



Article

Acyclic Arylamine-Based Ionophores as Potentiometric Sensors for Zn^{2+} and Ni^{2+} Ions

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Abstract: Two receptor molecules *N*-(2-nitrophenyl)benzene-1,2-diamine (DPA) and *N,N*-bis(2-nitrophenyl)benzene-1,2-diamine (TPA) are proposed as Zn^{2+} and Ni^{2+} -selective electrodes, respectively. The two electrodes respond to Zn^{2+} and Ni^{2+} ions with the detection limits of 1.3×10^{-6} M and 2.8×10^{-6} M, respectively. Both the electrodes have a life time of four months and respond within 15 s and 20 s, respectively, for Zn^{2+} and Ni^{2+} over a wide pH range (3–9). The electrodes show very good selectivity towards the primary ions in presence of some alkali, alkaline earth, and transition metal ions.

Keywords: acyclic arylamines; zinc ion; nickel ion; PVC membrane; potentiometry; DFT studies; ISE

1. Introduction

The design and synthesis of artificial ionophores for selective recognition of ions is a field of significant interest due to their key role in major biological and chemical processes [1]. A large number of receptors based on pyrroles, lactams, aliphatic amines, hydrazines and urea have been reported where the amine group ($-\text{NH}-$) acts as the anion or cation binding site [2–6]. Selectivity of the ionophore to act as a cation sensor depends upon availability of the electron pair on nitrogen and the pre-organisation of the cavity size, while anion sensing is governed by chemical interactions [2–4]. Further, receptor properties of an ionophore are governed by a delicate balance between rigidity, required for high selectivity, and flexibility, for a sufficiently fast ion exchange. Macrocyclic arylamines offer advantages of both rigidity and flexibility. The rigidity is due to its planar aromatic ring and the flexibility due to rotation around amine linkages. Thus, two new ionophores, diphenyl amine (DPA) and triphenyl amine (TPA), were designed and synthesized to explore their sensing properties by potentiometric methods. Potentiometry offers an advantage over other electrochemical methods in terms of cost, sensitivity, and selectivity [5–7]. The results indicated strong affinity for Zn^{2+} ions in case of DPA, while TPA was selective towards Ni^{2+} ions.

Determination of both zinc and nickel in trace amounts is important in biological, pharmaceutical, and environmental monitoring. The role of zinc as an essential element (8 to 15 mg/day in humans) for immune functioning, DNA synthesis, and enzyme activity is well known [8–10]. Also, extensive use of both the metals in pharmaceutical, electroplating, and paint industries increases its concentration in water, air, and soil [11]. Similarly, deficiency as well as excess of nickel is detrimental to animal and plant systems [12–15]. It has been known that the presence of nickel ions beyond a tolerable limit in drinking water (2.5 mg/mL) can cause disorders of the central nervous system, asthma, dermatitis, and cancer [16,17].

There are a number of reports in literature where analytical techniques such as atomic absorption spectrometry, voltammetry, atomic emission, and UV-Vis spectroscopy have been used for the detection of trace amounts of zinc [18–30] and nickel ions [31–35]. However, potentiometry, due to

its inexpensive, wide, and linear range, is a fast and a simple procedure that has an advantage. A number of ions selective membranes (ISM) have been reported with various compounds for the detection of both zinc and nickel. This includes [Bzo₂Me₂Ph₂(16)hexaeneN₄] [36], PME-6,7:14,15-Bzo₂-10,11-(4-methylbenzene)-[15]-6,8,12,14-tetraene-9,12-N₂-1,5-O₂ [37], Dibenzo-24-crown-8 [26], 3-[(2-Furylmethylene)amino]-2-thioxo-1,3-thiazolidin-4-one [38], *N,N*-Bis(acetylacetone)ethylene diamine [25] for zinc ions and porphyrins, crown ethers, cyclams, amines, and Schiff bases-based molecules for nickel ions [33,34,39–43].

In this work, we report the use of two acyclic arylamine-based ionophores, *N*-(2-nitrophenyl)benzene-1,2-diamine (DPA) and *N,N*-bis(2-nitrophenyl)benzene-1,2-diamine (TPA), for preparing highly selective Zn²⁺ and Ni²⁺ membrane electrodes, respectively. To the best of our knowledge, this is the first report where diphenylamines have been reported as potentiometric sensors for Zn²⁺ and Ni²⁺ ions.

