292.6
Sr^{2+}	−29.5426	−607.3073	−124.6
K^+	−27.6374	−605.2845	−52.8
Cs^+	−19.4811	−597.1074	−37.9
Be^{2+}	−13.4423	−591.1854	−111.7
Li^+	−7.1454	−584.5921	−71.6

[a]The total energy of the uncomplexed ligand is −577.57 Hartree.

Where, $E_{complex}$, E_{ligand} and E_{cation} are the total energies of the complex, uncomplexed FTT and metal ion, respectively.

Optimization of the uncomplexed FTT was also carried out with the semi-empirical PM_3 method using Hyper Chem software (Version 6.01). No adequate parameterization of the metal ions was available in PM_3, so that semi-empirical calculations could not be carried out on the complexes.

Table 1 summarizes the theoretical data about the stability of the FTT complexes with Li^+, K^+, Ca^{2+}, La^{3+}, Cs^+, Sr^{2+}, Be^{2+}, Cd^{2+}, and Zn^{2+} ions. Inspection of Table 1 reveals that the cation binding energy with FTT shows a pronounced dependence on the nature of metal ions used. In fact, the stability of the resulting complexes is expected to decrease in the order of:

$$La^{3+} > Zn^{2+} > Cd^{2+} > Ca^{2+} > Sr^{2+} > Be^{2+} > Li^+ > K^+ > Cs^+$$
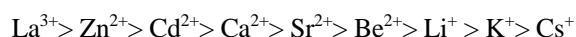
Althogh there is not a complete coordination between this pattern, and that obtained from the selectivity determination experiments, specially in the case of La^{3+}, which could have risen from the approximations made in the calculations, like the assumption of the reactions to take place in gas phase, ignoring the type of the solvent, the consequent solvation energies, and the extent of solvation, which have a great impact on the selectivity of a membrane, the pattern still partially in coordinance with the selectivity patterns.

The optimized structures of uncomplexed FTT and its Zn^{2+}-complex are shown in Figures 2(a and b) and some of their selected geometric parameters are summarized in Table 2, As it is seen from Figure 2b, FTT is not coplanar in the complexed form. It is immediately obvious that the optimized free FTT structure reveled that the S group and the O and N groups to be far enough from each other to minimize the possible intermolecular repulsive forces.

So, that all two donating atoms of the FTT molecule will be in suitable proximity of the central metal ion for proper binding interactions. Of course, the contribution of a change in solvation–desolvation energies of the metal ions, in both aqueous and membrane phases on the stability order of the deferent metal ions' complexes with FTT can not be ignored. The obtained results revealed that among the different metal ions tested, only Zn^{2+} ion posses the desired
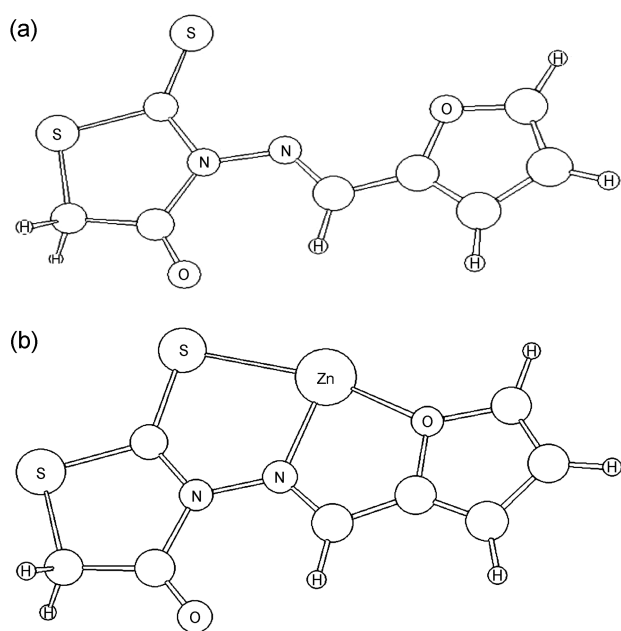
Figure 2. Optimized structure of uncomplexed FTT (a) and **Zn(II)-complex** (b).

