



ORIGINAL ARTICLE

Polyvinyl chloride-based 18-crown-6, dibenzo18-crown-6 and calix-[6]-arene zinc(II)-potentiometric sensors



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Abstract Polyvinyl chloride (PVC) based membranes of 18-crown-6 (18C6), dibenzo 18-crown-6 (DB18C6) and calix[6]arene (CAX), as ionophores, with dioctylphenylphosphonate (DOPP), bis(ethylhexyl)sebacate (DOS) dioctyl phthalate (DOP), 2-nitrophenyloctylether (*o*-NPOE) and didecylphthalate (DDP) as plasticizing solvent mediators are prepared and constructed for the determination of Zn(II). Of the 15 membranes constructed, only the PVC based membranes of DB18C6 and 18C6 ionophores with DOPP, as plasticizer, in the ratio (w/w) PVC:ionophore:DOPP (60:2:120) give the best results in terms of working concentration range (1.0×10^{-5} – 1.0×10^{-1} M) with a Nernstian slope of 29.0 mV/decade of activity for membrane composed of DOPP + DB18C6(1a) and (1.0×10^{-5} – 1.0×10^{-1} M) with a Nernstian slope of 30.0 mV/decade of activity for membrane composed of DOPP + 18C6(1b). The usable pH range of the sensors is 3.0–8.0, beyond which a drift in potential is observed. The response time of the sensors is ≤ 15 s with a lifetime of 2 months during which they can be used without any measurable divergence. The selectivity coefficient values indicate that the electrode is highly selective for Zn^{2+} over a number of other cations except Pb^{2+} and Ag^{+} . The electrodes have successfully been used to determine Zn(II) in real alloys and standard samples with a precision as relative standard deviation (RSD) $< 2\%$ for each of the cited electrodes. The results obtained by the proposed ISEs are in good agreement with the results obtained by direct flame AAS method.

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1. Introduction

Ion selective electrodes are being widely used in the environmental, industrial, agricultural and medical fields as they offer several advantages over other methods of analysis. The most attractive features of this technique are the speed with which samples can be analyzed, portability of the device, sample non-destruction, online monitoring, cost effectiveness and large measuring range. Some commercialized sensors for alkali

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and alkaline earth metals, halides, etc., are available, however, more efforts are required to develop ion-selective electrodes of commercial standards for heavy metal ions, which are toxic beyond a certain concentration level.

Besides its carcinogenic and mutagenic nature, the toxicity of zinc arises from its synergistic/antagonistic interaction with other heavy metals, particularly its homolog cadmium (Moore and Ramamoorthy, 1984). Zinc compounds are widely used in electroplating, pharmaceuticals, paint, rubber, dye, wood preservatives, ointments and batteries. So, the wastes from these industries need to be frequently analyzed. Common zinc compounds found at hazardous waste sites include zinc chloride, zinc oxide, zinc sulfate and zinc sulfide. Besides, it is also present in high protein foods and its large doses can cause fever, chills, pulmonary manifestation, gastroenteritis, vomiting, nausea, anemia and renal failure. In view of its toxicity, the determination of zinc becomes important.

Most of the reported zinc ion selective electrodes have poor sensitivity, selectivity, long response time and short life time. An electrode was fabricated by incorporating zinc salts of bi(4-octylphenyl)hydrogen phosphate in PVC matrix (Gorton and Fiedler, 1977) but the electrode showed serious interference from some metals. Linarsund and Bhatti (1979) tried zinc complex of bis(2-ethylhexyl)phosphate, an extractant, as electroactive material for preparing Zn^{2+} -selective electrodes but it had a very narrow working pH of range 4.5–6.0.

Lebedeva and Jansons (1987) prepared Zn^{2+} -selective electrodes using saturated solutions of Zn-quinoline-8-carbodi-thioate in chloroform. Kojima and Kamata (1994) used tetrabutylthiuram disulfide as the carrier in PVC based membrane electrode. Zinc orthophosphate and zinc mercuric thiocyanate were used by Rocheleaw and Purdy (1990) as electroactive materials on a carbon support for the fabrication of Zn^{2+} -selective sensors. The electrode worked well but suffered interference from Cu^{2+} , Cd^{2+} and Pb^{2+} . Another electrode, based on salicylaldehyde-formaldehyde resin, for zinc (Srivastava et al., 1995) exhibited a working concentration range of 3.0 μM –0.1 M with a near Nernstian slope. A zinc-selective electrode was used by Obmetho et al. (1988) for the determination of zinc in alloys. Srivastava et al. (1996) used a cryptand for the fabrication of zinc selective sensor but it exhibited a non-Nernstian response.

Zn-bis(2,4,4-trimethylpentyl) thiophosphinic acid complex was also used for fabricating Zn^{2+} -selective sensor (Gupta et al., 1998) but it suffers interference from copper. Shamsipur et al. (1999) reported a zinc-selective sensor based on benzo substituted macrocyclic diamides. An electrode based on 5,6,14,15-dibenzo-1,4-dioxo 8,12-diazacyclopentadecane-5,14-diene showed response for zinc (Fakhari et al., 2001). It has a working concentration range of 5 μM –100 mM in the pH range of 1.5–7.0. A significant number of macrocycles, from crown ethers to calixarene derivatives, have been used in the construction of poly(vinyl)chloride (PVC) membrane electrodes for alkali metal and alkaline earth metal cations (Liu et al., 2000). The selectivity of these electrodes is based on the high bonding affinity of the ionophores containing oxygen or nitrogen atoms for the acceptors.

Membranes of dibenzo-24-crown-8 (I) as an ion active material in poly(vinylchloride) (PVC) based matrix have been tried for zinc(II)-selective sensors (Gupta et al., 2005). The effect of anion excluder, sodium tetraphenylborate (NaTPB) and plasticizers, tris(2-ethylhexyl)phosphate (TEP), tributylphosphate

(TBP), dibutylphthalate (DBP), dibutyl(butyl)phosphonate (DBBP), 1-chloronaphthalene (CN) and dioctylphthalate (DOP) on the performance of the membrane electrodes has also been studied. It was observed that the membrane having the composition (I): PVC:NaTPB:DOP in the ratio 10:200:2:100 gave the best results with a wide working concentration range of 9.2×10^{-5} to 1.0×10^{-1} M, Nernstian slope of 29.0 ± 0.5 mV/decade of activity, fast response time of 12 s and good selectivity over a number of mono-, bi-, and trivalent cations. The sensor works well in a pH range 4.8–6.2. The practical utility of the sensor has been demonstrated by using it as an indicator electrode in the potentiometric titration of Zn^{2+} with EDTA and also for the determination of Zn^{2+} in a real sample analysis of wastewater.

A literature survey revealed that crown ethers based Zn(II) ion selective electrodes are rarely reported (Gupta, 1999; Gupta et al., 2005) and no attempt has been found concerning the use of DB18C6, 18C6 and/or CAX, ionophores, and the DOPP, solvent mediator, for the fabrication of Zn(II) electrodes.

