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Fabrication of Pb^{2+} Ion Selective Electrode Based on 1-((3-((2-Hydroxynaphthalen-1-yl)Methyleneamino)-2,2-Dimethylpropylimino) Methyl) Naphthalen-2-ol as New Neutral Ionophore

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The potentiometric investigation of complexation of 1 - ((3 - ((2 – hydroxynaphthalen – 1 – y l) methyleneamino) – 2 , 2 – dimethylpropylimino) methyl) naphthalen-2-ol (HMDMN) show strong interaction between HMDMN and Pb^{2+} ion while their formation constant was evaluated using potentiometric data. The suitability of the HMDMN for construction of new Pb^{2+} ion PVC membrane electrode and its potentiometric determination was investigated. The influence of variables including pH, membrane ingredients was optimized and set as PVC: DBP: carrier: NaTPB: NaTPB /carrier mole ratio with the percent mass ratio of 28.9:57.8: 8.0: 5.33: 0.83. At optimum values of all variables the electrode response is linear in the concentration range of 1.0×10^{-6} to 0.1 M with detection limit 4.0×10^{-7} M with nernstian slop of 25.79 mV/decade over the pH range of 5.0-7.2. This electrode with appropriate response time about 10s and suitable reproducibility (RSD), can be used for a at least 2 month without any measurable divergence in response properties. The proposed sensor reveals good selectivity toward pb^{2+} ion with respect to many alkali, alkaline earth, transition and heavy metal ions. It was applied to the determination of pb^{2+} in water and soil samples.

Keywords: pb^{2+}-selective electrode; PVC membrane electrode; 1-((3-((2-hydroxynaphthalen-1-yl)methyleneamino)-2,2-dimethylpropylimino) methyl) naphthalen-2-ol (HMDMN); Potentiometry.

1. INTRODUCTION

Lead widely has been applied in industrial and therefore its arrival to natural water, potable water, soils and air lead to generation of serious hazardous to human health [1-3]. Therefore, there is an urgent requirement for the assessment and monitoring of Pb^{2+} ion content in various real samples with complicated matrices. Some of the previously reported Pb^{2+} ion determination [4-8], suffer from limitations such as expensive instruments, well-controlled experimental conditions and/or are timeconsuming. Thus, the development of a more convenient direct method for the quick and inexpensive assay of Pb^{2+} ion in different samples is of urgent need.

Potentiometric detectors based on ion-selective electrodes (ISEs) are efficiently suitable for accurate, reproducible and selective determination of various metal ions. Because of some offer mention advantages including selectivity, sensitivity, good precision, simplicity and so on. These methods allow direct on-line monitoring of concentration of selected species without any significant prior pretreatment [9–13].

Because of the urgent need for fast and accurate determination of Pb^{2+} ion in wide concentration range in various real samples with complicated matrices, Pb^{2+}-selective electrodes based on different ionophore has been reported [14–17]. Since preparation of Pb^{2+} -ISEs associated with serious difficulties [18, 19], relatively high effort has been focused to the development of Pb^{2+} -ISEs.

In this paper, a newly synthesized Schiff base successfully has been applied as an appropriate neutral carrier for construction of Pb^{2+}-selective PVC membrane sensor for its potentiometric determination of Pb^{2+} ion. The proposed electrode exhibits significantly good selectivity to Pb^{2+} over alkali, alkaline earth and several transition and heavy metal ions.

