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LEAD (II)-SELECTIVE POLYMERIC ELECTRODE USING PVC MEMBRANE BASED ON A COMPLEX OF 1,3-DIPHENYL-5-P-NITRO PHENYL FORMAZAN AND LEAD (II) AS AN IONOPHORE

Hajar Nasser [1]* Mossab Barakat Khalil*[2]

*1. **Associate professor, Department of Chemistry, College of Sciences, Tishreen University, Latakia, Syria.**
2.PhD student, Dept. of chemistry, Associate Professor, Department of Chemistry, college of Sciences, Tishreen University, Latakia, Syria.

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ABSTRACT

A PVC membrane electrode for lead ion based on 1,3-diphenyl-5-p-nitro phenyl formazan As an Ionophore was prepared. The electrode exhibits a Nernstion response (29.524mv/decade) for lead ion over a relatively wide concentration rang (1.0×10^{-6} to1.0×10^{-1}) with a limit detection 5.37×10^{-7}M. It has a relatively fast response time (<10 s). The proposed membrane electrode revealed very good selectivity in the PH= 4-8. The influence of membrane composition enthe electrode response was studied. The proposed electrode was used for the determination of lead ion in wastewater, water and wastewater of manufactory.

INTRODUCTION

Ion-selective sensors have been used for analytical determination of a wide variety of ions since the 1970s. Ion-selective sensor's utility and simplicity have replaced other wet analytical methods that were often far slower and more cumbersome to perform. Ionophore plays a key role in the sensitivity of an ion-selective electrode (ISE). The creation of cavities and cleft in the ionophore that are complementary to the size and charge of a particular ion can lead to very selective interactions. One of the most important figures of merit for ISEs is the selectivity towards a specific analyte, which is generally limited by the interaction of ionophore within the membrane with other ions in solution. Recently, there has been much focus on the construction of anion-selective electrodes that function on the basis of chemical recognition principle [1]. The demand for ionophores with either new or improved selectivities in the field of ion selective

*Corresponding Author:
Hajar Nasser
Associate professor, Department of Chemistry, College of Sciences, Tishreen University, Latakia, Syria

electrodes (ISEs) is high particularly in the area of anion-selective electrodes.

The ion-selective electrode (ISE) dynamic response is generated by the selective complexation of the target ion by the ion carrier that is dispersed in a poly(vinyl chloride) (PVC) matrix. The ISEs that are based on polymeric membranes incorporated with ionophores are well known to be very useful tools for clinical, chemical and environmental analysis. Until now, large numbers of ionophores with high selectivity for specific metal ions have been developed as potentiometric sensors for the determination of the respective metal ions. The ISEs for determining the lead ion have received much interest, and many ligands have been studied for their use as sensing ionophores[2-5]. Piroxicam, quinaldic acid, capric acid, diaza-crown, dibenzyl phosphate, benzyl sulfide, acyclic diamide, anthraquinone, calix-azo, calixphosphine oxides, thiacrown 5,5'-dithiobis-2-nitrobenzoic acid, crown-ethers, polyaminoanthraquinone 1,2- bis(salicylidin aminooxy)ethane, and porphyrins as ionophores have been used for lead-ISEs[6-15]. The presence of toxic heavy metal ions in industrial wastewater has generated considerable concern in recent years. Heavy metal contamination exists in aqueous waste streams of many industries, such as metal plating facilities, mining operations and tanneries. The soils surrounding many military bases are also contaminated and pose a risk of metal ground water and surface water contamination. Among the toxic heavy metal ions which present potential danger to human health are copper, lead, cadmium, chromium and mercury. these heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders [16-22]. The feature of Schiff bases allow geometric and cavity control of the host-guest complexation and modulation of its lipophilicity, and this produces remarkable selectivity, sensitivity and stability for a specific ion. The resulting Schiff base complexes have attracted increasing attention in the field of ionic binding due to their unique properties and reactivity. In order to improve the selectivity for the lead ion compared with the other ions, we used a new ionophore. Therefore in the present study, we describe the preparation and characterization of new ISEs that are based on as a new ionophore. The coordinating effect for the selective response of the lead ion was investigated by using PVC membranes. Polymeric ISEs provide one of the most powerful sensing methods because it is possible to select various sensory elements according to the shape and size of the target ion. The ISE based on 1,3-diphenyl-5-p-nitro phenyl formazan exhibits good sensitivity and selectivity towards the lead ion.[23-26]

