ORIGINAL ARTICLE

Polymeric membrane and coated graphite electrode based on newly synthesized tetraazamacrocyclic ligand for trace level determination of nickel ion in fruit juices and wine samples

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Abstract Novel polymeric membrane electrode (PME) and coated graphite electrode (CGE) for nickel ion were prepared based on 2,9-(2-methoxyaniline)$_2$-4,11-Me$_2$-[14]-1,4,8,11-tetraene-1,5,8,12-N$_4$ as a suitable neutral ionophore. The addition of lipophilic anion excluder (NaTPB) and various plasticizers viz o-nitrophenyloctylether (o-NPOE), dioctylphthalate (DOP), dibutylphthalate (DBP), 1-chloronaphthalene (CN) and tri-n-butylphosphate (TBP) have found to improve the performance of the sensors. The best performance was obtained for the membrane sensor having a composition of **I**:NaTPB:TBP:PVC in the ratio 6:4:100:90 (w/w; mg). The electrodes exhibit Nernstian slopes for Ni^{2+} ions over wide concentration ranges of 4.6×10^{-7}–1.0×10^{-1} M for PME and 7.7×10^{-8}–1.0×10^{-1} M for CGE with limits of detection of 2.7×10^{-7} M for PME and 3.7×10^{-8} M for CGE. The response time for PME and CGE was found to be 10 and 8 s respectively. The potentiometric responses are independent of the pH of the test solution in the pH range 3.0–8.0. The proposed electrodes revealed good selectivities over a wide variety of other cations including alkali, alkaline earth, transition and heavy metal ions. The coated graphite electrode was used as an indicator electrode in the potentiometric titration of nickel ion with EDTA and in direct determination in different fruit juices and wine samples.

Keywords Tetraazamacrocycle · Nickel selective sensor · Coated graphite electrode · Ion selective electrodes · Chemical sensors

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Introduction

Ion selective electrodes (ISEs) for different cations have been widely used with polymeric membranes containing appropriate carriers (i.e. ionophore). These ionophores have been examined so that they could be incorporated to form complexes with metal ion within the membrane. The quest for the new ligands capable of specific and effective molecular recognition of metal ions in carrier assisted membranes or polymeric membranes based on ion selective electrodes (ISEs) is a topic of current interest [1–3]. Macrocycles are a favoured class of compounds in this area as their complexes have high stability constants, lipophilicity to remain in the membrane phase and sufficient conformational flexibility for rapid ion exchange [4]. Synthetic macrocycles are a growing class of compounds with varying chemistry, a wide range of different molecular topologies and sets of donor atoms [5–9]. The chemical properties of macrocyclic complexes can be tuned to force metal ions to adopt unusual coordination geometry. Currently a great deal of attention is being focussed on macrocyclic ligands because they play an important role in many aspects of chemistry, medicine and the chemical industry.

The need for selective determination of heavy metal ions has increased immensely during the last few decades due to the growing environmental problems. One of the heavy metal which is of considerable interest is nickel. Nickel is extensively used in a variety of commercially important industries, including stainless steel production, manufacture of coins, jewellery and nickel catalysts. The main source of nickel in aquatic systems is dissociation of rocks and soil, biological cycles and especially industrial processes and water disposal [10]. The maximum recommended concentration of nickel ions in drinking water for

livestock is 2.5 mg mL^{-1} [11]. Nickel is also present in food of both animal and plant origins such as red meat, cotton seed, corn meal, unsaturated oils, chocolates, baking powder and certain spices. Beverages like wine, beer, milk are also a rich source of nickel.