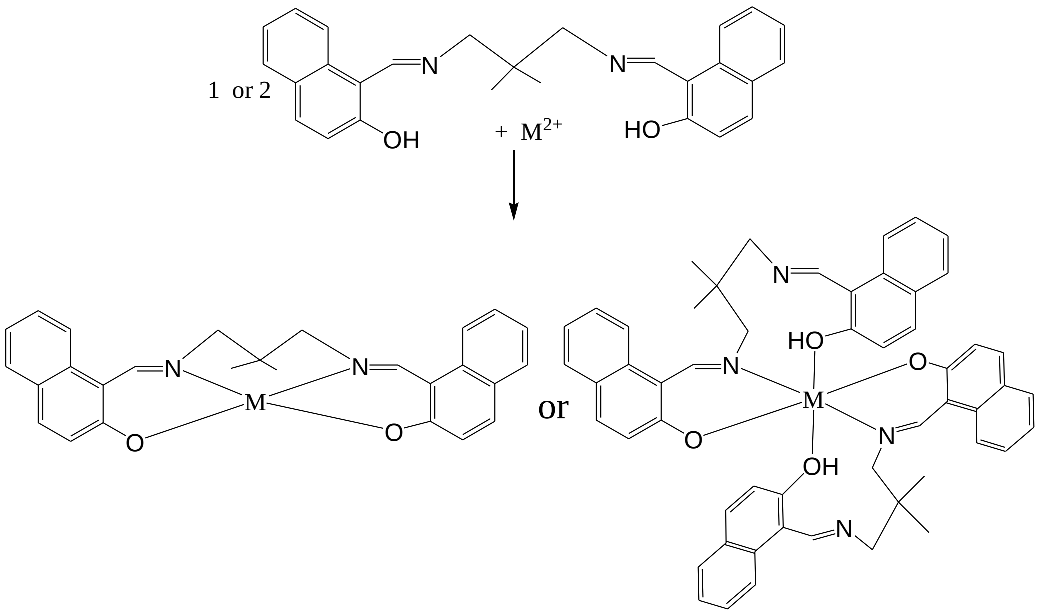
2. EXPERIMENTAL

2.1. Apparatus, reagents and materials

All the potential and pH measurements were carried out with a pH/Ion meters model 691 (Metrohm). The UV–VIS model Perkin Elmer (Lambda25) spectrophotometer with 1.0 cm glass cell was used for absorbance measurement. All chemicals (analytical reagent grade) and doubly distilled water were used throughout. Reagent grade dibutylphthalate (DBP), dimethyl sebacate (DMS), diethyl sebacate (DES) high relative molecular weight poly vinyl chloride (PVC), sodium tetraphenylborate (NaTPB) were purchased from sigma Aldrich (Germany) and used as received. Tetrahydrofuran (THF) was distilled before use. The stock solution of 0.5 M Pb^{2+}ion was prepared by dissolving appropriate amount of its nitrate salt in 100 ml of doubly distilled water.

2.2. Preparation of 1-((3-((2-hydroxynaphthalen-1-yl) methyleneamino)-2,2-dimethylpropylimino) methyl) naphthalen-2-ol (HMDMN)

A solution of 2,2-dimethyl-1,3-propylenediamine (0.51 g, 5 mmol) in absolute EtOH (20 mL) was added to a solution of 2-hydroxy-1-naphthaldehyde (1.722 g, 10 mmol) in absolute EtOH (20 mL) and boiled under reflux for 4 h. The reaction mixture was placed in the refrigerator overnight and then kept for several days to reduce solvent. The powder was filtrated and washed twice with cooled ethanol and dried under air (81 % yields). Elemental analysis, % $C_{27}H_{26}N_2O_2$: C, 79.00; H, 6.38; N, 6.82; found: C, 78.9; H, 6.4; N, 6.5. IR(KBr, cm^{-1}): 2500-3500(bm, νOH), 3053(w, CH- Aromatic), 2960(w, CH- Aliphatic), 2931,(w, CH- Aliphatic), 2873(w, CH- iminic), 1628(vs, -C=N), 1545(m, C=C), 1516(m, C=C), 1491(m, C=C), 1471(m, C=C), 1354(m), 1274(s, C-N), 1250(m), 1209(m), 1186(m, C-O), 1143(m), 827(s), 747(s), 506(w). The schematic diagram of interaction of pb^{2+} with proposed ligand is illustrated in scheme 1.



Scheme 1. Formation of ML and/or ML_2.

2.3. Electrode preparation

The coated-graphite electrodes were prepared according to previously reported method [20-22]. Graphite rods (3 mm diameter and 10 mm long) were prepared from spectroscopic grade graphite. A shielded copper wire was glued to one of graphite rod with silver loaded epoxy resin and the rod was inserted into the end of a PVC tube. The working surface of the electrode was polished with a polishing cloth. The electrode was rinsed with water and methanol and allowed to dry. A mixture of PVC, plasticizer, NaTPB and ionophore was added to about (total mass of 100 mg) 2 mL of THF.

The polished graphite electrode was then coated by repeated dipping (several times, a few minutes between dipping) into the membrane solution. A membrane was formed on the graphite surface and was allowed to set overnight. After complete dissolution, the mixture was poured in the acrylic rings placed on a smooth glass plate and allowed to evaporate at room temperature. The resulting 0.5 mm thick transparent membrane was cut to size and attached to Pyrex tube. It was finally conditioned for 1 day by soaking in a 0.5 M Pb^{2+} solution.

