# Nickel(II) selective poly(vinyl chloride) membrane ISE using a novel macrocyclic compound 1,10-diaza-4,7-dioxo-3,8-dibenzoyl-cyclotetradeca-2,9(2)-diene as neutral carrier

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**Abstract :** A PVC membrane based nickel(II) selective electrode was constructed using 1,10-diaza-4,7-dioxo-3,8-dibenzoyl-cyclotetradeca-2,9(2)-diene (DADOCTD) as a neutral carrier. The sensor exhibits a Nerstian response for $Ni^{II}$ ions over a wide concentration range of $3.9 \times 10^{-6}$ to $1.0 \times 10^{-1}$ mol/L with a slope of 29.0 mV/decade. It has a relatively fast response time and can be used for 120 days without any considerable divergence in potentials. The proposed sensor revealed relatively good selectivity and high sensitivity for $Ni^{II}$ over a wide variety of other metal ions and could be used in a pH range of 3.0-8.0. It was used as an indicator electrode in potentiometer titration and in analysis of concentration of nickel in practical samples.

**Keywords :** $Ni^{2+}$, PVC electrodes, slope.

## Introduction

Chemical sensor technology creates a potentially fundamental aspect for the determination of several biologically relevant ions, environmental monitoring and industrial effluents analysis. The ion selective electrodes provide a rapid, accurate and low-cost method of analysis without any pre-treatment of samples. Due to toxic nature of nickel, there is urgent need for monitoring it in the clinical samples, industrial effluents, food and environmental samples[1,2].

In recent time macrocyclic compounds are considered as potential ionophore for development of highly sensitive and selective ISE because they generally behave as neutral charge (electron) carrier and they can generally made to have two different binding states. These two states can be easily and reversibly interconvert by external forces such as pH gradients[3,4], light[5], temperature[6], and redox gradients[7-9]. Macrocyclic compounds due to moderately preorganized three-dimensional frameworks. In the present communication, efforts have been taken to describe the new PVC based ISE using i.e. DADOCTD as ionophore, which shows better or compatible response towards selectivity, sensitivity and another parameters for $Ni^{2+}$-selective electrodes, over a number of previous reported electrodes[10,11].

## Experimental

*Reagents :* All the reagents used were of analytical grade. High molecular weight PVC, tetrahydrofuran (THF), 1,2-dibromoethane, ethylenediamine and salicyldehyde were procured from Aldrich. Plasticizers dibutylphthalate (DBP), dioctylphthalate (DOP), nitrobenzene (NB), tetraphenylborate (TPB) and tris(2-ethylhexyl)phosphate (TEP) are obtained from Fluka. Metal nitrate and chloride salts, and all other analytical grade, solvents were used as received from Merck.
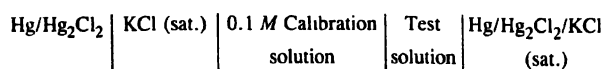
*Instrumentation :*

IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrophotometer. $^1H$ NMR spectrum was recorded in deuterated dimethyl sulfoxide with TMS as internal standard on a Varian mercury spectrometer at 300 MHz.

*Potential measurement :*

All the membrane electrode potential measurements were performed at constant temperature (25 ± 0.5 °C) using digital pH meter, potentiometer (Elico L1-10, India) in conjugation with saturated calomel electrodes as reference electrodes. The representative electrochemical

cell for the EMF measurements is as follows :

| Hg/Hg$_2$Cl$_2$ | KCl (sat.) | 0.1 $M$ Calibration solution | Test solution | Hg/Hg$_2$Cl$_2$/KCl (sat.) |
|---|---|---|---|---|