2. Results and Discussion

2.1. Potentiometric Studies

2.1.1. Determination of Binding Constants

Preliminary studies to determine the binding affinity of the ionophores with different metal ions were done potentiometrically using sandwich membrane method. A poly vinylchloride (PVC) membrane consists of plasticizer, *o*-nitrophenyloctylether (*o*-NPOE), lipophilic salt, and sodium tetraphenylborate (NaTPB), and a required amount of the ionophore was pressed against a blank membrane (without ionophore) for each ionophore, as shown in Figure 1. Binding constants for both the ionophores were calculated by measuring EMF using a known procedure [44,45] and following equation where *L_T*, *R_T*, and *Z_I* are the concentration of ionophore, lipophilic salt, and charge carried by primary ion, respectively. Expressions *R*, *T*, and *F* carry their usual meanings and *n* represents stoichiometry of the metal ion-ionophore complex.

$$\beta_{ILn} = (L_T - nR_T/Z_I)^{-n} \exp(E_M Z_I F / RT)$$

The values calculated for Fe²⁺, Co²⁺, Ca²⁺, Mn²⁺, Cu²⁺, and Zn²⁺ for their affinity with DPA were 5.3, 4.7, 4.1, 3.7, 5.8, and 7.4, respectively. Thus Zn²⁺ ions displayed highest affinity towards DPA. Similarly, values calculated with TPA indicated more stable complex in case of Ni²⁺ ions. Formation constant values with Ca²⁺, Cu²⁺, Ni²⁺, Mg²⁺, Zn²⁺, and Co²⁺ ions were found to be 3.4, 6.2, 8.3, 3.8, 4.8, and 3.6, respectively.

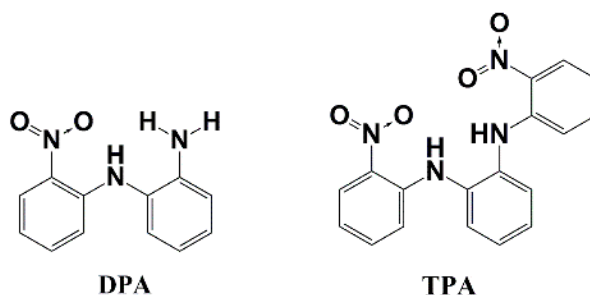


Figure 1. Structure of ionophores.

2.1.2. Membrane Optimization

It is well known that response, mechanical strength, and life time of any liquid membrane electrode is significantly dependent upon its composition [1,46–49]. While PVC provides mechanical strength to the membrane and is inert to the chemical interactions, the *o*-NPOE used as a plasticizer

serves as a membrane solvent with reduced viscosity and ensures high mobility of the membrane constituents. The plasticizer also helps in improving selectivity and is compatible with other membrane components. The role of lipophilic reagent (NaTPB, in our case) is to introduce Donnan exclusion of ion in the membrane, i.e., to introduce permselectivity in the membrane so that no counter ions are co-extracted from the solution to the membrane phase. The presence of sufficient amount of non-exchangeable lipophilic ions in the membrane ensures that the concentration of primary ions is much higher than the co-extracted amount. Optimization of the ratio of ionophore: NaTPB is very critical to ensure the best response of the electrode. The amount of lipophilic ions was carefully monitored to get the optimized ratio of ionophore: lipophilic salt. Thus, based on preliminary experiments (Figure 2) and values of the binding constants for both DPA and TPA, membranes were optimized to get lowest detection limit with closest Nernstian response.

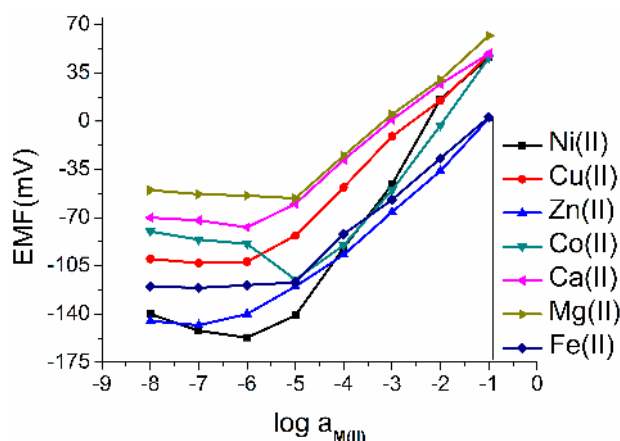


Figure 2. Trends of electromotive force (EMF) responses as a function of concentration by *N,N*-bis(2-nitrophenyl)benzene-1,2-diamine (TPA) towards different metal ions.

Table 1 shows different compositions of DPA-based membrane and its response to Zn^{2+} ions. Figure 3 shows that any change in the ionophore less or greater than 3% leads to non-Nernstian responses. Variation in the plasticizer, lipophilic salt, and PVC within the permissible limit gave membrane electrode no. 3, having composition PVC: o-NPOE: DPA: NaTPB as 33:61:3:3 (*w/w*) as the optimum composition with closest Nernstian response. This composition was used for further studies in case of DPA.

