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ORIGINAL RESEARCH ARTICLE

Ni^{2+} ion sensitive sustainable sensors based on 4-vinyl pyridine-ethyl acrylate copolymer

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ABSTRACT

Toxic metal ions present in environmental water samples and other samples need to be detected for their removal. The detection of trace metal ions using an ion selective electrode (ISE) holds great significance in analytical chemistry. A 4-vinyl pyridine-ethyl acrylate copolymer-polyvinyl chloride (VE-PVC) based polymeric matrix (electrode) has been fabricated by free radical bulk polymerization method which is an example of a green and sustainable method capable of detecting Ni^{2+} ions even in trace amounts. To fabricate the polymeric matrix (electrode) (PME), VE has been used as an ionophore. Further, the effectiveness of Ni^{2+} ion ISE has also been investigated in the presence of surfactants and detergents. Its performance has also been analyzed in the presence of plasticizers. The electrode is found to be very useful for the estimation of Ni^{2+} ions using ethylenediaminetetraacetic acid by potentiometric titration and also in the estimation of presence of Ni^{2+} ions in water. Compared to other metal ions, the fabricated membrane electrode developed in this work has been found to show efficient and better selectivity towards Ni^{2+} ions.

Keywords: 4-vinyl pyridine-ethyl Acrylate; Copolymer; Ni^{2+} Ion Selective Electrode; Potentiometry; PVC Membrane

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1. Introduction

Nickel is a toxic metal[1]. Thus, it is a cause of serious concern for the environmentalists. Industrial processes including battery production, mining, electroplating, refining processes, and natural processes like soil erosion contribute to the discharge of nickel ions into water bodies[2–5] endangering human life and livestock. Nickel can cause serious health hazards like pneumonitis, dermatitis, asthma, and cancer[6]. It is also responsible for kidney and blood disorders[7,8]. Due to these severe effects, selective monitoring of Ni^{2+} ions in industries, biological systems, environment and food samples[9–12] becomes imperative.

Numerous analytical techniques as well as HPLC and fluorometric methods[13,14] have been employed to determine the presence of Ni^{2+} ions in reported literature. Conventional methods like liquid-liquid extraction and analytical techniques are time-consuming and expensive besides using chlorinated organic solvents in the process. In contrast, the use of chelating polymer matrices for the determination of Ni^{2+} ions is an environmentally friendly green method of analysis[15,16]. The estimation of ions can be done by potentiometric titration method using ISE effectively. Several such electrodes have been described for the selective identification of ions[17–22].

Potentiometric estimation using an ion-selective electrode (ISE) includes easy preparation methods, effortless operation, fast response time and wide concentration ranges. The electrode is more selective for the ion to be estimated as compared to other interfering ions. This estimation technique is passive towards colour change and turbidity of the solution in which the ion has to be analyzed. Hence it becomes an effective tool that may be used to estimate analyte ions in industrial or environmental samples. Likewise, the requirement of estimation of Ni^{2+} ions in ecology and medicine has ignited interest of researchers in potentiometric sensors. As a result, numerous efforts have been put in to create Ni^{2+} ion selective membrane electrodes based on various ionophores[23–26]. However, several of these electrodes still have a number of drawbacks. The concentration range for working of the electrode is limited, and the period in which it gives response is more. Further, if the procedure is repeated, the same result is seldom obtained. Therefore, efforts to develop a Ni^{2+} ion selective electrode whose concentration range is greater and the detection limit is low, is an active field of research. Till now, extensive research has been reported on homopolymers. However, research in the field of copolymers has been explored to a smaller extent.

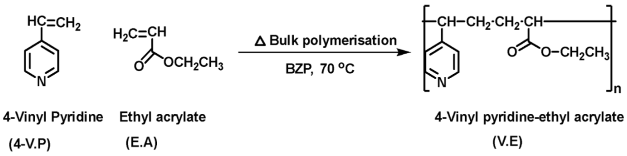
The present work reports the synthesis of a novel polymeric matrix (electrode) whose basis is the synthesized VE copolymer, which behaves as an effective ionophore for the identification of nickel ions.

2. Experiment

4-vinyl pyridine (V, E Merck), and ethyl acrylate (E, E Merck) were used after purification. THF, NaTPB, DBBP, TBP, DOP, DBP, NPOE, and polyvinyl chloride were all acquired from Aldrich (Wisconsin, USA). All solutions were prepared in deionized water. A digital potentiometer, and a pH meter from Elico-LI-MODEL-120 was used in our study.

