Ni\textsuperscript{2+} Selective Membrane Sensors Based on Sulfamethoxazole Diazonium Resorcinol in Poly (Vinyl Chloride) (PVC) Matrix

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Abstract PVC-based membranes of sulfamethoxazole diazonium resorcinol (SDR) as electroactive material with dioctylphthalate (DOP), Dioctylsebacate (DOS), \( \alpha \)-Nitrophenyloctylether (\( \alpha \)-NPOE) as plasticizing solvent mediators have been found to act as Ni\textsuperscript{2+} selective sensor, the best performance was obtained with the sensor having a membrane of composition plasticizer:PVC:ionophore in the ratio 200:100:5 mg. The sensor exhibits Nernstian response in the activity range \( 5 \times 10^{-6} \) to \( 1.0 \times 10^{-1} \) M, performs satisfactorily over a wide pH range (5–9), with a fast response time (10 s). The sensor was found to work satisfactorily in partially different internal solution concentrations and could be used over a period of 2 months. Potentiometric selectivity coefficients determined by matched potential method (MPM) indicate excellent selectivity for Ni\textsuperscript{2+} ions. The sensors could be used successfully in the estimation of nickel as an indicator electrode in potentiometric titration.

Keywords Poly (vinyl chloride) · PVC membrane · Nernstian slopes · Nickel ion sensor · Potentiometry · Ion selective electrodes · Sulfamethoxazole diazonium resorcinol

1 Introduction

Nickel is widely used in electroplating, manufacture of Ni–Cd batteries, rods for arc welding, pigments for paints, ceramics, surgical and dental processes, magnetic tapes of computers and as catalysts. Its widespread use results in its presence normally at low concentration level in raw meats, chocolates, hydrogenated oils, milk and milk products, canned food, etc. and in various industrial and domestic effluents. Nickel is a moderately toxic element and is known to cause cancer of the respiratory system [1], skin disorder known as nickel–eczema [2], acute pneumonitis, asthma and increase in blood cells. Thus, it is important to know its concentration in various samples. A number
of methods such as flow injection spectrometry, flame and graphite furnace atomic absorption spectrometry, ICP-AES and flame photometry are used for its determination. These methods provide accurate results but are not very appropriate for analysis of large number of environmental samples because they require expertise and good infrastructure. On the other hand, selective ion sensors are very useful for the monitoring of heavy metals in large number of samples as they are convenient, fast, easy to operate, generally require no sample pre-treatment, suitable for online monitoring and cost little. Therefore, a number of nickel sensors based on heterogeneous membranes of porphyrins [3,4] crown ethers [5–8], cycles [9–11], ion exchangers [12,13], pentacyclooctaaza [14], 2,5-thiophenylbis(5-tertbutyl-1,3-benzexazole) [15], dioxime derivative [16] and Schiff bases [17–19] in PVC, nickel phosphate [20] in parafin and silicone rubber and nickel complex of 1,4,8,11-tetraazacyclotetradecane [21] in araldite have been reported. However, their performance is poor with regard to one or more sensor characteristics, i.e., working activity range, selectivity, response time, pH range and lifetime. In addition to these solid membrane sensors, liquid membrane sensors have also been investigated [22–24]. However, they are of limited use in view of attrition of liquid membrane during experimentation. To achieve wider applicability, these limitations need to be removed. Efforts in this direction are on experimentation. To achieve wider applicability, these limitations need to be removed. Efforts in this direction are on using different materials for preparation of membranes.