If nickel concentration exceeds the normal level, it may become a potential health hazard. Ni toxicity can cause acute pneumonitis, dermatitis, asthma, cancer of lungs, stomachaches, adverse effects on blood and kidneys, disorders of central nervous system and cancer of nasal cavity and lungs [12]. Though human requirement for nickel is very low which probably does not exceed 100 µg day^{-1} but deficiency of nickel can cause low blood glucose level, abnormal bone growth, poor absorption of ferric ion and altered metabolism of calcium, Vitamin B-12 and energy nutrients. Thus, due to vital importance of nickel in biological system and industry, a narrow window of concentration between essentiality and toxicity warrants the determination of nickel. A number of sophisticated techniques such as flow injection spectrophotometry, flame and graphite furnace, atomic absorption spectrophotometry, ICP-AES and flame photometry have been employed for trace level determination of nickel. However, these methods are disadvantageous as they require sample pre-treatment and infrastructure back up and are therefore not very convenient for routine analysis of large number of environmental samples. Therefore there is critical need for the development of selective, portable, inexpensive diagnostic tools for determination of Ni. Recently ion selective electrodes have been proved promising alternative which overcomes or minimizes the above drawbacks since they are fast, convenient, require no sample treatment, suitable for online analysis, easily handled and do not require large infrastructure backup. Extensive efforts have been made to develop a good sensitive sensor for nickel ion using different ionophores. A survey of literature reveals that the first nickel selective electrode was reported by Pungor and co-workers using a nickel–dimethylglyoxime complex [13]. Later heterogeneous membrane of nickel complex of 1,4,8,11-tetraazacyclotetradecane in araldite [14], nickel bis-(2-ethyl hexyl) phosphate in PVC [15] and nickel phosphate in paraffin and silicone rubber [16] were used for preparing electrodes. In recent years, Ni(II) selective electrode have been reported based on several neutral carriers viz porphyrins [17], 3,4:11,12-dibenzo-2,5,10, 13-tetraoxa-1,6,9,14-tetraazacyclohexadecane [18], dibenzo[e,k]2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclo decane-1,3,5,7,9,11-hexaene [19], tetraazaannulene [20], octaaza macrocycle [21], dibenzocyclamnickel(II) [22], N,N′-bis-(4-dimethyl-amino-benzylidene)-benzene-1,2-diamine [23], mercapto compound [24], porphines [25], benzylbis (thiosemi carbazone) [26], benzooxazole [27], Schiff chelates [28], tert-octylcalix[6]arene derivative [29] and crown ethers [30–32]. However, most of them possess either one, two or in some cases, all of the following problems such as poor selectivity, narrow working concentration range, non-Nernstian response, long response time and poor reproducibility [12–15, 17, 27, 31–35].

In order to achieve wider applicability, these limitations need to be removed. An important requirement for the preparation of a selective ion sensor is that the electroactive material, which is used in the membranes, should exhibit high lipophilicity and strong affinity for a particular metal ion to be determined and poor affinity for others. Sensors comprising macrocyclic ligands as electroactive ingredient have been reported to exhibit excellent selectivity for specific metal ions. Taking into account of the highly desirable attributes of such type of ligands, we have synthesised a macrocyclic ligand (2,9-(2-methoxyaniline)$_2$-4,11-Me$_2$-[14]-1,4,8,11-tetraene-1,5,8,12-N$_4$ (**I**) which can act as a very suitable neutral ionophore for the preparation of polymeric membrane (PME) and coated graphite electrodes (CGE) for highly selective and sensitive determination of nickel ion.

Experimental

Reagents

Reagent grade sodium tetraphenylborate (NaTPB), dibutylphthalate (DBP), tri-n-butylphosphate (TBP), dioctylphthalate (DOP), o-nitrophenyloctyl ether (o-NPOE), 1-chloronaphthalene (CN), tetrahydrofuran (THF) and high molecular weight poly (vinylchloride) were purchased from E. Merck (Germany) and used as received. Ethylenediamine and o-acetoacetanisidide were procured from Aldrich (USA). The chloride salts of all the cations used were of analytical grade and used without any further purification. The solutions of metal salts were prepared in doubly distilled water and standardized whenever necessary.

Synthesis of macrocycle

The macrocyclic ionophore 2,9-(2-methoxyaniline)$_2$-4, 11-Me$_2$-[14]-1,4,8,11-tetraene-1,5,8,12-N$_4$ (Fig. 1) was synthesized by dissolving equimolar amounts of ethylenediamine (0.01 M) and o-acetoacetanisidide (0.01 M). Ethylenediamine was dissolved in minimum quantity of methanol and to this solution o-acetoacetanisidide dissolved in methanol was added dropwise with stirring. The resulting mixture was refluxed for 8 h and then was concentrated to half of its original volume on a water bath, followed by cooling and keeping aside for 1 day. The shiny creamish coloured product thus obtained was filtered off,

