Talanta 82 (2010) 44–50

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Comparative study on 2-amino-1,4-naphthoquinone derived ligands as indium (III) selective PVC-based sensors

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ARTICLE INFO

Article history:
Received 19 February 2010
Received in revised form 26 March 2010
Accepted 26 March 2010
Available online 1 April 2010

Keywords:
Indium (III)
PVC
Ion-selective electrode
2-Amino-1,4-naphthoquinone

ABSTRACT

The three different ligands (Q_2 to Q_4) based on 2-amino-1,4-naphthoquinone (Q_1), have been synthesized and explored as neutral ionophores for preparing polyvinyl chloride-based membrane sensors selective to indium (III). The addition of potassium tetrakis(4-chlorophenyl) borate and various plasticizers, viz., *o*-NPOE, DBP, DBBP, DOP and CN has been found to substantially improve the performance of the sensors. The best performance was obtained with the sensor no. 16 having membrane of ligand (Q_2) with composition (%, w/w) ionophore Q_2 (3.0%):PVC (30.0%):*o*-NPOE (63.0%):KTpClPB (4.0%). This sensor exhibits Nernstian response with slope 19.8 mV/decade of activity in the concentration range 2.5×10^{-7} to 1.0×10^{-2} M indium (III), performs satisfactorily over wide pH range of (2.5–7.5) with a fast response time (10 s). The sensor was also found to work satisfactorily in partially non-aqueous media up to 20% (v/v) content of acetonitrile, ethanol and methanol. The proposed sensor can be used over a period of 3.5 months without significant drift in potentials. The quantitative application of sensor was also evaluated by comparative analysis of artificially made sea water with AAS.

1. Introduction

Indium (III) is a very soft, silver-white, relatively rare true metal with bright luster. Indium has huge industrial applications; transparent electrodes from indium tin oxide in liquid crystal displays and touch screens, as a thin film to form lubricant layer and to form low melting point alloys. It also shows application in nuclear medicine for the treatment of tumors [1]. There is also some harmful effect with the listed above applications. The continuous treatment of hepatocytes with indium chloride at concentration of 100 μM to 1 mM for 2 h resulted in dose-dependent inhibition of gap junctional communication between hepatocytes and long term treatment causes the accumulation of indium in liver, spleen and bone marrow with excretion in the urine [2]. Considering these views its determination is very crucial for commercial and health purposes, therefore many analytical techniques have been applied for the analysis of indium in different samples; ICP-MS [3–5], AAS [6–12], HPLC [13–18], etc. All these sophisticated techniques are costly and required manpower as a technical expert even pre-sample treatment is also required before the analysis of samples.

A simplest analytical technique; ion-selective electrodes (ISEs) has been utilized first time in determination of indium (III) from different real samples. ISE is a low-cost portable device and can be used without pre-treatment of samples. This has led to increasing interest by our research group in the development and application of ion-selective membrane sensors using various organic ionophores and ion-pairs for the determination of metal [19–24], nonmetals [25–29], organic molecules [29–33] and some selective drugs [34–37]. In the present study the different quinone derivatives of 2-amino-1,4-naphthoquinone have been synthesized and explored in different PVC-based membrane sensors as ionophores for comparative analysis.

2. Experimental

2.1. Reagents and materials

High molecular weight polyvinyl chloride (PVC), 2-amino-1,4-naphthoquinone and isopropanaldehyde Aldrich (Wisconsin, USA), *o*-nitrophenyl octyl ether (*o*-NPOE), CH_2Cl_2, HCHO, dioctylphthalate (DOP) and triflouroacetic acid (CF_3COOH) Fluka (Ronkonkoma, NY), tri-*n*-butylphosphate (TBP) BDH (Poole, England), chloronapthalene (CN), dibutylphthalate (DBP), sodium tetraphenylborate (NaTPB) and dibutyl(butyl) phosphonate (DBBP) Mobile (Alabama, USA), potassium fluoroborate (KBF_4), potassium tetrakis (p-chloropheny1)borate

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doi:10.1016/j.talanta.2010.03.055

(KTpClPB) and oleic acid (OA) Sisco Research Lab. (Mumbai, India).

2.2. Synthesis of ligands

2.2.1. 1H-2,4-dihydronaphtho[2,3-d]1,3-oxazine-5,10-diones (Q_2)

To a solution of 2-amino-1,4-naphthoquinone (Q_1) (250 mg, 1.45 mmol) and 1 mL (excess) of the appropriate formaldehyde in 50 mL of chloroform, triflouroacetic acid (3 drops) was added. The reaction mixture was stirred at room temperature for few days (7 days). Then, the solvent was removed and the residue (Q_2) was recrystallized from CH_3OH.

Q_2: Color: Red needles. Yield: 210 mg, 66%. m.p.: 188–190 °C. IR (KBr): 3354(s), 1672(m), 1618(s) and 1504(s) cm^{-1}. ^1H NMR δ_H (acetone-d6): 4.62 (s, 2H), 4.90 (s, 2H), 7.30 (br, NH), 7.69 (dt, J_1 = 7.5 Hz, J_2 = 1.3 Hz, 1H), 7.78 (dt, J_1 = 7.5 Hz, J_2 = 1.3 Hz, 1H) and 8.97 (m, 2H). C-13 NMR δ: 63.01, 73.56, 112.54, 125.99, 126.06, 130.38, 132.18, 133.00, 134.61, 142.61, 179.93 and 180.07. m/z: 215 (M^+, 100%). Anal. Calcd. for $C_{12}H_9NO_3$: C, 66.97; H, 4.22; N, 6.51. Found: C, 66.71; H, 4.12; N, 6.36 on the basis of structure given in Fig. 1.