In the present study, we tried DB18C6, 18C6 and CAX as active materials in PVC matrix for the fabrication of Zn^{2+} -selective sensors using different types of solvent mediators. The different factors affecting the response characteristics of tested electrodes have been thoroughly investigated. The electrodes incorporating DB18C6 + DOPP (type 1a) and 18C6 + DOPP (type 1b) gave the best potential response characteristics. They have been used for the determination of Zn(II) in real alloy samples. The results obtained by the adopted ISEs were compared with the results obtained by direct flame AAS determination.

2. Experimental

2.1. Equipments

A Perkin–Elmer Spectrometer model 2380 was used for flame AAS determination of zinc. The electromotive force (EMF) of each potentiometric cell was measured at room temperature (25 ± 1 °C) with a Cole Parmer 5986 pH/mV meter having a sensitivity of ± 0.1 mV. The reference electrode is an Orion model 900-200 Ag/AgCl electrode. An Orion model 420A ionalyzer with its combined glass electrode was used for measuring the pH values.

2.2. Chemicals and solutions

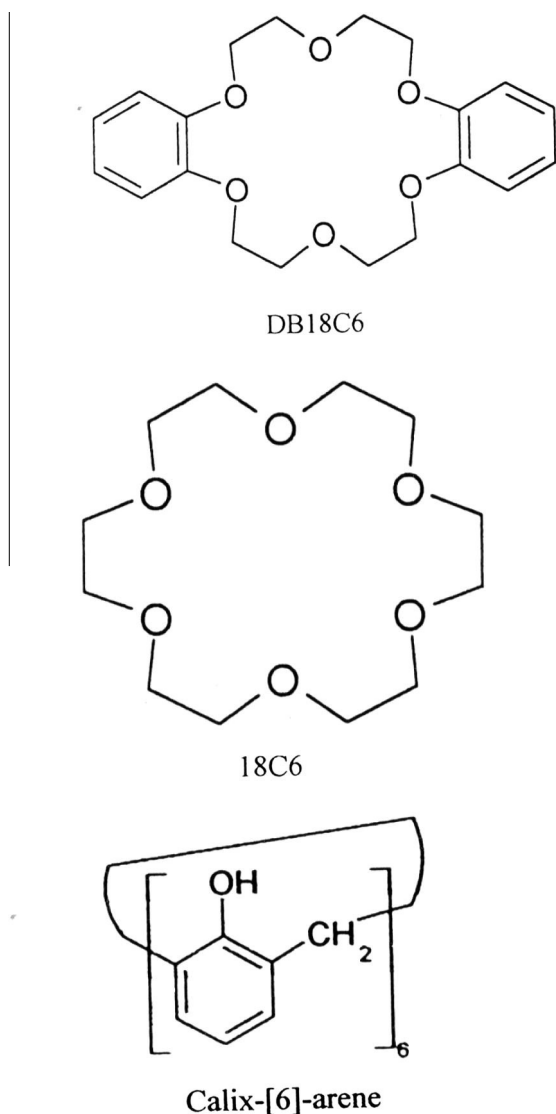
All reagents used in the investigations were of analytical reagent grade. Doubly distilled water (DDW) was used for preparing all aqueous solutions.

Polyvinyl chloride (PVC) is a high molecular weight solid of highest purity (99%) which was provided by Fluka Chemical Co.

2.2.1. Ionophores (Scheme 1)

1,4,7,13,16-Hexaoxacyclooctadecane (18-crown-6) (18C6) and dibenzo (18-crown-6) (DB18C6) are of highest purity (98%) supplied by (Fulka, Germany).

37,38,39,40,41-Penta-kis(diethoxythiophosphoryl)-oxy-5, 11,17,23,24,35-hexa-kis (1,1-dimethylethyl)calix[6]arene-42-ol (CAX), Scheme 1, were synthesized from *p*-tert-butyl-calix[6]arene by Wroblewski et al. (1996). This method is based



Scheme 1 Molecular structures of DB18C6, 18C6 and calyx[6]arene.

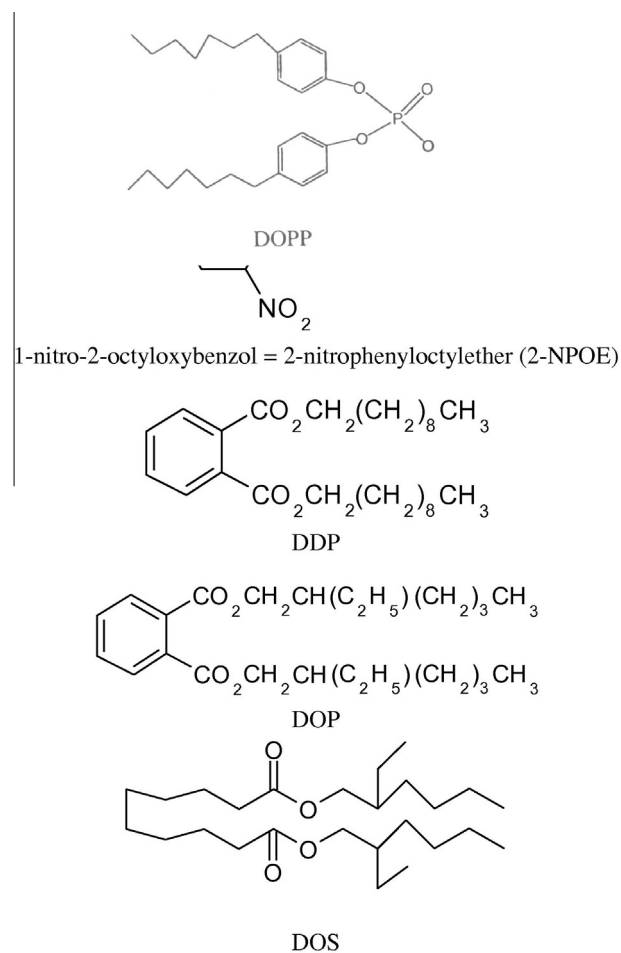
on the addition of freshly grounded solid NaOH (1.5 g), diethoxythiophosphoryl chloride (2.4 ml) and tetrabutylammonium bromide (1.5 g) to a solution of *p*-*tert*-butylcalix[6]arene (1.5 g) CH_2Cl_2 . The suspension was stirred for 10 h at room temperature. The organic layer was then washed with 1 M HCl, water, brine and dried over MgSO_4 .

2.2.2. Solvent mediators (Scheme 2)

Diocetylphenylphosphonate (DOPP), bis(ethylhexyl)sebacate (DOS), dioctyl phthalate (DOP), 2-nitrophenyloctylether (*o*-NPOE) and didecylphthalate (DDP), Scheme 2, are pure liquids of highest purity supplied by Aldrich Chemical Company.

