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# Anion recognition through amide-based dendritic molecule: A poly(vinyl chloride) based sensor for nitrate ion

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## ABSTRACT

Poly(vinyl chloride) (PVC)-based membranes of N,N-bis-succinamide-based dendritic molecule with tetrabutyl ammonium bromide (TBAB) as a cation inhibitor and dibutylphthalate (DBP), dioctylphthalate (DOP), dibutyl (butyl) phosphonate (DBBP) and 1-chloronaphthalene (CN) as plasticizing solvent mediators were prepared and used as nitrate ion-selective electrodes. Optimum performance was observed with the membrane having I–PVC–TBAB–DBP in the ratio 1:33:1:65 (w/w). The electrode has a linear response to nitrate with a detection limit of $3.9 \times 10^{-5} \pm 0.07$ M and Nernstian compliance ($57.0 \pm 0.2$ mV/decade) between pH 2.8 and 9.6 with a fast response time of about 20 s. The selectivity coefficient values of the order of 0.001 for mono-; bi- and trivalent anions; indicate high selectivity for nitrate ions over these anions. The preparation procedure of the electrode is very easy and inexpensive. The electrodes were used over a period of 45 days with good reproducibility. The analytical usefulness of the proposed electrode has been evaluated by its application in the determination of nitrate ions in waste water samples.

## 1. Introduction

The development of potentiometric membrane-based anion sensors with analytical useful selectivity remains a formidable challenge. Indeed, there are relatively few types of lipophilic ionophores, required for preparation of such sensors that display significant preference for one anion over others [1,2]. Anions play fundamental roles in a wide number of environmental and biological processes and due to their importance the development of anion sensors and chemosensors has grown in importance in recent years and has become an important sub-area within the field of anion chemistry [3–11]. But still, the challenge of developing potentiometric sensor for anions lies because of wide range of geometries, low charge radii ratio, pH sensitivity and high solvation energy exhibited by anions [12,13]. The determination of nitrate anion is important as it is ubiquitous within environmental, food, industrial and physiological systems. An important aspect associated with nitrate chemistry is its chemical transformation or biodegradation into nitrite, which is an indication of faecal pollution of natural waters. Nitrite, due to its interaction with blood pigment produces methemoglobinalmia which has harmful impacts on human health [14]. The current WHO drinking water guideline is 50 mg nitrate/L. Nitrate in drinking water is a major health concern because of its toxicity; especially to young children. The average human daily intake of nitrate/nitrite is 95 mg/day in adults [15]. The amount of nitrate in various samples such as natural and waste waters, food products, industrial materials, tobacco and industrial effluents, has been determined by different methods [16–23]. Among the different analytical methods developed so far for determination of nitrate, potentiometric detection methods based on ion-selective electrodes (ISEs) have emerged as one of the most promising tools for this purpose. So far few electrodes have been reported for the determination of nitrate ions. Some of which are based on ion exchangers that provide Hofmeister-type selectivities [24,25] while in the recent years electrodes based on other ionophores have also been developed which show selectivity towards nitrate ions [26–31].

Dendrimers are perfect and unified macromolecules with regular and highly branched architectures that are obtained from a

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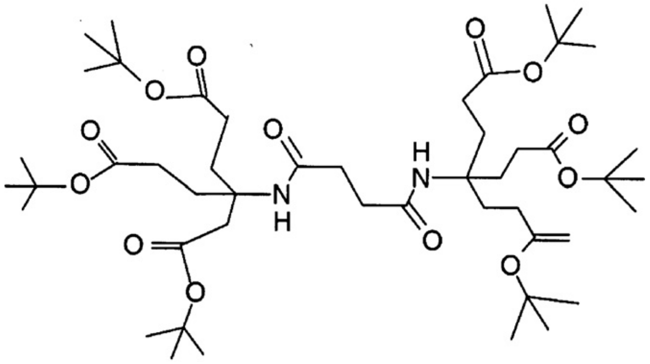