MATERIALS & METHODS

The 1,3-diphenyl-5-p-nitro phenyl formazan As an Ionophorethat was tested as a lead(II) ionophore is shown in (Fig.1). High molecular weight PVC, Dioctylesebacate (DOS), Dibutyle phthalate (DBP), and Tetrahydrofuran (THF), Sodium tetraphenyl borate(NaTPB) were all obtained from Merck, and these substances were used to prepare the PVC membranes. The nitrate salts of the cations we used (all from Merck) were of the highest purity available. Doubly distilled water in a quartz apparatus was used to prepare all the aqueous electrolyte solutions. The typical composition of the PVC-based lead (II)-selective electrodes was 35.4% PVC, 57.0% plasticizer, 7% ionophore and 0.6% additive. The ionophore, plasticizer, additive and PVC were dissolved in the appropriate volume of THF and this was mechanically stirred. All the membrane cocktails were cast in glass rings placed on glass plates for creating the conventional ion-selective electrodes. The solvent from the PVC membrane was allowed to evaporate for at least 24 hours at room temperature. The thickness of the resulting membrane, as measured by a micrometer, was about 0.3mm. The tube was then filled with internal filling solution (1×10^{-3}M)Pb(NO3)2. The electrode was finally conditioned for 24 h by soaking in a 1×10^{-2}M solution of lead (II) nitrate. A silver/silver chloride electrode was used as an internal reference electrode. The ratio of various ingredients, concentration of equilibrating solutions, and time of conditioning were optimized in order we have reproducible membranes and the potentials with relatively little noise. The composition of the membrane electrode is summarized in Table1. All emf requirements were carried out with the following cell assembly

Ag/AgCl| 3MKCl| samplesolution| electrodemembrane| 1.0×10−3MPb (NO3)2| 3MKCl| Ag/AgCl

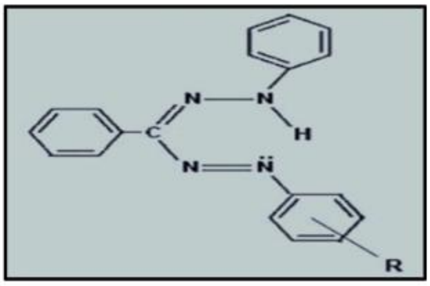

Figure 1. structure of ionophore 1,3-diphenyl-5-p-nitro phenyl formazan : R=NO_2

Table 1 Optimization of membrane ingredients of Pb2+-selective electrode

No	Composition %				Concentration range M	Slope
	additive	Plasticizer	PVC	Ionophore		
1	7	36.6	56.4 DOP	--	16.7	1×10^{-5}- 10^{-1}
2	3	38.0	58.0 DOP	1 NaTPB	35.379	3×10^{-4} – 10^{-1}
3	4	31.0	64.0 DOP	1 NaTPB	21.92	3×10^{-4} – 10^{-1}
4	7	27.0	65.0 DOP	1 NaTPB	20.133	1×10^{-4} – 10^{-1}
5	7	30.0	61.4 DOP	1.6 NaTPB	36.195	3×10^{-5} – 10^{-1}
6	7	30	62 DOP	1 NaTPB	35.081	9×10^{-5} – 10^{-1}
7	7	35.4	57.0 DOP	0.6 NaTPB	28.6	1×10^{-6} – 10^{-1}
8	7	34.0	57.0 DOP	2 NaTPB	21.409	9×10^{-5} – 10^{-1}
9	7	36.0	56.0 DOP	1 NaTPB	14.155	3×10^{-4} – 10^{-1}
10	7	36.0	55.4 DOP	1.6 NaTPB	21.02	9×10^{-5} – 10^{-1}
11	7	35.4	57.0 DOP	0.6 PbSO4	--	--
12	7	35.4	57.0 DOP	0.6 PbS	--	--
13	7	35.4	57.0 DOP	0.6 PbI2	--	--
14	7	35.4	57.0 DOP	0.6 PbCl2	--	--
15	7	35.4	57.0 DBP	0.6 NaTPB	29.524	1×10^{-6} – 10^{-1}

Table2 Selectivity coefficients (-Log $K^{MPM}_{Pb^{+2},M^{+n}}$) for the various different lead ion selective electrodes, No.15 in Table 1

Interference ion	Piroxicam	Dibenzyl phosphate	Calix phosphine oxide	Schiff base BTEA	Schiff base BTPD	PAAQ Polyaminoanthraquinone	This work
Cu2+	1.9	4.5	4.3	3.3	3.1	1.23	1.6
Ba2+	2.2	×	×	2.6	3.0	2.44	1.88
Cd2+	2.3	3.2	5.3	3.4	3.5	-	1.5
Zn2+	2.9	5.2	4.5	3.7	3.8	-	3.69
Ca2+	4	2.3	2.3	4	4.0	2.51	3.79
Mg2+	2.4	×	×	4.6	×	-	2.4
Na+	1.4	3.5	0.8	3.2	3.0	2.14	2.4
K+	2.2	2.8	2.5	3.1	3.0	2.36	1.69
Ni2+	×	×	×	×	×	-	2.6
Co+2	×	×	×	×	×	-	1.79
Reference	[11]	[13]	[14]	[16]	[21]	[22]	--