2.3. Electrode preparation

The general procedure to prepare the PVC membranes was to mix 60 mg of powdered PVC and 2 mg of ionophore (DB18C6, 18C6 or CAX) with 120 mg of plasticizer (DOPP, DOP, DDP, DOS or *o*-NPOE) as solvent mediators. Then, the mixture was



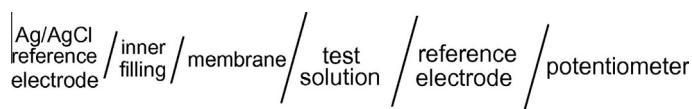
Scheme 2 The molecular structure of the used plasticizer (solvent mediators).

thoroughly dissolved in approximately 2 ml of tetrahydrofuran (THF) by vigorous shaking and poured into 5 cm glass rings resting on clean glass plates. The solvent was allowed to evaporate at 25 °C for 24 h. The resulting membrane was peeled off from the glass mold. Then, disks of 7 mm diameter were punched from the membranes and mounted into Philips Is-560 electrode bodies (Eindhoven, The Netherlands) filled with an aqueous solution of 10^{-2} M ZnCl_2 . The electrodes were, then, conditioned for at least 24 h in a fresh 10^{-2} M ZnCl_2 solution in a dark place. Table 1 summarizes the composition of all the fabricated membranes.

2.4. Analytical procedures

2.4.1. Electrode calibration

The calibration of electrodes was done using the following electrochemical system.



where the reference electrode is an Orion model 900-200 Ag/AgCl electrode.

Table 1 Composition of PVC-based membranes of Zn²⁺-ISEs.

Electrode	Composition		
	PVC, 60 mg	Ionophore, 2 mg	Plasticizer, 120 mg
1a	PVC	DB18C6	DOPP
2a	PVC	DB18C6	DOP
3a	PVC	DB18C6	2-NPOE
4a	PVC	DB18C6	DOS
5a	PVC	DB18C6	DDP
1b	PVC	18C6	DOPP
2b	PVC	18C6	DOP
3b	PVC	18C6	2-NPOE
4b	PVC	18C6	DOS
5b	PVC	18C6	DDP
1c	PVC	CAX	DOPP
2c	PVC	CAX	DOP
3c	PVC	CAX	2-NPOE
4c	PVC	CAX	DOS
5c	PVC	CAX	DDP

Aliquots (50 ml) of solutions between 10⁻⁷ and 10⁻¹ M of zinc chloride were transferred into 70 ml beakers. Each proposed Zn²⁺ electrode in conjunction with Ag/AgCl reference electrode was immersed into the solution. Stirring was started and the stable potential reading for each concentration was recorded and plotted against p [Zn²⁺].

From the resulting curves the slope, linear working range and detection limit of the zinc electrodes were determined.

2.4.2. Effect of pH on the electrode potential

The pH effect of the test solutions on the potential reading of the electrode system for 10⁻², 10⁻³, 10⁻⁴ M of ZnCl₂, was tested. Forty-five milliliters of each of the tested solutions were transferred to a 100 ml beaker then the proposed Zn(II)-selective electrode in conjunction with Ag/AgCl reference electrode and a combined glass electrode system was immersed in the same solution. Potential and pH readings were simultaneously measured. The pHs of the solutions were varied over the range 1.0–11.0 by the addition of 0.1 M HCl or 0.1 M NaOH solutions and the mV readings were plotted against the pH values.

2.4.3. Selectivity measurements

The selectivity with respect to selected inorganic cations was tested. The separate technique (Gosofret and Buck, 1984; Gadzekpo and Christian, 1984) was applied by measuring the potential readings of 10⁻³ M for Zn²⁺ and 10⁻³ M of the interfering ion. Then, the selectivity coefficient K_{Zn}^{pot}, X^{Z+} is calculated by applying the following equation.

$$\log K_{Zn}^{pot}, X^{Z+} = E_2 - E_1/S + \log[Zn^{2+}] - \log[X^{Z+}]^{1/Z} \quad (1)$$

where E_1 is the electrode potential of 10⁻³ M of Zn²⁺, E_2 is the electrode potential of 10⁻³ M solution of the interfering cation X, S is the slope of the calibration curve at room temperature and Z is the charge of the interfering ion.

2.4.4. Response time

Four concentrations of zinc chloride solutions, i.e., 10⁻¹, 10⁻², 10⁻³ and 10⁻⁴ M were chosen for measuring the time dependent potential of the selective electrode (response time). Approximately 45 ml aliquot of each solution was put in

potentiometric cell then the cited zinc selective electrode and the reference electrode were directly immersed in the solution. The potential response was plotted against the time. This method is called immersion method. The time dependence of the electrode potential (Toth et al., 1971) may be presented by the equation:

$$E_t = E_{st} + (E_i - E_{st}) \exp(-t/\tau)$$

where E_i is the initial potential of the ion selective electrode, E_{st} is the final potential of the steady state and τ is the relaxation time which is identified with its response time.

2.4.5. Effect of soaking on the electrode potential

The prepared electrodes were soaked in 10⁻² M ZnCl₂ solution at room temperature 25 ± 1 °C. A calibration graph was constructed for each electrode after different time intervals covering the range 1 day to 2 months. The measurements were stopped when the slope of the calibration curve was deviated largely from the theoretical Nernstian value.

2.5. Sample analysis

2.5.1. Analysis of standard reference samples

In order to validate the accuracy of the proposed ISE methodology, two standard reference samples were analyzed by the adopted ISEs namely phosphate 1 and phosphate 2 prepared by Nuclear Materials Corporation, Egypt.

A 0.25 g of each standard reference sample was weighed and dissolved in a Teflon beaker with a mixture of 45 mL HF, 15 mL conc. H₂SO₄ and 5 mL conc. HNO₃. After complete dissolution, the solution was evaporated nearly until dryness. The residue was dissolved in 10 mL DDW. A known aliquot of this solution was pipetted into a 50 ml calibrated flask. The pH was adjusted between 4 and 8. The potential readings of the two ISEs were referred to a calibration graph constructed previously for Zn(II). The results obtained by the proposed ISEs were compared with those obtained by flame AAS.

2.5.2. Analysis of Devarde's alloy

Devarde's alloy (50% Cu, 45% Al and 5% Zn) is a BDH laboratory reagent powder manufactured in UK.

Dissolve 1.0 g of Devarde's alloy sample in 10 ml of (1:1) HCl, then add minimal amount of (1:1) HNO₃, boil to remove the oxides of nitrogen, cool, transfer to a 100 volumetric flask and dilute to volume with DDW. A known aliquot of this solution was pipetted into a 50 ml calibrated flask. The pH was adjusted between 4 and 8. The potential readings of the two ISEs were referred to a calibration graph constructed previously for Zn(II). The results obtained by the proposed ISEs were compared with those obtained by flame AAS.

3. Results and discussion

3.1. Performance characteristics of sensors

It is well known that the sensitivity, linearity, and selectivity obtained for a given ionophore depends significantly on the membrane composition. Thus, the influence of the type of ionophore and the nature of plasticizers on the potential response of the membrane sensors, were investigated. The response

Table 2 Response characteristics of zinc-electrodes based on DB18C6 and different solvent mediators.