Fig. 1 Synthesis of 2,9-(2-methoxyaniline)$_2$-4,11-Me$_2$-[14]-1,4,8,11-tetraene-1,5,8,12-N$_4$ ionophore (**I**) by reaction with *o*-acetoacetanisidide and ethylenediamine in MeOH
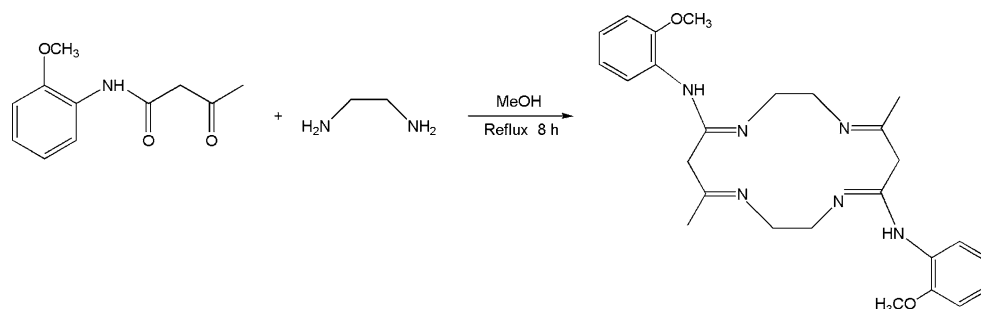
washed with cold methanol and recrystallized from ethanol/acetonitrile (1:1) and dried in vacuo. Yield: 86%, M.P.: 178 °C. Anal. calcd. for [$C_{26}H_{34}N_6O_2$] (%): C, 67.49; H, 7.35; N, 18.17; O, 6.92; observed (%): C, 67.51; H, 7.41; N, 18.17; O, 6.92. ^{1}H NMR (CDCl$_3$, 500 MHz) δ_{ppm}: 6.82–7.29 (m, H–Ar, 8H), 4.7 (bs, NH, 2H), 3.86 (s, –OCH$_3$, 6H), 3.36–3.40 (t, N–CH$_2$–C, 8H), 2.75 (s, –C–CH$_2$–C–, 4H), 1.93 (s, –CH$_3$, 6H). IR (KBr, cm^{-1}): 1,620 (C=N); 3,425 (–NH); 783, 648 (–CH$_2$).

Electrode preparation

The membranes were prepared as suggested by Craggs et al. [36]. It is known that the sensitivity, linearity and selectivity obtained for a given ionophore depends significantly on membrane composition and nature of plasticizer used [37]. The PVC-based membrane was prepared by dissolving appropriate amounts of macrocyclic ligand (i.e. ionophore), anion excluder (NaTPB), and plasticizers DBP, TBP, *o*-NPOE, DOP, CN and PVC in THF (3 mL). The homogeneous mixture was obtained after complete dissolution of all the components, concentrated by evaporating THF and was poured into polyacrylate rings placed on a smooth glass plate. The viscosity of the solution and solvent evaporation was carefully controlled to obtain membranes with reproducible characteristics and uniform morphology and thickness otherwise have shown a significant variation, which ultimately affected the sensor response. The membranes (2.4 cm diameter) were glued to one end of a "Pyrex" glass tube by careful removal from the glass plate. Thus, several membranes (1.8 cm diameter in cell) of varying composition were prepared and investigated and the membrane that gave reproducible results and best performance was selected for detailed studies.

To prepare the coated graphite electrodes, spectroscopic grade graphite rods 10 mm long and 3 mm in diameter were used. A shielded copper wire was glued to one end of the graphite rod, and the electrode was sealed into the end of a PVC tube of about the same diameter with epoxy resin. The working surface of the electrode was polished with fine alumina slurries on a polishing cloth, sonicated in

distilled water and dried in air. The polished graphite electrode was dipped into the membrane solution mentioned above, and the solvent was evaporated. A membrane was formed on the graphite surface, and the electrode was allowed to stabilize overnight.

Equilibration of membranes and potential measurements

The time of contact and concentration of equilibrating solution were optimized so that the sensors generated stable and reproducible potentials at relatively short response times. The polymeric membrane electrode and coated graphite electrode were equilibrated for 4 and 2 days respectively in a 1.0×10^{-1} M NiCl$_2$ solution. The potentials were measured by varying the concentration of NiCl$_2$ in test solution in the range 1.0×10^{-9}–1.0×10^{-1} M. Standard NiCl$_2$ solution were obtained by gradual dilution of 0.1 M NiCl$_2$ solution. The emf measurements with the polymeric membrane electrode and the coated graphite electrode were carried out on Orion 4 pH meter at 25 ± 0.1 °C using saturated calomel electrode (SCE) as reference electrode with the following cell assemblies:

Hg/Hg$_2$Cl$_2$ | KCl (satd.) | internal solution (0.1 M NiCl$_2$) ‖ PVC membrane ‖ sample solution | Hg–Hg$_2$Cl$_2$, KCl (satd.) (PME)

Graphite surface | PVC membrane | sample solution ‖ Hg/HgCl$_2$ | KCl (satd.) (CGE)

Activity coefficients were calculated according to the Debye-Huckel procedure, using following equation [38].

$$\log\gamma = -0.511z^2\left[\mu^{1/2}/\left(1 + 1.5\mu^{1/2}\right) - 0.2\mu\right] \qquad (1)$$

where μ is the ionic strength and z the valency.

