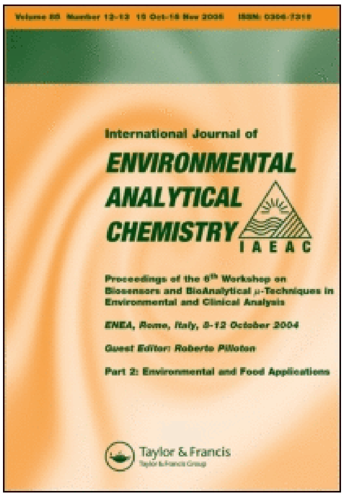

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Perchlorate selective sensor based on a newly synthesized hydrogen-bonding diamide receptor

Ajay Kumar Jain[a]; Jitendra Raisoni[a]; Ravindra Kumar[a]; Shalabh Jain[b]
[a] Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee, India [b] Department of Chemistry, Gurukul Kangri University, Haridwar, India

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Perchlorate selective sensor based on a newly synthesized hydrogen-bonding diamide receptor

AJAY KUMAR JAIN*†, JITENDRA RAISONI†,
RAVINDRA KUMAR† and SHALABH JAIN‡

†Department of Chemistry, Indian Institute of Technology
Roorkee, Roorkee 247667, India
‡Department of Chemistry, Gurukul Kangri University, Haridwar, India

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The novel ionophore, N^1,N^3-di(1H-benzoimidazole-2-yl)isophthalamide receptor (I) has been synthesized and characterized by UV, IR, and CHN analysis. Polyvinyl chloride (PVC)-based membranes of (I) have been prepared and explored as ClO_4^- selective sensors. The effect of various plasticizers, viz. tris(2-ethylhexyl) phosphate (TEHP), dibutyl phosphate (DBP), dioctyl phosphate (DOP), diethyl phosphate (DEP), tricresyl phosphate (TCP), and a cation excluder, tridodecylmethylammonium chloride (TDDMACl), was studied in detail, and an improved performance was observed in several instances. Optimum performance was observed with the membrane having (I)-PVC-TDDMACl-DOP in the ratio 1 : 120 : 1 : 200 (mg). The sensor works satisfactorily in the concentration range 1.8×10^{-5} to 1.0×10^{-1} M with near Nernstian compliance (52.0 mV per decade of activity) between pH 4.0 and 10.0 with a fast response time of about 12 s. The potentiometric selectivity coefficient values as determined by the Fixed Interference Method indicate a selective response for ClO_4^- in the presence of interfering ions. The sensor exhibits adequate shelf-life (~2 months) with a good reproducibility (SD ± 0.4 mV).

Keywords: Perchlorate; Ionophore; Sensor; Plasticizer; Membrane

1. Introduction

Perchlorate is a component of solid-phase rocket fuel and other industrial products that is being discovered with increasing frequency in the environment. It interferes with iodine uptake by the thyroid gland and is associated with disruption of thyroid function [1–3]. The US Environmental Protection Agency (EPA) stipulated a protective health level dosage of ClO_4^- as $3 \times 10^{-5}\,mg^{-1}\,kg^{-1}\,day^{-1}$ [4]. A number of methods such as ion chromatography [5], spectrophotometry [6], indirect atomic absorption spectrometry [7], and conductometric titration [8] have been developed for the quantification of perchlorate. These methods generally require sample pretreatment and infrastructure

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*Corresponding author. Fax: +91-1332-273560. Email: akjaincy@iitr.ernet.in

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backup, and are not very convenient for the analysis of a large number of samples. Ion sensors are analytical tools which are expedient and fast, often requiring no sample treatment, and are also suitable for 'on-line' analysis. Several perchlorate selective sensors have been reported recently in the literature [9–19]. However, their utility for perchlorate estimation has been limited due to the high degree of interference with lipophilic anions such as Sal^- and SCN^-. Therefore, efforts are still being made to develop a better perchlorate selective sensor which is sufficiently selective and sensitive.

In recent times, intensive research has been directed towards the preparation of a variety of selective receptors for anions [20–23]. These have included Lewis acids, pyrroles, guanidium, metalloreceptors, and amides. Such receptors are now used for anion recognition and their sensing [22, 23]. Among these, structurally simple diamide receptors show strong and selective anion binding due in part to their flexibility which allows adjustment in cavity size as well as the formation of strong hydrogen bonds [24–26]. With this in mind, we have synthesized a novel hydrogen bonding N^1,N^3-di(1H-benzoimidazole-2-yl)isophthalamide receptor containing strong hydrogen-bond donor sites and employed it for developing a perchlorate sensor. The results of these investigations are presented in this communication and show that the sensor of the synthesized receptor has turned out to be a selective and sensitive sensor for perchlorate.