2.2.2. 1H-2,4-dihydro-2,4-diisopropylnaphtho[2,3-d]1,3-oxazine-5,10-diones (Q_3) and (Q_4)

To a solution of 2-amino-1,4-naphthoquinone (Q_1) (250 mg, 1.45 mmol) and 1 mL (excess) of the appropriate isopropanaldehyde in 50 mL of chloroform, triflouroacetic acid (3 drops) was added. The reaction mixture was stirred at room temperature for few days (5 days). Then, the solvent was removed and the residue (Q_3 and Q_4) was recrystallized from CH_3OH. The mixture of Q_3 and Q_4 was obtained as red crystals (230 mg, 54%), that was further chromatographed on silica gel using CH_2Cl_2 as eluant to isolate the two isomers (Q_3 and Q_4).

Q_3: Yield (170 mg, 39%), m.p.: 117–119 °C. IR (KBr): 3370(m), 2960(m), 1674(m), 1606(s), 1596(s), 1564(s), 1490(s) and 1364(m). ^1H NMR $\delta_H(CDCl_3)$: 0.75(d, J = 7 Hz, 3H), 1.06 (d, J = 7 Hz, 3H), 1.07 (d, J = 7 Hz, 3H), 1.17 (d, J = 7 Hz, 3H), 1.98 (septet of doublet, J_1 = 7 Hz, J_2 = 2.4 Hz, 1H), 2.79 (septet of doublet, J_1 = 7 Hz, J_2 = 2.4 Hz, 1H), 4.39 (dd, J_1 = 4.5 Hz, J_2 = 1.7 Hz, 1H), 4.78 (d, J = 2.4 Hz, 1H), 5.85 (br, NH), 7.59 (m, 1H), 7.70 (m, 1H), 8.00 (m, 1H), 8.06 (m, 1H). C-13 NMR δ: 14.75, 16.37, 17.19, 20.01, 30.18, 32.05, 77.41, 84.39, 115.91, 125.73, 126.23, 130.38, 131.93, 133.63, 134.59, 145.27, 180.16 and 180.27. Anal. Calcd. for $C_{18}H_{21}NO_3$: C, 72.22; H, 7.07; N, 4.68. Found: C, 72.12; H, 7.11; N, 4.54 on the basis of structure given in Fig. 1.

Q_4: Yield (60 mg, 14%). m.p.: 126–128. IR (KBr): 3350(m), 1672(m), 1600(s), 1570(s), 1502(s), and 1372(m). ^1H NMR $\delta_H(CDCl_3)$: 0.98 (d, J = 7 Hz, 3H), 1.05 (d, J = 7 Hz, 6H), 1.08 (d, J = 7 Hz, 3H), 1.97 (septet of doublet, J_1 = 7 Hz, J_2 = 1.8 Hz, 1H), 2.07 (septet of doublet, J_1 = 7 Hz, J_2 = 1.6 Hz, 1H), 4.65 (d, J = 8.6 Hz, 1H), 4.71 (dd, J_1 = 2.4 Hz, J_2 = 1.2 Hz, 1H), 6.02 (br, NH), 7.60 (m, 1H), 7.71 (m, 1H), 8.05 (m, 2H). C-13 NMR δ: 16.32, 17.30, 18.76, 18.96, 32.37, 32.55, 75.17, 80.71, 113.56, 125.81, 126.36, 130.34, 131.80, 133.56, 134.65, 141.93, 179.85 and 180.40. Anal. Calcd. for $C_{18}H_{21}NO_3$: C, 72.22; H, 7.07; N, 4.68. Found: C, 72.08; H, 7.02; N, 4.51 on the basis of structure given in Fig. 1.

2.3. Fabrication of membrane sensor

The membranes have been fabricated as suggested by Craggs et al. [38]. The PVC-based membranes have been prepared by dissolving appropriate amounts of ionophores (Q_1 to Q_4), different anionic additives NaTPB, OA, KTpClPB, KBF4 and plasticizers DBBP, DBP, *o*-NPOE, CN, DOP, THB and PVC in THF (5 mL). The components were added in terms of weight percentages. The homogeneous mixture was obtained after complete dissolution of all the components, concentrated by evaporating THF and it has been 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 thickness otherwise the response of the membrane sensors have shown a significant variation. The membranes of 0.4-mm thickness were removed carefully from the glass plate and glued to one end of a “Pyrex” glass tube. It is known that the sensitivity, linearity and selectivity obtained for a given ionophore depends significantly on the membrane composition and nature of plasticizer used [39]. Thus, the ratio of membrane ingredients, time of contact, concentration of equilibrating solution, etc. were optimized after a good deal of experimentation to provide membranes, which generate reproducible and stable potentials. The membranes having only PVC as membrane ingredient (dummy membranes) have also been prepared to observe whether any background potentials being produced due to binding material or not. The potentials were not generated without the electroactive material in the membrane. The activities of metal ions were calculated from the modified form of the Debye–Huckel equation.