Results and discussion

Optimization of membrane composition

It is well understood that the sensitivity, linearity and selectivity obtained for a given ionophore depends significantly on the membrane composition and nature of the

plasticizers used [39–43]. Thus, several membranes of varying plasticizer/PVC/carrier ratios were tested.

The optimum membrane ingredient showing the most sensitive, reproducible and stable results was obtained with a plasticizer/PVC ratios of ~ 1.1 together with 6 mg of ionophore. A study of the influence of the plasticizer on the potentiometric response characteristics were conducted by using TBP, DBP, o-NPOE, DOP and CN and the results are shown in Fig. 2. It can be seen from Table 1, that the membrane without any plasticizer (membrane no. 1) gave a narrow working concentration range of 4.8×10^{-5}–1.0×10^{-1} M with a slope of 38.4 mV decade^{-1} of activity. It has been shown that the presence of lipophillic ionic additives in the ion-selective membrane sensors is necessary to introduce perm selectivity [44]. Considerable improvements were observed, when ionic additives and different plasticizers were added to the membrane ingredients. The best performance was exhibited by membrane no. 2 containing TBP as solvent mediator with the composition **I**:NaTPB:TBP:PVC (6:4:100:90) (w/w; mg). This sensor displayed the widest working concentration range of

4.6×10^{-7}–1.0×10^{-1} M and a Nernstian slope of 29.5 ± 0.3 mV decade^{-1} of activity. The limit of detection, as determined from the intersection of two extrapolated segments of the calibration curve was 2.7×10^{-7} M. The other membranes having DBP, o-NPOE and CN (membrane nos. 3, 4 and 6) as plasticizers showed the improved working concentration ranges as well as slope values. The membrane containing DOP as plasticizer did not show much improved response characteristics. Thus, membrane no. 2, i.e. containing TBP as plasticizer was selected to prepare both the polymeric membrane electrode (PME) and the coated graphite electrode (CGE) for the Ni^{2+} ion. The critical response characteristics of the proposed electrodes were assessed according to IUPAC recommendation [45].

The EMF response of the polymeric membrane and coated graphite electrode (Fig. 3) indicates their Nernstian behaviour over a wide concentration range. The slopes, linear ranges and detection limit of the resulting EMF-pNi^{2+} graphs are given in Table 2. The improved performance characteristics of the CGE over those of the
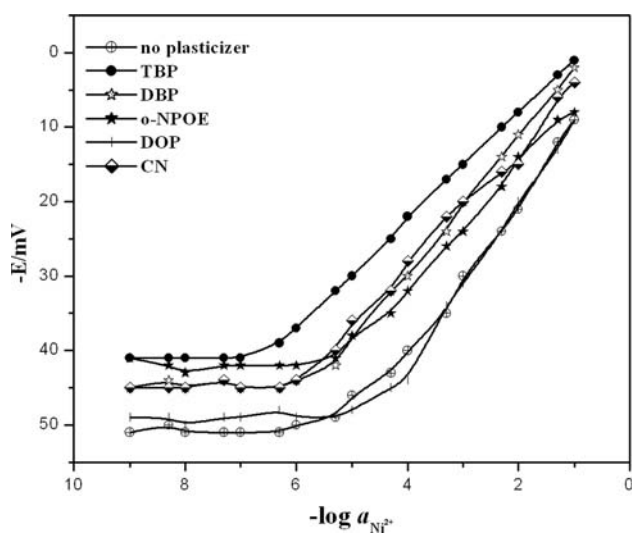

Fig. 2 Plots showing variation of membrane potential with the concentration of Ni^{2+} ions based on **I** with different plasticizers
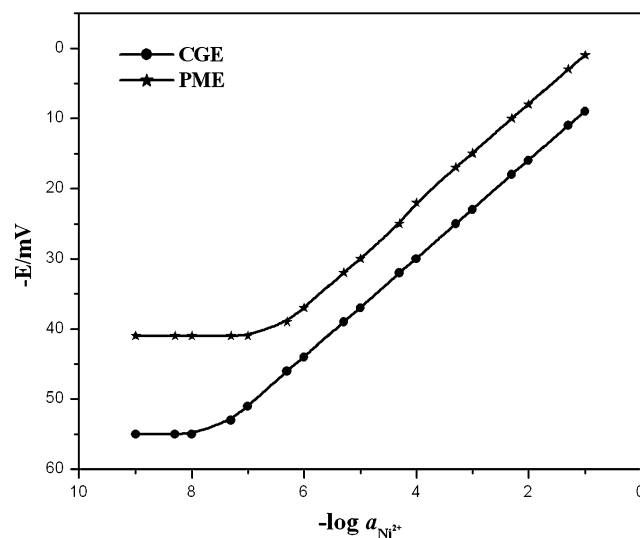