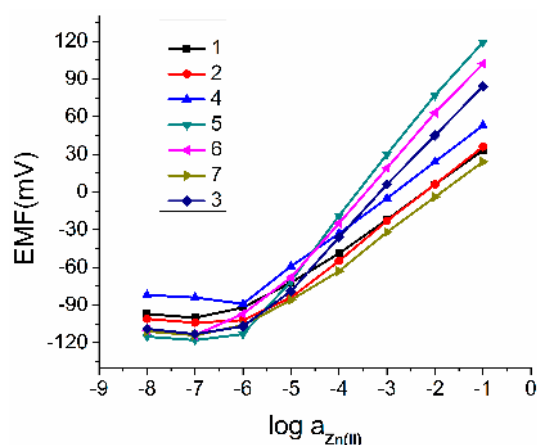


Figure 3. Response of *N*-(2-nitrophenyl)benzene-1,2-diamine (DPA) towards different membrane compositions given in Table 1.

Table 1. Optimization of membrane components for Zn^{2+} selective electrode based on diphenylamine derivative.

Membrane Electrode No.	PVC (Wt %)	Plasticizer (Wt %)	Ionophore (Wt %)	NaTPB (Wt %)	Slope, mV/Decade	Detection Limit, (M) (Zn^{2+})
1	33	63	1	3	20	1.0×10^{-5}
2	33	64	2	1	21	8.2×10^{-5}
3	33	61	3	3	30	1.3×10^{-6}
4	34	61	2	3	21	3.2×10^{-5}
5	33	60	4	3	36	6.3×10^{-5}
6	32	60	5	3	33	1.2×10^{-5}
7	32	59	6	3	20	3.6×10^{-5}

Similarly, Table 2 shows different compositions tried for TPA-based membrane and its response towards Ni^{2+} ions. Here again, membranes with 3% of ionophore gave closest Nernstian response, having slope in the range of 25–30 mV/decade (membrane electrodes no. 9–11). It can be observed (Table 2) that any deviation from 3% of ionophore leads to significant divergence in the Nernstian response of the membrane. Thus, membrane electrode no. 9, having composition of TPA: PVC: o-NPOE: NaTPB as 3:32:62:3 (*w/w*), was selected for further studies as Ni^{2+} selective electrode. The response of blank membranes (membrane electrode no. 1 and 2) towards Ni^{2+} ions was insignificant.

Table 2. Optimization of membrane components for Ni^{2+} ISE based on triphenylamine derivative.

Membrane Electrode No.	Ionophore (% <i>w/w</i>)	PVC (% <i>w/w</i>)	NPOE (% <i>w/w</i>)	NaTPB (% <i>w/w</i>)	Slope, mV/decade	Detection Limit, (M) (Ni^{2+})
1	-	33	67	-	-	-
2	-	33	65	2	-	-
3	1	33	65	1	14.3	2.4×10^{-4}
4	1	32	65	2	15.2	7.1×10^{-4}
5	2	33	64	1	20.8	6.8×10^{-4}
6	2	32	65	1	19.8	2.7×10^{-4}
7	2	32	64	2	21.2	8.2×10^{-5}
8	2	33	63	2	21.8	7.6×10^{-5}
9	3	32	62	3	30.0	2.8×10^{-6}
10	3	33	61	3	26.5	9.2×10^{-6}
11	3	33	63	1	25.8	1.2×10^{-5}
12	4	33	60	3	37.0	4.3×10^{-6}
13	4	32	61	3	35.2	3.8×10^{-5}
14	5	32	61	2	34.0	1.2×10^{-5}
15	5	32	60	3	33.2	8.7×10^{-5}

2.1.3. Calibration Curve, Response Time, and Life Time of the Electrode

The effect of internal solution concentration was studied on the working of membrane electrodes to know the best performing concentration, as per International Union of Pure and Applied Chemistry (IUPAC) recommendations [50]. Three internal solution concentrations in the range 1×10^{-3} M to 1×10^{-1} M were used with best response observed in case of 1×10^{-1} M concentration. This concentration of the internal solution was used to draw a calibration curve for the Zn^{2+} selective electrode (Membrane no. 3, Table 1) over a concentration range of 10^{-8} M to 10^{-1} M of the primary ion (Zn^{2+}). Figure 4 shows the calibration curve with workable concentration range of 1×10^{-6} M to 1×10^{-1} M and a Nernstian slope of 30 mV/decade. The lower detection limit obtained was 1.3×10^{-6} M for the Zn^{2+} ions, as calculated according to IUPAC recommendation [48]. Similarly, the calibration curve drawn for the Ni^{2+} —selective electrode containing triphenylamine as an ionophore gave best response with membrane electrode no. 9 (Table 2) having a slope of 30 mV/decade.