2.1 Synthesis of copolymer-VE

To avoid polymerization, 4-vinyl pyridine and ethyl acrylate monomers were purified by distillation in a nitrogen atmosphere and stored below 5 °C. The purification of benzoyl peroxide was done in chloroform and methanol. While different solvents were refined by distillation prior to use, various initiators were also purified by recrystallization. Using benzoyl peroxide as an initiator and free radical bulk polymerization at 70 °C, VE copolymers were prepared and precipitated using methanol as shown in **Reaction 1**.



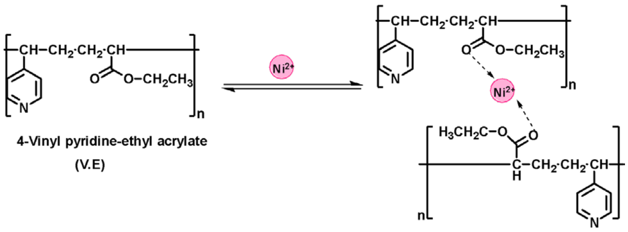
Reaction 1. Preparation of VE copolymer.

2.2 Synthetic procedure for the VE-PVC based sensor (polymer matrix electrode)

Fixed amounts of ionophore (VE copolymer) and PVC powder with and without plasticizer along with the anion additive in THF were taken to prepare the desired sensor. The resulting viscous mixture was allowed to rest in a circular ring kept on a glass plate. This was then kept undisturbed for 12 hours, to evaporate, which enabled the formation of an even, elastic and steady membrane of 1 mm thickness. This transparent membrane was then pasted on a hollow Pyrex tube, using araldite for fabricating the desired sensor and left for drying at room temperature overnight.

2.3 Equilibration of membrane

The electrode was conditioned for 2 days in 0.1 M Ni $(NO_3)_2$ for attaining the selectivity of the ion at the junction of the polymer matrix and the aqueous metal ion. **Reaction 2** shows the representative interaction between VE copolymeric membrane and Ni^{2+} ions. After this optimized equilibrium time, it was observed that the potential values thus obtained were steady and could be reproduced.



Reaction 2. Method of complex formation of VE copolymer with Ni^{2+} ion.

2.4 Measurement of electromotive force

The cell assembly used to determine the potential of the prepared sensor at room temperature was:

Calomel electrode (internal)/0.1 M nickel nitrate inside solution/polymer matrix/solution for detection/calomel electrode (external).

We recorded the electromotive force of the electrode at regular time intervals of 5 minutes to determine the response time.

3. Results and discussions

VE copolymer was prepared via free radical bulk polymerisation at 70 °C and its composition as listed in **Table 1** is determined from the 1H-NMR spectrum[27].

Table 1. Composition data of VE Copolymer

S. No.	Sample	f_v	F_v
1	VE-6	0.40	0.50
2	VE-7	0.30	0.42
3	VE-8	0.20	0.35

Note: f_v and F_v represent the mole fraction of V-unit in feed and copolymer, respectively.

3.1 Comparison of potential response of Ni^{2+} vs other metal ions

The potential response of the prepared membranes conditioned for 48 hours in 0.1 M solution of various metal ions were recorded as a function of concentration and it can be seen from **Figure 1** that sensors based on VE copolymer exhibited good response with Ni (II) ion in comparison to other cations which showed little or no response.

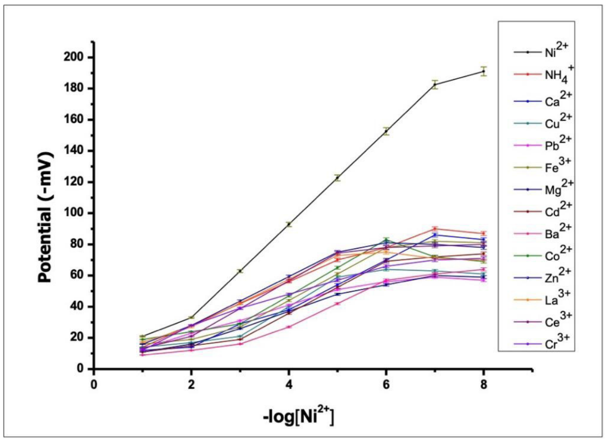


Figure 1. Potential responses of respective metal ions with concentration.