Fig. 3 Calibration characteristics of Ni^{2+} selective electrodes (PME and CGE) based on ionophore **I**

Table 1 Optimization of membrane compositions and their potentiometric response for Ni^{2+} ion selective membrane based on ionophore (**I**)

| S. no. | Composition of membrane (w/w; mg) | | | | | | | | Working concentration range (M) | Slope (mV decade^{-1} of activity) | Detection limit (M) |
	I	PVC	NaTBP	TBP	DBP	NPOE	DOP	CN			
1	6	190	4	–	–	–	–	–	1.0×10^{-1}–4.8×10^{-5}	38.4	3.1×10^{-6}
2	6	90	4	100	–	–	–	–	1.0×10^{-1}–4.6×10^{-7}	29.5	2.7×10^{-7}
3	6	90	4	–	100	–	–	–	1.0×10^{-1}–5.0×10^{-6}	37.2	2.1×10^{-6}
4	6	90	4	–	–	100	–	–	1.0×10^{-1}–4.4×10^{-6}	31.5	7.6×10^{-6}
5	6	90	4	–	–	–	100	–	1.0×10^{-1}–5.2×10^{-5}	44.3	2.3×10^{-5}
6	6	90	4	–	–	–	–	100	1.0×10^{-1}–5.4×10^{-6}	33.4	1.4×10^{-6}

Table 2 Response characteristics of the nickel ion-selective electrodes based on PME and CGE

Properties	Values/range	
	PME	CGE
Optimized membrane composition	(**I**) (6 mg):PVC (90 mg): TBP (100 mg):NaTPB (4 mg)	(**I**) (6 mg):PVC (90 mg):TBP (100 mg):NaTPB (4 mg)
Conditioning time	4 Days in 0.1 M NiCl$_2$	2 Days in 0.1 M NiCl$_2$
Working concentration range (M)	4.6×10^{-7}–1.0×10^{-1}	7.7×10^{-8}–1.0×10^{-1}
Detection limit (M)	2.7×10^{-7}	3.7×10^{-8}
Slope (mV decade^{-1} of activity)	29.5	29.5
S.D. of slope	±0.3	±0.2
Response time (s)	10	8
Life span	4 Months	5 Months
pH range	3.0–8.0	3.0–8.0

PME presumably originate from the coated graphite technology, where an internal 1.0×10^{-1} M NiCl$_2$ solution, in the case of PME, has been replaced by a copper wire of much higher electrical conductivity, in the case of CGE. A comparison of data given in Table 2 revealed that, while both electrodes show a nice Nernstian behaviour with fast response, the linear range and the limit of detection of the coated graphite electrode are significantly improved relative to those of polymeric membrane electrode. It is well known that the higher limit of detection of PME than that of CGE is mainly due to some leakage of the internal solution into the test solution via polymeric membrane [44].

Response and life time of proposed sensors

The response time i.e. the time required by the electrode assembly to generate stable and reproducible potentials was found to be 10 s for the polymeric membrane electrode and 8 s for the coated graphite electrode (Table 2) over the full range of concentrations. Potentials generated by the developed sensors remained stable for more than ∼5 min after which a very slow divergence were recorded. The much higher electrical conductivity of the copper wire (in CGE) than that of the internal solution (in PME) is expected to result in lower response time of the CGE in comparison with the PME.

The polymeric membrane electrode and coated graphite electrode could be used over a period of 4 and 5 months respectively at a stretch without observing any significant change in response time, slope and working concentration range. After this period there was a slight change in slope and response time and this could be corrected by re-equilibrating the membrane with 0.1 M Ni^{2+} solution for 3 days. With this treatment the assembly could be used for two more months and then it was replaced by a fresh membrane. During usage, they were stored in 0.1 M Ni^{2+} solution.