RESULTS AND DISCUSSIONS

Formazans dyes as ligands seem to have potential to serve as ionophores for soft heavy metal ions in the PVC membrane electrodes because of their excellent metal-binding properties, their water insoluble and their rapid exchange kinetics. 1,3-diphenyl-5-p-nitro phenyl formazan As an Ionophorewas used as an ionophore for preparing the PVC membrane ion-selective electrodes for a wide variety of metal ions. Table 1 shows the compositions of the ionophore, the plasticizer, the additive and the PVC. Figure 4 shows the pH dependence for the potentiometric response of the novel membrane electrode in a variety of pH solutions. It is clear from Fig. 4 That the potentials were found to stay constant from pH 4 to 8, beyond which the potential changes considerably. The sharp change in potentials at higher pH values may be due to the hydrolysis of the Pb^{2+} ions to form lead hydroxide while at lower pH values, there is an increase in potential of the electrode which indicates that the sensor responds to hydrogen ions. The Pb^{2+}-ISE membrane compositions were optimized to obtain the best sensitivity and selectivity towards the lead ion because the sensitivity and selectivity of the ion-selective electrodes were dependent upon the nature of ionophore used, as well as being significantly dependent on the membrane composition and the additives that were used. The optimization was carried out by varying the ratio of the PVC membrane components such as the PVC, the plasticizer, the ionophore and the additive (NaTPB).

Table 3 Comparison of the Pb^{+2} selective electrodes with reported electrodes

Ionophore	Slope mv/decade	Working concentration range M	Detection limit M	Response time S	pH range	Reference
Bis(acetylacetone)-p-phenylenediamine-lead(II)[LPb(NO3)2]H2O complex ionohore	30	$1{\times}10^{-5}$- $1{\times}10^{-1}$	$2{\times}10^{-6}$	10<		5
N,N'-bis(5-methyl salicylidene)-p-diphenylene methane diamine	29.4	$5{\times}10^{-6}$- $1{\times}10^{-1}$	$2{\times}10^{-6}$	10<		17
N,N'-bis(3-methyl salicylidene)-p-henylene methane diamine	30.3±0.6	$2{\times}10^{-5}$ – $1{\times}10^{-1}$	$1{\times}10^{-5}$	10<		18
1,10-dibenzyl-1,10-diaza-18-crowne-6	29.1,28.9	$5{\times}10^{-6}$- $1{\times}10^{-1}$	$3{\times}10^{-6}$	10<		19
N,N'-bis-thiophene-2-ylmethylene- ethane-1,2-diamine	29.79	$1{\times}10^{-5}$- $1{\times}10^{-1}$	$2.04{\times}10^{-6}$	10<		16
N,N'-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane(I)	30±0.1	$8.2{\times}10^{-6}$–$1{\times}10^{-1}$	$8.2{\times}\ 10^{-6}$	10<		20
thioamide functionalized calyx [4] arenes	28.7	$1{\times}10^{-6}$ –$1{\times}10^{-2}$	$5{\times}{\times}10^{-6}$	< 10	3 - 6	23
1, 10-dibenzyl-1, 10-diaza-18-crown-6 (DBzDA18C6)	25.79	$1{\times}10^{-6}$ –$1{\times}10^{-1}$	$4{\times}10^{-7}$	≤10	5-7.2	24
1,2- bis(salicylidin aminooxy)ethane	26.49±0.7	$1{\times}10^{-6}$ – $1{\times}10^{-1}$	$7.6{\times}10^{-7}$	10<		25
N,N'-N"-tris(2-pyridyloxymethyl) ethane	30	$1{\times}10^{-5}$ –$1{\times}10^{-1}$	$1{\times}10^{-5}$	15±2	2.6-6.3	26
This work	29.524	$1{\times}10^{-6}$ – $1{\times}10^{-1}$	$5.37{\times}10^{-7}$	≤10	4-8	