2.4. Emf measurements

The emf measurements were carried out with the following cell assemblies: PVC membrane│Sample solution│Reference electrode that a double junction Ag/AgCl was used as reference electrode with a pH/mV meter. The pH of the sample solutions was monitored simultaneously with a conventional glass pH electrode. The performance of each electrode was investigated by measuring its potential in Pb^{2+} ion concentration in the range of $1 \times 10^{-1} – 1 \times 10^{-7}$ M by serial dilution of the 0.5 M stock solution at constant pH. The solutions were stirred and potential readings recorded when they reached steady state values. The data were plotted as observed potential versus the logarithm of Pb^{2+} ion concentration.

2.5. Potentiometric Titration

The jacketed cell containing test solution was equipped with a magnetic stirrer and a tightly fitting cap, through which the electrode system and 10-ml capacity Metrohm piston burette were inserted and sealed with clamps and O-rings. The atmospheric CO_2 was excluded from the titration cell with a purging steam of purified nitrogen gas. 30 mL of HMDMN 2.67×10^{-3} M, 50% dioxane-50% water solution was titrated in the absence and presence of 1.33×10^{-3} M metal ion with a standard carbonate-free NaOH solution (0.086M), while strength was adjusted to 0.1 M with $NaClO_4$. In the first pH was measured and allowed system sufficient time for the establishment of equilibrium. HMDMN protonation constants and stability constants of its metal ion complexes were evaluated using the BEST program described by Martell and Motekaitis [20]. The value of autoprotolysis constant for 50% dioxane-50% water (v/v) solvent (Ks = $[H^+]$ $[OH^-]$) was calculated according literature [20].

2.6. Procedure for the determination of Pb^{2+} in water and soil samples

Twenty grams of homogenized soil sample in a 200 mL beaker was digested with addition of 10 mL concentrated HNO_3 and 2 mL of $HClO_4$ 70% (w/w) using a heated for 1 h. The content of beaker was filtered through a Whatman No. 40 filter paper into a 250 mL calibrated flask and its pH was adjusted to about 4.0 and diluted to mark with de-ionized water and its Pb^{2+} ion content was determined by standard addition method. Water and soil samples containing different Pb^{2+} ion concentrations were prepared by adding known amounts of Pb^{2+} ion to blank water and soil. The Pb^{2+} ion selective and reference electrodes were immersed in these samples and the Pb^{2+} ion concentrations were determined by direct potentiometry and using the standard addition technique. A blank value for the corresponding blank water or soil samples was also obtained to correct the above results.

3. RESULTS AND DISCUSSION

3.1. Potentiometric investigation of complexation of ionophore with Pb^{2+} ion

It HMDMN is insoluble in acidic and in neutral aqueous solution while it is soluble in some organic solvents. In order to obtain a clue about its efficiency and suitability for application as efficient Pb^{2+} ion ionophore, its complexation with Pb^{2+} ion was investigated potentiometrically in 50% dioxane-50% water (v/v) solvent. In preliminary experiments, the HMDMN was titrated with a standard NaOH in a 50% dioxane-50% water (v/v) solvent (Fig.1a), to obtain some information about its protonation constants. The protonation constants of HMDMN in a 50% dioxane-50% water solvent were calculated for the first time by fitting the potentiometric pH data using BEST program according to previous publication [19-21] and the results are shown in Table 1. The HMDMN is tetradentate with two adjacent weak amine donors and two strongly basic phenolate groups. According to these results, it can be concluded that in pH> 5.0 HMDMN has two protonation constants, while 12.05 and 23.41 are related to the protonation of two phenol oxygen's.