3.2 Concentration of solution inside the polymer matrix

When the membrane's inside diffusion potential becomes noticeable, the solution which is inside has a significant impact on the membrane's sensing capabilities. In order to explore how the inside solution affects the various parameter, the electromotive force was recorded for 0.1 M, 0.05 M and 0.01 M solutions of Ni^{2+} ions. Since the internal solution with concentration 0.1 M demonstrated optimum effectiveness, for all subsequent studies an optimum concentration of 0.1 M was maintained.

3.3 Concentration range in which the electrode shows optimum effectiveness

Investigating the electromotive force of the polymer matrices VE-6, VE-7 and VE-8 in relation to Ni^{2+} ion activity yielded the results depicted in the representative calibration curve shown in **Figure 2**, wherein potential vs log of Ni^{2+} concentration was plotted. In **Table 2**, the variations in membrane electrode properties caused by the composition of different VE copolymers are listed. Thus, it can be seen from the table that Ni^{2+} ions can be best estimated using the VE-7 membrane electrode as it has the maximum working concentration range and minimum response time as compared to VE-6 and VE-8.

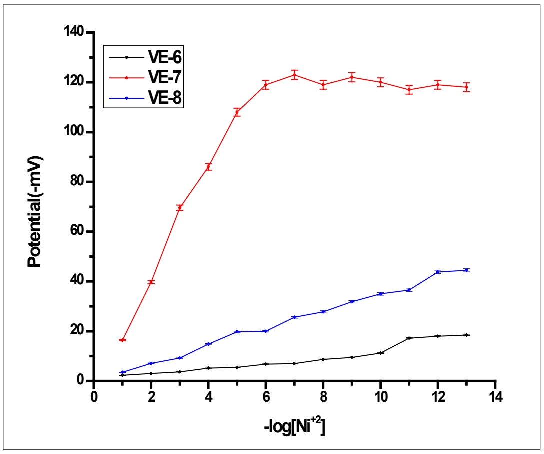


Figure 2. Plot of potential vs concentration of Ni^{2+} ion.

3.4 Effect of plasticizers

A required quantity of plasticizer was added to the membrane to check its enhanced performance. The role of the plasticizer is to increase the mobility of the membrane by increasing its softness and elasticity[28]. A marked improvement in the work performance and stability of the electrode was seen. It also

Table 2. Properties of various of compositions VE Copolymers

S. No.	Sample	Range of working concentration (M)	Slope (mV/Decade)	Response time (s)
1	VE-6	5×10^{-5}–1×10^{-1}	2.30 ± 0.05	90
2	VE-7	1×10^{-7}–1×10^{-1}	33.20 ± 0.60	10
3	VE-8	5×10^{-5}–1×10^{-1}	6.70 ± 0.10	85

remained in usable condition for a longer period of time. It was deduced that the zero current ion was able to fluidize from the membrane into the solution which helped in augmenting the components of the membrane and also those of the inner electrolyte.

Different amounts of NaTPB were chosen for the preparation of the membrane as shown in **Table 3** to analyze its effect as an anion excluder[29]. Apart from this, the factors affecting the properties of the sensor were found to be the amount of ionophore, nature and the quantity of plasticizers and ionic additives. Thus, several membranes (PME-1 – PME-8) were synthesized with different amounts of ionophore, plasticiser, PVC and anion excluder (NaTBP). **Table 3** lists the various synthesized sensors, their composition and performance, from which it is observed that PME-3 containing 3.0 mg of the ionophore is optimal for the electrode to function properly. Since the membrane is affected to quite an extent by the plasticizers, hence five different kinds of plasticizers of different polarities were chosen to study their effect on the proposed electrode which were DOP, DBP, DBBP, TBP and NPOE. Among the five plasticizers chosen and studied, DBP showed the maximum sensitivity and linear range implying thereby that Ni^{2+} ion can be easily identified with the help of DBP.