Figure 3. Potential responses of the different ion-selective electrodes based on FTT.

energy changes for the FTT.

Due to the very low solubility of FTT in water and the existence of three donating atoms (one nitrogen and two donating sulfur) in its structure, FTT seemed to be a potential ionophore for transition and heavy metal ions in the PVC-based membrane sensors. Thus, in preliminary experiments, it was used to prepare a number of PVC membrane ion-selective electrodes for a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. The potential responses of the most sensitive sensors are depicted in Figure 3. As can be seen from Figure 3, among the cations used, those of hard acid character (*i.e.* alkali, alkaline earth ions),[20] show negligible responses due to their weak interactions with the nitrogen and sulfur atoms of the ionophore as soft bases. On the other hand, the metal ions of soft acid character (*i.e.* Zn^{2+}, Hg^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, and Pb^{2+})[20] and, especially, Zn^{2+} show the most sensitive potential responses in the series, among which Zn^{2+} ion provides the most suitable ion-selective electrode. It is thus obvious that the Zn^{2+} ions are more easily attracted to the PVC–FTT membrane which results in a Nernstian potential–concentration response over a wide range.

Since the sensitivity and selectivity obtained for a given ion carrier depend significantly on the membrane ingre-
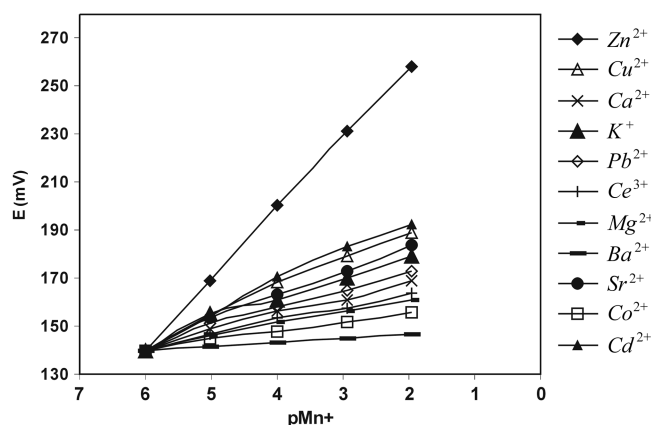
dients and the nature of solvent mediators and additives used,[10-13,21] we investigated the influence of membrane composition on the potential response of the Zn^{2+} selective electrode and the results are given in Table 3. As can be seen from Table 3, increasing the amount of FTT, up to a value of 3%, resulted in the best sensitivity and linear range, although the slope of emf versus log concentration plot in this case is lower than the expected Nernstian value (nos. 1-4). However, addition of 5% NaTPB will increase the sensitivity of the electrode response considerably (no. 5), and the membrane sensor exhibits a Nernstian behavior. It is well known that the presence of lipophilic anions as an additive in cation-selective membrane electrodes not only diminishes the ohmic resistance[22] and enhances the response behavior

Table 3. Optimization of membrane ingredients

Number of membrane	Composition(wt.%)				Slope (mV/decade)
	PVC	Plasticizer	FTT	NaTPB	
1	30	NB, 68	2	0	15.6 ± 0.4
2	30	NB, 67	3	0	17.3 ± 0.3
3	30	NB, 66	4	0	16.4 ± 0.5
4	30	NB, 66	3	1	19.5 ± 0.4
5	30	NB, 64	3	3	23.7 ± 0.6
6	30	NB, 62	3	5	29.6 ± 0.4
7	30	DBP, 62	3	5	23.5 ± 0.5
8	30	BA, 62	3	5	23.4 ± 0.4
9	30	NB, 67	3	–	19.4 ± 0.4
10	30	NB, 65	–	5	5.0 ± 0.3

Table 2. Selective geometric parameters for free FTT and its Zn^{2+} complex[a]

	< SCN	< NNC	< CCN	Torsion angle of < CNNC	Atomic Charge N	Atomic Charge S	O–Zn	S–Zn	< SZnO
Ligand Free	129.06	116.32	118.67	179.10	−0.08 −0.19	−0.36	–	–	–
Complex with Zn^{+2}	126.80	112.95	114.61	−180.00	−0.23 −0.16	−0.23	1.98	2.62	165.98