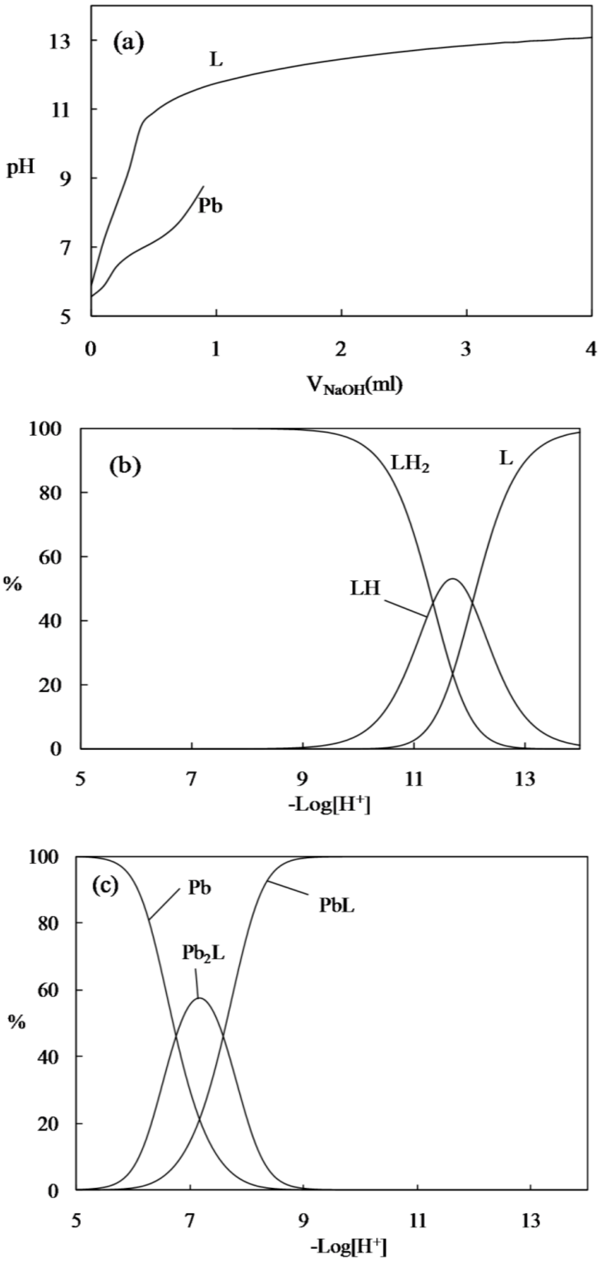


Figure 1. Potentiometric titration curves of HMDMN (L) (a) in the absence and presence of Pb^{2+} ion with NaOH 0.086 M in 50% dioxane-50% water (v/v) solvent at 25 °C and μ=0.1 M $NaClO_4$ and distribution diagrams of L (b) and of L/Pb^{2+} binary system(c).

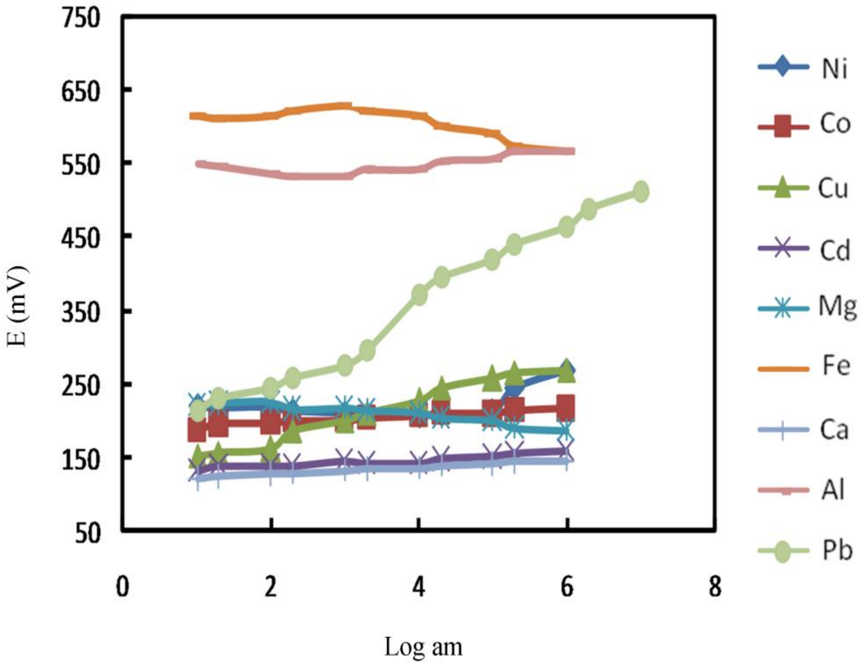


Figure 2. Potential response of various ion-selective membranes based on PVC- HMDMN.

In order to evaluate the stoichiometry and stability of the Pb^{2+} ion complexes with HMDMN (50% dioxane-50% water solvent) 2.67 $\times 10^{-3}$ M concentration of HMDMN in the presence of the 1.25×10^{-2} M Pb^{2+} ion were titrated with a 0.086 M solution of NaOH at 25±0.1 °C and 0.1 M ionic strength maintained by $NaClO_4$ (Fig. 1a). It was seen that the potentiometric titration curve of HMDMN is depressed considerably in the presence of the Pb^{2+} ion and distribution diagram for HMDMN is shown in Fig. 1b. Titration of HMDMN in the presence of metal ion continued till the formation of precipitate in solution.