*Synthesis of the ionophore :*

The ionophore chosen here to develop a nickel(II) selective electrode is a macrocyclic compound 1,10-diaza-4,7-dioxo-3,8-dibenzoyl-cyclotetradeca-2,9(2)-diene (DADOCTD), which is prepared by two step complete condensation reaction, occurring in a closed single pot. In a 500 mL three-necked round bottle flask, fitted with water condenser and a mechanical stirrer at its two necks, 100 mL ethanolic solution of 30.5 mL salicyldehyde (0.5 $M$) was taken using a dropping cylindrical funnel at the third neck of the flask. The solution was warmed upto 40 °C followed by addition of 100 mL ethanolic solution of 21.25 mL 1,2-dibromoethane (0.25 $M$) in the presence of Na$_2$CO$_3$ with slow mechanical stirring. After closing the stopper of the dropping funnel the reaction mixture was refluxed for about 4 h at 60 °C with stirring. It was allowed to get cooled upto approx. 40 °C and then a 100 mL ethanolic solution of 27 mL ethylenediamine (0.25 $M$) was added with continuous stirring and refluxed for next 6 h when brownish viscus liquid was obtained which on cooling produced bright yellow precipitate. It was filtered, washed with water and then by ethanol. Finally very bright lemon yellow colored compound was obtained and was stored in vacuum-desiccator for further use in characterization and as ionophore. The yield was 70%, m.p. 276 °C and the compound was soluble in DMF. IR (KBr) spectra exhibits $v_{str.}$C=N bands in 1588–1635 cm$^{-1}$ region and the absence of uncondensed functional groups (NH$_2$, C=O); $^1$H NMR ($\delta$ ppm) (300 MHz, 298 K) $\delta$ :

1.25 (4H, s, C–N), 3.94 (4H, s, C–O), 6.83 (2H, t, aromatic), 6.92 (2H, d, aromatic), 7.21 (2H, t, aromatic), 7.31 (2H, d, aromatic), 8.36 (2H, s, -CH) (Found : C, 64.01; H, 3.75; N, 32.24. Calcd. for C$_{18}$H$_{18}$N$_2$O$_2$ : C, 73.47; H, 6.12; N, 9.52; O, 10.89%).

*Electrode preparation :*

The membranes were prepared using the basic method given by Craggs *et al.*[12] with certain variations in compositions of PVC, ionophore and plasticizers/solvent mediators like DBP, NB, DOP, NBA, TBP etc. The PVC membrane solution was prepared by through mixing of the ionophore (macrocyclic compound) (1% wt.), DBP as plasticizer (66% wt.) and PVC (33% wt.) and dissolving in THF. The resulting PVC-THF solution was poured into a glass mould and THF was allowed to evaporate off at room temperature over 24 h. A flexible membrane with a thickness of 0.2–0.4 mm was obtained. The discs of 6 mm diameter were cut and pasted onto a glass-tube. After getting dried, this tube was filled with an 0.01 $M$ internal solution of nickel and immersed in the 0.01 $M$ nickel nitrate solution, at least for 2–3 days prior to use.

*Analysis of nickel(II) in milk and chocolate samples :*

A suitable amount of milk powder or chocolate (about 10 mL milk or 2 g chocolate) was burnt at 450 °C in a porcelain crucible for about 1.5–2 h. About 2 mL of conc. HNO$_3$ was added into the residue and gently heated to dissolve. The resulting solution was diluted with minimum amount of water followed by its filtration and transfer to a 250 mL beaker with multiple washing by water. Final volume of the solution in the beaker was made upto 50 mL. The volume of this solution was reduced upto
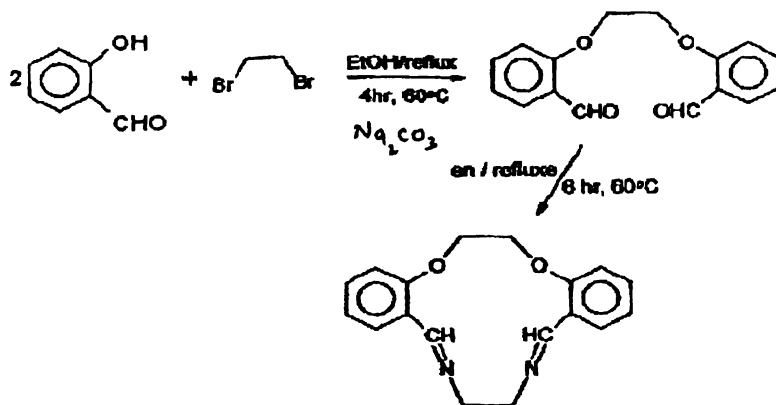


**Scheme 1**

20-25 mL. Finally this solution was transferred properly into a 100 mL volumetric flask followed by make-up of volume.