Table 3. Performance features of nickel (II) selective electrode

Electrode	PVC (mg)	Plasticizer (mg)	Ionophore (mg) VE-7	NaTPB (mg)	Nernstian slope (mV/decade)	Concentration range M
PME-1	33	59 (DOP)	2	6	25.1 ± 0.7	1.0×10^{-5} to 1.0×10^{-2}
PME-2	32	64 (DBP)	4	2	27.4 ± 0.2	1.0×10^{-6} to 1.0×10^{-2}
PME-3	32	63 (DBP)	3	2	38.7 ± 0.4	1.0×10^{-7} to 1.0×10^{-1}
PME-4	32	61 (DBP)	4	1	27.1 ± 0.1	1.0×10^{-6} to 1.0×10^{-2}
PME-5	34	62 (DBBP)	3	1	21.2 ± 0.2	1.0×10^{-6} to 1.0×10^{-2}
PME-6	33	60 (TBP)	4	3	24.5 ± 0.3	1.0×10^{-5} to 1.0×10^{-2}
PME-7	32	60 (NPOE)	6	2	21.1 ± 0.5	1.0×10^{-7} to 1.0×10^{-2}
PME-8	32	60 (NPOE)	6	2	23.2 ± 0.4	1.0×10^{-7} to 1.0×10^{-2}

3.5 pH effect

The pH effect was examined on two different concentrations of Ni^{2+} ion (1×10^{-4} and 1×10^{-6} M), with pH ranging from 1.0–13.0, by using 0.1 M of either hydrochloric acid or sodium hydroxide. **Figure 3** represents the graph between potential and pH wherein a constant electromotive force is observed within the pH range 1.8 to 8.5. Beyond pH 8.5, the potential decreases gradually. This can be due to $Ni(OH)_2$ formation at a higher pH[30]. At lower pH (acidic medium), an increase in potential is observed as the nitrogen present in the ionophore may be protonated[31]. Hence this range of pH 1.8 to 8.5 may be considered as the functioning range.

3.6 Dynamic time in which the polymer matrix responds and its longevity

Dynamic time in which the polymer matrix responds is the time in which the polymer matrix attains 90% of the stable potential value. This is obtained after successive immersions of the electrode in solutions differing in concentration by ten times. The dynamic time of the prepared electrode was determined by measuring cell potential at concentrations from 1 µM to 0.1 M[32–35]. **Figure 4** represents the actual potential vs dynamic response time.

From the above plot, it is evident that the electrode attains equilibrium within 10 seconds for the entire concentration range. In comparison to the previous membranes reported[36–39], the Nernstian slope and dynamic time in which the proposed polymer matrix (electrode) responds is found to be significantly good. This comparison is given in **Table 4**. The time period of the polymer matrix (electrode) is significant in its long-term usability. To determine the time period or longevity of the electrode, it was calibrated using solutions of known concentrations at a 10-day interval for 3 months.

Table 4. Comparative study of reported Ni^{2+} selective electrodes with prepared electrode

S. No.	Concn. M	Detection limit (mol L^{-1})	Nernstian slope (mV/decade)	pH	Dynamic time to respond (s)	Ionophore used	Ref.
1.	1.0×10^{-1}–5.0×10^{-6}	1.3×10^{-6}	29.9	3.6–7.4	20	Alizarin red-S-CTAB ion pair	[36]
2.	1.0×10^{-7}–1.0×10^{-2}	N.M.	30.5	2.5–7.5	18	Di-benzoyl-methane bis-(carbo-hydrazone)	[37]
3.	5.0×10^{-6}–1.0×10^{-2}	2.1×10^{-6}	29.7	3.5–7.5	<15	tris[2-(1-ethylbenzimidazolyl)] methylamine	[38]
4.	3.9×10^{-6}–1.0×10^{-1}	2.9×10^{-6}	29.5	2.5–7.7	8	Bis nitrato [4-hydroxy acetophenone semicarbazone)] nickel (II)	[39]
5.	1.0×10^{-7}–1.0×10^{-2}	5.1×10^{-8}	30	2.0–9.8	=10	Prepared electrode	Nil

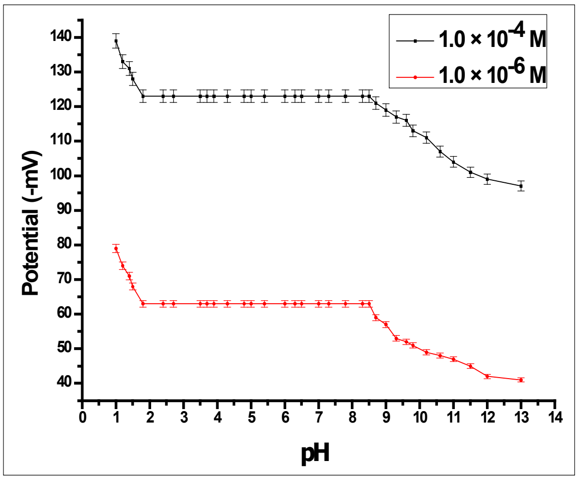


Figure 3. Plot of electromotive force vs pH.