2.4. Equilibration of membranes and potential measurements

The prepared membranes were equilibrated for two days in 0.01 M indium (III) solution. The potentials were measured by varying the concentration of In^{3+} in the test solution in the range 1.0×10^{-9} to 1.0×10^{-2} M using a buffer solution Tris–HCl (pH 4.0) having a equimolar concentration of sodium citrate with a digital potentiometer (model 5652 A, ECIL, India) by setting up the following cell assembly, employing saturated calomel electrodes (SCE) as a reference electrode.

SCE | test solution ‖ PVC membrane ‖ 0.01 M sodium citrate + 0.01 M $InCl_3$ | SCE.

3. Results and discussion

3.1. Determination of formation constant

Formation constant of the ion–ionophore complex within the membrane phase is a very important parameter that dictates the practical selectivity of the sensor. In this method, two membrane segments are fused together, with only one containing the ionophore, to give a concentration-polarized sandwich membrane. A membrane potential measurement of this transient condition reveals the ion activity ratio at both interfaces, which translates into the apparent binding constants of the ion–ionophore complex [40]. In this method complex formation constants obtained by neglecting ion pairing. As reported, the membrane potential E_M is determined by subtracting the cell potential for a membrane without ionophore from that for the sandwich membrane. The formation constant is then calculated from the following equation:

$$\beta_{IL_n} = \left(L_T - \frac{nR_T}{z_I}\right)^{-n} \exp\left(\frac{E_M z_I F}{RT}\right) \qquad (1)$$

where L_T is the total concentration of ionophore in the membrane segment, R_T is the concentration of lipophilic ionic site additives, n is the ion–ionophore complex stoichiometry, and R, T and F are the gas constant, the absolute temperature, and the Faraday constant. The ion I carries a charge of z_I. The determined formation constants ($\log \beta_{IL_n}$) for the examined different complexes were recorded in Table 1. The elapsed time between sandwich fusion and exposure to electrolyte was typically <1 min. The potential was recorded as the mean of the last minute of a 5-min measurement period in the appropriate salt solution. The potential of such sandwich membranes remains free of diffusion-induced potential drifts

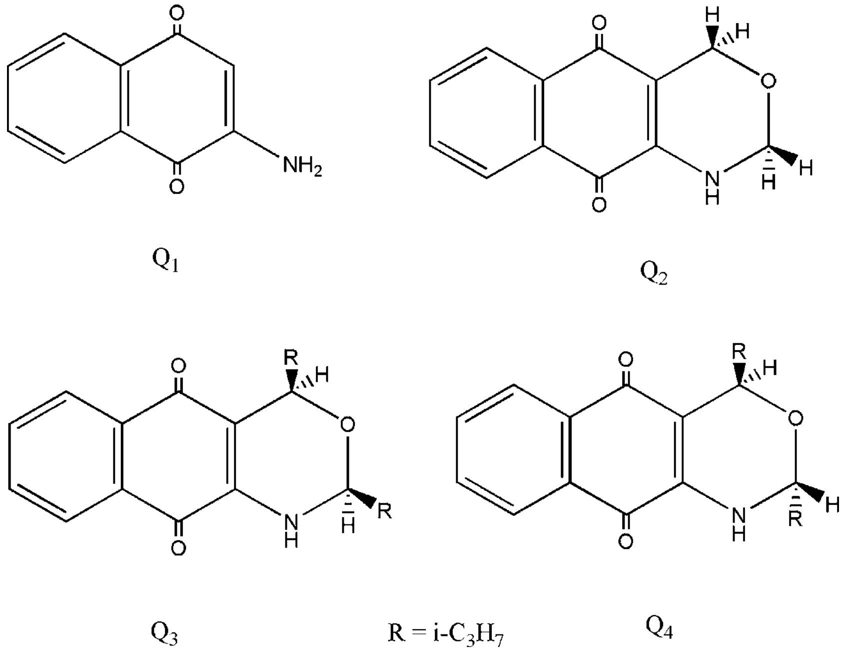

Fig. 1. The structures of 2-amino-1,4-naphthoquinone (Q_1) and its derived ligands Q_2 to Q_4.

for about 20 min. Standard deviations were obtained based on the measurements of sets of at least three replicate membrane disks that were made from the same parent membrane. A careful analysis of the data in Table 1, reveals that indium ion has significant cation-binding characteristics.

3.2. *Effect of internal solution*

The influence of the concentration of internal solution on the potential response of the polymeric membrane sensors for In^{3+} ion based on Q_1 to Q_4 ionophores were studied. The concentration was varied from 1.0×10^{-1} to 1.0×10^{-4} M and the potential response of the sensors has been observed. It was found that the best results in terms of slope and working concentration range has been obtained with internal solution of activity 1.0×10^{-2} M. Thus, 1.0×10^{-2} concentration of the reference solution was quite appropriate for the smooth functioning of the proposed sensors.

3.3. *Optimization of membrane composition*

In order to get the best responsive results from membrane sensors, the different membranes (Tables 2–5) with different composition have been prepared and their response characteristics were evaluated according to the IUPAC recommendations [41] as it is often known that selectivity is highly dependent on the incorporation of additional membrane components [42].