Electrode no.	Ionophore	Solvent mediator	Slope (mV/decade)	Linear range (M)	Detection limit (M)	R.S.D. (%) ($n = 3$)
Type-1a	DB18C6	DOPP	29	10^{-5} – 10^{-1}	7.5×10^{-6}	1.02
Type-2a	DB18C6	DOP	8	10^{-6} – 10^{-1}	Undetected	–
Type-3a	DB18C6	2-NPOE	9	10^{-5} – 10^{-1}	Undetected	–
Type-4a	DB18C6	DOS	11	10^{-6} – 10^{-1}	Undetected	–
Type-5a	DB18C6	DDP	12	10^{-3} – 10^{-1}	10^{-5}	2.9

Table 3 Response characteristics of zinc electrodes based on (DB18C6) and different solvent mediators.

Electrode no.	Ionophore	Solvent mediator	Slope (mV/decade)	Linear range (M)	Detection limit (M)	R.S.D. (%) ($n = 3$)
1b	18C6	DOPP	30	10^{-5} – 10^{-1}	1.5×10^{-6}	1.54
2b	18C6	DOP	7	10^{-6} – 10^{-1}	Undetected	–
3b	18C6	2-NPOE	10	10^{-5} – 10^{-1}	Undetected	–
4b	18C6	DOS	4	10^{-6} – 10^{-1}	Undetected	–
5b	18C6	DDP	21	10^{-3} – 10^{-1}	3×10^{-4}	3.0

Table 4 Response characteristics of zinc electrodes based on CAX and different solvent mediators.

Electrode no.	Ionophore	Solvent mediator	Slope (mV/decade)	Linear range (M)	Detection limit (M)	R.S.D. (%) ($n = 3$)
Type-1c	CAX	DOPP	20	10^{-4} – 10^{-1}	10^{-6}	2.2
Type-2c	CAX	DOP	2	10^{-6} – 10^{-1}	Undetected	–
Type-3c	CAX	2-NPOE	5	10^{-5} – 10^{-2}	Undetected	–
Type-4c	CAX	DOS	10	10^{-5} – 10^{-3}	Undetected	–
Type-5c	CAX	DDP	20	10^{-2} – 10^{-1}	3×10^{-4}	3.6

characteristics of the fabricated Zn ion selective electrodes are summarized in Tables 2–4. A comparison of the performance characteristics of all the sensors clearly revealed that the sensors 1a and 1b having membranes with DOPP plasticizer and DB18C6 and 18C6 ionophores, respectively, are the best. These sensors exhibit the widest working concentration range of 1×10^{-1} – 1×10^{-5} M, a Nernstian slope of 29 and 30 mV/decade for electrodes with membranes 1a and 1b, respectively, and a minimum response time of ≤ 15 s. Thus, all the further studies were carried out with the cells employing sensors 1a and 1b.

3.2. Ionophores (ion carrier)

As with many ionophore-based membrane electrodes, the electrochemical response of the electrode toward Zn^{2+} , depends on the type of ionophore incorporated in the membrane. As shown in Table 1, three types of ionophores (neutral carriers) are used *viz.*: DB18C6, 18C6 and calix-6-aren (CAX), for preparing Zn^{2+} selective electrodes in the present study. Table 5 shows the effect of changing the type of ionophore on the electrode response after one day time soaking in ZnCl_2 solution.

As it can be seen, the response of the electrodes with membrane types 1a, 1b gives a best typical Nernstian response toward Zn^{2+} . The obtained slope values of the calibration graphs are: 29 ± 1 and 30 ± 1 mV/decade for electrodes with membranes incorporating DB18C6 and 18C6 ionophores, respectively. But in case of using CAX as ionophore (membrane 1c), the response was a poor Nernstian response of ~ 20 mV/decade. From these results, it can be concluded that when using the same plasticizer (DOPP) and the same membrane matrix (PVC) the response varied with changing the type of ionophore. The best Nernstian response was obtained in case of using crown ether derivatives DB18C6 and 18C6 not in using calix-[6]-arene (CAX). This may be attributed to the structure of crown ether which is able to carry the charged Zn^{2+} ion; this ability improves the performance of the electrodes 1a and 1b.

3.3. Solvent mediators

One of the expected reasons for the presence of plasticizer is to give a homogeneous organic phase. Also the membrane solvent must be physically compatible with the polymer,

Table 5 Influence of ionophores on the characteristics Zn(II) ion selective electrodes.

Electrode	Ionophore	Solvent mediator	Slope (mV/decade)	Linear range (M)	Detection limit (M)	R.S.D. (%) ($n = 3$)
1a	DB18C6	DOPP	29	10^{-5} – 10^{-1}	7.5×10^{-6}	1.02
1b	18C6	DOPP	30	10^{-5} – 10^{-1}	1.5×10^{-6}	1.54
1c	CAX	DOPP	20	10^{-3} – 10^{-1}	10^{-5}	2.20

i.e., has plasticizing properties. To provide suitable mechanical properties, five types of plasticizers were used (DOPP,

DOP, DOS, DDP and 2-NPOE (with the two crown ethers DB18C6 and 18C6. Fig. 1 shows the effect of changing the

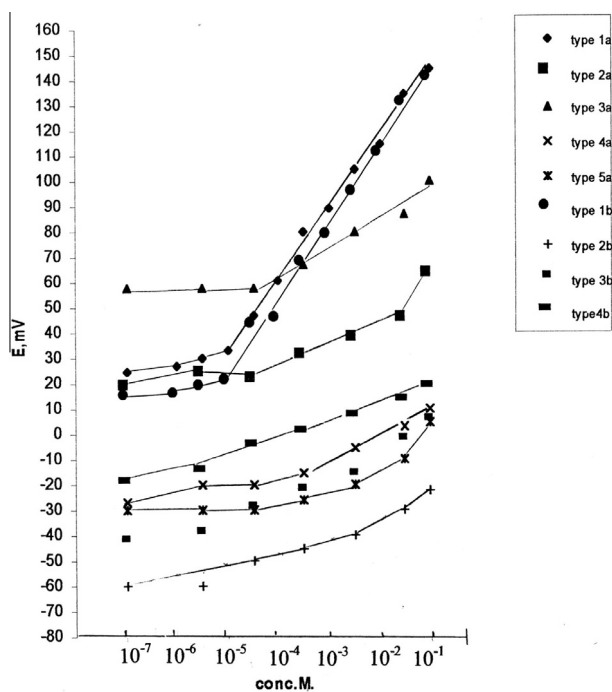


Figure 1 The effect of changing composition on the electrode response after one day time soaking in ZnCl₂ solutions.