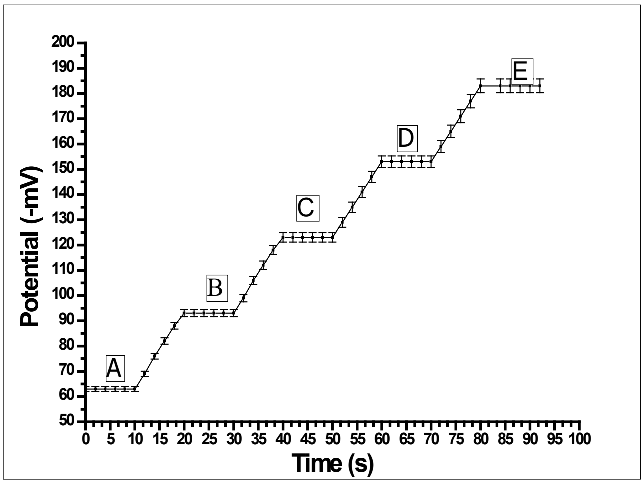


Figure 4. Actual potential vs dynamic response time.

3.7 Selectivity of the electrode

Selective behaviour of an electrode is its preferential response towards a metal ion over other ions present. It is expressed as KpotA,B. This depicts that synthesized polymer matrix (electrode) shows a selective behaviour for Ni^{2+} ions. **Table 5** gives the selectivity coefficient values obtained by FIM[34,40].

The membrane has the greatest affinity for Ni^{2+} ions due to higher formation constant of Ni^{2+} polymer matrix (electrode). Hence the transport of Ni^{2+} ions across the membrane is easier.

3.8 Analytical applications

3.8.1 Potentiometric titration

Samples of water from different places were taken and the nickel (II) concentration was estimated in them using the polymer matrix (electrode). This works suitably in laboratory conditions. In the present work, the titration of 25 mL of 0.0005 M $Ni(NO_3)_2$ solution vs 0.01 M EDTA was performed at a pH of 5.5 using the prepared polymer matrix. Upon titration, EDTA starts forming a complex with Ni^{2+} ions. As a result, the free Ni^{2+} ions decreases and

Table 5. Selectivity coefficient of the ionophore towards various cations (FIM)

Cations in solution	$K^{pot}_{A,B}$
Ni^{2+}	6.9×10^{-3}
Cu^{2+}	5.1×10^{-3}
Hg^{2+}	4.8×10^{-3}
Cr^{3+}	5.6×10^{-4}
Na^{+}	4.7×10^{-4}
Ce^{3+}	4.1×10^{-4}
Ba^{2+}	3.6×10^{-4}
Cd^{3+}	3.4×10^{-4}
Fe^{2+}	3.1×10^{-4}
Pb^{2+}	6.2×10^{-5}
Cd^{2+}	5.6×10^{-5}
La^{+}	4.8×10^{-5}
K^{+}	4.3×10^{-5}
Al^{3+}	3.9×10^{-5}
Mg^{2+}	2.9×10^{-5}
Co^{2+}	2.2×10^{-5}

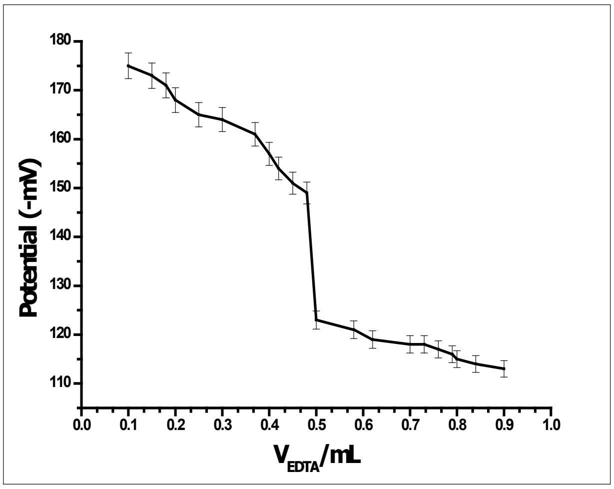


Figure 5. Variation of potential of 0.0001 M Ni^{2+} solution with volume of 0.01 M EDTA solution.

so the potential also decreases. The **Figure 5** shows the plot of the corresponding titration and exhibits a sharp inflexion at the equivalence point thus resulting in the estimation of nickel ion.