3.3.1. *Effect of addition of plasticizer*

Once the membrane sensors based on different ligands (Q_1, Q_2, Q_3 and Q_4) have been prepared and their responses checked against different concentration of In^{3+}, the effect of plasticizers was studied to get the best results. The membrane compositions have been optimized using different concentration of plasticizers having a different dielectric constants (ε); TEHP ($\varepsilon = 4.8$), DBBP ($\varepsilon = 4.6$), DBP ($\varepsilon = 6.4$), *o*-NPOE ($\varepsilon = 24$), CN ($\varepsilon = 5$), DOP ($\varepsilon = 5$) and PVC ($\varepsilon = 3.9$). It

Table 1
The formation constants of different ligands and metals.

Cations	Q_1 Formation constant (log β_{IL_n}) ± SD[a]	Q_2 Formation constant (log β_{IL_n}) ± SD[a]	Q_3 Formation constant(log β_{IL_n}) ± SD[a]	Q_4 Formation constant(log β_{IL_n}) ± SD[a]
Na^+	0.51 ± 0.05	0.81 ± 0.06	0.61 ± 0.03	0.71 ± 0.05
K^+	0.54 ± 0.03	0.82 ± 0.05	0.65 ± 0.04	0.79 ± 0.05
Ag^+	1.20 ± 0.08	2.45 ± 0.06	1.92 ± 0.03	2.15 ± 0.08
Cu^{2+}	2.21 ± 0.19	3.14 ± 0.21	2.41 ± 0.22	2.65 ± 0.12
Pb^{2+}	2.58 ± 0.15	3.82 ± 0.06	3.54 ± 0.11	3.74 ± 0.03
Cd^{2+}	2.55 ± 0.13	3.72 ± 0.11	3.51 ± 0.08	3.65 ± 0.14
Zn^{2+}	2.10 ± 0.16	2.28 ± 0.20	1.81 ± 0.22	2.12 ± 0.12
Co^{2+}	2.11 ± 0.12	3.47 ± 0.21	3.00 ± 0.11	3.44 ± 0.09
Cr^{3+}	3.40 ± 0.21	4.12 ± 0.09	3.71 ± 0.14	3.76 ± 0.15
Ce^{3+}	3.21 ± 0.25	4.15 ± 0.16	3.27 ± 0.09	3.38 ± 0.12
In^{3+}	5.21 ± 0.19	8.11 ± 0.17	6.77 ± 0.06	7.17 ± 0.13
Ga^{3+}	4.56 ± 0.25	5.56 ± 0.14	4.57 ± 0.12	4.67 ± 0.18
Al^{3+}	4.21 ± 0.25	4.81 ± 0.17	3.82 ± 0.11	4.17 ± 0.15
Tl^{3+}	4.36 ± 0.25	4.87 ± 0.14	3.88 ± 0.14	4.24 ± 0.16

[a] Mean value ± standard deviation (three measurements).

Table 2
The optimization of membrane compositions (%, w/w).