2. Experimental

2.1 *Reagents*

All reagents were of analytical grade and used without further purification. Isophthaloyl dichloride, Aldrich, Germany; 1H-benzo[d]imidazole-2-amine, Acros Organics, USA; triethylamine (Et_3N), tridodecylmethylammonium chloride (TDDMACl) and high-molecular-weight polyvinyl chloride (PVC), Aldrich, USA; tris(2-ethylhexyl) phosphate (TEHP), E. Merck, Germany; dibutyl phosphate (DBP), Reidel, India; dioctyl phosphate (DOP), diethyl phosphate (DEP), Reidel, India; tricresyl phosphate (TCP) Aldrich, USA were used as obtained. Analytical reagent-grade tetrahydrofuran (THF) and sulfuric acid were obtained from Ranbaxy, India. Standard solutions were prepared with double-distilled water. Working solutions of different concentrations were prepared by diluting 0.1 M stock solutions.

2.2 *Synthesis of* N^1,N^3*-di(1H-benzoimidazole-2-yl)isophthalamide receptor (I)*

The solution of isophthaloyl dichloride (1.014 g, 5 mmol) in 5 mL of dry THF was added dropwise to the mixture of Et_3N (1.4 mL), 1H-benzoimidazole-2-amine (1.330 g, 10 mmol) and 200 mL of dry THF over a period of 5 minutes. After continuous stirring for 24 h, the mixture was filtered and the filtrate evaporated. The solid residue obtained was purified by crystallization to yield (80%), yellow solid (figure 1) with the following characteristics: M.p. $>300°C$; $\lambda_{max} = 261$ nm; IR: $\nu(\text{–C=O, amide}) = 1644\ cm^{-1}$, $\nu(\text{–NH}) = 3434\ cm^{-1}$; Anal. Calcd for $C_{22}H_{16}N_6O_2$: C, 66.6; H, 4.0; N, 21.2%. Found: C, 66.0; H, 3.6; N, 20.1%.

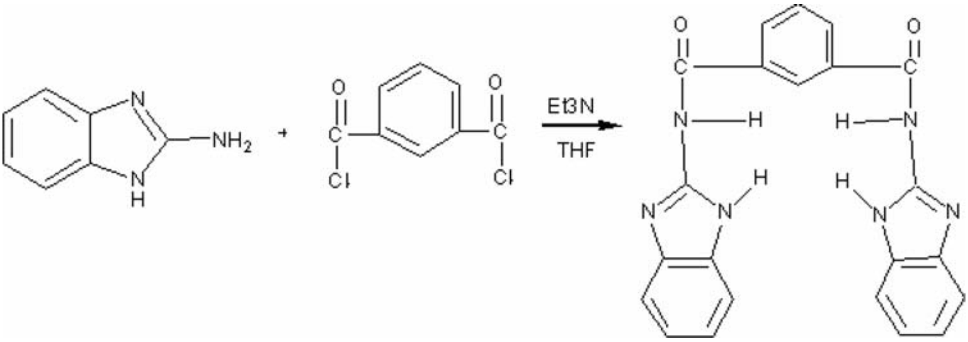

Figure 1. Synthesis of N^1,N^3-di(1H-benzoimidazole-2-yl)isophthalamide receptor (I).

2.3 *Preparation of membranes*

The PVC-based membranes were prepared by dissolving appropriate amounts of (I), TDDMACl, plasticizers (DOP, TEHP, DBP, DEP, and TCP), and PVC in THF (10 mL). After complete dissolution of all the components and thorough mixing, the homogeneous mixture was poured into polyacrylate rings placed on a smooth glass plate. THF was allowed to evaporate for about 24 h at room temperature. To obtain membranes with reproducible characteristics, the solvent evaporation was carefully controlled; otherwise, the morphology and thickness of the membranes show significant variations which ultimately affected the sensor response. Transparent membranes (0.5 mm in thickness) were removed carefully from the glass plate. A 5-mm-diameter piece was cut out and glued to one end of a 'Pyrex' glass tube. The membranes thus prepared were then equilibrated for 2 days in 0.1 M ClO_4^- solution.