(Figure 5). Workable concentration range in this case was 1×10^{-5} M to 1×10^{-1} M and the lower detection limit 2.8×10^{-6} M of Ni^{2+} . Response time was measured by recording EMF of the electrode as a function of time till a stable reading was achieved.

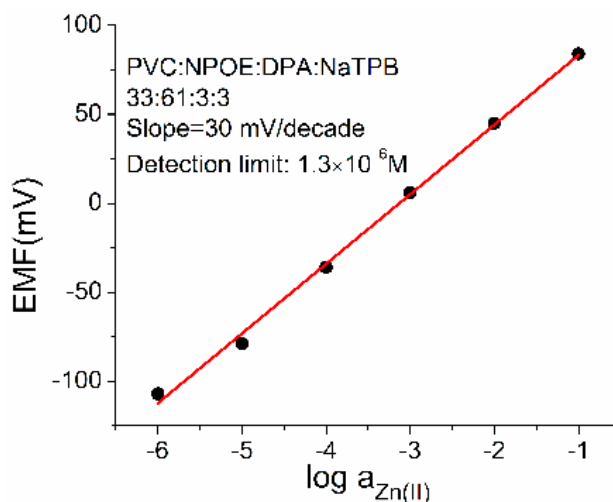


Figure 4. Potentiometric characteristics calibration curve for Zn^{2+} selective sensor based on DPA.

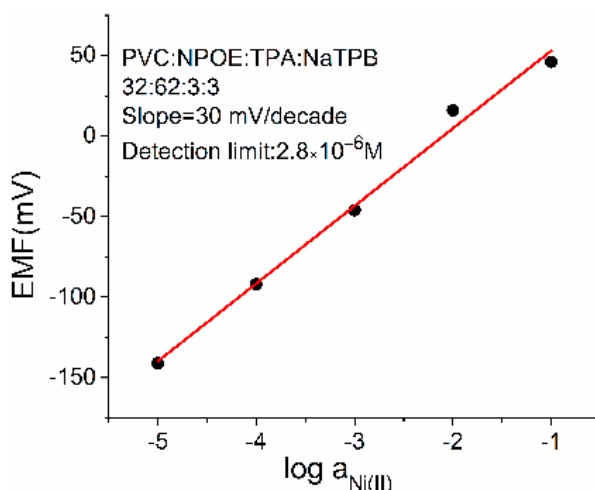


Figure 5. Potentiometric characteristics calibration curve for Ni^{2+} selective sensor based on TPA.

Response time: This is an important parameter to evaluate an electrode's working efficiency. The steady response that in case of DPA was found within 15 s after addition of Zn^{2+} ions, while nickel-selective, TPA-based electrode stabilized in 20 s. Both the electrodes could be used for 4 months without observing any considerable change when stored in 0.1 M respective ion solutions.

2.1.4. Effect of pH

In order to evaluate the behavior of electrodes in different working conditions, their EMF was measured over entire pH range. Figure 6a shows the response of the DPA ionophore for the zinc ions (10^{-2} M and 10^{-3} M) in the pH range 1 to 12. It can be observed that DPA has a steady response over wide pH range of 3.6–9.3. Similarly, the response of TPA remained unaffected in the pH range of 4.2–9.2 when different concentrations of Ni^{2+} (10^{-1} M and 10^{-2} M) were used (Figure 6b). A decrease in the potential at lower pH in case of TPA can be attributed to protonation of the donor NH groups that become unavailable to complex with respective metal ions. Furthermore, the electrodes may be

exhibiting interference due to hydrogen ions. At elevated pH, the coordinated metal gets hydrolysed and thus electrode response deviates.