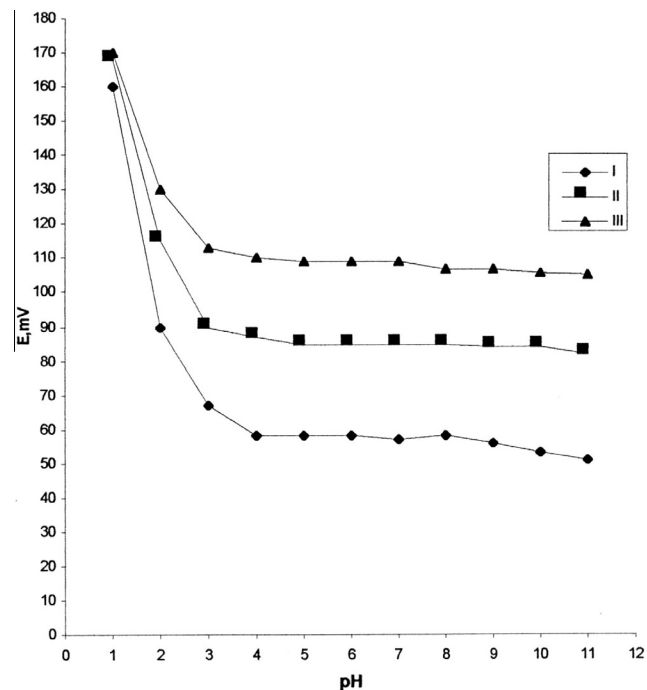


Figure 3 pH effect on the potential of zinc-responsive electrode with membrane type 1b (18C6 + DOPP) for Zn²⁺ solutions (I, 10⁻²; II, 10⁻³; III, 10⁻⁴ M).

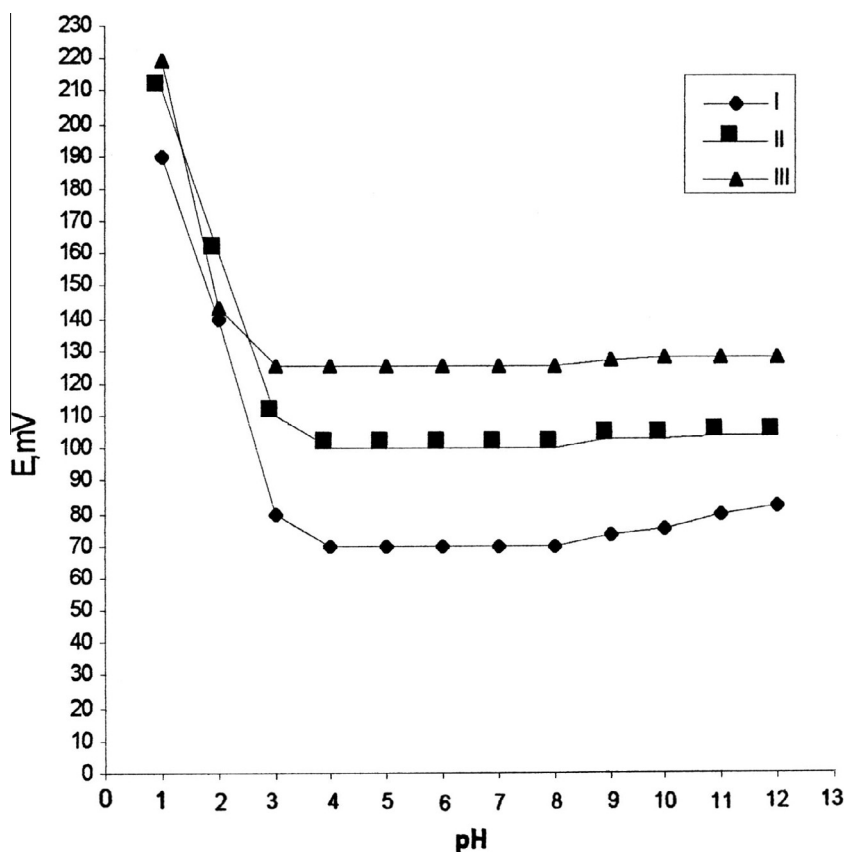
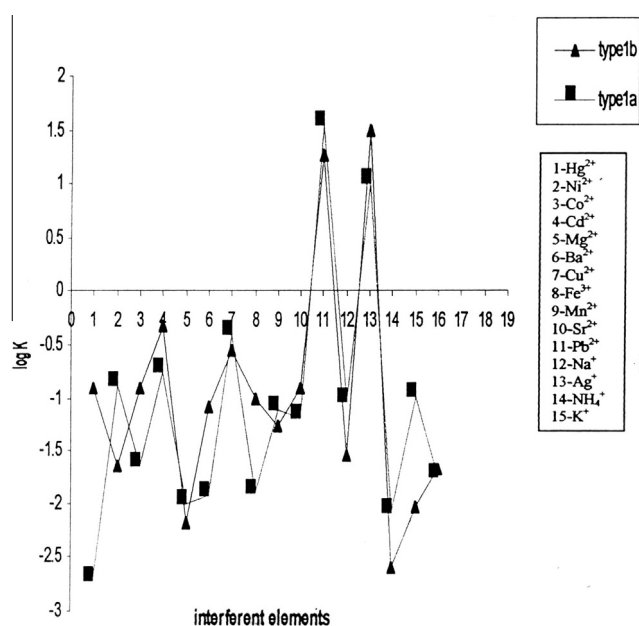


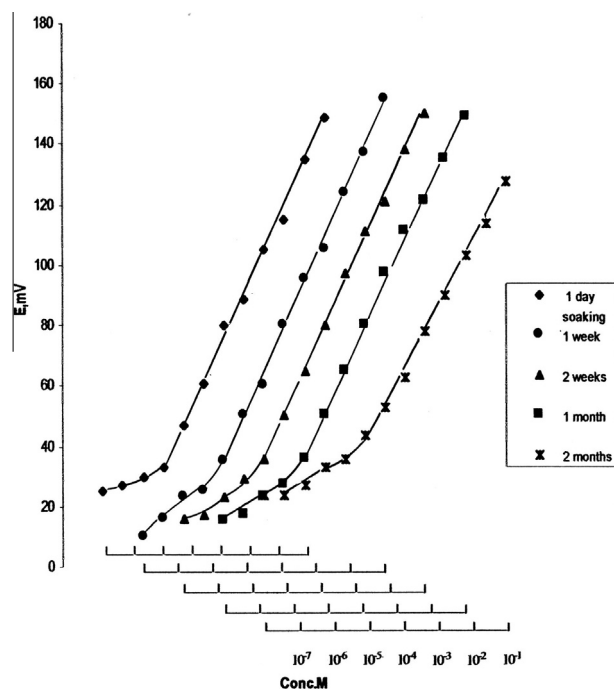
Figure 2 pH effect on the potential of zinc-responsive electrode with membrane type 1a (DB18C6 + DOPP) for Zn²⁺ solutions (I, 10⁻²; II, 10⁻³; III, 10⁻⁴ M).

Table 6 Logarithmic selectivity coefficient values for Zn²⁺ ISEs based on DB18C6 (type 1a) and 18C6 (type 1b).