## Results and discussion

Due to sufficient lipophilic character of macrocyclic ligands, we were prompted to investigate the bahaviour of the ligand with two donating nitrogen atoms as carrier in the construction of PVC-based membranes for the estimation of various bivalent ions concentrations in aqueous solution. As can be seen from the Fig. 1, the ionophore as a neutral carrier was found to be higly responsive to $Ni^{II}$ with respect to several metal ions such as $Li^I$, $K^I$, $Ca^{II}$, $Al^{III}$, $Sr^{II}$, $Be^{II}$, $Th^{IV}$ and $Cd^{II}$.
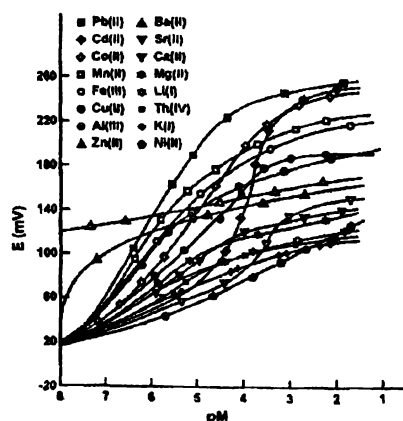


**Fig. 1.** Potential response of various ion-selective electrodes based on DADOCTD.

The molecular structures of the uncomplexed DADOCTD and its complexes with $Ni^{II}$ and other metal ions were optimized using the lanl2mb basis set for all atoms at restricted Hartree Fock (RHF) level. The binding energy (DE) was calculated with the enlarged basis sets using eq. (1) :

$$\Delta E = E_{complex} - (E_{ligand} + E_{cation}) \qquad (1)$$

where $E_{complex}$, $E_{ligand}$ and $E_{cation}$ are the total energies of the complex, uncomplexed DADOCTD and metal ion, respectively.

Inspection of Table 1 reveals that the cation binding energies with DADOCTD shows a pronounced dependence on the nature of metal ions used. In fact, the stability of the resulting complexes is expected to decrease in the order of :
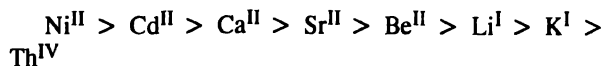
$Ni^{II} > Cd^{II} > Ca^{II} > Sr^{II} > Be^{II} > Li^I > K^I > Th^{IV}$

**Table 1.** Binding energy of complexes of the different metal ions with DADOCTD

| Metal ion | Total energy of metal ion (Hartree) | Total energy of the complex (Hartree) | Binding energy $(\Delta E)^a$ (kcal mol$^{-1}$) |
|---|---|---|---|
| $Ni^{II}$ | -62.6454 | -640.6321 | -269.4 |
| $Cd^{II}$ | -45.7232 | -623.6654 | -239.4 |
| $Ca^{II}$ | -35.6124 | -613.4141 | -147.5 |
| $Al^{III}$ | -29.5441 | -607.5722 | -292.6 |
| $Sr^{II}$ | -29.5426 | -607.3073 | -124.6 |
| $K^I$ | -27.6374 | -605.2845 | -52.8 |
| $Th^{IV}$ | -19.4811 | -597.1074 | -37.9 |
| $Be^{II}$ | -13.4423 | -591.1854 | -111.7 |
| $Li^I$ | -7.1454 | -584.5921 | -71.6 |

### *Effect of membrane composition :*

The characteristics of membrane, such as response time, lifetime, selectivity and chemical stability depends on the nature and amount of plasticizer as well as the ionophore. In fact the membrane composition especially in some cases, the nature of additive may have a significant influence on the sensitivity and selectivity obtained for a given electroactive material[13-15]. In general, the thickness of the membrane depends on the membrane content of PVC and there is a good correlation between membrane thickness and the PVC content of the membrane. The detection limit of the sensor increases with a decrease in the PVC content. However, if the membrane is too short, it losses its mechanical strength, and is easily broken[16]. Furthermore the stability of carrier complexes in membranes results from the electrostatic interaction between complexes and the surrounding membrane solvents[17]. Accordingly, for selecting solvent mediator for a metal ion selective electrode, a number of solvents, like dibutylphthalate (DBP), dibutylbutylphosphonate (DBBP), tributylphosphate (TBP), tris(2-ethyhexyl)phosphate (TEP) etc. were taken in varying amount and their effect on potentiometric response of ISE was observed (Table 2).