3.8.2 Estimation of Ni^{2+} in water from different places

Table 6 represents the estimation of Ni^{2+} ion concentration in water from various water bodies from different parts of India with the proposed electrode as the indicator. The Ni^{2+} ion concentration present in the analyzed water sample using the proposed VE-PVC based polymer matrix agrees well with that obtained by AAS.

3.9 Tolerance limits

The tolerance limit for interfering metal ions needs to be determined, because if the $K^{pot}A,B$ value of the electrode is small, then in that case, it is able to tolerate a greater concentration of interfering metal ion. Ba^{2+} ion was chosen as the interfering ion to determine the tolerance level of the electrode which have lower values of selectivity coefficient in comparison to Ni^{2+} ions. Keeping the Ba^{2+} ion concentration fixed as 0.0005, 0.0001, and 0.00005 M, the electromotive force of the polymer matrix was determined as a function of Ni^{2+} ion concentration. As seen from the plot in **Figure 6**, the potential of the sensor for Ba^{2+} ions and Ni^{2+} ions is the same up to a particular concentration. After that, a sudden change in potential is observed. The linear portion of the graph from where there is a sudden change in the potential is the working range of the sensor electrode for the determination of Ni^{2+} ions. Thus, 0.0005, 0.0001, and 0.00005 M concentrations of Ba^{2+} ions can be tolerated over reduced working concentration ranges of 0.001 to 0.1 M, 0.00005 to 0.5 M and 0.0005 to 0.1 M of Ni^{2+} ions respectively.

Table 6. Concentration of Ni^{2+} in water from various sources

S. No.	Water from various sources	Observed by proposed electrode (mg/L)	Observed by AAS (mg/L)
1	Ganga Canal, Khatoli	2.00 ± 0.03	1.98
2	Bore well, Khatoli	0.50 ± 0.03	0.52
3	Bore well, Tuglakabad	4.30 ± 0.03	4.33
4	Borewell, Baraut	3.50 ± 0.03	3.47
5	Tap water, Baghpat	3.47 ± 0.03	3.45

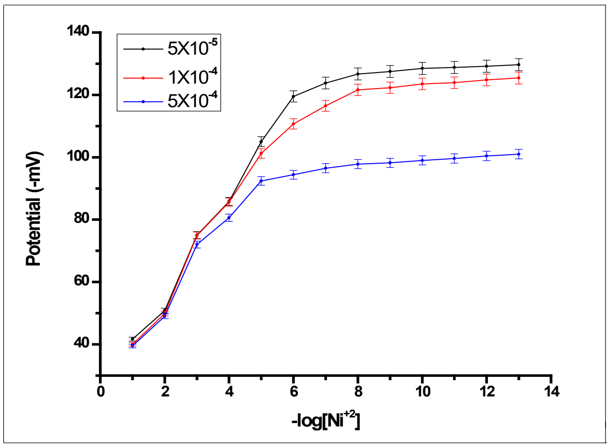


Figure 6. Changes in potential of the sensor with concentration of Ni^{2+} ions in presence of Ba^{2+} ions.

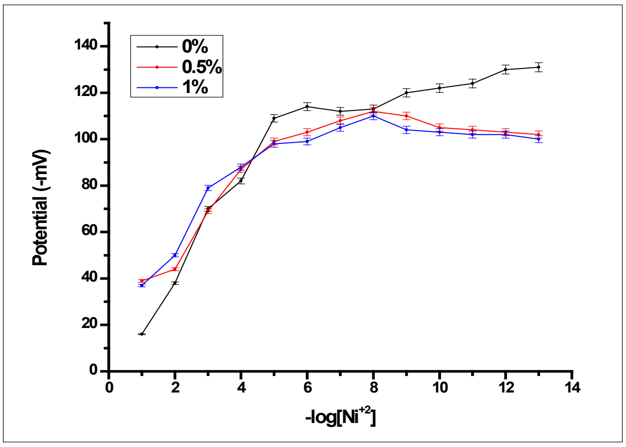


Figure 7. Effect of surfactant concentration on potential of VE-PVC based membrane sensor.