To investigate the suitability of the HMDMN as Pb^{2+} selective ion carrier in preliminary experiments it was applied for PVC membrane ion-selective electrodes for a variety of cations including alkali, alkaline earth and some transition metal ions and their potential responses after conditioning in the respective nitrate solution of each cation is shown in Fig. 2. As it can be seen, among all investigated cations, Pb^{2+} ion show the Nernstian potential response while for all other cations the slope of the corresponding potential–Log plots was much less than the expected Nernstian slopes (59.0 and 29.5 mV/decade for mono and divalent cations). This is most probably due to the selective behavior and interaction of the ionophore for Pb^{2+} over other metal ions as well as the rapid exchange kinetics of the resulting complex.

The extent of depression obviously depends to the stoichiometry and stability constant of resulting complexes and respective cumulative stability constants of $M_mL_lH_h$, β_{mlh}, defined according our previous publications [13-20]. M, L, and H represent metal ion, HMDMN and proton respectively and m, l, and h are the respective stoichiometry coefficients. The potentiometric pH titration curves of HMDMN in the presence of metal ions were fitted to the BEST program, and the corresponding distribution diagram is shown in Fig 1c and respective constants are presented in Table 1. These results revealed that, Pb^{2+} ion form strong complexes with HMDMN (L).

Table 1. Overall and stepwise protonation constants of HMDMN and stability constants of HMDMN/Pb^{2+} binary system in a 50% dioxane-50% water (v/v) solvent at 25 ˚C and $\mu = 0.1$M $NaClO_4$.

System	m	l	h	Logβ	LogK	Max %	at pH
HMDMN	0	1	1	12.06	12.05	52.95	11.66
	0	1	2	23.41	11.41	100	5.50-7.67
HMDMN-Pb^{+2}	1	1	0	11.90	11.90	100	10.04<
	2	1	0	15.71	3.81	57.70	7.16

In the Pb^{2+}-HMDMN binary system computer refinement of the titration data showed the presence of PbL and Pb_2L species. Due to high stability constant and its low tendency for dissolving in suitable carrier for construction of Pb^{2+} ion selective electrode.

3.2. Influence of membrane composition

The nature of incorporated ionophore, amount of carrier and additive and plasticizer/PVC ratio has strongly influence on the performance of each ISE. [23-25]. Thus, different aspects of membrane based on DBP for concentration of a new Pb^{2+}-ISE were optimized and the results are summarized in Table 2. As can be seen a near-Nernstian response, low detection limit and good calibration reproducibility were obtained. The optimization of perm- selectivity of membrane sensors is known to be dependent on the incorporation of additional membrane compounds. Generally, membrane additives by reducing ohmic resistance [26], improving the response behavior and selectivity of electrode [27] and increasing the extraction capability and efficiency of ionophore lead to significant improvement in electrode response [28]. Moreover, the additives may catalyze the exchange kinetics at the sample-membrane interface [27,29]. The results obtained with different membrane compositions show the membrane composition (number 14) of PVC: DBP: carrier: NaTPB: NaTPB /carrier (mole ratio = 0.83) with the percent mass ratio of 28.9:57.8: 8.0: 5.33 was selected in subsequent works for the evolution of performance of proposed electrode. The slope and detection limit of the electrode were evaluated from repeatedly carrying out the calibration between 1.0×10^{-6} and 1.0×10^{-1} M and the respective calibration parameters are presented in Table 2.

The results show that this ISE has a rapid response even to low concentrations of Pb^{2+} ion. The dynamic response time of the membrane was measured at various concentrations (1.0×10^{-5} to 1.0×10^{-2} mol L^{-1} of pb^{2+} ion (10 time difference in concentration) and respective results are presented in Fig. 3. As it can be seen in the whole concentration range the electrode reaches equilibrium response within about 10 s. The life time and stability of the electrodes were tested by repeated monitoring of potentials and plotting calibration curve over a period of 2 months. It was seen that the proposed electrode at optimum values of all variables show very slight gradual decrease in the calibration slopes of the electrodes during this period shows the applicability of the proposed electrode for accurate and fast determination of pb^{2+} ion concentration. The slope of electrode was 25.79±0.80 which indicate high reproducibility of proposed electrode. The repeatability of electrode response by calculating the standard deviation of six replicate measurements with one electrode at fixed concentration of Pb^{2+} ion respective to linear range and slope was ±0.42 and 1.15 that indicate the repeatability of response of proposed electrode.