Sensor no.	Composition of membrane sensors (%, w/w)				Working range (M)	Slope[a] ± 0.5	Response time (s)
	Ionophore	PVC	Additives	Plasticizer			
1	0.0 (Q_1)	30.0	4.0 (KTpClPB)	66.0	–	–	20
2	13.0 (Q_1)	73.0	14.0 (KTpClPB)	0.0	4.5×10^{-3} to 1.0×10^{-2}	16.0	25
3	3.0 (Q_1)	30.0	4.0 (KTpClPB)	63.0 (DBP)	7.5×10^{-4} to 1.0×10^{-2}	17.6	18
4	3.0 (Q_1)	30.0	4.0 (KTpClPB)	63.0 (DBBP)	5.4×10^{-4} to 1.0×10^{-2}	16.8	21
5	3.0 (Q_1)	30.0	4.0 (KTpClPB)	63.0 (TEHP)	2.8×10^{-4} to 1.0×10^{-2}	17.0	19
6	3.0 (Q_1)	30.0	4.0 (KTpClPB)	63.0 (CN)	5.4×10^{-5} to 1.0×10^{-2}	18.0	17
7	3.0 (Q_1)	30.0	4.0 (KTpClPB)	63.0 (DOP)	8.4×10^{-5} to 1.0×10^{-2}	17.8	15
8	**3.0 (Q_1)**	**30.0**	**4.0 (KTpClPB)**	**63.0 (*o*-NPOE)**	**2.4×10^{-5} to 1.0×10^{-2}**	**19.5**	**11**
9	0.0 (Q_2)	30.0	4.0 (KTpClPB)	66.0	–	–	24
10	13.0 (Q_2)	73.0	14.0 (KTpClPB)	0.0	7.5×10^{-4} to 1.0×10^{-2}	17.8	13
11	3.0 (Q_2)	30.0	4.0 (KTpClPB)	63.0 (DBP)	4.3×10^{-4} to 1.0×10^{-2}	18.9	17
12	3.0 (Q_2)	30.0	4.0 (KTpClPB)	63.0 (DBBP)	6.5×10^{-5} to 1.0×10^{-2}	18.5	14
13	3.0 (Q_2)	30.0	4.0 (KTpClPB)	63.0 (TEHP)	4.5×10^{-5} to 1.0×10^{-2}	18.7	12
14	3.0 (Q_2)	30.0	4.0 (KTpClPB)	63.0 (CN)	7.4×10^{-6} to 1.0×10^{-2}	18.8	11
15	3.0 (Q_2)	30.0	4.0 (KTpClPB)	63.0 (DOP)	3.6×10^{-6} to 1.0×10^{-2}	19.2	11
16	**3.0 (Q_2)**	**30.0**	**4.0 (KTpClPB)**	**63.0 (*o*-NPOE)**	**2.5×10^{-7} to 1.0×10^{-2}**	**19.8**	**10**
17	0.0 (Q_3)	30.0	4.0 (KTpClPB)	66.0	–	–	24
18	13.0 (Q_3)	73.0	14.0 (KTpClPB)	0.0	9.2×10^{-4} to 1.0×10^{-2}	16.5	14
19	3.0 (Q_3)	30.0	4.0 (KTpClPB)	63.0 (DBP)	6.3×10^{-4} to 1.0×10^{-2}	17.4	17
20	3.0 (Q_3)	30.0	4.0 (KTpClPB)	63.0 (DBBP)	8.2×10^{-5} to 1.0×10^{-2}	18.5	18
21	3.0 (Q_3)	30.0	4.0 (KTpClPB)	63.0 (TEHP)	6.2×10^{-5} to 1.0×10^{-2}	18.6	14
22	3.0 (Q_3)	30.0	4.0 (KTpClPB)	63.0 (CN)	9.1×10^{-6} to 1.0×10^{-2}	17.5	15
23	3.0 (Q_3)	30.0	4.0 (KTpClPB)	63.0 (DOP)	5.4×10^{-6} to 1.0×10^{-2}	18.4	12
24	**3.0 (Q_3)**	**30.0**	**4.0 (KTpClPB)**	**63.0 (*o*-NPOE)**	**5.5×10^{-7} to 1.0×10^{-2}**	**19.5**	**12**
25	0.0 (Q_4)	30.0	4.0 (KTpClPB)	66.0	–	–	22
26	13.0 (Q_4)	73.0	14.0 (KTpClPB)	0.0	8.5×10^{-4} to 1.0×10^{-2}	16.4	13
27	3.0 (Q_4)	30.0	4.0 (KTpClPB)	63.0 (DBP)	5.4×10^{-4} to 1.0×10^{-2}	17.4	15
28	3.0 (Q_4)	30.0	4.0 (KTpClPB)	63.0 (DBBP)	7.4×10^{-5} to 1.0×10^{-2}	18.3	14
29	3.0 (Q_4)	30.0	4.0 (KTpClPB)	63.0 (TEHP)	5.5×10^{-5} to 1.0×10^{-2}	18.5	13
30	3.0 (Q_4)	30.0	4.0 (KTpClPB)	63.0 (CN)	8.2×10^{-6} to 1.0×10^{-2}	18.8	13
31	3.0 (Q_4)	30.0	4.0 (KTpClPB)	63.0 (DOP)	4.3×10^{-6} to 1.0×10^{-2}	19.5	11
32	**3.0 (Q_4)**	**30.0**	**4.0 (KTpClPB)**	**63.0 (*o*-NPOE)**	**3.3×10^{-7} to 1.0×10^{-2}**	**19.7**	**11**

[a] mV/decade of activity.

Table 3
The effect of anionic additives on the performances of In^{3+} selective sensors.

Membrane sensor composition	Anionic additives	Working concentration range (M)	Detection limit ± 0.5 (M)	Slope[a] ± 0.5
Q_1:PVC:*o*-NPOE (%, w/w) 3.0: 30.0:63.0	–	4.5×10^{-4} to 1.0×10^{-2}	3.8×10^{-4}	17.0
	KTpClPB	2.4×10^{-5} to 1.0×10^{-2}	1.2×10^{-5}	19.5
	NaTPB	3.5×10^{-5} to 1.0×10^{-2}	2.5×10^{-5}	19.5
	KBF_4	3.8×10^{-5} to 1.0×10^{-2}	2.3×10^{-5}	18.8
	OA	5.5×10^{-5} to 1.0×10^{-2}	4.4×10^{-5}	18.9
Q_2:PVC:*o*-NPOE (%, w/w) 3.0:30.0:63.0	–	4.3×10^{-4} to 1.0×10^{-2}	3.5×10^{-4}	17.5
	KTpClPB	2.5×10^{-7} to 1.0×10^{-2}	1.2×10^{-7}	19.8
	NaTPB	2.8×10^{-7} to 1.0×10^{-2}	1.5×10^{-7}	19.8
	KBF_4	3.2×10^{-6} to 1.0×10^{-2}	2.4×10^{-6}	19.4
	OA	5.6×10^{-6} to 1.0×10^{-1}	4.1×10^{-6}	18.9
Q_3:PVC:*o*-NPOE (%, w/w) 3.0:30.0:63.0	–	5.6×10^{-4} to 1.0×10^{-2}	4.2×10^{-4}	17.0
	KTpClPB	5.5×10^{-7} to 1.0×10^{-2}	4.4×10^{-7}	19.5
	NaTPB	6.5×10^{-7} to 1.0×10^{-2}	5.2×10^{-7}	19.2
	KBF_4	4.5×10^{-6} to 1.0×10^{-2}	3.3×10^{-6}	18.9
	OA	7.7×10^{-6} to 1.0×10^{-2}	6.2×10^{-6}	18.6
Q_4:PVC:*o*-NPOE (%, w/w) 3.0:30.0:63.0	–	5.6×10^{-4} to 1.0×10^{-2}	4.2×10^{-4}	17.7
	KTpClPB	3.3×10^{-7} to 1.0×10^{-2}	2.1×10^{-7}	19.7
	NaTPB	3.7×10^{-7} to 1.0×10^{-2}	2.3×10^{-7}	19.5
	KBF_4	4.0×10^{-6} to 1.0×10^{-2}	3.6×10^{-6}	19.3
	OA	6.3×10^{-6} to 1.0×10^{-2}	5.9×10^{-6}	18.7

[a] mV/decade of activity.