The main requirement to impart selectivity to the ion sensor is to use membranes of a material which shows strong affinity for a particular metal ion and poor to others. The main problem in the development of a good sensor is that such materials are not easily available. Thus, newer materials synthesized are continuously being examined for such roles. Continuing efforts in this direction, we have recently synthesized diverse porphyrin and studied their membranes in PVC matrix as Ni2+ selective sensors. Besides this, Schiff bases with N and O donor atoms are well known to form strong complexes with transition metal ions. Some of the Schiff bases are reported to form strong complexes with a specific ion due to geometric factors [25,26]. As a result, Schiff base complexes have attracted increasing attention in solvent extraction [27,28], ion exchangers [29,30] and catalytic studies [31,32]. Thus, Schiff bases offer a good possibility to be used as Ni2+ selective ionophore. PVC-based membranes of meso-tetrakis-4-tris-(4-allyl dimethylsilylphenyl)silyl-phenylporphyrin (I) and (sal)2 trien (II) [33], Ni (II) selective sensors based on Schiff bases membranes [34] have been studied as Ni2+ selective sensors and the results reported in the present communication show that they perform well and could be used for its selective quantification. Ion selective methods for determination of Ni2+ [35–42], Spectrophotometric methods [43–63], electrochemical methods [64], Titration methods [65], Potentiometric sensors for heavy metals, nickel (II) [66,67], Cadmium (II) [68,69], Pb (II) [70–73], Iron (III) [74], Aluminum (III) [75], Chromium (III) [76], Mercury (II) [77,78], Zinc (II) [79], Vanadium, zirconium and molybdenum [80–86].

2 Experimental

2.1 Apparatus

All Potentiometric measurements were made at 25 ± 1 °C with an Orion (Model 720) pH/mV meter. Double junction Ag/AgCl reference electrode was used. An Orion electrode (Model 90-02) filled with 10% (w/v) potassium chloride was used in the outer compartment. Combination glass (Ross pH) electrode (Orion Model 81-02) was used for all pH measurements.

2.2 Reagents and Materials

All chemicals were of analytical reagent grade unless otherwise stated and doubly distilled water was used throughout. Nickel chloride (Ni2+), PVC powder of molecular weight ∼10,000, Tetrahydrofuran (THF), Butylatedhydroxytoluene, o-NPOE, DOP and DOS, a plasticizer with a purity of ~99% were obtained from Aldrich Chem. Co. (Milwaukee, WI, USA). (Ni2+) (10−2 M) stock solution was prepared by dissolving 0.073 g of (Ni2+) in 25 ml of (0.05 M) phosphate buffer solution (pH 7). (Ni2+) (10−1 to 10−6 M) standard solutions were prepared by appropriate dilution of the stock (Ni2+) solution with 0.05 M phosphate buffer solution of pH 7.

The following cations and compound solutions were prepared and standardized using the standard methods. Dilute solutions (10−2 to 10−6 M) of these cations and compounds were prepared by tenfold dilution of the stock solutions with 0.05 M phosphate buffer solution of pH 7.

3 Synthesis of Ionophore

The azo products of sulfamethoxazole were prepared by coupling of sulfamethoxazole diazonium salts with the resorcinol [87]. Empirical formula (Molecular weight C16H14O5N4S (374) color orange, m.p. 198–200 °C. Elemental analysis % Calc. (found) %C: 51.34 (48.59), %H 3.74 (2.63), %N: 14.97 (13.89).

IR spectra for compound C16H14O5N4S ν OH: (3,543) (w), ν NH: (3,159)m, ν C=N: (1,614), ν N=N: (1,404), ν SO2: (1,341) (w), 1,163 (m).

UV spectrum The UV–visible absorption spectrum of the compound in ethanol within the wavelength ranges 200–800 nm. The spectrum shows two bands. The first band lying
at 267 nm is attributed to the low energy $\pi-\pi^*$ transition within the phenyl moiety. The second band located at 398 nm corresponds to $n-\pi^*$ transition of the N=N group.

$^1H\text{NMR}$ (CDCl$_3$, 300 MHz); (ppm) 7.2 (3H CH$_3$), 8.0 (H ph), 10.9 (HN), (11–12.1 d,d HO…N), (12.3–12.7 d,d H ph).