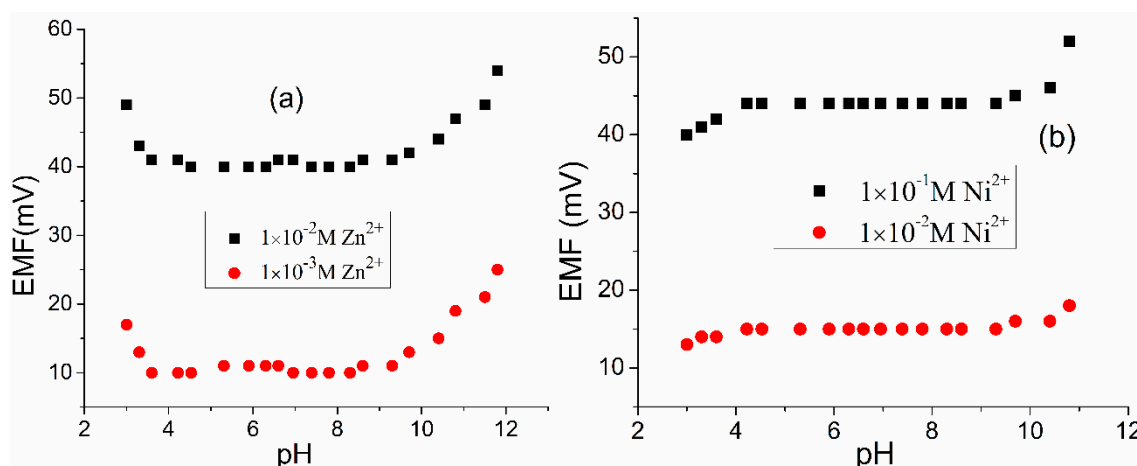


Figure 6. Effect of pH on the potential response of (a) Zn^{2+} ISE based on DPA and (b) Ni^{2+} ISE based on TPA.

2.1.5. Effect of Interfering Ions on Potentiometric Selectivity of Electrodes

The behavior of both the electrodes was studied in the presence of interfering ions in order to ascertain their selectivity. This is expressed as the potentiometric selectivity coefficient $-\log K_{M^{n+},B}^{\text{Pot}}$ and was determined by IUPAC-recommended, fixed-interference method (FIM) [50]. Addition of a fixed concentration of interfering ions (1.0×10^{-2} M) to a varying concentration (1×10^{-8} M to 1×10^{-1} M) of the target ion showed hardly any interference from the other ions. The selectivity coefficients values so determined for DPA and TPA electrodes have been compiled in Tables 3 and 4, respectively.

Table 3. Potentiometric selectivity coefficient values for DPA electrode by fixed interference method.

Metal Ion	$\log K_{\text{Zn}^{2+},B}$	Metal Ion	$\log K_{\text{Zn}^{2+},B}$
K^+	−1.4	Ni^{2+}	−2.0
Ca^{2+}	−2.7	Cu^{2+}	−2.5
Na^+	−1.9	Sr^{2+}	−2.3
Mg^{2+}	−2.1	Ba^{2+}	−3.1
Pb^{2+}	−2.4	Cd^{2+}	−1.9
Fe^{2+}	−2.8	Co^{2+}	−2.7

From the $\log K$ values obtained for both DPA and TPA electrodes, it can be proposed that electrodes have high selectivity for Zn^{2+} and Ni^{2+} ions, respectively, over other ions and can be conveniently used for the determination of their respective ions.

Table 4. Potentiometric selectivity coefficient values for TPA electrode by fixed interference method.

Metal Ion	$\log K_{\text{Ni}^{2+},B}$	Metal Ion	$\log K_{\text{Ni}^{2+},B}$
Na^+	−1.0	Pb^{2+}	−2.6
Sr^{2+}	−3.1	Fe^{2+}	−3.2
Cu^{2+}	−1.9	Ca^{2+}	−3.1
Cd^{2+}	−2.9	Ba^{2+}	−3.5
Mg^{2+}	−2.8	Zn^{2+}	−2.1
Co^{2+}	−3.1	Mn^{2+}	−3.2

2.1.6. Applications

Applicability of both DPA and TPA membranes was evaluated as indicator electrodes in the potentiometric titrations with 1×10^{-2} M solutions of Zn^{2+} and Ni^{2+} ion, respectively, by titrating against Ethylene Diamine Tetra Acetic Acid (EDTA) solutions. Figure 7a shows an inflection point corresponding to 1:1 stoichiometry for Zn^{2+} -EDTA complex in case of DPA membrane electrode. Similarly, Figure 7b shows decrease in the EMF as an increasing volume of EDTA is added to fixed volume of 1×10^{-2} M Ni^{2+} ions. Here again, titration curve shows sharp inflexion point corresponding to 1:1 stoichiometry of the complex. Therefore, both the membranes can be used as indicator electrodes for the potentiometric determination of equivalent point.