2.4 *Potential measurement and apparatus*

The potential and pH measurements were carried out at $25 \pm 0.1^\circ C$ with a digital potentiometer (Model 5652 A, ECIL, India) and Century Microvoltmeter (Model CVM 301, India) by setting up the following cell assembly, employing saturated calomel electrode (SCE) as a reference electrodes: SCE/internal solution (0.1 M, ClO_4^-)/membrane/test solutions/SCE.

IR spectra were recorded on a Perkin–Elmer 1600 series FT–IR spectrophotometer. The melting points were determined on a Buchi SMP 20 melting point apparatus. Elemental analysis was performed using a Vario EL III instrument. The activity was calculated by a modified form of the Debye–Huckel equation [27].

3. Results and discussion

In preliminary investigations, the potentiometric response of the membranes containing (I) as electroactive material was tested for a number of anions. The potential responses of various sensors are shown in figure 2. Among the anions, the best response was observed for ClO_4^- ion, so the ionophore was selected as a suitable sensor material for the ClO_4^- -selective sensor.

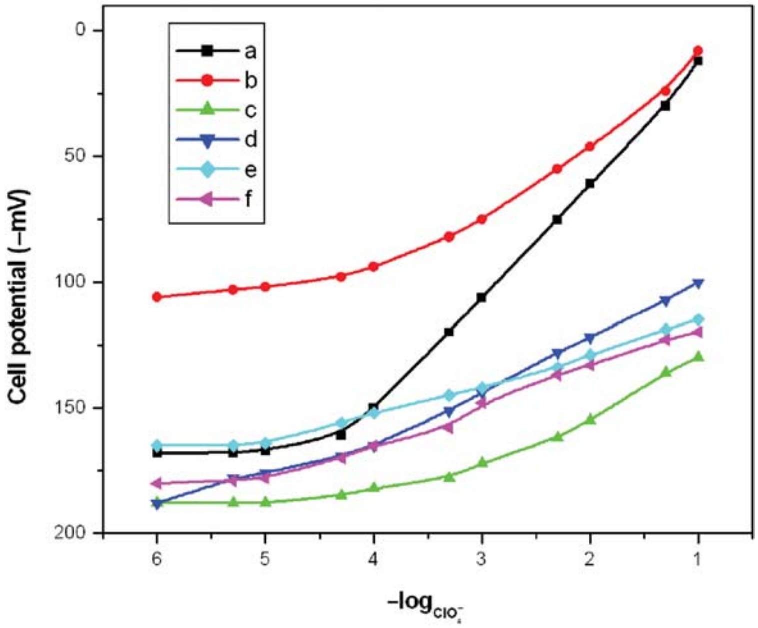

Figure 2. Response of the N^1,N^3-di(1H-benzoimidazole-2-yl)isophthalamide receptor-based membranes (without plasticizer) to (a) perchlorate, (b) dichromate, (c) sulfate, (d) bicarbonate, (e) nitrate, and (f) thiocyanate.

3.1 *Working concentration range and slope*

Before starting any potential studies, the membranes were equilibrated with 0.1 M ClO_4^- solution. It was found that an equilibration time of 2 days was optimal, as equilibrated membranes gave reproducible results, and no drift in potential was observed. The potential of sensors employing membranes with and without plasticizers was determined as a function of ClO_4^- activity, which is taken as a test solution and with an internal solution with a concentration of 1.0×10^{-1} M ClO_4^-. The potential thus determined is plotted against ClO_4^- activity in figure 3. From these plots, a working concentration range (linear potential response) and slope were calculated, and these have been compiled in table 1. It can be seen from table 1 that the sensor number 1 with a membrane without a plasticizer works in the concentration range of 4.4×10^{-5} to 1.0×10^{-1} M with a slope of 49.0 mV per decade of activity. The slope of this membrane is near-Nernstian, and the working concentration range is narrow. It can be further seen that the addition of different plasticizers to the membrane has affected the performance to different extents. Of all the plasticized membranes, that with the DOP plasticizer (sensor number 2) performs best, as it exhibits the widest working concentration range of 1.8×10^{-5}–1.0×10^{-1} M with a near Nernstian slope of 52.0 mV per decade of activity. The potential generated by the sensor was reproducible, and repeated monitoring of potential (15 measurements) at the same concentration (1.0×10^{-3} M) gave a standard deviation of ±0.4 mV. It is important to mention here that internal solutions of different concentrations, viz. 1.0×10^{-2}, 5.0×10^{-2}, and 1.0×10^{-1} M were tried, but the best results were obtained with the internal solution of 1.0×10^{-1} M ClO_4^-.