[a]Distances in A°, angles in degrees.
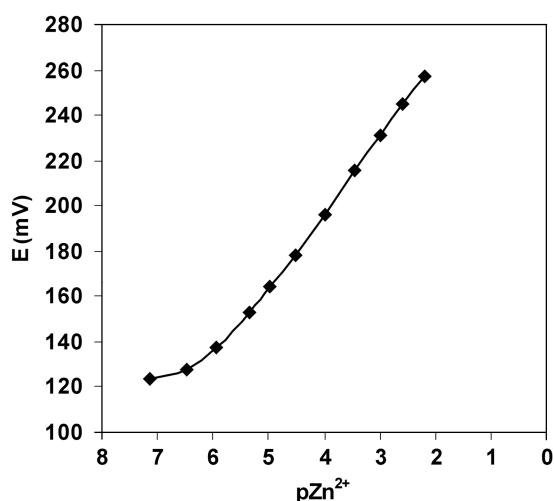
Figure 4. Calibration curves of the Zn^{2+} membrane sensor based on FTT.

Figure 5. Dynamic response time of the Zn^{2+} membrane sensor for step changes in the concentration of Zn^{2+} solutions: A) 1.0×10^{-6} M, B) 1.0×10^{-5} M, C) 1.0×10^{-4} M, D) 1.0×10^{-3} M, E) 1.0×10^{-2} M.

Figure 6. Effect of the pH of the test solution (1.0×10^{-3} M of Zn^{2+}) on the potential response of the Zn^{2+} ion-selective electrode.

and selectivity,[23] but also, in cases where the extraction capability is poor, increases the sensitivity of the membrane electrodes.[21-23] In order to make sure that the membrane selectivity arises only from the used ionophore, and not from the additive, we did our experiments by making a membrane containing all of the membrane ingredients except the ionophore. (No. 10) the potential responses of this membrane proved our hypothesis especially when compared with a membrane lacking the lipophilic additive, but incorporating the ionophore.

Table 3 shows that among the membranes 6-8, the membrane 6 containing NB with higher polarity than BA and DBP, exhibits a nice Nernstian behavior. However the best performance was obtained with membrane sensor containing 30% PVC, 62% NB, 3% FTT, and 5% NaTPB.

The critical response characteristics of the Zn^{2+} PVC-based membrane sensor were assessed according to IUPAC recommendations.[24] The emf response of the membrane at varying activity of Zn^{2+} (Fig. 4) indicates a rectilinear range from 1.0×10^{-2} to 1.0×10^{-6} M. The slope of the calibration curve was 29.3 ± 0.3 mV per decade of Zn^{2+} concentration. The limit of detection of the proposed sensor, as determined from the intersection of the two extrapolated segments of the calibration graph, was 8.5×10^{-7} M. The standard deviation of nine replicate measurements was ± 0.7 mV.

The average time required for the Zn^{2+} sensor to reach a potential within ± 1 mV of the final equilibrium value after successive immersion in a series of Zn^{2+} solutions, each having a 10-fold difference in concentration, was measured. The dynamic response time thus obtained was less than 20 s in the whole concentration ranges (Fig. 5). The potentials remained constant for more than 4 min, after which only a very slow divergence was recorded (± 2.5 mV).