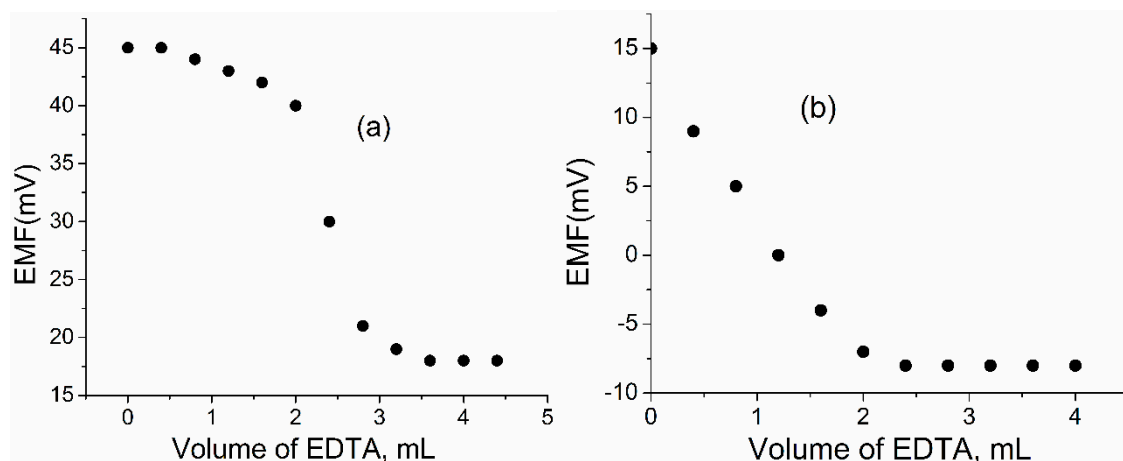


Figure 7. Potentiometric titration of (a) Zn(II) (25 mL of 1×10^{-2} M) with EDTA (1×10^{-1} M) using Zn(II)-selective electrode based on DPA and (b) Ni(II) (20 mL of 1×10^{-2} M) with EDTA (1×10^{-1} M) using Ni(II)-selective electrode based on TPA.

2.1.7. Comparison of the Proposed Sensors with Other Electrodes

Performance of the membrane electrodes has been compared with the earlier literature reports for the lower detection limit, slope of calibration curve, and pH range. Tables 5 and 6 show that both DPA and TPA electrodes are more close to the Nernst Equation and thus determine the concentration of the target species closer to the actual values.

Table 5. Comparison of proposed DPA-based zinc selective electrode with the reported electrodes.

S. No.	Ionophore	Detection Limit (M)	pH Range	Slope (mV/Decade)	Ref
1	[Bzo ₂ Me ₂ Ph ₂ (16)hexaeneN ₄]	2.24×10^{-6}	2.5–8.5	28.5	[36]
2	(4-methylbenzene)-[15]-6,8,12,14-tetraene-9,12-N ₂ -1,5-O ₂	3.3×10^{-7}	3.0–8.0	28.8	[37]
3	Dibenzo-24-crown-8	9.2×10^{-5}	4.8–6.2	29.0	[26]
4	3-[(2-Furylmethylene)amino]-2-thioxo-1,3-thiazolidin-4-one	8.5×10^{-7}	3.0–7.0	29.3	[38]
5	<i>N,N</i> -Bis(acetylacetone)ethylenediamine	8.9×10^{-5}	3.2–7.1	30.0	[25]
6	This work (DPA)	1.3×10^{-6}	3.6–9.3	30.0	-

Table 6. Comparison of proposed TPA-based Ni^{2+} selective electrode with the reported electrodes.

S. No.	Ionophore	Detection Limit (M)	pH Range	Slope (mV/decade)	Ref
1	Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene diperchlorate	1.0×10^{-5}	1.7–5.4	Near-Nernstian	[33]
2	[Me ₄ Bzo ₂ TAA]	7.9×10^{-6}	2.7–7.6	30	[34]
3	<i>N</i> -(2-hydroxybenzylidene)- <i>N</i> -(2-picolyl)ethylenediamine	3.2×10^{-6}	2.2–5.9	29	[39]
4	<i>N</i> 1, <i>N</i> 2-bis((naphthalen-1-yl)-methylene)ethane-1,2-diamine	1.3×10^{-6}	3.6–7.4	29.9	[40]
5	2,3,7,8,12,13,17,18-octamethyl-21H, 23H-porphine	1.0×10^{-5}	2–7	29	[41]
6	1,10-dibenzyl-1,10-diaza-18-crown-6	2.0×10^{-5}	4–8	Nernstian	[42]
7	5,7,8,14-tetramethyldibenzo[b,i]-1,4,8,11-tetrazacyclo tetradecane	7.0×10^{-6}	2–7.6	29.8	[43]
8	This work (TPA)	2.8×10^{-6}	4.2–9.2	30.0	-

2.2. Theoretical Studies

In an attempt to better understand the nature of ionophores and their interaction with metal ions, theoretical studies were carried out using density functional theory method (DFT). B3LYP function with 6–31 G basis set was used for quantum chemical calculations of ionophores, independently and along with metal ions on Gaussian 03W programme.