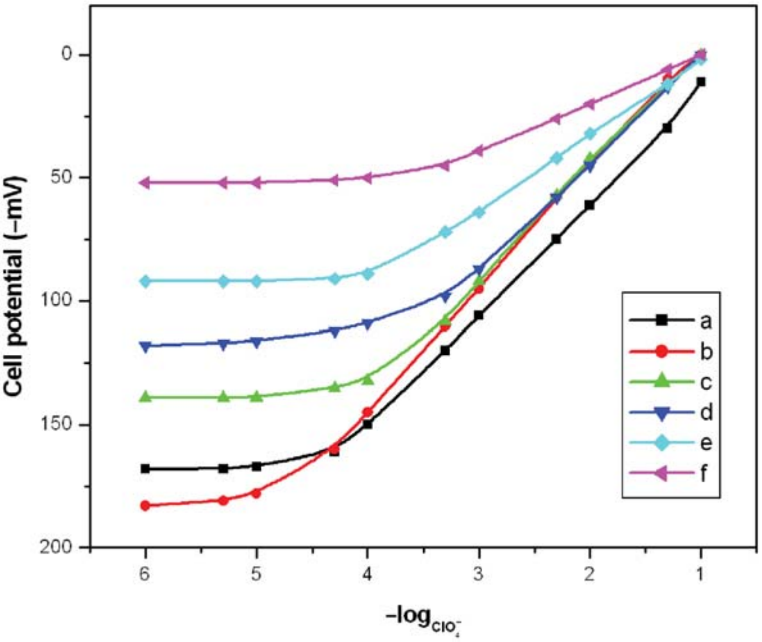

Figure 3. Variation of membrane potential with activity of ClO_4^- ions of PVC-based membranes of (I): (a) without plasticizer and with plasticizer, (b) DOP, (c) TEHP, (d) TCP, (e) DBP, and (f) DEP.

3.2 *Response and lifetime*

The response time has been measured as the time taken by the sensor to attain a stable potential. It has been determined for all six sensors and is mentioned in table 1. It can be seen from the table that the response time of the sensor with a membrane (number 1) without a plasticizer is sufficiently high (45 s). However, with the addition of plasticizers to the membranes (numbers 2–6), the response time is sufficiently reduced. This could be due to the change in properties of the membranes caused by the addition of the plasticizers, which brings the transition temperature of the polymer matrix to near ambient temperature [28]. Among all the sensors prepared with different plasticizers, sensor number 2 with the DOP plasticizer improved the response time to a maximum extent. This sensor generates a stable and reproducible potential within 12 s. The sensors could be used over a period of two months. However, the membranes were stored in 0.5 M ClO_4^- solution when not in use. Since the sensor (number 2) exhibited the best performance characteristics, the same was chosen for further studies.

3.3 *pH and solvent effect*

In order to investigate the pH effect on the potential response of the sensor, the potential was measured at a fixed concentration of ClO_4^- solution, i.e. 1.0×10^{-3} M with different pH values. The pH of the solution was varied from 1.0 to 12.0 with the addition of HNO_3 or ammonia. The potential variation as a function of pH is plotted on figure 4. It can be seen that the useful pH range for this sensor is 4.0–10.0 because in this range, the potential remains constant. The performance of the sensor system

Table 1. Composition of PVC-based membranes of *N*[1],*N*[3]-di(1H-benzoimidazole-2-yl)isophthalamide receptor (I) and performance characteristics of ClO_4^- selective sensors based on them.