Life time of the proposed sensor was evaluated by the measuring of the slope of the three sensors during ten weeks. Each sensor was used for one hour per day (after using, it washed and dried). After nine weeks, the slopes of Zn^{2+} ion-selective membrane sensors, began to reduce (from 28.9 to
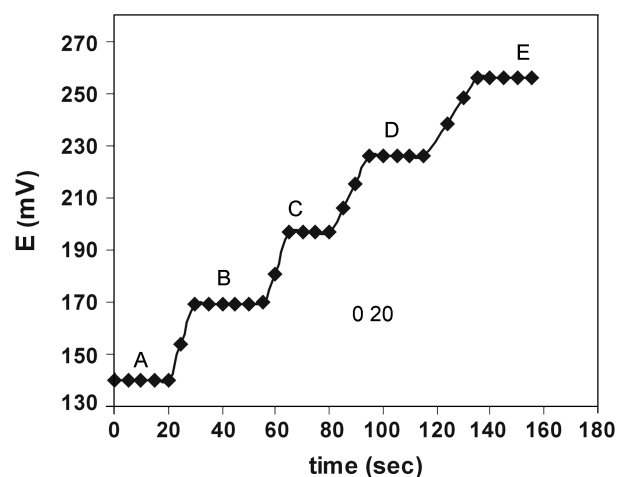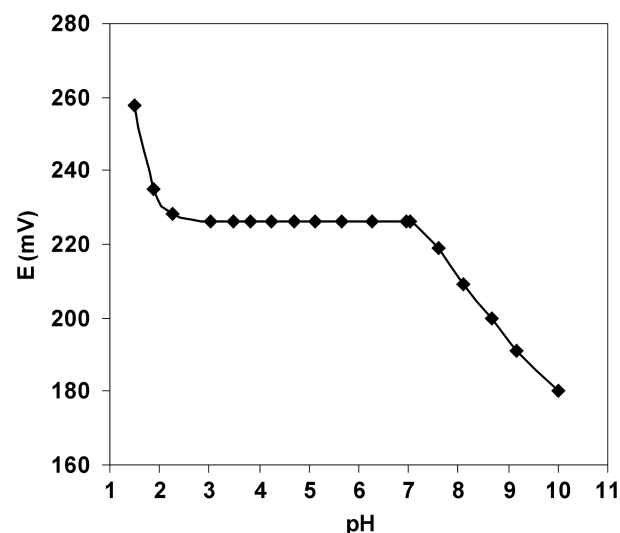
26.2 mV per decade).

The pH dependence of the Zn^{2+} membrane sensor at a concentration of 1.0×10^{-3} M was tested over the pH range 1.5-10.0, and the results are depicted in Figure 6. As it is seen from Figure 6, the potential response of the sensor is independent of pH in the range 3.0-7.0. At higher and lower pH than this range, potential was decreased and increased, respectively. The increasing in the potential is due to the responds of the membrane to hydronium ions (some protonation of ion carrier in the membrane). The decreasing in the potential is due to the formation of some hydroxy complexes of Zn^{2+} ions, that reduces the concentration of Zn^{2+} in solution.

The selectivity of the Zn^{2+} sensor was evaluated by the matched potential method.[25] The potentiometric selectivity coefficients of the sensor towards different ions (Zn^{2+}, Cu^{2+}, Ca^{2+}, K^+, Pb^{2+}, Ce^{3+}, Mg^{2+}, Ba^{2+}, Sr^{2+}, Co^{2+}, Cd^{2+}) was determined and the results are summarized in Table 4. As

Table 4. Selectivity coefficients of various interfering ions [M^{n+}]

Cation	$\log K_{Zn^{2+},M}^{MPM}$
Pb^{2+}	−3.35
Cu^{2+}	−2.90
Cd^{2+}	−2.76
Co^{2+}	−3.75
Ni^{2+}	−3.42
Mg^{2+}	−3.60
Sr^{2+}	−2.90
Ca^{2+}	−3.20
Ba^{2+}	−3.85
K^{+}	−3.25
Na^{+}	−3.60
Ce^{3+}	−3.52
La^{3+}	−3.44
Cr^{3+}	−2.76
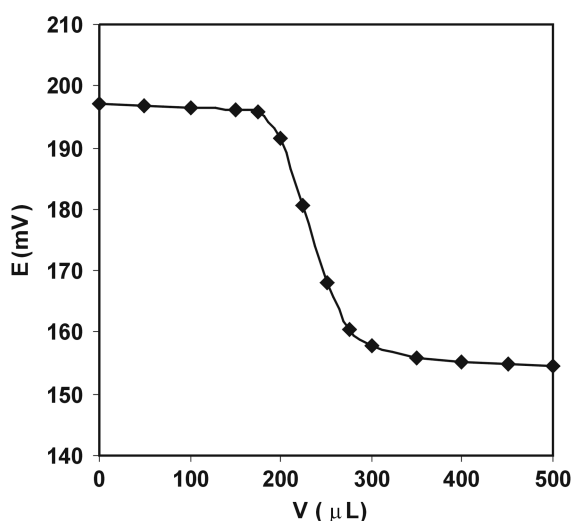
Figure 7. Potentiometric titration curve of 25.0 mL 1.0×10^{-4} M solution of Zn^{2+} with 1.0×10^{-2} M of EDTA.