### *Working concentration range :*

The potential response of the membrane, as a function of $Ni^{2+}$ activity is shown in Table 1 and in Fig. 2. It is observed that membrane No. 1, without plasticizer has a narrow working concentration range and near Nerstian slope 25.0 mV/decade activity. Further it attains stable potential value in 50 s at higher concentration ($1.0 \times 10^{-1}$ *M*) and in 90 s lower concentration ($7.8 \times 10^{-4}$ *M*).

**Table 2.** Comparison and response characteristics of Ni$^{II}$-selective PVC based membrane having (DADODBCT) as electroactive material

| Membrane No. | Ratio of various compositions in membrane (w/w) | | | | | | | | Working concentration range ($M$) | Slope (mV/ decade) | Response time (s) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | I | NaTBP | DOP | NB | TEP | TBP | DBP | PVC | | | |
| 1 | 5 | – | – | – | – | – | – | 33 | $7.8 \times 10^{-4}$ to $1.0 \times 10^{-1}$ | 25.0 | 50–90 |
| 2 | 5 | 2 | 60 | – | – | – | – | 33 | $6.0 \times 10^{-8}$ to $1.0 \times 10^{-1}$ | 29.5 | 10 |
| 3 | 5 | 2 | – | 60 | – | – | – | 33 | $7.2 \times 10^{-5}$ to $1.0 \times 10^{-1}$ | 28.2 | 30 |
| 4 | 5 | 2 | – | – | 60 | – | – | 33 | $3.8 \times 10^{-5}$ to $1.0 \times 10^{-1}$ | 24.4 | 24 |
| 5 | 5 | 2 | – | – | – | 60 | – | 33 | $9.7 \times 10^{-5}$ to $1.0 \times 10^{-1}$ | 29.1 | 19 |
| 6 | 5 | 2 | – | – | – | – | 60 | 33 | $6.8 \times 10^{-4}$ to $1.0 \times 10^{-1}$ | 31.0 | 22 |
| 7 | 3 | 2 | – | – | – | – | – | 33 | $5.3 \times 10^{-5}$ to $1.0 \times 10^{-1}$ | 28.9 | 18 |
| 8 | 2 | 2 | – | – | – | – | – | 33 | $4.1 \times 10^{-4}$ to $1.0 \times 10^{-1}$ | 27.3 | 17 |
| 9 | 8 | 2 | – | – | – | – | – | 33 | $6.5 \times 10^{-4}$ to $1.0 \times 10^{-1}$ | 28.4 | 15 |
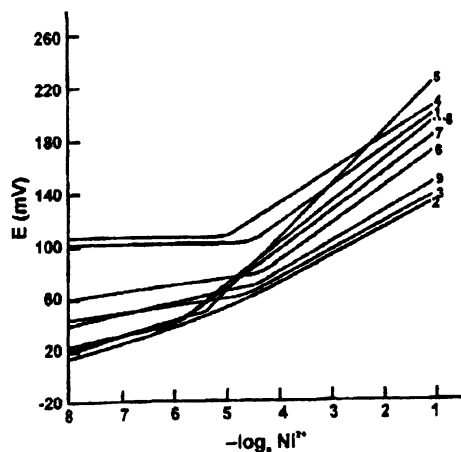


**Fig. 2.** Calibration graphs of Ni$^{II}$-selective PVC based membrane containing DAOBTD with different compositions.

However, the addition of plasticizer improves the response characteristics of the membrane, which not only shows significant potential response in improved and wider concentration range but the slope value also approached closer to the Nernstan value of 29.5 for bivalent metal ions. Especially the membrane No. 2, which contains DOP as plasticizer, exhibits linearity in the concentration range $3.9 \times 10^{-6}$ to $1.0 \times 10^{-2}$ with a slope of 29.5 mV/ decade of activity. All the further studies were performed with the membrane No. 2, which has the optimized composition for best potential response towards Ni$^{II}$ selectivity.