Table 2. Optimization of membrane ingredients.

N	PVC (mg)	Plastisizer (mg)			Carrier (mg)	NaTPB (mg)	R^2	L. R. (µM-M)	Slope (mV/decade)
		DMS	DES	DBP					
1	30	-	-	60	2.0	4.0	0.992	0.1-0.1	15.13
2	30	-	-	60	4.0	4.0	0.993	1.0-0.1	12.04
3	30	-	-	60	6.0	4.0	0.992	5.0-0.1	20.31
4	30	-	-	60	8.0	4.0	0.994	10-0.1	22.3
5	30	-	-	60	10.0	4.0	0.976	1.0-0.1	21.01
6	29.4	58.6	-	-	8.0	4.0	0.854	0.1-0.1	21.14
7	29.4	-	58.6	-	8.0	4.0	0.983	1.0-0.1	19.78
8	29.4	-	-	58.6	8.0	4.0	0.985	0.1-0.1	24.50
9	29.33	-	-	-	8.0	4.0	0.870	1.0-0.1	14.50
10	30.7	-	-	61.3	8.0	0	0.995	1.0-0.1	10.10
11	30.2	-	-	60.44	8.0	1.34	0.991	1.0-0.1	20.60
12	29.8	-	-	59.6	8.0	2.67	0.997	1.0-0.1	24.07
13	29.3	-	-	58.66	8.0	4.00	0.995	1.0-0.1	23.96
14	28.9	-	-	57.8	8.0	5.33	0.991	1.0-0.1	25.79
15	28.4	-	-	56.88	8.0	6.68	0.992	1.0-0.1	19.98

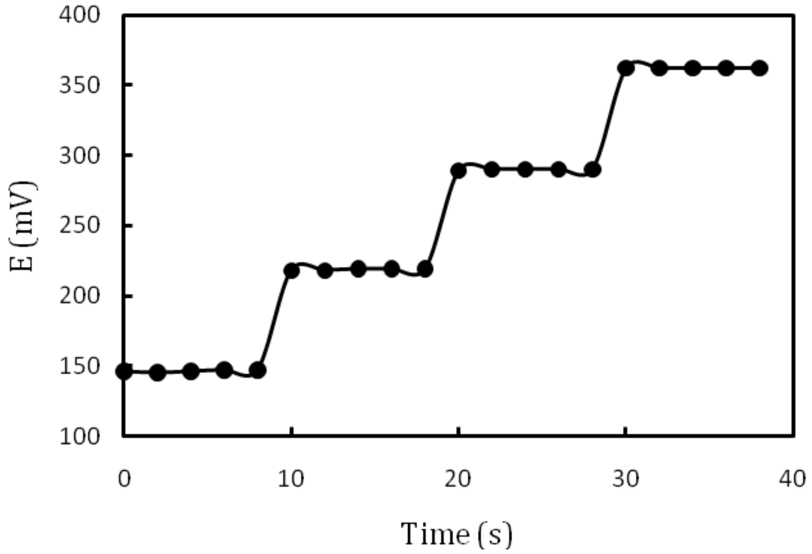


Figure 3. Response time of proposed of the Pb^{2+} ion selective electrode based on PVC- HMDMN in the presence of different concentrations ($1.0\times10^{-5} – 1.0 \times 10^{-2}$) of Pb^{2+} ions**.**

3.3. effect of pH

The effect of pH on the electrode potential at various Pb^{2+} ion concentrations was studied by adding diluted solutions of HCl or NaOH in the range of 1.5–9.5 (Fig. 4) [29].