Table 4
The comparative evaluation of best In^{3+} selective membrane sensors.

Sensor no.	Working range (M)	Detection limit (M) ± 0.5	Slope[a] ± 0.5	Response time (s)
8	2.4×10^{-5} to 1.0×10^{-2}	1.2×10^{-5}	19.5	11
16	2.5×10^{-7} to 1.0×10^{-2}	1.2×10^{-7}	19.8	10
24	5.5×10^{-7} to 1.0×10^{-2}	4.4×10^{-7}	19.5	12
32	3.3×10^{-7} to 1.0×10^{-2}	2.3×10^{-7}	19.7	12

[a] mV/decade of activity.

Table 5
Selectivity coefficient ($\log K^{\mathrm{Pot}}_{\mathrm{In}^{3+},\mathrm{B}}$) values observed for best In(III) selective sensors as calculated by fixed interference method.

Interfering ion (B)	Selectivity coefficient (no. 16) FIM[a]	Selectivity coefficient (no. 32) FIM[a]
Na^+	−3.79	−4.62
K^+	−3.14	−4.43
Cu^{2+}	−2.67	−2.43
Pb^{2+}	−2.47	−2.39
Cd^{2+}	−2.01	−1.82
Zn^{2+}	−2.95	−2.37
Co^{2+}	−2.10	−1.96
Cr^{3+}	−1.78	−1.48
Ce^{3+}	−1.88	−1.67
Al^{3+}	−1.77	−1.55
Ga^{3+}	−1.67	−1.59
Tl^{3+}	−1.73	−1.61

[a] Fixed interference method.

is well known that the sensitivity and selectivity of cation-selective membrane sensors strongly depend on the membrane composition and the nature of the plasticizer used [43,44]. The effect of plasticizer on In^{3+} membrane sensors based on different ligands is shown in Table 2. It is clear from the table that *o*-NPOE is more effective plasticizer than others in preparing the In^{3+} ISEs because of its high dielectric ($\varepsilon = 24$) constant that increases the indium (III) selectivity for proposed ionophores. The plasticizers except *o*-NPOE has less dielectric constant therefore they will solvate the extracted cations in ionophore-free membranes or membrane segments more strongly than *o*-NPOE-based membranes, which lead to smaller binding constants. It is noteworthy that the lipophilicity of plasticizer influences both dielectric constant of the polymeric membranes and the mobility of the ionophore and its metal complex [45,46].

3.3.2. *Effect of addition of anionic additives*

To determine the effect of different lipophilic anionic additives added to the membrane phase influencing the working sensitivity of the sensor, a series of membranes was studied by using lipophilic additives like NaTPB, KTpClPB, OA and KBF_4 (Table 3). Incorporating KTpClPB in the membrane composition in the proportion of 4.0% (w/w) relative to the total membrane composition showed best performance characteristics. This is due to fact that KTpClPB acts as a charge compensating counter ion in the membrane and thus facilitate the process of ion charge transduction.

3.4. *Response of the membrane sensors based on different ligands (Q_1 to Q_4)*

The response studies of membrane sensors based on different ligands (Q_1 to Q_4) have been studied and it was found that the selectivity and sensitivity of membrane sensors were in order of $Q_2 > Q_4 > Q_3 > Q_1$ respective ligands. The low sensitivity of Q_1-based sensor can be understood by having only two oxygen donating sites in comparison to others. Whereas Q_2 based is found to highly selective because of three oxygen donating sites with least steric effect in comparison to other all. The membrane sensor based on Q_4 is more selective in comparison to Q_3-based membrane sensor because of least steric effect of alkyl groups attached in trans manners in Q_4. The best responsive characteristics of different ligand (Q_1 to Q_4)-based membranes are shown in Fig. 2 and Table 4.

3.5. *Potentiometric selectivity of In^{3+} selective membrane sensors against different cationic species*

The selectivity coefficient values of the best responsive membrane sensors (16 and 32) for different cationic species (M^{n+}) was evaluated by using fixed interference method (FIM) [47]. In the FIM, the selectivity coefficient was evaluated from potential measurement on solutions containing a fixed concentration of interfering ion (1.0×10^{-2} M) and varying amount of In^{3+} ions. The selectivity coefficient is calculated from the following equation:

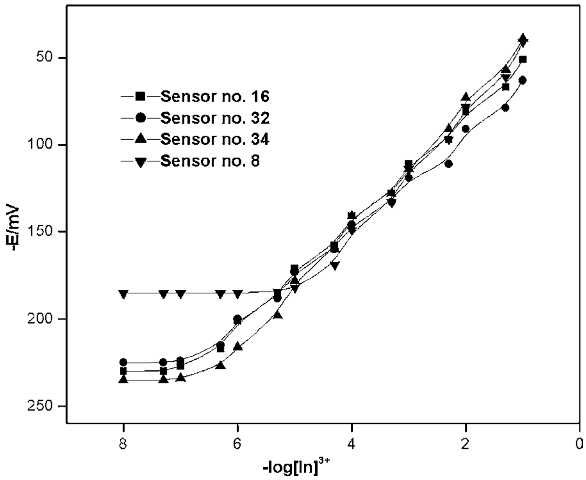

Fig. 2. The comparative evaluation of Q_1 to Q_4-based fabricated best responsive membrane sensors.

$$\log K^{\mathrm{Pot}}_{\mathrm{In}^{3+},\mathrm{B}} = \frac{a\mathrm{In}^{3+}}{(aB)^{zA/zB}} \qquad (2)$$

where $a\mathrm{In}^{3+}$ is the activity of the primary ion (In^{3+}) at the lower detection limit in the presence of interfering ion B with activity of aB, having zA and zB their respective charges. The values of selectivity coefficient so determined for best responsive membrane sensor (16 and 32) are compiled in Table 5. It is clear from the corresponding table that the selectivity of sensor no. 16 towards In^{3+} is higher over most of the cations. As sensor no. 16 is better than the other membrane sensors in terms of wider working concentration range, lower detection limit, high selectivity and Nernstian compliance, further studies were carried out with it only.

3.6. *pH and non-aqueous effect*

Due to the interference of H^+ at lower pH range (1–3) and OH^- at higher pH range (higher to pH 8) in the aqueous solution. It is necessary to find the optimum pH range where the sensors functions without interference from the hydrogen or hydroxyl ions. The pH dependence of the sensor (16) has been tested over the pH range 1.0–12.0 at two fixed concentrations (1.0×10^{-2} and 1.0×10^{-3}) of In^{3+} with the equimolar concentration of sodium citrate. The pH was adjusted with dilute nitric acid or sodium hydroxide solutions. The potential of the sensor was determined as a function of pH and the results are demonstrated in Fig. 3. The potential remained constant over the pH range of 2.5–7.5, which may be taken as the working pH range of the sensor assembly. It is expected that $In(OH)_3$ will precipitate at pH 3.64 for 0.01 M In. Contrary to this the observed results show otherwise which may be due to the fact that indium (III) has been taken with the equimolar concentration of sodium citrate as reported earlier by other workers also [48,49]. However still it may be better to work on pH of more than 4.5 to avoid any chance of hydrolysis. The performance of the sensor no. 16 was further assessed in partial non-aqueous media, i.e. methanol–water, ethanol–water and acetonitrile–water mixture. The results obtained are compiled in Table 6 and show that up to 20% non-aqueous content no significant change occurs in the slope and working concentration of the sensor. However, above 20% non-aqueous content, the working concentration of the sensor

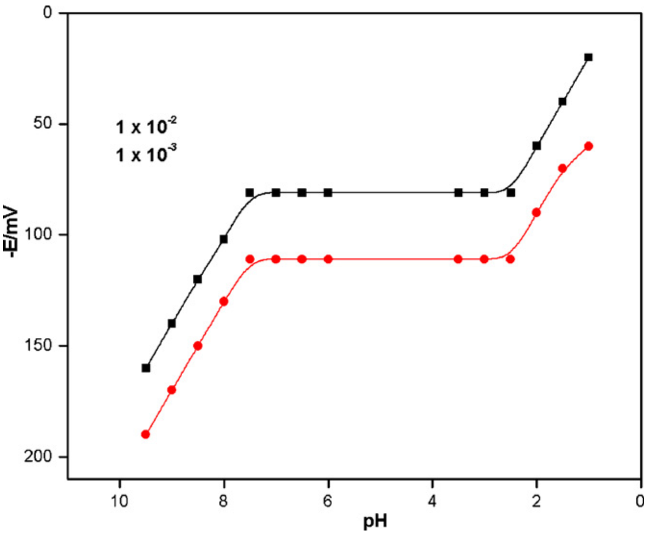

Fig. 3. The pH response study of Q_2-based best selective and responsive membrane sensor (sensor no. 16).

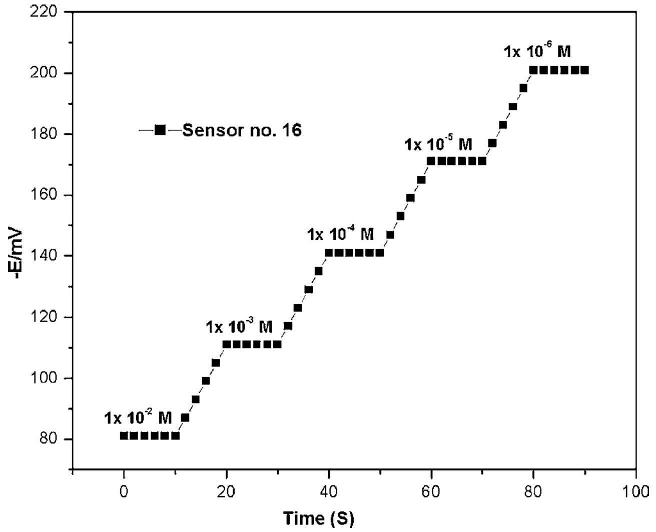

Fig. 4. The dynamic response of sensor no. 16.