No.	Interferant (10 ⁻³ M)	log K ^{pot} at 10 ⁻³ M Zn ²⁺	
		ISE (1a)	ISE (1b)
1	Hg ²⁺	-1.920	-1.707
2	Ni ²⁺	-0.815	-1.910
3	Co ²⁺	-2.107	-1.776
4	Cd ²⁺	-1.460	-1.224
5	Mg ²⁺	-1.895	-2.189
6	Ba ²⁺	-2.320	-1.090
7	Cu ²⁺	-0.607	-0.552
8	Fe ³⁺	-1.831	-1.431
9	Mn ²⁺	-1.500	-1.707
10	Sr ²⁺	-1.286	-1.466
11	Pb ²⁺	+1.330	+1.293
12	Na ⁺	-2.740	-2.397
13	NH ₄ ⁺	-1.857	-2.259
14	K ⁺	-2.390	-2.328
15	Al ³⁺	-1270	-1.966
16	Ag ⁺	+0.724	+0.965

**Figure 4** Separate solution selectivity coefficient at 10⁻² M ZnCl₂ solution of Zn²⁺-selective electrode with membrane type 1a (DB18C6 + DOPP) and type 1b (18C6 + DOPP).

type of the solvent mediator on the electrode response after one day time soaking in ZnCl₂ solution. The response of the electrodes with membrane types 1a and 1b gives a best typical Nernstian response toward Zn²⁺. The presence of DOPP rather than DOP, DOS, 2-NPOE or DDP is the reason for the electrode response toward Zn²⁺ ion. This is confirmed by comparing the calibration graphs of the DB18C6 based membranes, one membrane contains DOPP (type-1a), while others contain DOP (type-2a), 2-NPOE (type-3a), DOS (type-4a) or DDP (type-5a). The slope of the calibration graph of the electrode with membrane (type-1a) is a better Nernstian response of 29 mV/decade and a wider linear range of 10⁻⁵–10⁻¹ M and detection limit (7.5 × 10⁻⁶ M) while other types did not show Nernstian response (Fig. 1, Table 2). Similar results were obtained in case of using 18C6 as an ionophore, Table 3, for preparing electrodes with different solvent mediators. Only the membrane plasticized with DOPP (electrode with membrane type 1b) gave a typical Nernstian response with slope of 30 ± 1 mV/decade and a wider linear range 10⁻⁵–10⁻¹ M and detection limit (1.5 × 10⁻⁶ M) (Table 3). The response

**Figure 5** Effect dopping time in 10⁻³ M ZnCl₂ on the performance of the electrode type 1a (DP18C6 + DOPP).**Table 7** Nernstian response and rectilinear range LCR of Zinc electrode with membrane DB18C6 (type 1a) and 18C6 (type 1b) for some selected cations.

Membrane type	Property	Hg ²⁺	Ni ²⁺	Co ²⁺	Cd ²⁺	Mg ²⁺	Ba ²⁺	Cu ²⁺	Fe ²⁺	Mn ²⁺	Sr ²⁺	Pb ²⁺	Na ²⁺	NH ₄ ⁺	K ⁺	Al ³⁺	Ag ⁺
Ia	Slope (mV/decade)	10	11	24	30	12	20	7	20	27	28	28	30	37	23	16	34
DB18C6 + DOPP	LCR, pM	4.0–2.0	6–1	3–1	4–1	4–1	4–1	4–1	5–2	4–1	3–1	6–3	3–1	3–1	3–1	5–2	4–1
Ib	Slope (mV/decade)	28	20	26	30	16	30	6	29	26	30	30	35	30	5	31	41
18C6 + DOPP	LCR, pM	5–3	3–1	3.5–1	4–1	3–1	4–1	6–1	5–1	5–1.0	3–1	5–1	3–1	2–1	6–1	5–1	4–1

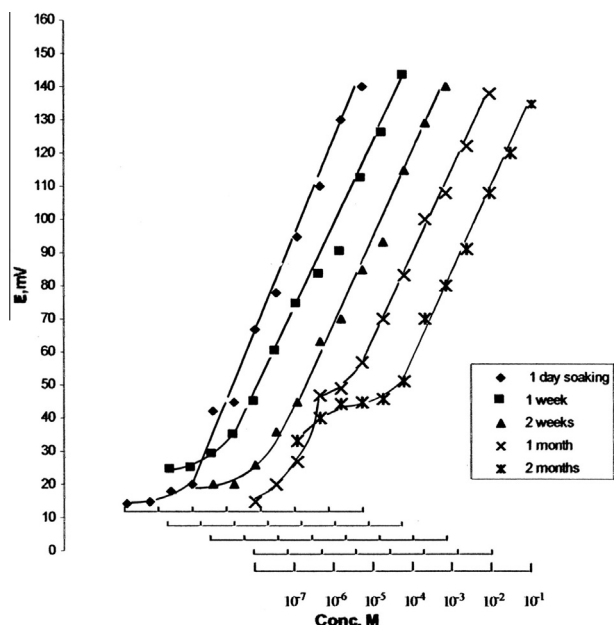


Figure 6 Calibration curves for Zn-selective electrodes with PVC membrane type 1b (18C6 + DOPP) at various time of soaking.

of electrodes with membranes 1a and 1b is improved upon using DOPP as a solvent mediator. This is because DOPP ensures the mobility of the free and complexed ionophore and provides suitable mechanical properties of the membranes improving the performance of the electrodes with membranes 1a and 1b.

3.4. Effect of pH on the membrane response

The effect of pH is considered to be one of the main characteristics of ion selective electrodes. The pH-profiles of the electrodes with membranes 1a and 1b have been constructed to find the optimum pH-range of each electrode. The pH dependence of each electrode response was examined using 10^{-4} , 10^{-3} and 10^{-2} M Zn^{2+} solutions. The pH has been adjusted by using hydrochloric acid (0.1 M) and sodium hydroxide (0.1 M). For electrode with membrane 1a the working pH ranges of the electrodes are 3–8, 4–8 and 4–8 for concentrations 10^{-4} , 10^{-3} and 10^{-2} M, $ZnCl_2$ solution, respectively, Fig. 2. Similar behavior was obtained when using the electrode

with membrane 1b in which the working pH ranges are (3–8), (3–9) and (3–8) for concentrations 10^{-4} , 10^{-3} and 10^{-2} M, $ZnCl_2$ solution, respectively, Fig. 3. The break down of the curves in the basic medium is due to the hydrolysis of zinc ions. In acidic medium, on the other hand, a sudden change is observed at pH 3 in case of electrode with membrane 1b for all the concentrations tested (10^{-2} , 10^{-3} and 10^{-4} M). But in case of the electrode with membrane 1a the change is observed at pH 3 in case of concentration 10^{-4} and pH 4 for concentrations 10^{-3} and 10^{-2} M. Finally the break in acidic medium pH < 3.0 and 4.0 is due to the protonation of the corresponding ionophore in the membranes. Under these conditions zinc ions cannot freely be exchanged.