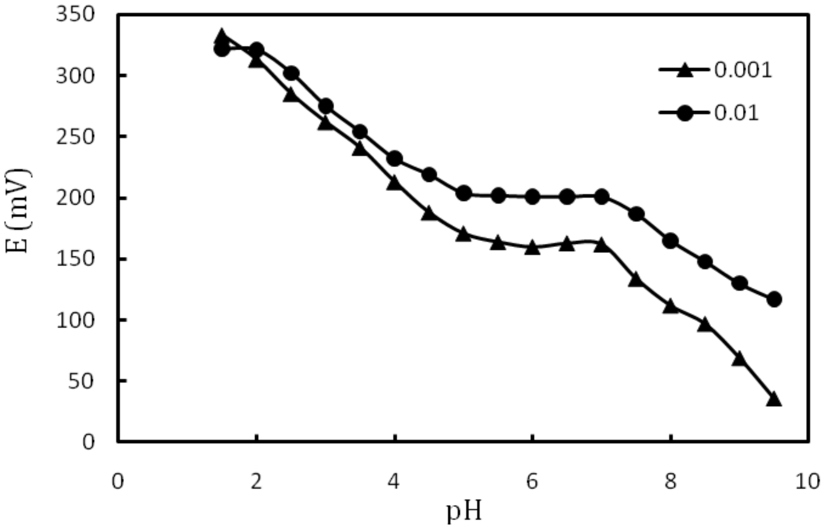


Figure 4. Effect of pH test solution on the potential response of the Pb^{2+}-ISE based on PVC- HMDMN in the presence of 1.0×10^{-2} and 1.0×10^{-3} M Pb^{2+} ion.

The results showed that its electrode potential was independent on the pH of solution in the range of 5–7.2. Drastic potential changes are observed at higher and lower pH values. This is most probably due to the simultaneous response of the electrode to Pb^{2+} and OH−, at pH >7.2, and at pH

<5.0 probably due to protonation of the N atoms of ionophore which lead to the decomplexation process the electrode response decrease significantly.

3.4. Selectivity coefficients of Pb^{2+} ion selective electrode

Potentiometric selectivity coefficient of any proposed electrode (relative response to other ions present in solution) depend on the activity and the method of their determination can be evaluated using different methods such as separate solution method (SSM) and mixed solution method (MSM) [30-32]. The Nicolskii coefficient is often determined by the so-called separate solution method by comparing two solutions, each containing a salt of the primary and interfering ion only. The selectivity coefficient, K_{IJ}^{SSM}, is determined by following Eq. (1):

$$ln_{IJ}^{SSM} = \frac{Z_I F[E_2 - E_1]}{RT} - ln\alpha_1(1 - \frac{Z_I}{Z_J}) \qquad (1)$$

In Eq. (1) it is considered that $\alpha_I = \alpha_J$. E_1 and E_2 are the response of the electrode to main and interfering ion, respectively. In the fixed interference method (FIM) which is a type of the mixed solution method (MSM), selectivity coefficients of the Pb^{2+} sensor were evaluated graphically with a fixed concentration of the interfering ions (1.0×10^{-3} mol L^{-1}) and different amounts of the Pb^{2+} ion; the results are shown in Table 3.

Table 3. The selectivity coefficients ($Log_{pb,M}^{pot}$) of diverse ions.

Ion	-Log K	
	SSM	FIM
Cr^{2+}	0.30	0.24
Ni^{2+}	1.90	1.95
Ca^{2+}	0.15	0.21
Co^{2+}	1.30	1.31
Zn^{2+}	1.50	1.59
Cu^{2+}	0.40	0.52
Mn^{2+}	2.03	2.02
Ba^{2+}	3.6	3.65
Cd^{2+}	2.90	2.98
Na^{+}	1.56	1.64

The MSM based on the semi empirical Nikolskii–Eisenman equation is of questionable validity when ions of different charge are present; therefore the MPM was applied to these ions. The meaning of selectivity coefficients K_{IJ}^{FIM} determined with this method is intuitively convincing, because they clearly reflect what is observed with real-world sensors in relevant samples. The selectivity coefficient, K_{IJ}^{FIM} , is determined by the following Eq. (2):

$$K_{IJ}^{FIM} = \frac{\alpha_1(DL)}{\alpha_J(BG)^{z_I/z_J}} \qquad (2)$$

From Table 3, it can be seen that the electrodes based on HMDMN is highly selective response for Pb^{2+} ion toward with variety of cations. There is a satisfactory agreement between the two sets of results obtained for several cations by the SSM and FIM methods. The order of selectivity for the ionophore clearly indicates that there is a strong and selective interaction between HMDMN and Pb^{2+} ion[33].

3.5. Applications

Characteristic performance and properties of this new proposed Pb^{2+}-ISE is presented in Table 4. The new Pb^{2+} ion-selective electrode was applied for the determination of Pb^{2+} ion in river and well water and soil samples and respective results are presented in Table 5. The investigated accuracy of analysis assessed using the standard addition technique show good recoveries for all samples.