	Composition of membranes (amount (mg) of different components added)										
Sensor number	(I)	PVC	TDDMACl	DOP	TEHP	DEP	DBP	TCP	Working concentration range (M)	Slope (mV per decade of activity)	Response time (s)
1	1	120	1						4.4×10^{-5}–1.0×10^{-1}	49.0	45
2	1	120	1	200					1.8×10^{-5}–1.0×10^{-1}	52.0	12
3	1	120	1		200				1.6×10^{-4}–1.0×10^{-1}	50.0	16
4	1	120	1			200			2.5×10^{-4}–1.0×10^{-1}	19.0	20
5	1	120	1				200		3.1×10^{-4}–1.0×10^{-1}	31.0	15
6	1	120	1					200	1.7×10^{-4}–1.0×10^{-1}	42.0	15

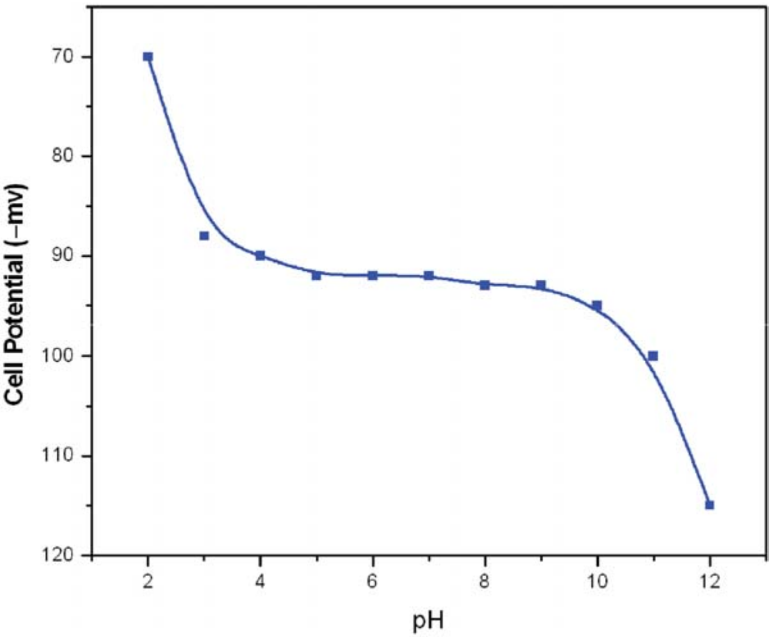

Figure 4. Variation of membrane potential with pH.

was also investigated in a partially non-aqueous medium using a methanol–water, ethanol–water, and acetone–water mixture. Thus, the potential response of the sensor as a function of ClO_4^- ion activity was determined in 10, 20, and 30% (v/v) methanol–water, ethanol–water, and acetone mixtures and is given in figures 5–7. From these plots, the working concentration range and slope were evaluated and are compiled in table 2. It can be seen from the table that the sensor worked satisfactorily up to 20% (v/v) non-aqueous content as, in these mixtures, the working concentration range and slope remain almost the same. However, above a 20% non-aqueous content, the slope and working concentration range are appreciably decreased.

3.4 *Selectivity*

Selectivity is an important characteristic of a sensor that delineates the extent to which the device may be used in the estimation of analyte ion in the presence of other ions. Potentiometric selectivity coefficients of the proposed sensor were determined by the Fixed Interference Method [29]. In this, the potential was measured for solutions containing varying concentration of ClO_4^- and fixed interfering ion concentration (1.0×10^{-2} M). The selectivity coefficients thus calculated by this method are summarized in table 3. As can be seen, the sensor exhibits a selective response toward the ClO_4^- ion and follows a selectivity pattern for several anions in the order $ClO_4^- > SCN^- > I^- > C_6H_5COO^- > CrO_4^{2-} > CH_3COO^- > CO_3^{2-} > Cr_2O_7^{2-} > NO_3^- > H_2PO_4^- > HCO_3^- > HPO_4^{2-} > SO_4^{2-} > F^-$. A selectivity coefficient value equal to 1.0 indicates that the membrane responds equally to primary as well as interfering ions. A value smaller than 1.0 indicates that it responds more to primary ions than