3.5. Potentiometric selectivity

The influence of interfering ions on the response behavior of ion selective membrane electrode is usually described in terms of selectivity coefficient $K_{A,B}^{pot}$. Most often it is expressed as the logarithm of ($K_{A,B}^{pot}$). Negative values indicate a preference for the target ion relative to the interfering ion. Positive values of $\log K_{A,B}^{pot}$, on the other hand, indicate the preference of an electrode for the interfering ion. The experimental selectivity coefficients depend on the activity and the method of their determination. Different methods of the selectivity determination can be found in the literature. The IUPAC suggests two methods: separate solution method (SSM) and fixed interference method (FIM). There is also an alternative method of the selectivity determination called matched potential method (MPM). In the present study, the selectivity coefficient values were determined using SSM method. Several inorganic cations are chosen for the selectivity measurements. The resulting selectivity coefficient values are summarized in Table 6 and represented in Fig. 4. As it can be seen, for all ions used (except Pb^{2+} and Ag^+) the $\log K_{Zn,M}^{pot}$ values were negative indicating that they would not significantly disturb the functioning of the Zn ion selective membranes. The positive interfering effects of Pb^{2+} and Ag^+ ions could be related to the tendency of these cations to coordinate with crown ethers (Zareh et al., 2001). So for this reason, the measurements of electrode comprising membranes 1a and 1b must be carried out after isolation of silver and lead. The resulting selectivity coefficients, also, show that there is no marked difference in the selectivity coefficient values between the two electrodes with membrane types 1a and 1b except for Ni^{2+} . The $\log K_{Zn,Ni}^{pot}$ is improved in case of using 18C6 as ionophore.

Table 8 Effect of soaking time in 10^{-2} M $ZnCl_2$ on the performance of Zn^{2+} electrodes with membrane types 1a, 1b.

Membrane type	Soaking time	Slope (mV/decade)	Linear range (M)	Detection limit (M)
Type-1a DB18C6 + DOPP	One day	29	10^{-5} – 10^{-1}	6.5×10^{-6}
	One week	28	5×10^{-5} – 10^{-1}	2.5×10^{-6}
	Two weeks	27	10^{-4} – 10^{-1}	2.9×10^{-6}
	One month	27	10^{-4} – 10^{-1}	9×10^{-6}
	Two months	27	10^{-4} – 10^{-1}	1.5×10^{-5}
Type-1b 18C6 + DOPP	One day	30	10^{-5} – 10^{-1}	1.5×10^{-6}
	One week	29	10^{-5} – 10^{-1}	1.5×10^{-6}
	Two weeks	29	10^{-4} – 10^{-1}	2.5×10^{-6}
	One month	28	5×10^{-4} – 10^{-1}	5×10^{-6}
	≥ 2 months	28	10^{-4} – 10^{-1}	7.2×10^{-6}

By measuring the potential values for 10^{-5} – 10^{-1} M concentrations of the interfering ions, a complete picture of the selectivity of the studied Zn^{2+} electrodes is obtained. A comparison of the obtained results with those for the electrodes whenever Zn^{2+} is the measured cation is shown in Table 7.

3.6. Effect of soaking and electrode age

To investigate the electrode age, it was soaked in 10^{-2} M zinc chloride solution for interval ranging from one day till the electrode lost its Nernstian behavior. The response of each electrode was checked by recording the calibration graph at 25 °C, at different intervals. Representative calibration curves for the effect of soaking on the performance characteristics of zinc electrodes with membrane types 1a and 1b as a function of the soaking time are shown in Figs. 5 and 6, respectively. The results listed in Table 8, summarize the effects of soaking time on slope, detection limit and usable linear concentration range of the proposed electrodes. As it can be noticed, the electrodes have a long working period extending up to 2 months. They are ready for measurements after preconditioning period one day with a Nernstian slope reaching 29 and 30 mV/decade for electrodes with membrane types 1a and 1b, respectively. A small drift, then, occurs (not more than 2 mV) after 2 months. The decrease in the performance of the electrodes after 2 months soaking could be attributed to the leaching out of all or some membrane constituents (neutral carriers or plasticizer), i.e., they become insufficient to complete the ionic exchange process at the membrane interface.

3.7. Response time

The response time of an ion-selective electrode represents the dynamic response of the ion-exchange process at the

Table 9 Response time values by seconds for membrane types (1a, 1b) of Zn^{2+} -electrodes.

Concentration (M)	Electrode	
	Response time (s)	
	ISE 1a	ISE 1b
10^{-4}	15	15
10^{-3}	7	7
10^{-2}	6	4
10^{-1}	3	3

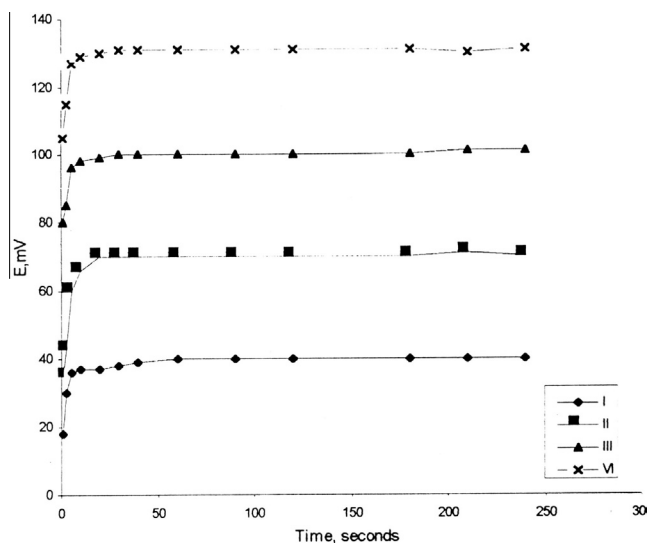


Figure 8 Response time curves for zinc electrode type 1b (18C6 + DOPP) for (I, 10^{-1} ; II, 10^{-2} ; III, 10^{-3} and VI, 10^{-4} M).

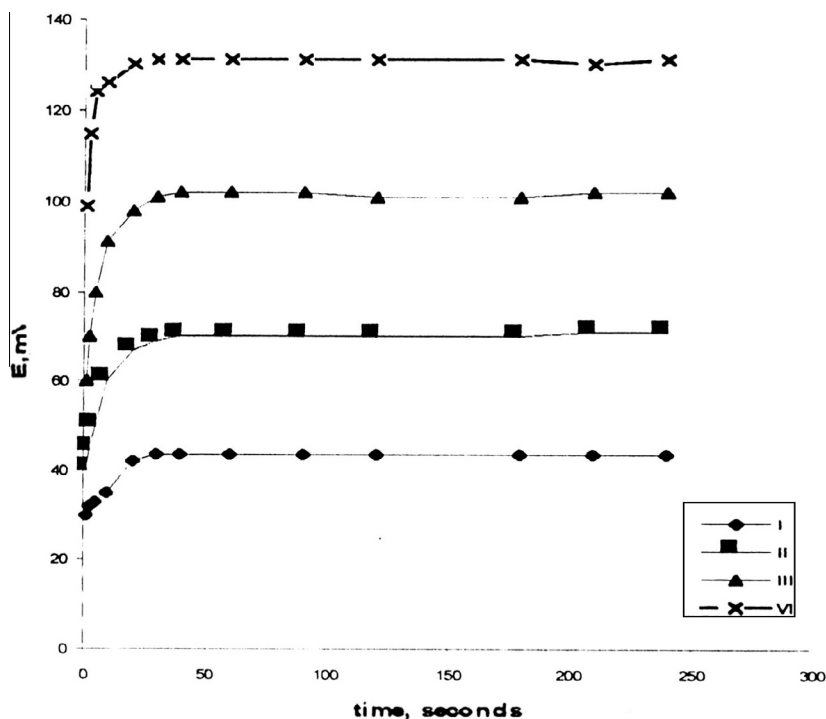


Figure 7 Response time curves for zinc electrode type 1a (DB18C6 + DOPP) for (I, 10^{-1} ; II, 10^{-2} ; III, 10^{-3} and VI, 10^{-4} M).