*Response time and lifetime* :

Membrane No. 1, without plasticizer shows a response time of 50–90 s. Such high response time was reduced significantly, when solvent mediator was used. The best response time was observed as 10 s for membrane No. 2, having plasticizer DOP. Potential generated by this membrane remains stable for 150 s and start deviating slowly. The electrode was used over a period of 4 months without observing any significant change in potential response for whole working concentration range.

*Effect of pH* :

The pH dependence of the electrode was tested over the range 1.0–12 using test solution of nickel nitrate in the concentration range of $1.0 \times 10^{-2}$ to $1.0 \times 10^{-4}$, which is depicted in Fig. 3. The pH of test solution was adjusted by the addition of dilute nitric acid and dilute
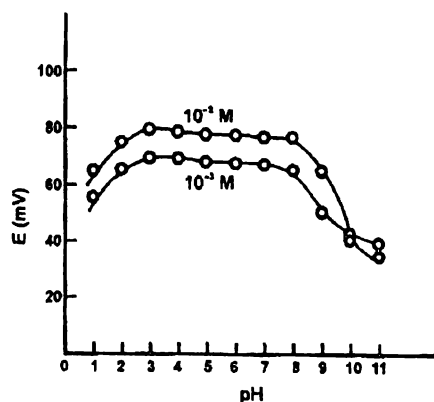
**Fig. 3.** The effect of the pH of the test solutions $(1.0 \times 10^{-2}$ mol $L^{-1}$ and $1.0 \times 10^{-3}$ mol $L^{-1})$ on on the potential response of the nickel sensor (membrane No. 2).

NaOH solutions. Fig. 3 clearly shows that the useful pH range is 3.0 to 8.0 as potential remains constant in this range, in both different concentrations.

*Potentiometric selectivity* :

Selectivity is the most important characteristic of any ion selective electrode. To investigate the selectivity of the proposed membrane electrode, its potential response was investigated in the presence of various interfering foreign cations using the matched potential method $(MPM)^{18,19}$. According to MPM, the selectivity coefficient is defined as the activity (concentration) ratio of the primary ion and the interfering ion, which gives the same potential change in a reference solution[20]. The concentration of $Ni^{2+}$ used, as the primary ion in this study,

was $1.0 \times 10^{-2}$ $M$. The resulting selectivity coefficients are summarized in Table 3. The selectivity coefficient values $<1$ for various interfering ion studied indicate that most of the hard, soft and borderline metal ions used did not significantly disturb the functioning of the $Ni^{2+}$-selective electrode. In Table 4, the response characteristics of the proposed membrane sensor are compared with those of the best $Ni^{2+}$-selective electrode reported earlier[21-23].

**Table 3.** Selectivity coefficients of the nickel selective electrode based on (DAOBTD) using the matched potential method (MPM)

| Interfering ion (B) | Selectivity coefficients, $K^{pot}$ $Ni^{2+}$(B) |
|---|---|
| $Li^I$ | $3.1 \times 10^{-4}$ |
| $K^I$ | $7.4 \times 10^{-4}$ |
| $Mg^{II}$ | $8.5 \times 10^{-4}$ |
| $Ca^{II}$ | $7.2 \times 10^{-4}$ |
| $Ba^{II}$ | $9.2 \times 10^{-4}$ |
| $Al^{III}$ | $5.4 \times 10^{-3}$ |
| $Zn^{II}$ | $6.1 \times 10^{-3}$ |
| $Co^{II}$ | $5.0 \times 10^{-4}$ |
| $Cu^{II}$ | $8.3 \times 10^{-4}$ |
| $Cd^{II}$ | $3.7 \times 10^{-3}$ |
| $Pb^{II}$ | $4.3 \times 10^{-4}$ |
| $Mn^{II}$ | $7.1 \times 10^{-4}$ |
| $Sr^{II}$ | $6.5 \times 10^{-3}$ |
| $Fe^{II}$ | $7.9 \times 10^{-4}$ |
| $Th^{IV}$ | $2.2 \times 10^{-4}$ |