4 Potentiometric Selectivity

The selectivity is the most important characteristic, as it determines the extent of utility of a sensor in real sample measurement. The selectivity coefficient values were determined by matched potential method (MPM), which was proposed by Gadzekpo and Christian [88] to overcome difficulties in obtaining selectivity coefficient values when ions of unequal charges are involved. In this procedure, the selectivity coefficient $K_{Ni^{2+}}^{\text{pot}}$ is calculated by the expression

$$K_{Ni^{2+},B}^{\text{pot}} = \frac{\Delta a_{Ni^{2+}}}{\Delta a_B} = \frac{a_{Ni^{2+}} - a_B}{a_{Ni^{2+}} - a_B}$$

and is, therefore, determined by measuring the change in potential upon increasing by a definite amount the primary ion activity from an initial values of $a_{Ni^{2+}}$ to $a_{Ni^{2+}}$ and $a_B$ represents the activity of interfering ion (B) added to the same reference solution of activity $a_{Ni^{2+}}$ which causes the same potential change. The values of $a_{Ni^{2+}}$ and $a_{Ni^{2+}}$ were taken to be $1 \times 10^{-3}$M and $5 \times 10^{-3}$ M, whereas the values of $a_B$ were experimentally determined. The values determined by MPM are given in Table 1.

It is seen that the selectivity coefficients are much smaller than 1.0 showing that both the sensors are sufficiently selective over all the interfering ions studied.

5 Preparation of Membranes

The PVC-based membranes were prepared by dissolving ionophore solvent mediators DOP, DOS, o-NPOE and PVC in THF (5–10 mL). After complete dissolution of all the components and thorough mixing, the resulting mixture was poured into polyacrylates ring placed on a smooth glass plate and was allowed to evaporate. The transparent membranes of 0.4 mm thickness formed were removed carefully from the glass plate. A 5 mm diameter piece was cut out and glued to one end of a “Pyrex” glass tube. The membranes thus prepared were equilibrated for 8 days in 0.1 M Ni$_2$+ solution. Membranes of different composition were prepared and investigated and those, which gave reproducible results and better performance characteristics, were selected for further studies. The optimum composition of membranes for best performance is given in Table 2. The activity coefficient ($\gamma$) of metal ions was calculated from the modified form of the Debye–Huckel equation [89].

6 Results and Discussion

6.1 Working Activity Range and Slope

The potential generated across the membrane was investigated as a function of Ni$_2$+ activity in the range $5.0 \times 10^{-6}$ to $1.0 \times 10^{-1}$ M and the results obtained are shown in Fig. 1.

The coordination chemistry of Ni$_2$+ ions reveals that the ions have a remarkable preference for formation of square planar amine complexes. This has been extensively exploited in synthesizing a variety of thermodynamically stable N4 macrocycle complexes with varying ring size [95,96]. The 12-membered tetraphenyl substituted macrocycle was chosen as an ionophore for Ni$_2$+ -ISE as it has a flat and highly electron delocalized structure, and owing to its planar geometry and appropriate cavity size it is expected to greatly influence the chemical and physical properties of Ni$_2$+ ions. The tetra phenyl groups add the lipophilicity and thermodynamic stability for the rapid exchange of metal ions [97] sulfamethoxazole diazonium resorcinol (SDR). Therefore, it was used as an ion-active phase in Ni$_2$+ -ISE. SDR was

Table 1 Potentiometric selectivity coefficients ($K_{Ni^{2+}}^{\text{pot}}$) for the three proposed electrodes at $10^{-2}$ M internal solution

| Interferon’s | o-NPOE | DOS | DOP |
|-------------|--------|-----|-----|
| K$^{1+}$    | 1.3 x 10^{-3} | 2.1 x 10^{-3} | 1.6 x 10^{-3} |
| Na$^{2+}$   | 2.2 x 10^{-3} | 1.3 x 10^{-3} | 1.3 x 10^{-3} |
| Ca$^{2+}$   | 3.3 x 10^{-3} | 1.9 x 10^{-3} | 1.8 x 10^{-3} |
| Zn$^{2+}$   | 2.9 x 10^{-3} | 3.5 x 10^{-3} | 3.4 x 10^{-3} |
| Fe$^{3+}$   | 3.4 x 10^{-3} | 3.3 x 10^{-3} | 2.6 x 10^{-3} |
| Pb$^{2+}$   | 1.6 x 10^{-4} | 2.4 x 10^{-3} | 3.4 x 10^{-3} |
| Sn$^{2+}$   | 1.1 x 10^{-4} | 1.9 x 10^{-3} | 1.5 x 10^{-3} |
| Cd$^{2+}$   | 1.4 x 10^{-4} | 2.5 x 10^{-3} | 1.3 x 10^{-4} |
| Co$^{2+}$   | 1.3 x 10^{-4} | 1.7 x 10^{-3} | 1.4 x 10^{-4} |
| Cu$^{2+}$   | 1.6 x 10^{-3} | 1.5 x 10^{-3} | 1.5 x 10^{-4} |
| Mn$^{2+}$   | 1.7 x 10^{-3} | 1.1 x 10^{-3} | 2.7 x 10^{-4} |
| Ba$^{2+}$   | 1.4 x 10^{-3} | 1.4 x 10^{-4} | 1.3 x 10^{-3} |
| Sr$^{2+}$   | 1.2 x 10^{-4} | 1.9 x 10^{-3} | 1.2 x 10^{-3} |
| Ca$^{2+}$   | 1.8 x 10^{-3} | 1.4 x 10^{-4} | 1.6 x 10^{-3} |
| Mg$^{2+}$   | 1.4 x 10^{-3} | 1.3 x 10^{-4} | 2.5 x 10^{-3} |
Table 2 Response characteristics for Ni\(^{2+}\) membranes