Table 6. Determination of Zn^{2+} in three industrial wastewater samples using AAS and direct potentiometry with the membrane based on FTT

Sample No.	ISE (PPm)	AAS (PPm)
1	$1.43^a \pm 0.04$	$1.40^a \pm 0.02$
2	6.52 ± 0.03	6.45 ± 0.04
3	0.34 ± 0.02	0.32 ± 0.02

^{a}Results are based on three measurements

can be seen, with the exception of Cd^{2+}, for all cations used, the selectivity coefficients are in the order of 1.7×10^{-3} or smaller, indicating they would not significantly disturb the functioning of the Zn^{2+} sensor.

Table 5 compares the selectivity coefficients, detection limit, and dynamic linearity range of the proposed sensor with the best previously reported Zn^{2+} sensors.[1-4,6-9] As seen, the proposed sensor not only, in term of selectivity, but also, in terms of detection limit and linearity range is superior than the reported Zn^{2+} sensors.

The proposed Zn^{2+} membrane sensor was found to work well under laboratory conditions. It was successfully applied to the titration of a 1.0×10^{-4} M Zn^{2+} solution with a 1.0×10^{-2} M EDTA solution, and the resulting titration curve is shown in Figure 7. As it is seen, the amount of Zn^{2+} in solution can be determined with the good accuracy.

The electrode was also applied to the monitoring of Zn^{2+} in a wastewater industrial zinc electroplating sample. The results (Table 6) obtained with the sensor and those of atomic absorption spectrometric (AAS) analysis, were close enough for us conclude that the proposed sensor could be used in the environmental monitoring of Zn^{2+}.

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Table 5. Comparison of the selectivity coefficients, detection limit, and dynamic linearity range of different Zn^{2+} electrodes

Dynamic Linearity Range (M)	Detection Limit (M)	$\log K_{Zn^{2+},M}^{MPM}$													Ref
		Cr^{3+}	Ni^{2+}	La^{3+}	Ce^{3+}	Pb^{2+}	Cd^{2+}	Co^{2+}	Ba^{2+}	Sr^{2+}	Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}	
1.0×10^{-1}-5.6×10^{-6}	5.6×10^{-6}	–	−0.56	–	–	–	−0.47	−0.57	–	–	−1.50	−2.00	–	−2.30	1
1.0×10^{-1}-1.5×10^{-5}	–	−1.00	0.42	–	−0.96	−0.80	−0.39	−0.23	−0.77	−1.00	−0.96	−0.70	−0.68	−0.21	2
1.0×10^{-1}-5.0×10^{-5}	–	−1.74	−1.41	–	–	−1.72	−1.45	−1.45	−2.00	−1.90	−1.47	−1.72	−1.60	−1.30	3
1.0×10^{-1}-6.2×10^{-6}	–	−0.88	−0.51	–	−0.96	−0.92	−0.88	−0.51	−0.66	−0.85	−0.72	−0.20	−1.00	−0.23	4
1.0×10^{-1}-1.3×10^{-5}	–	−1.55	−1.70	–	–	−1.60	−1.22	−1.70	–	−1.60	−1.88	–	−1.70	−1.19	7
1.0×10^{-1}-5.0×10^{-5}	3.0×10^{-5}	−2.77	−1.74	–	–	−3.09	−2.67	−2.53	–	−2.65	−3.21	–	−3.70	–	8
1.0×10^{-1}-9.0×10^{-5}	5.0×10^{-5}	–	−2.74	–	–	−2.96	−2.08	−3.00	−2.57	−2.47	−2.34	–	−1.65	−1.58	9
1.0×10^{-2}-1.0×10^{-6}	8.5×10^{-7}	−2.76	−3.42	−3.44	−3.52	−3.35	−2.76	−3.75	−3.85	−2.90	−3.20	−3.60	−3.25	−3.60	This work

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