Effect of pH on sensor performance

The potentiometric response of the proposed sensor was found to be sensitive to pH changes. Thus, the pH dependence of the electrodes was tested by measuring the potential response of solution containing 1.0×10^{-3} and 1.0×10^{-4} M of the Ni^{2+} ion in the pH range 1.0–11.0. The pH was adjusted by using 0.1 M solution of either HCl or NaOH and the results are shown in Figs. 4 and 5 for PME and CGE respectively. It can be seen that potential response for both electrodes remains constant over the pH range 3.0–8.0 and the same can be taken as the working pH range of the electrodes. The significant change in potential response observed at pH below 3.0 can be reasonably related to the response of the sensor to the hydrogen ions. On the other hand, the observed potential drift at pH values could be due to the formation of some hydroxyl complexes of Ni^{2+} in solution. Therefore, the best performance for the
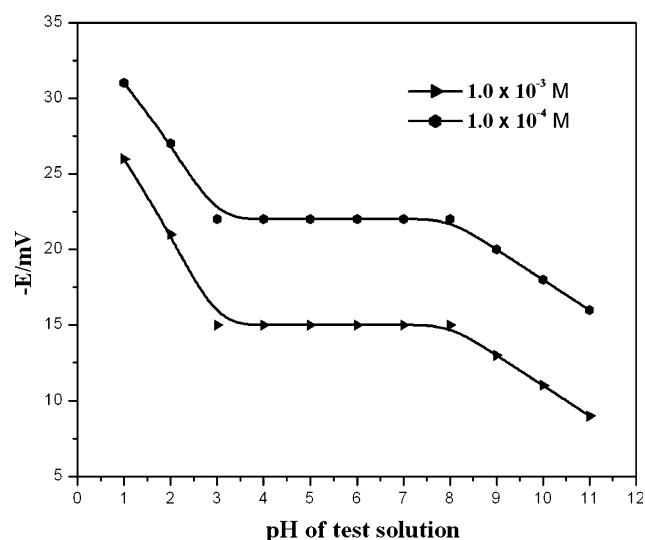
Fig. 4 Effect of pH of the test solutions on the potential responses of the PME
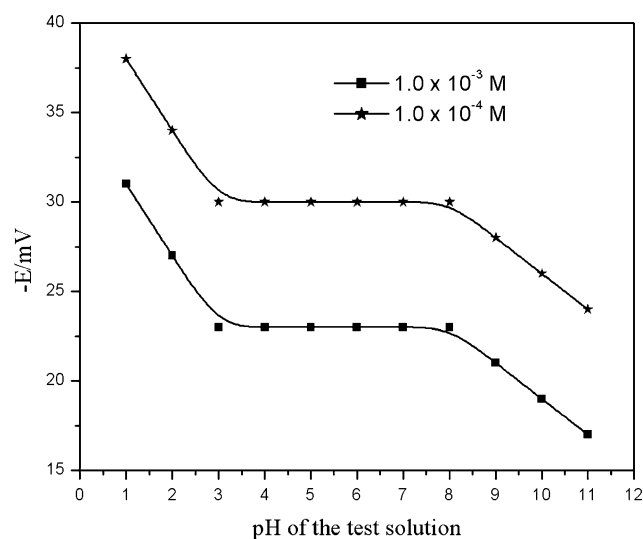
Fig. 5 Effect of pH of the test solutions on the potential responses of the CGE

proposed sensor should be achieved in the pH range 3.0–8.0.

Effect of interfering ions on sensor performance

Potentiometric selectivity coefficients, describing the preference of the ion-selective electrodes for an interfering ion, B, relative to Ni^{2+} ion, A, were determined by the matched potential method, which is recommended [46] to overcome the difficulties associated with the methods based on the Nicolsky-Eisenman equation [47]. According to this method, the specified activity (concentration) of the primary ion (A) is added to a reference solution and the potential is measured. In a separate experiment, the interfering ions (B) are successively added to an identical reference solution until the measured potential matched that obtained before by adding the primary ions. The matched potential method selectivity coefficient, $K_{A,B}^{MPM}$ is then given by the resulting primary ion to interfering ion activity ratio, $K_{A,B}^{MPM} = \Delta a_A / a_B$. The activity of Ni^{2+} as reference solution was taken as 1.0×10^{-2} M in this study. The resulting values for both nickel(II) ion-selective electrodes are listed in Table 3. From Table 3, it is immediately obvious that the proposed nickel(II) ion-selective electrodes are highly selective with respect to other common cations. The selectivity coefficients are in the order of 10^{-2} (for PME) and 10^{-3} (for CGE) or lower, which seems to indicate that these cations have negligible impact on the functionality of the Ni^{2+} ion selective sensor. Meanwhile, the data given in Table 3 revealed that, in all cases, the selectivity coefficients obtained for the coated graphite electrode are lower than those for the polymeric