| Electrode composition  | Internal solution (M) | Slope (mV) | Measuring range (M) | Detection limit (M) |
|------------------------|-----------------------|------------|---------------------|---------------------|
| PVC:NOPE:SDR (100:200:5) | 10\(^{-3}\)         | 29         | 1 \times 10\(^{-6}\) to 1 \times 10\(^{-1}\) | 5 \times 10\(^{-6}\) |
|                         | 10\(^{-2}\)         | 29         | 1 \times 10\(^{-6}\) to 1 \times 10\(^{-1}\) | 5 \times 10\(^{-6}\) |
|                         | 10\(^{-1}\)         | 30         | 1 \times 10\(^{-6}\) to 1 \times 10\(^{-1}\) | 1 \times 10\(^{-5}\) |
| PVC:DOP:SDR (100:200:5) | 10\(^{-3}\)         | 28         | 1 \times 10\(^{-6}\) to 1 \times 10\(^{-1}\) | 5 \times 10\(^{-6}\) |
|                         | 10\(^{-2}\)         | 29         | 1 \times 10\(^{-6}\) to 1 \times 10\(^{-1}\) | 5 \times 10\(^{-6}\) |
|                         | 10\(^{-1}\)         | 29         | 1 \times 10\(^{-6}\) to 1 \times 10\(^{-1}\) | 1 \times 10\(^{-5}\) |
| PVC:DOS:SDR (100:200:5) | 10\(^{-3}\)         | 28         | 1 \times 10\(^{-6}\) to 1 \times 10\(^{-1}\) | 5 \times 10\(^{-6}\) |
|                         | 10\(^{-2}\)         | 28         | 1 \times 10\(^{-6}\) to 1 \times 10\(^{-1}\) | 5 \times 10\(^{-6}\) |
|                         | 10\(^{-1}\)         | 29         | 1 \times 10\(^{-6}\) to 1 \times 10\(^{-1}\) | 1 \times 10\(^{-5}\) |

Fig. 1 Calibration curves and the optimum responses of the SDR with (\(\alpha\)-NPOE, DOP, and DOS) for Ni\(^{2+}\) at phosphate buffer solution pH = 8

used as a ionophore in the construction of ISEs for various metal ions. The potential response obtained is given in Table 2. As can be seen from the figure, the ligand gives the best potential response to Ni\(^{2+}\) ions in comparison to other alkali, alkaline earth, transition and heavy metal ions. Further, the response characteristics of the Ni\(^{2+}\)-selective electrode based on SDR were tested as a function of the membrane composition, nature of the plasticizer and the amount of the ionophore used. To achieve good selectivity, it is essential that no significant amount of other ions should enter the membrane phase. Tetraphenylborate (NaTPB) was added to all prepared membranes to reduce the interference from anions, optimize sensing selectivity and reduce bulk membrane impedance [98]. It is seen from Fig. 1 that the sensors having \(\alpha\)-NPOE plasticizer exhibit maximum activity range (linear response) of 2.5 \times 10^{-6} to 1.0 \times 10^{-1} M with Nernstian slope of 29.5 mV/decade of activity. Two plasticizers namely DOP and DOS were added in an attempt to improve the performance of the sensors and the results obtained are also shown in Fig. 1. All performance characteristics of the sensors determined from this figure are compiled in Table 2. It is seen that the addition of plasticizers to the membranes and the data are compared by atomic absorption spectroscopy (AAS) for the determination of nickel.