The potentiometric response of the membranes was evaluated as to the slope and the detection limit towards the lead ion. The effects of the membrane composition, the nature of plasticizers, the ionophores and the lipophilic additive on the potentiometric response of the Pb^{2+}-ISE were investigated and the results are summarized in Table 1. A membrane prepared displays a good Nernstian response to Pb^{2+} over a wide range. The slope of the calibration curve was 29.524mV/decade of the Pb^{2+} concentration at room temperature, and the limit of detection (LOD) of the log a (M) was equal to −6.27. The effect of the plasticizer on the Pb^{2+}-ISE membrane electrodes based on the **1,3-** diphenyl-5-p-nitro phenyl formazan As an Ionophore is shown in Figure 5. The response time of the membrane electrode thus obtained was < 10 s for the addition of 1.0×10^{-3} M Pb^{2+} to the 1.0×10^{-5} M lead ion (Fig.6). The potentiometric selectivity coefficients measure the response of the electrode for the primary ion in the presence of foreign ions Table 2.That shows potentiometric selectivity coefficient data of Pb(II)-selective electrode for interferingcations relative to Pb^{2+}, which indicate that the ISE is selective towards lead over the transition metal, alkali and alkaline earth metals, and other heavy metal ions. The optimized formulation of the sensor no. 15 was compared in terms of analytical performance with membranes employing different neutral ionophores that had been studied previously. Table 3 represents the main analytical features of some Lead(II) ionselective electrodes. The sensor is superior to existing sensors in terms of selectivity over anumber of cations while comparable with regard to other parameters such as working concentration range, slope, pH range, response time and reproducibility. Further, this sensor could be used in real sample analysis.

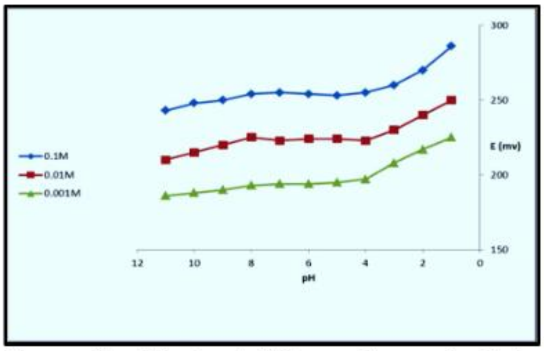

Figure 4. Effect of PH on the potential response the Pb^{+2} ion- selective electrode at different concentrations: 1×10^{-1}M , 1×10^{-2} M, 1×10^{-3}M

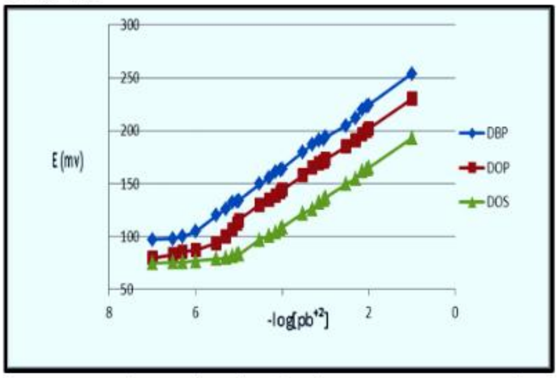

Figure 5. electrode The lead-ion responses of the membranes prepared by using different plasticizers

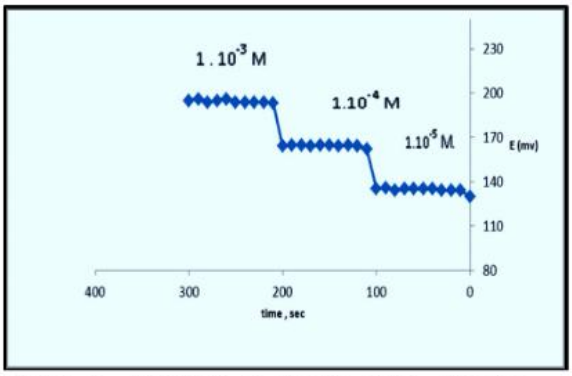

Figure 6. Dynamic response time of the membrane electrode based . 1,3-diphenyl-5-p-nitro phenyl formazan for step change in concentration of Pb+2 : 1×10-5M ,1×10-4M, 1× 10-3M .

CONCLUSIONS

The membrane electrode incorporating **1,3-** diphenyl-5-p-nitro phenyl formazan as an ion carrier can be used for the development of a lead ion-selective electrode. The membrane has a linear dynamic range between 1.0 × 10^{-1} M - 1.0 × 10^{-6} M with a Nernstian slope of 29.524 mV per decade, and its detection limit was 5.37× 10-7 M. The potentiometric response is independent of PH range of 4-8. Most of the metal ions would not seriously affect the selectivity of the lead electrode. It can be concluded that the membrane electrode has a rapid

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