Table 4. Response characteristics of the proposed Pb^{2+} ion selective electrode

Properties	Values / Range
Optimized membrane composition (% by weight)	PVC (28.9), DBP (57.8), carrier(8.0), NaTPB (5.33)
Electrode type	Coated-graphite (solid contact) electrode
pH range	5-7.2 for both electrodes
Conditioning time	at least 18 h in 0.1 M $Pb(NO_3)_2$
Linear range (Pb^{+2} M)	1×10^{-6} - 1×10^{-1}
Slope (mV/decade)	25.79
Detection limit (M)	4×10^{-7}
Standard deviation of slope (within electrode variation, mV/decade)	± 0.8
Response time (s)	≤ 10

The presented results, in Table 5 indicate that the amount of Pb^{2+} ion evaluated with the help of the sensor is in good agreement with those obtained by the standard addition method, thereby reflecting its utility for evaluating the Pb^{2+} ion content in real samples with complicated matrices.

Table 5. Application of the proposed Pb^{2+} selective electrode for determination of Pb^{2+} ions concentration in real samples.

Sample	Add value	Found	RSD (%)	Recovery
Soil	0.0*	32	2.1	
	10.0	43.6	2.2	116
River water	0.0	40	3.0	
	10.0	51.9	2.0	119
Well water	0.0	60	2.5	
	10.0	73.9	2.3	139

*All values are in μM.

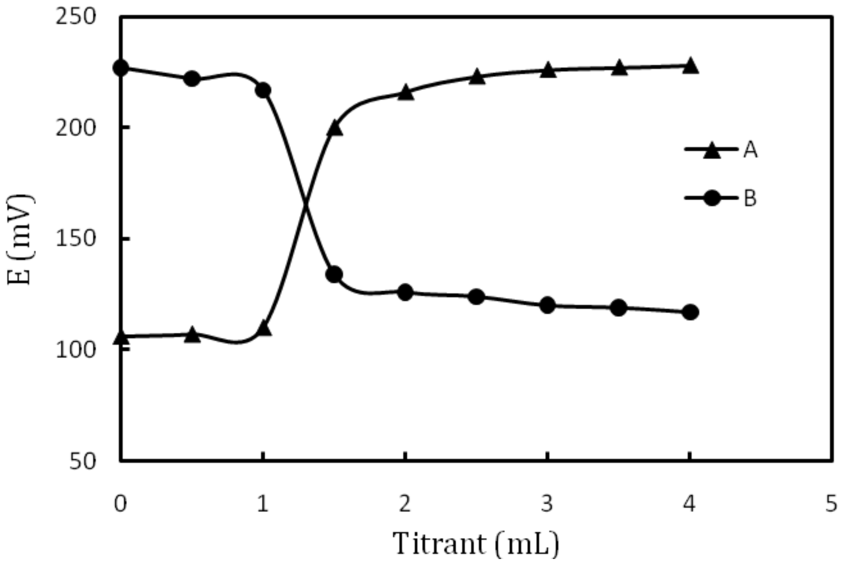


Figure 5. Titration curve of 1.3 mL of 0.01 M of Pb^{2+} ion with 0.1 EDTA (A) and reverse (B) at optimum condition of Pb^{+2}-ISE according to Table 2.

The proposed electrode was also successfully applied as an indicator electrode in conjunction with Ag/AgCl reference electrode for the potentiometric titration of CrO_4^{2-} solutions with Pb^{2+} ion and vice versa. The results of the titration for 1.3 ml of 0.01 M $EDTA^-$ with 0.1 M Pb^{2+} ion showed in Fig. 5. It can be seen that, the amount of CrO_4^{2-} and Pb^{2+} ion in solution could be accurately determined with the proposed electrode. A very good inflection point (165 mV) observed in the titration plot shows the perfect stoichiometry.

4. CONCLUSIONS

The newly synthesized 1-((3-((2-hydroxynaphthalen-1-yl) methyleneamino)-2,2-dimethylpropylimino) methyl) naphthalen-2-ol efficiently has been applies as good ionophore for the development of PVC-based Pb^{2+} ion-selective electrode. The electrode responded to Pb^{2+} ion in a

Nernstian fashion and displayed a low limit of detection 4×10^{-7} and wide linearity 1×10^{-6} - 1×10^{-1} Pb^{2+} ion. The electrode characteristics such as linear range, response time and specially selectivity were comparable to the previously reported Pb^{2+} ion-selective electrodes. The electrode can be successfully applied to the recovery of Pb^{2+} ions from various real samples with complicated matrices.

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