6.2 Effect of pH

The effect of pH on the performance of two sensors was also seen at two Ni\(^{2+}\) activities of 1.0 \times 10^{-3} and 1.0 \times 10^{-4} M. The potential of the sensors remains constant over a pH range of 6.0–9.5 (Fig. 2). This can be taken as the useful pH working range.
6.3 Effect of Internal Solution

The influence of the concentration of internal solution on the emf response of all Ni$^{2+}$ ion-selective electrodes was studied, and the results show that variation in the concentration range ($1 \times 10^{-1}$ to $1 \times 10^{-4}$ M) of the internal solution does not significantly change the electrode response of slope while parameters like measuring range and detection limit [99] changed to considerable extent (Table 2). A $1 \times 10^{-3}$ M concentration of internal solution gave the best response (Fig. 3) and was chosen for further studies.

6.4 Response and Lifetime

The response time of the sensor has been determined by measuring the time required to achieve a steady potential for $1.0 \times 10^{-4}$ M solution, when Ni$^{2+}$ ion activity was rapidly increased tenfold from $1.0 \times 10^{-5}$ to $1.0 \times 10^{-4}$ M. The response time of the membrane without plasticizer is found to be 8 s. The low response time of the sensors are most probably due to the fast exchange of Ni$^{2+}$ between ionophore and the bulk solution occurring at the membrane interface. It is well known that the dynamic response time of a sensor is one of the most important factors in its evaluation. To measure the dynamic response time of the proposed sensor the concentration of the test solution has been successively changed from $1.0 \times 10^{-6}$ to $1.0 \times 10^{-2}$ M. The resulting data depicted in Fig. 4 show that the time needed to reach a potential within ±1 mV of the final equilibrium value after successive immersion of a series of Ni$^{2+}$ ions, each having a tenfold difference in concentration, is 8 s for (electrode). This is most probably due to the fast exchange kinetics of complexation–decomplexation of Ni$^{2+}$ with the ionophore at the test solution-membrane interface. To evaluate the reversibility of the electrode, a similar procedure in the opposite direction was adopted. The measurements have been performed in the sequence of high-to-low from $1.0 \times 10^{-2}$ to $1.0 \times 10^{-3}$ M sample concentrations and the results showed that the potentiometric response of the electrodes was reversible; although the time needed to reach equilibrium values (50 s) was longer than that of low-to-high sample concentrations. The life time of membrane is 2 months. To evaluate the reversibility of the electrode, a similar procedure in the opposite direction was adopted. The measurements have been performed in the sequence of high-to-low from $1.0 \times 10^{-2}$ to $1.0 \times 10^{-3}$ M sample concentrations and the results showed that, the potentiometric response of the electrodes was reversible; although the time needed to reach equilibrium values (50 s) was longer than that of low to high sample concentrations. Reproducibility of the electrode was examined using six similar constructed electrodes under the optimum conditions. The result showed good reproducibility (±0.4 mV) for the electrode.

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**Fig. 3** Effect of internal solution concentration on the membrane electrode for $\sigma$-NOPE

**Fig. 4** The response time of the membranes SDR

**Fig. 5** Potentiometric titration curve of Ni$^{2+}$ ($1.0 \times 10^{-3}$ M, 10 mL) with EDTA ($1.0 \times 10^{-2}$ M), using the sensor $\sigma$-NPOE
Table 3 Comparison of the potentiometric parameters of the proposed nickel sensor with the literature of reported nickel selective sensors