Table 10 Statistical evaluation for analysis of some standard reference samples using the proposed Zn²⁺-selective electrodes ($n = 5$). Comparison of experimental mean (\bar{X}), ppm, with true value (μ), by $|t|_1$ test.

Sample	Method		
	Flame AAS	ISE type 1a	ISE type 1
<i>Phosphate 1^a</i>			
\bar{X}	65.20	65.09	14.95
μ	65.30	65.30	15.0
S	0.09	031	0.186
$ t _1$	2.50	21.5	2.4
RSD	0.14	0.48	
<i>Phosphate 2^a</i>			
\bar{X}	252.9	251.8	253.0
μ	252.4	252.4	252.4
S	0.48	0.70	0.64
$ t _1$	2.3	1.9	2.1
R.S.D.	0.19	0.28	0.25

(\bar{X}): experimental value, (μ) true value. $|t|_1$: for $P = 0.05$ and $n = 5$ (4 degree of freedom) = 2.78. R.S.D.%:

^a Prepared by Nuclear Materials Corporation, Egypt.

membrane-test solution interface. In the present work the average time required for the Zn²⁺-selective electrode to reach a potential within ± 1 mV of the final equilibrium value after successive immersion of series of zinc ion solutions, each having a 10-fold difference in concentration, was measured. The results are shown in Figs. 7 and 8 and summarized in Table 9. The static response time thus obtained was less than 15 s over the entire concentration range, and the potentials stayed constant for

more than 5 min, after which only a very slow divergence was recorded. The sensing behavior of the membrane remained unchanged when the potential was recorded either from low to high concentration or vice versa. Moreover, it is observed that the response times for higher concentrations are shorter than those for the diluted solutions, Table 9. This can be explained to be due to the enhancement of the ion exchange process of the electrodes at higher concentrations (see Fig. 8).

3.8. Application

3.8.1. Analysis of standard reference samples

In order to validate the ISE procedure, the proposed zinc selective electrodes were applied to two standard reference materials *viz.*: phosphate 1 and phosphate 2 prepared by Nuclear Materials Corporation, Egypt. The average contents of Zn ions ($n = 5$) in the standard reference materials are shown in Table 10 with a precision as relative standard deviation (R.S.D.) up to 2.5%.

Table 10, also, shows a comparison of the experimental mean (\bar{X}) and the true value (μ) by the $|t|_1$ test. From Table 10 it can be noticed that $|t|_1 = 1.5$ – 2.5 for the investigated Zn ions. This means that for all the metal ions the null hypothesis of $|t|_1$ for $P = 0.05$ and $n = 5$ is retained where the calculated experimental values of $|t|_1$ are less than the tabulated value ($|t|_1 = 2.78$). This means that all the pre-concentrated samples are not subject to any systematic error, *i.e.*, they are accurate.

3.8.2. Analysis of alloys

The analytical employability of the adopted zinc(II) ion selective electrodes 1a and 1b was investigated. The electrodes

Table 11 Analysis of Zn(II) in real alloy samples by the proposed ISEs and flame AAS.

Sample	AAS method			ISE method membrane 1a			ISE method membrane 1b		
	Zn(II) found (ppm)	Mean recovery (%)	R.S.D. (%) ($n = 3$)	Zn(II) found (ppm)	Mean recovery (%)	R.S.D. (%) ($n = 3$)	Zn(II) found (ppm)	Mean recovery (%)	R.S.D. (%) ($n = 3$)
Devarde's Alloy samples	500	100	0.96	490	98	1.1	496	99.2	0.97
	50	99.9	1.20	49.0	98	2.3	48	96.6	1.30
	5	99.5	1.36	4.70	94	2.0	4.8	96.0	1.80

Table 12 Comparison of the responsive characteristics of different Zn ion selective electrodes.

Carrier	Working range	Slope (mV/decade)	pH range	Interfering ions	Reference
(2,4,4-Trimethylphenyl)dithiophosphinic acid	1×10^{-1} – 1×10^{-5}	30.1	2.1–6.9	–	Gupta et al. (1998)
12-Crown-4	1×10^{-1} – 1×10^{-5}	29.5	2.8–5.5	Na	Gupta (1999)
1,13-Diaza-2,3,11,12,15,18-tribenzo-4,7,10-trioxacyclononaoctane-14,19-dione	1×10^{-1} – 1×10^{-5}	30.0	3.0–7.0	–	Shamsipur et al. (1999)
5,10,15,20-Tetraphenyl-21H, 23H-porphine	1×10^{-1} – 1×10^{-5}	29.0	3.8–7.7	–	Gupta et al. (2001a,b)
Protoporphyrine IX dimethyl ester	1×10^{-1} – 1×10^{-5}	29.0	2.1–4.0	Na, Cd	Gupta et al. (2001a,b)
Bis(2-nitrophenyl)disulfide	3.2×10^{-2} – 2.9×10^{-7}	29.9	2–9	–	Gholivand and Mozaffari (2003)
DB24C6	1×10^{-1} – 1×10^{-5}	29.0	4.8–6.2	–	Gupta et al. (2005)
DB18C6	1×10^{-1} – 1×10^{-5}	29.0	4.0–8.0	Pb, Ag	Present work
18C6	1×10^{-1} – 1×10^{-5}	30.0	4.0–8.0	Pb, Ag	Present work

were successfully applied to determine Zn(II) in real alloy samples; the results are shown in Table 11 with a relative standard deviation < 2.0 for each of the tested electrodes.

As it can be seen from Table 11, there is a satisfactory agreement between the values obtained by the ISEs and AAS methods.

4. Conclusion

The plasticized PVC-based membranes incorporating DB18C6 and 18C6 as ionophores and DOPP as solvent mediator in a PVC matrix in the ratio 2:60:120 (w/w) (ionophore:PVC:DOPP) could be used to determine Zn^{2+} in the concentration ranges 1×10^{-1} – 1×10^{-5} M with slopes of 29 and 30 mV/decade for electrodes 1a and 1b, respectively. The sensors work in a wide pH range 4–8 with response times ≤ 15 s. The selectivity of the electrodes toward Zn^{2+} is quite good over other cations and the life time of each assembly is ~ 2 months. Each of the adopted electrodes was successfully applied to the determination of Zn in alloy and ore samples with good precision as R.S.D.

In Table 12, the response characteristics of the proposed ISEs are compared with those of the best Zn^{2+} -selective electrodes reported previously. From the data listed therein it can be noticed that not only the concentration range and detection limits of the proposed electrodes but, also their pH range are in good agreement or even better than some other previously reported Zn^{2+} ion-selective electrodes.

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