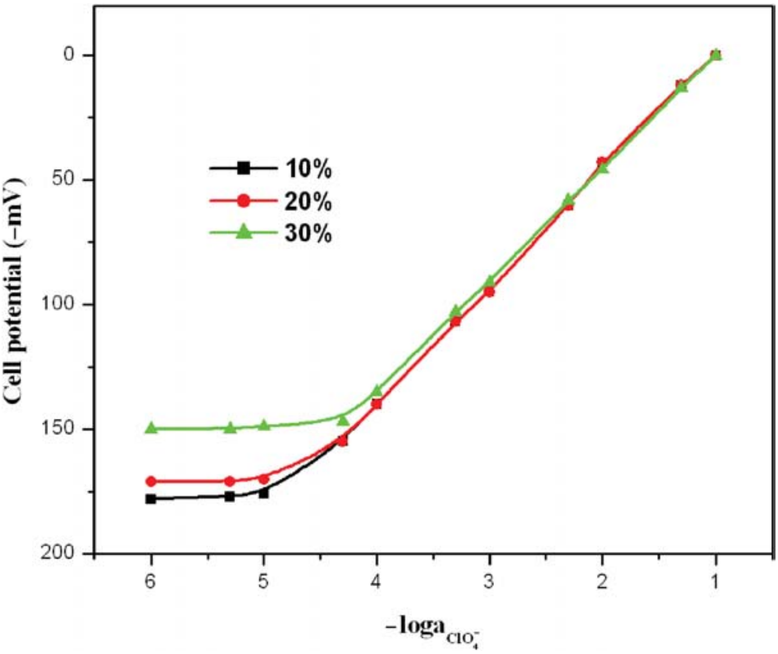

Figure 5. Potential response of the sensor in the presence of 10, 20, and 30% methanol.

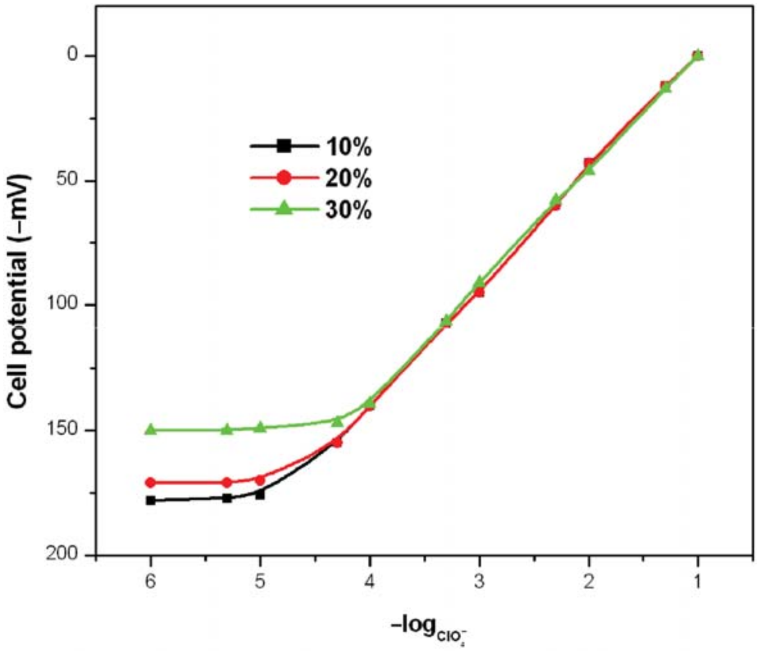

Figure 6. Potential response of the sensor in the presence of 10, 20, and 30% ethanol.

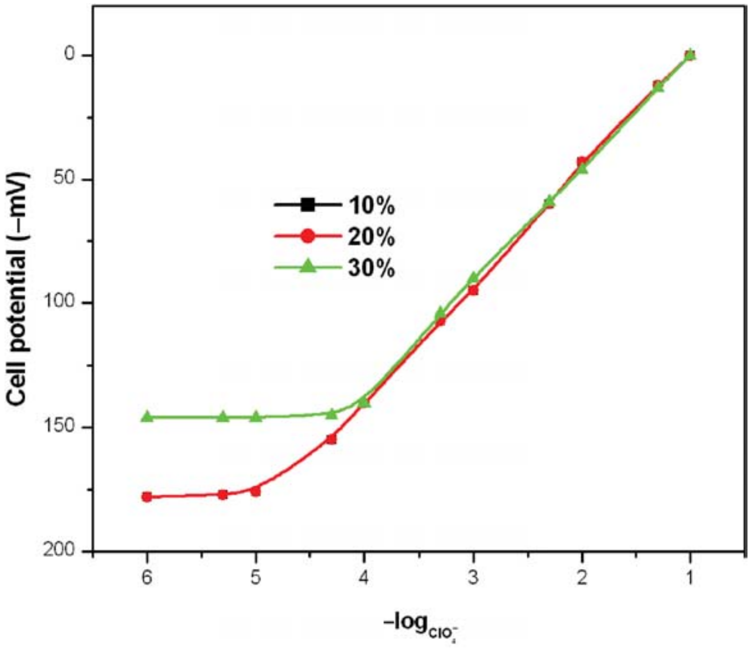

Figure 7. Potential response of the sensor in the presence of 10, 20, and 30% acetone.