Table 3 Selectivity coefficient of various interfering ions for Ni^{2+} selective electrodes based on ionophore **I**

Interfering cations	Selectivity coefficient ($K_{A,B}^{MPM}$)	
	PME	CGE
Co^{2+}	4.6×10^{-2}	6.2×10^{-3}
Cu^{2+}	6.2×10^{-2}	6.0×10^{-3}
Na^+	5.5×10^{-2}	5.2×10^{-3}
Cd^{2+}	4.5×10^{-2}	4.0×10^{-3}
K^+	3.5×10^{-3}	1.4×10^{-3}
Ba^{2+}	4.1×10^{-3}	2.1×10^{-3}
Ca^{2+}	4.7×10^{-3}	4.2×10^{-4}
Cr^{3+}	3.4×10^{-3}	3.8×10^{-4}
Zn^{2+}	2.8×10^{-3}	3.4×10^{-4}
Sr^{2+}	2.5×10^{-3}	3.0×10^{-4}
Mn^{2+}	2.3×10^{-3}	2.7×10^{-4}
Hg^{2+}	2.2×10^{-3}	2.6×10^{-4}
Fe^{3+}	1.8×10^{-3}	2.1×10^{-4}
Pb^{2+}	1.5×10^{-3}	1.6×10^{-4}
Al^{3+}	1.2×10^{-3}	1.1×10^{-4}
Bi^{3+}	2.8×10^{-4}	4.1×10^{-5}

membrane electrode, emphasizing the superiority of the CGE in this respect as well.

Effect of non-aqueous content

The real samples may contain non-aqueous content, so the performance of the sensor was also investigated in partially non-aqueous media using 10%, 20%, 25%, 30% and 35% (v/v) using non aqueous content in methanol–water, ethanol–water and acetonitrile–water mixtures (Table 4). It was found that the membranes do not show any appreciable change in working concentration range and slope in methanol–water and ethanol–water mixtures up to 25% (v/v) non-aqueous contents, whereas in acetonitrile–water mixture, membrane could tolerate up to 20% (v/v) non-aqueous content. However, above these mentioned non aqueous contents, the slope and working concentration range decreases appreciably, consequently reliable measurements could not be obtained. The drift in potentials in the organic phase may be probably due to swelling in membrane which was too high that membrane became mechanically weak and leaching of ionophore from membrane to non-aqueous solution took place.
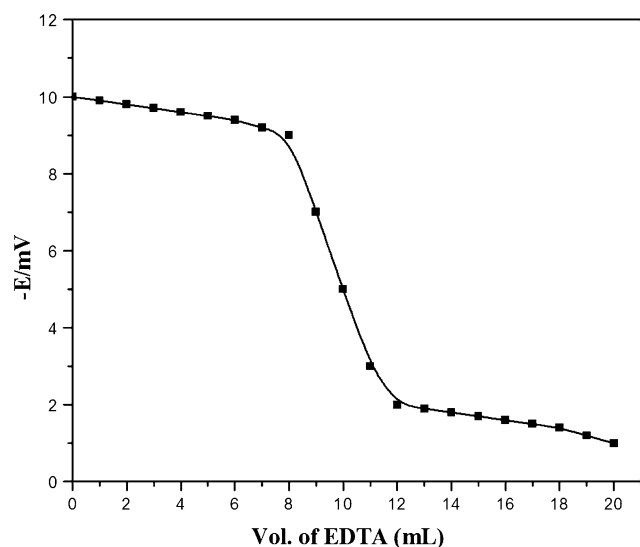
Analytical applications

The proposed coated graphite electrode was found to work well under laboratory conditions. The CGE was used as an indicator electrode in the successful titration of 20 mL of

Table 4 Effect of partially non-aqueous medium on the working of Ni^{2+} selective sensor (CGE) based on **I**

Non-aqueous content (%; v/v)	Working concentration range (M)	Slope (mV decade^{-1} of activity)
0	7.7×10^{-8}–1.0×10^{-1}	29.5
Methanol		
10	7.7×10^{-8}–1.0×10^{-1}	29.5
20	7.7×10^{-8}–1.0×10^{-1}	29.5
25	7.4×10^{-8}–1.0×10^{-1}	29.3
30	9.2×10^{-7}–1.0×10^{-1}	26.5
35	3.2×10^{-7}–1.0×10^{-1}	21.8
Ethanol		
10	7.7×10^{-8}–1.0×10^{-1}	29.5
20	7.7×10^{-8}–1.0×10^{-1}	29.5
25	7.1×10^{-8}–1.0×10^{-1}	29.4
30	8.7×10^{-7}–1.0×10^{-1}	25.8
35	4.1×10^{-7}–1.0×10^{-1}	19.2
Acetonitrile		
10	7.7×10^{-8}–1.0×10^{-1}	29.5
20	7.7×10^{-8}–1.0×10^{-1}	29.5
25	9.8×10^{-7}–1.0×10^{-1}	27.3
30	8.3×10^{-7}–1.0×10^{-1}	24.3
35	5.2×10^{-6}–1.0×10^{-1}	18.4