Quantum chemical calculations carried out for energy optimization of DPA independently and along with other metal ions showed highest energy decrease (1778 a.u.) with Zn^{2+} ions. The decrease in the energy with Mn^{2+} , Fe^{2+} , Ni^{2+} , and Cu^{2+} was 1150, 1263, 1507, and 1639 a.u., respectively. Thus, theoretical results were consistent with the experimental outcome. A look at the minimum energy configuration of DPA (Figure 8a) shows presence of a pseudo-cavity constituted by the three nitrogens. Two of these nitrogens contribute from amino and one from nitro groups. In the presence of metal ions, the nitrogen atoms align themselves in a way to fit metal in the cavity. The best fit alignment is obtained in case of Zn^{2+} ions with minimum energy (Figure 8b).

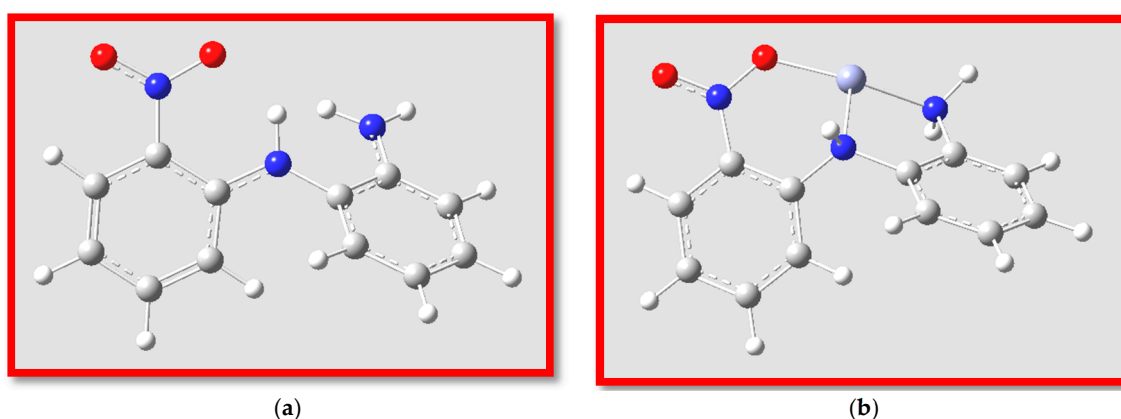


Figure 8. DFT optimized structures of DPA (a) and DPA- Zn^{2+} complex (b). White, red, blue, grey, and purple spheres refer to H, O, N, C, and Zn^{2+} , respectively.

Similar calculations done with TPA show a decrease in the energy decreases from -1213 a.u. to -2721 a.u after addition of Ni^{2+} , thus indicating the formation of highly stable TPA- Ni^{2+} complex. Figure 9 shows the three dimensional structure of TPA, in which two amine nitrogens along with one of the nitro groups are involved in composing a pseudo cavity for the trapping of metal ion. The nitro

groups on the terminal phenyl ring were observed to be trans to each other. However, in the presence of Ni^{2+} ions, the trans nitro group flips to take cis position, where all the four nitrogens are involved in complexation with metal ion.

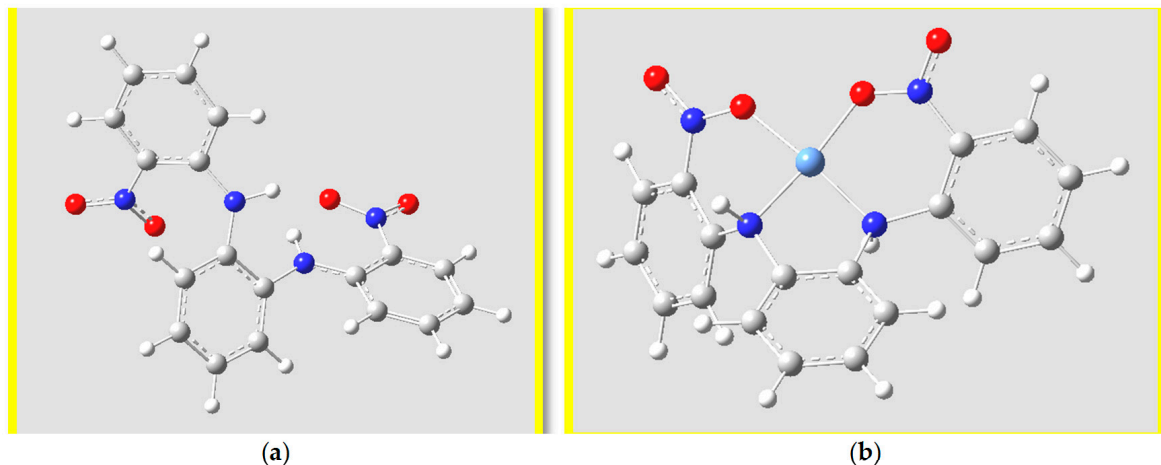


Figure 9. DFT optimized structures of TPA (a) and TPA- Ni^{2+} complex (b). White, red, dark blue, grey and light blue spheres refer to H, O, N, C, and Ni^{2+} , respectively.