**Table 4.** Comparison of the reported electrode with proposed electrode assembly

| Sl. no. | Working concentration range (M) | Slope (mV/decade of activity) | pH range | Response time (s) | Life time (weeks) | Refs. |
|---|---|---|---|---|---|---|
| 1. | $3.2 \times 10^{-6} - 5.0 \times 10^{-2}$ | $29.0 \pm 0.4$ | 2.2–5.9 | ~10 | 16 | 3 |
| 2. | $1.0 \times 10^{-7} - 1.0 \times 10^{-2}$ | – | 5.0–8.5 | <15 | 4 | 6 |
| 3. | $1.0 \times 10^{-6} - 1.0 \times 10^{-1}$ | ~30.0 | 1.7–5.4 | 15 | 24 | 7 |
| 4. | $1.0 \times 10^{-5} - 1.0 \times 10^{-1}$ | 29.5 | 2.6–6.8 | <25 | 16 | 8 |
| 5. | $2.0 \times 10^{-5} - 5.5 \times 10^{-3}$ | 29.8 | 4.0–8.0 | 300 | 6 | 11 |
| 6. | $7.9 \times 10^{-6} - 1.0 \times 10^{-1}$ | $30.0 \pm 1.0$ | 2.7–7.6 | 15 | Not mentioned | 12 |
| 7. | $1.0 \times 10^{-6} - 1.0 \times 10^{-1}$ | 30.5 | 3.0–6.0 | <40 | ≥8 | 14 |
| 8. | Not mentioned | 2.0 | 2.8–7.6 | 15 | 8 | 15 |
| 9. | $1.0 \times 10^{-7} - 1.0 \times 10^{-2}$ | $30 \pm 1.0$ | 4.5–9.0 | <10 | 2 | 16 |
| 10. | $1.0 \times 10^{-8} - 1.0 \times 10^{-3}$ | – | – | <40 | – | 17 |
| 11. | $6.0 \times 10^{-8} - 1.0 \times 10^{-1}$ | 29.5 | 2.5–8.5 | 10 | 16 | Present work |

*Application of the proposed ISE :*

The proposed electrode was successfully applied as indicator electrode in conjugation with SCE in the potentiometric titration of $Ni^{2+}$ solution with EDTA as a suitable titrant. $Ni^{2+}$ solution (10 mL of $1.0 \times 10^{-3}$ M) was brought to pH 6.0 with hexamine and then titrated against $1.0 \times 10^{-2}$ M EDTA solutions. The potential data are plotted against volume of EDTA as shown in Fig. 4. The plot is of conventional sigmoidal shape, indicating sufficient selectivity of the sensor for $Ni^{2+}$ ions and 1 : 1 stoichiometry of Ni-EDTA complex at the end point.
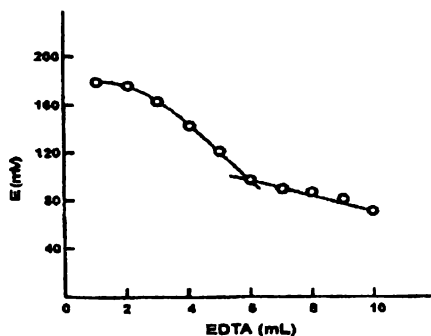


**Fig. 4.** Potentiometric titration curve of 10 mL solution of $Ni^{2+}$ ($1.0 \times 10^{-3}$ mol $L^{-1}$) with $1.0 \times 10^{-2}$ mol $L^{-1}$ of EDTA.

The nickel contents were determined successfully in the various samples of dairy milk and chocolates using the proposed sensor. The results clearly indicated that the values are at par the evaluation of the same samples by atomic absorption spectroscopy (Table 5).

**Table 5.** Nickel content in various samples of milk and chocolate analyzed

| Sample | Using proposed electrode (mg $K^{-1}$) | AAS (mg $K^{-1}$) |
| --- | --- | --- |
| Milk (1) | $1.70 \pm 0.10$ | $1.80 \pm 0.10$ |
| Milk (2) | $1.75 \pm 0.10$ | $1.90 \pm 0.10$ |
| Chocolate (1) | $0.67 \pm 0.05$ | $0.68 \pm 0.05$ |
| Chocolate (2) | $0.58 \pm 0.10$ | $0.60 \pm 0.10$ |

## Acknowledgement

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