Table 5 Determination of nickel(II) in some fruit juice samples with the sensor (CGE) based on **I**

Type of juices	ISE[a] (mg L^{-1})	AAS[a] (mg L^{-1})	Confidence limit (%)
Grapes juice	0.019 ± 0.001	0.02 ± 0.002	95
Pineapple juice	0.27 ± 0.02	0.28 ± 0.03	98
Lime juice	0.39 ± 0.01	0.40 ± 0.02	95
Lemon juice	0.019 ± 0.001	0.02 ± 0.001	95

[a] Results are based on triplicate measurements

Ni^{2+} ion solution (5.0×10^{-3} M) with a EDTA (1.0×10^{-2} M) at pH 5.5. The resulting titration curve is shown in Fig. 6, indicating that the amount of Ni^{2+} ion can be accurately determined with the CGE.

The nickel selectivity exhibited by the CGE makes it potentially useful for monitoring the low level concentration

of Ni^{2+} ion in real samples. In this regard, experiments were performed to measure Ni^{2+} ion in fruit juices and wine samples. In the analysis of fruit juices, they were first centrifuged for 15 min to obtain pulp free liquid then were filtered and diluted in 1:20 ratio and analyzed by the proposed electrode. The results obtained have been shown in Table 5. The analysis of wine samples requires sample preparation. A 10 mL portion of sample (wine) was treated with 1 mL of 65% (v/v) HNO_3 and 2 mL of H_2O_2 in a pyrex glass tube placed in an aluminium block and heated at 100 °C overnight. Aliquots of H_2O_2 were added until the solution remained transparent and clear. The solutions were left to cool at room temperature and diluted with de-ionised Milli-Q-water. The resulting solution was then analyzed by the proposed sensor and results obtained are presented in Table 6. The results obtained were also compared with those from Atomic Absorption Spectroscopy analyzer. It is clear from values in Tables 5 and 6, that these were in good agreement with those obtained by AAS. Hence, the sensor can be successfully employed for the estimation of Ni^{2+} ion in real samples.

Conclusion

On the basis of the results discussed in this paper, the tetraazamacrocyclic ligand 2,9-(2-methoxyaniline)$_2$-4,11-Me$_2$-[14]-1,4,8,11-tetraene-1,5,8,12-N$_4$ can be regarded as a potential carrier for the construction of polymeric membrane electrode and coated graphite electrode to determine the low level concentration of nickel ion. The best performance was obtained for the membrane sensor having a composition of **I**:NaTPB:TBP:PVC in the ratio 6:4:100:90 (w/w; mg). The EMF response of the polymeric membrane and the coated graphite electrode indicates their Nernstian behaviour over a wide concentration range. Proposed nickel ion selective sensor shows maximum selectivity, widest working concentration range and minimum response time. Comparison of data (Table 2) revealed that coated graphite electrode is superior to the polymeric membrane electrode with regard to detection limit (3.7×10^{-8} M),

Fig. 6 Potentiometric titration curve of 20 mL of 5.0×10^{-3} M solution of Ni^{2+} ion with 1.0×10^{-2} M EDTA at pH 5.5 using CGE as indicator electrode

Table 6 Analytical data of nickel(II) concentration in wine samples as determined with CGE and AAS

Wine samples	Concentration of Ni^{2+} as determined by ISE[a] ($\mu g\,L^{-1}$)	Concentration of Ni^{2+} as determined by AAS[a] ($\mu g\,L^{-1}$)	Confidence limit (%)
Red wine	46.6 ± 0.1	46.3 ± 0.2	95
White wine	33.5 ± 0.2	33.2 ± 0.3	99
Rose wine	22.3 ± 0.1	22.1 ± 0.2	96
Champagne	17.9 ± 0.1	17.4 ± 0.3	95

[a] Results are based on triplicate measurements

response time (8 s) and selectivity. Thus, the coated graphite electrode was selected for the trace level determination of nickel ions in fruit juices and wine samples and can also be used as an indicator electrode in potentiometric titration.

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