3.10 Effect of detergent and surfactant

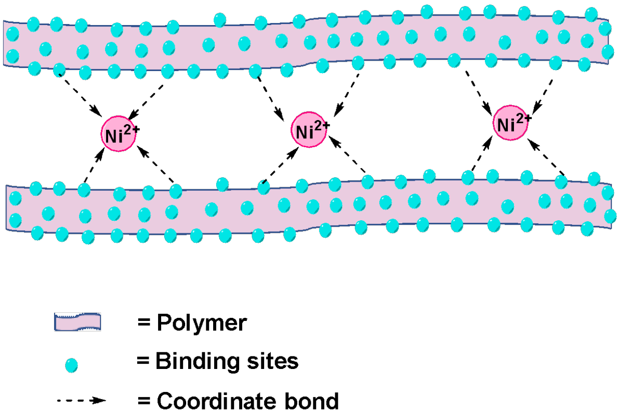
The value of potential decreases with increase in the concentration of detergent (like Nirma, Ariel, and Rin) (**Table 7**) and surfactant (sodium lauryl sulphate) (**Figure 7**) over a varied range of Ni^{2+} ion concentration. As the concentration of the detergent increases, the EMF of the cell decreases. The EMF of the cell decreases with the increasing concentration of the detergent.

3.11 Mechanism

Scheme 1 suggests the coordination scheme with nickel as the central metal ion in the copolymer. The copolymer structure of the ion selective membrane (ionophore) is such that it affects the interaction of the metal ion with the anions as the membrane is permeable only towards the required ion, hence being responsible for the selectivity of the ionophore towards Ni^{2+} ions[41,42].

Table 7. Working of Ni (II) selective electrode in presence of detergent

Volume of 1×10^{-5} M of solution (mL)	Concn. 5 mL of detergent (%)	Potential (mV) Nirma	Potential (mV) Ariel	Potential (mV) Rin
20	1	25 ± 0.3	25 ± 0.3	26 ± 0.3
20	2	22 ± 0.3	21 ± 0.3	20 ± 0.3
20	3	19 ± 0.3	19 ± 0.3	20 ± 0.3
20	4	18 ± 0.3	17 ± 0.3	17 ± 0.3
20	5	14 ± 0.2	14 ± 0.2	15 ± 0.2



Scheme 1. Sensing of Ni^{2+} ion by copolymer membrane.

4. Conclusion

In the reported work, a new Ni^{2+} ISE has been synthesized and calibrated. The calibration confirms its good response between 0.1 μM to 0.1 M. The investigations using PME in a concentration range of 0.1 μM to 0.1 M exhibit the best Nernstian slope of 33.2 mV/decade for Ni^{2+} ions having a detection limit of 0.1 μM. The performance of the membrane electrode is enhanced by adding plasticizers. The best outcome is observed with the membrane ratio [DBP: PVC: I: NaTPB] = 63:32:3:2, showing that a concentration range of 0.1 μM to 0.1 M is appropriate for the working of the electrode. Sufficient amounts of surfactant and detergents also have the ability to change the potential. The electrode can be used effectively as an indicator in the estimation of Ni^{2+} ions potentiometrically using EDTA. The time response of the electrode is 10 s and the time period is 84 days in the pH range 1.8–8.5. On the basis of obtained results, it is suggested that the technique developed in this work offers a modest, quick and reasonable estimation of Ni^{2+} ions in ecological samples with good precision. This proposed method can be used to synthesize other ion selective electrodes too and can serve as an important method of detection of other toxic metals in the environment.

Abbreviations

DBBP: Dibutyl butyl phosphate
NaTPB: Sodium tetra phenyl borate
THF: Tetrahydrofuran
TBP: Tri-n-butyl phosphate
DOP: Dioctyl phthalate
DBP: Dibutyl phthalate
NPOE: 2-nitrophenyl octyl ether
VE: 4-vinyl pyridine-ethyl acrylate
EDTA: Ethylenediaminetetraacetic acid

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Conflict of interest

The authors declare no conflict of interest.

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