Table 7
The comparative study of membrane sensor no. 16 with AAS in determination of In^{3+} in artificially made sea water.

Sample no.	Sensor no. 16[a]	AAS[a]	t-Test ($P = 0.05$; $t_{\text{theoritical}} = 2.20$)
1 (15 mg/mL)	14.8 ± 1.2	14.6 ± 0.4	$t_{\text{experimental}} = 2.11$
2 (20 mg/mL)	19.7 ± 1.1	19.5 ± 0.3	$t_{\text{experimental}} = 2.09$
3 (25 mg/mL)	24.9 ± 1.3	24.7 ± 0.5	$t_{\text{experimental}} = 2.11$
4 (30 mg/mL)	29.8 ± 1.2	29.6 ± 0.4	$t_{\text{experimental}} = 2.10$
5 (35 mg/mL)	34.9 ± 1.2	34.4 ± 0.4	$t_{\text{experimental}} = 2.11$

[a] Triplicate measurement.

is significantly reduced, and thus the sensor can only be utilized in mixtures containing up to 20% non-aqueous content.

3.7. *Dynamic response and life time*

It is well known that the dynamic response and life time of a sensor are 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 1.0×10^{-6} to 1.0×10^{-2} M. The resulting data depicted in Fig. 4, shows that the time needed to reach a potential with in ±1 mV of the final equilibrium value after successive immersion of a series of In^{3+} ions, each having a tenfold difference in concentration is 10 for sensor no. 16. This is most probably due to the fast exchange kinetics of complexation–decomplexation of indium (III) ions with the Q_2 ionophore at the test solution–membrane interface.

The degradation of the sensitivity in the polymeric membrane may be dependent upon the lipophilicity and chemical stability of the ionophores, which can result in the ionophore bleeding from the membrane. Since indium (III) chelates of ionophores are the compounds having high lipophilicity, the membranes containing them should provide very low bleeding of the ionophore. The membrane could be used over a period of 3.5 months without significant drift in potentials. However, it is important to emphasize that it should be stored in 0.01 M In^{3+} solution when not in use.

Table 6
The performance of best In^{3+} selective sensor (no. 16) in non-aqueous content.

Non-aqueous content (%, v/v)	Working concentration range (M)	Slope (±0.5 mV/ decade of activity)
0	2.5×10^{-7} to 1.0×10^{-2}	19.8
Methanol		
10	2.5×10^{-7} to 1.0×10^{-2}	19.8
20	2.6×10^{-7} to 1.0×10^{-2}	19.8
25	6.8×10^{-7} to 1.0×10^{-2}	19.6
30	2.6×10^{-6} to 1.0×10^{-2}	19.4
35	4.4×10^{-6} to 1.0×10^{-2}	19.4
Ethanol		
10	2.5×10^{-7} to 1.0×10^{-2}	19.8
20	2.5×10^{-7} to 1.0×10^{-2}	19.8
25	7.5×10^{-7} to 1.0×10^{-2}	19.7
30	3.2×10^{-6} to 1.0×10^{-2}	19.6
35	5.2×10^{-6} to 1.0×10^{-2}	19.5
Acetonitrile		
10	2.5×10^{-7} to 1.0×10^{-2}	19.8
20	2.5×10^{-7} to 1.0×10^{-2}	19.8
25	8.5×10^{-7} to 1.0×10^{-2}	19.6
30	5.1×10^{-6} to 1.0×10^{-2}	19.5
35	7.1×10^{-6} to 1.0×10^{-2}	19.5

3.8. *Analytical applications*

The analytical application of proposed sensor plan was evaluated by the comparative estimation of indium (III) in different real samples with AAS. To determine the indium (III) a synthetic sea water was prepared according to Haraguchi and Fuwa [50] by dissolving 2.67 g of NaCl, 0.54 g of $MgCl_2$, 0.11 g of $CaCl_2$ and 0.08 g of KCl (3.40% salanity) in a PTFE beaker containing deionized water and 1 mL (15 mg/mL) of In^{3+} standard solution was added to the solution and total content was transferred in to 100 mL volumetric flask (pH 7.2). Similarly the different indium concentration's solutions (20%, 25%, 30% and 35%) were prepared and the concentration of indium (III) was determined with the sensor and compared with AAS, the obtained results are compiled in Table 7. The results clearly demonstrate the applicability of the proposed sensor for indium determination.

4. Conclusion

The proposed work describes the comparative study of 2-amino-1,4-naphthoquinone derived different ligand-based membrane sensors selective to In^{3+}. The sensor no. 16 based on Q_2 ligand found to be best selective for In^{3+}. In the working range of 2.5×10^{-7} to 1.0×10^{-2} M indium (III), performs satisfactorily over wide pH range of 2.5–7.5 with a fast response time (10 s). It was also found to work satisfactorily in partially non-aqueous media up to 20% (v/v) content of acetonitrile, ethanol and methanol and can be used over a period of 3.5 months without significant drift in potentials. The quantitative application of proposed sensor no. 16 was also tested by comparative analysis of artificially made sea water with AAS.

Acknowledgements

The authors acknowledge King Fahd University of Petroleum and Minerals (KFUPM) for supporting this work. One of the authors Manoj Kumar Pal is thankful to ministry of Human Resource Development (MHRD), New Delhi, India, for financial support.

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