| Ionophore                                                                 | Linear range (M)          | Slope  | pH range | Response time (s) | References |
|--------------------------------------------------------------------------|---------------------------|--------|----------|------------------|------------|
| N1,N2-Bis((naphthalen-1-yl)-methylene)ethane-1,2-diamine (NED)           | 1.0 × 10⁻¹ to 5.0 × 10⁻⁶  | 29.9   | 3.6–7.4  | 15               | [90]       |
| (2E,3E)-2H-1,4-Benzothiazine-2,3(4H)-Dioninediole                        | 1.0 × 10⁻⁶ to 1.0         | 30.0   | 2.0–6.5  | <10              | [91]       |
| 3,4:12,13-Dibeno-1,6,10,15-tetraazacyclododecane                          | 2.82 × 10⁻⁶ to 1.0 × 10⁻¹ | 30.5   | 2.5–7.5  | 18               | [92]       |
| 4,4,4,4-21H,23H-Porphine-5,10,15,20-tetratylyl tetrakis (benzoic acid)(TBAP) and 2,3,7,8,12,13,17,18-octamethyl-21H,23H-porphine (OMP) | 2.0 × 10⁻⁶ to 1.0 × 10⁻¹ and 1.0 × 10⁻⁵ to 1.0 × 10⁻¹ | 29.6 and 29.0 | 2.0–7.0 | 10–15 | [93] |
| 3-Hydroxy-N-[2-[(3-hydroxy-Nphenylbutyrimidoyl)-amino]-phenyl] Sulfamethoxazole diazonium resorcinol (SDR) | 1.6 × 10⁻⁷ to 1.0 × 10⁻² | 30.0 ± 0.2 | 1.0–12.0–12 | 12 | [94] |

Table 4 Comparison of the potentiometric parameters of the proposed nickel sensor with AAS

| Number of samples | Standard solutions | Ni found (M) | Real samples⁴ | References |
|-------------------|--------------------|--------------|---------------|------------|
|                   | ISE (M)            | AAS (M)      | ISE (M)       | AAS (M)    |
| 1                 | 1 × 10⁻¹           | 1.6 × 10⁻¹  | 1.7 × 10⁻¹    | 3.0 × 10⁻⁵ | 2.9 × 10⁻⁵ |
| 2                 | 1 × 10⁻²           | 1.2 × 10⁻²  | 1.1 × 10⁻²    | 5.1 × 10⁻⁵ | 4.8 × 10⁻⁵ |
| 3                 | 1 × 10⁻³           | 1.1 × 10⁻³  | 1.1 × 10⁻³    | 3.1 × 10⁻⁵ | 3.4 × 10⁻⁵ |
| 4                 | 1 × 10⁻⁴           | 1.3 × 10⁻⁴  | 1.2 × 10⁻⁴    | 9.1 × 10⁻⁴ | 1.1 × 10⁻⁴ |
| 5                 | 1 × 10⁻⁵           | 1.1 × 10⁻⁵  | 1.1 × 10⁻⁵    | 8.8 × 10⁻⁴ | 9.8 × 10⁻⁴ |
| 6                 | 1 × 10⁻⁶           | 1.7 × 10⁻⁶  | 1.3 × 10⁻⁶    | 2.1 × 10⁻⁵ | 2.2 × 10⁻⁵ |

7 Analytical Applications

7.1 Potentiometric Titration

The analytical application of the sensor ω-NOPE was tested and it was used as an indicator electrode to determine the endpoint in the potentiometric titration of Ni²⁺ with EDTA. 10 mL of a 1.0 × 10⁻³ M Ni²⁺ solution was titrated against a 1.0 × 10⁻² M EDTA solution at pH 6.0.

The plot obtained (Fig. 5) is of sigmoid shape, the sharp inflexion point observed corresponds to the stoichiometry of the Ni²⁺–EDTA complex. Thus, Ni²⁺ can be successfully determined potentiometrically using this sensor.

8 Conclusion

The PVC-based membrane electrode of ligand (SDR) with a composition of 5 mg ligand, 100 mg PVC and 200 mg ω-NOPE exhibits the best performance characteristics. The sensor exhibited good reproducibility with a useful life-time of 2 months. The proposed electrode was successfully applied in determining Ni²⁺ in the activity range 5 × 10⁻⁶ to 1.0 × 10⁻¹ M, performs satisfactorily over wide pH range (5–9) with a fast response time (10 s). Comparison of the potentiometric parameters of the proposed nickel sensor with the literature reported nickel selective sensors are shown in Tables 3 and 4.

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