3. Materials and Methods

3.1. Materials and Instrumentation

Reagents for the synthesis of DPA and TPA were purchased from LOBA Chemie (Mumbai, India) and Sd Fine (Mumbai, India) and used as such. All solvents were distilled before column chromatography. For TLC, precoated plates were used, and for column chromatography, silica gel (mesh 100–120) was used. Characterization of the synthesized ionophores was done using ^1H NMR and ^{13}C NMR spectra that were recorded on a Bruker AVANCE—400 MHz NMR spectrometer in CDCl_3 with SiMe_4 as the internal standard. Membranes were prepared using high molecular weight poly vinylchloride (PVC), o-nitrophenyloctylether (o-NPOE), and sodium tetraphenylborate, tetrahydrofuran (THF) that were purchased from Aldrich (India) and used as received. All metal salts used were of AR grade and used as nitrates by dissolving in double-distilled water. Solutions were prepared by serial dilutions and the potentials measured with an Equip-Tronics (EQ-602, accuracy, ± 0.1 mV) potentiometer (Mumbai, India).

3.2. Synthesis of Ionophores

Ionophores DPA and TPA were synthesized by “Modified Ullmann reaction” [51], which involves a copper mediated reaction between an aryl halide and an amine to get the corresponding arylamine. The two ionophores were then tested for binding with different metal ions by potentiometric and theoretical studies.

3.3. Potentiometric Studies

3.3.1. Preparation of Electrode

Membrane components, PVC, ionophore, ortho—nitrophenyloctylether, and sodium tetraphenylborate, as per Tables 1 and 2, were dissolved in 2–3 mL of tetrahydrofuran (THF) [52]. The homogeneous mixture obtained after complete dissolution was poured in a glass ring of diameter 20 mm, placed on dust free glass plate, and allowed to evaporate for 24 h at room temperature. To obtain membranes with similar characteristics, viscosity of the casting solution and the rate of solvent evaporation were controlled so that thickness and morphology of the membranes remain almost unchanged. Transparent membranes

so obtained were then removed from the glass ring and circular pieces of 1.25 cm diameter were cut and glued on the ground end of pyrex glass tube with araldite. Membranes were conditioned with 0.1 M metal salt solutions for 24 h.

3.3.2. EMF Measurement

The ratio of different membrane ingredients and the contact time were optimized to provide membranes, which resulted in reproducible and stable potentials. The activities of metal ions were calculated by using modified form of the Debye-Huckel equation [53]. All EMF measurements were carried out with the following assembly:

SCE || Internal Solution (0.1M M^{n+}) | PVC Membrane | Test solution M^{n+} || SCE

The concentrations of test solution were varied from 1×10^{-8} M to 1×10^{-1} M. The potential measurements were carried out at 25 ± 0.1 °C with a digital Equip-Tronics potentiometer.

3.4. Quantum Chemical Calculations

The quantum chemical study was carried out by density functional theory (DFT) method using Gauss View 4.1.2 software (Gaussian Inc., Wallingford, CT, USA). B3LYP method with 6–31 G basis set was employed for the optimization of ionophores, independently and along with metal ions.

4. Conclusions

Two ion-selective PVC membrane electrodes incorporating acyclic arylamines DPA and TPA as ionophores were used to determine Zn^{2+} and Ni^{2+} , respectively. The nernstian slope of 30 mV/decade of activity of respective ions was displayed by both the electrodes with detection limits of the order of 10^{-6} M. The electrodes responded very fast within 15 s and 20 s, respectively, for Zn(II) and Ni(II) ions. The electrodes can be used for 4 months over a wide pH range of 3–9. The potentiometric sensors were successfully used as indicator electrodes in potentiometric titration of Zn^{2+} and Ni^{2+} with EDTA.

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Author Contributions: Harpreet Kaur performed the experiments, analyzed the data, created the figures, and wrote the manuscript. Susheel K. Mittal and Manmohan Chhibber supervised the project.

Conflicts of Interest: The authors declare no conflict of interest.

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