Table 2. Performance of ClO_4^- selective sensor number 2 in non-aqueous media.

Non-aqueous content (% v/v)	Slope (mV per decade of activity)	Working concentration range (M)
0	52	1.8×10^{-5}–1.0×10^{-1}
Methanol		
10	52	1.8×10^{-5}–1.0×10^{-1}
20	52	2.0×10^{-5}–1.0×10^{-1}
30	45.7	6.0×10^{-5}–1.0×10^{-1}
Ethanol		
10	52	$1.\ 8 \times 10^{-5}$–1.0×10^{-1}
20	52	2.0×10^{-5}–1.0×10^{-1}
30	45.6	6.3×10^{-5}–1.0×10^{-1}
Acetone		
10	52	1.8×10^{-5}–1.0×10^{-1}
20	52	1.8×10^{-5}–1.0×10^{-1}
30	44.8	6.8×10^{-5}–1.0×10^{-1}

to interfering ions, and in such a case, the sensor is said to be selective to primary ions over interfering ions. Furthermore, the smaller the selectivity coefficient value, the higher the selectivity order. It can be seen from the table that the selectivity coefficients are in the order of 10^{-3} or lower for almost all diverse ions tested. Thus, these ions would not cause any significant interference in the estimation of ClO_4^- ions by this sensor unless present in large amounts. In view of the good selectivity of the sensor, it can be used for ClO_4^- determination in the presence of many foreign ions by direct potentiometry.

Table 3. Selectivity coefficients of sensor number 2 as determined by the Fixed Interference Method (FIM).

Interfering ion (M)	Selectivity coefficient $(K^{\mathrm{Pot}}_{\mathrm{ClO}_4^-},\mathrm{B})$
SCN^-	1.4×10^{-2}
HCO_3^-	2.2×10^{-3}
SO_4^{2-}	1.9×10^{-3}
CH_3COO^-	3.9×10^{-3}
I^-	7.9×10^{-3}
CO_3^-	3.9×10^{-3}
CrO_4^{2-}	4.4×10^{-3}
$C_6H_5COO^-$	5.6×10^{-4}
NO_3^-	3.1×10^{-3}
F^-	1.1×10^{-3}
HPO_4^{2-}	2.5×10^{-3}
$H_2PO_4^-$	2.2×10^{-3}

Table 4. Comparison of the proposed sensor number 2 with the reported sensors.

Sensor number	Working concentration range (M)	Slope (mV per decade of activity)	pH range	Response time (s)	Lifetime	Reference
1	1.0×10^{-7}–5.0×1.0^{-1}	59.5	3.0–11.0	10	15 days	[9]
2	5.0×10^{-7}–4.0×10^{-1}	59.9	2.5–9.5	8	2 months	[10]
3	1.0×10^{-5}–1.0×10^{-1}	59	4.0–9.0	NM[a]	8 months	[11]
4	5.2×10^{-6}–1.0×10^{-1}	52.5	2.0–10.0	NM	2 months	[12]
5	8.0×10^{-6}–1.6×10^{-1}	57.8	4.0–10.0	NM	2 months	[13]
6	1.0×10^{-6}–1.0×10^{-2}	56	1.5–13.5	10	9 months	[17]
7	1.8×10^{-5}–1.0×10^{-1}	52	4.0–10.0	12	2 months	Proposed sensor

[a] NM: not mentioned.

4. Conclusion

The results indicate that the membranes of the N^1,N^3-di(1H-benzo[d]imidazole-2-yl) isophthalamide receptor (I) are sufficiently selective for the ClO_4^- ion over a number of other ions. The addition of plasticizers to the membranes improved the performance of the sensors as the working concentration range was increased, and the response time was drastically reduced from 45 to 12 s. Of all the sensors investigated, sensor number 2 with a membrane with a composition of 1 : 1 : 120 : 200 mg (I : TDDMACl : PVC : DOP) was the best. The performance of this sensor was comparable with the reported ClO_4^- sensors in terms of the working concentration range, slope, pH effect, and reproducibility (table 4). However, the sensor is superior to existing sensors in terms of selectivity as reported sensors exhibit significant interference with SCN^- and I^- ions, whereas these ions do not interfere with its performance. Thus, the sensor can be used for the determination of ClO_4^- in the presence of various interfering ions by direct potentiometry.

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