**Fig. 1.** Structure of N,N-bis-succinamide-based dendrimer (I).

repetitive procedure. They are characterized by the presence of a large number of functional groups on the surface which results in solubility, viscosity, and thermal behaviors different from those of more classical polymers. They are also characterized by the presence of internal cavities which can be functionalized and by a core that does or does not bear functional groups. While they have found their potential applications in the fields of molecular electronics, material science (high performance polymers, catalysts, adhesives, etc.), the field of membrane chemistry still remain unattended, though, their unique structures make them suitable candidates for host–guest chemistry. Multiple identical end groups allow multiple binding of guest molecules at the periphery, which can lead to specific molecular recognition. Thus, in the recent years there has been considerable interest in the incorporation of functional units on the surface or in the interior core of the dendrimer so as to generate supramolecular assemblies having applications in chemical sensors [32–36]. Incorporation of desired functional units in proper number and location within the macromolecular superstructure can be achieved by a convergent growth method, a divergent method or a combination of both the methodologies. In the present studies our approach to design and synthesize nitrate ionophores has focused on the use of N,N-bis-succinamide-based dendritic molecule (I, Fig. 1). It can be seen from the figure that in this amide based dendrimer molecule the number of branches increases with the step number (the dendrimer generation). Thus, the branches crowd at the outer surface while the inner part of the dendrimer has ample empty space. Therefore, this dendrimer can behave like a capsule, encapsulating the guest ion. The structural mobility of this ionophore may further drive it to stably trap the nitrate anion by orienting the hydroxyl oxygen resulted due to keto-enol tautomerization and surrounding the nitrate oxygen without distorting the geometry of nitrate ion.

This compound has earlier been tried to develop an iodide sensor [37] where nitrate ion had shown some interference and thus, it is expected that this material may be a good ionophore for $NO_3^-$ ions. The results on the PVC-based membranes of this ionophore as nitrate-selective electrodes are presented in this paper. The response characteristics of the membrane electrode with the ionophore in terms of Nernstian slope, response time, detection limit and selectivity over other anions are discussed as well.

## 2. Materials and methods

### 2.1. Reagents and apparatus

All reagents used were of analytical reagent grade and were used without further purification; high molecular weight poly(vinyl chloride) (PVC) were obtained from Aldrich, USA, tetrabutyl ammonium bromide (TBAB), BDH, England, dibutylphthalate (DBP); and dioctylphthalate (DOP), Reidel India; dibutyl (butyl) phosphonate (DBBP), Mobil, USA, 1-chloronaphthalene (CN); E. Merck, Germany and tetrahydrofuran (THF) was obtained from Ranbaxy, India. Carbonate, bicarbonate, bromide, chloride, iodide, fluoride, acetate, sulphate, sulphite, nitrate, phosphate, nitrite, dichromate, permanganate, etc. solutions were prepared from sodium or potassium salts and were obtained from Ranbaxy, India.

N,N-bis-succinamide-based dendritic molecule used as the ionophore (I) in this work was synthesized by Chandra et al. [38].

Potentiometric measurements were carried out on a Mettler Toledo pH/ion analyser (model MA235).

### 2.2. Membrane preparation

The membranes were prepared by adding THF (5–10 ml) to 1% of ionophore, I and PVC (33%), cation excluder, TBAB (1%), solvent mediators (DBP, DOP, DBBP and CN) (65%) were further added to obtain membranes of different compositions (Table 1). The optimum composition of the membranes was obtained after a good deal of experimentation. 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 at room temperature, after 24 h, transparent membranes of 0.5 mm thickness were obtained. A 5 mm diameter piece was cut out and glued to one end of a Pyrex glass tube [39–43].

### 2.3. Equilibration of membranes and potential measurements

Proper equilibration of a membrane, to be used as a sensor, is essential for generating stable and reproducible potentials and to avoid long response time. It is necessary to optimize the concentration of the contacting solution and the time required for complete equilibration.

The membranes were found to be equilibrated within 3–5 days in 1.0 M $NO_3^-$ solution and the potentials were measured at $25 \pm 0.1\,^{\circ}C$ using PVC matrix membranes in conjunction with saturated calomel electrodes (SCE) by setting up the following cell assembly:

| | | | | |
|---|---|---|---|---|
| Internal reference electrode | Internal solution | Membrane | Test solutions | External reference electrode |

A fixed concentration of $NO_3^-$ was taken as internal solution (0.1 M) and a saturated calomel electrode was used as a reference electrode. The performance characteristics of the electrodes were examined by measuring potentials of the primary ion solutions with a concentration range of $10^{-6}$ to $10^{-1}$ M. Selectivity values ($K_{A,B}^{Pot}$) were evaluated using the 'fixed interference method' [44]. The initial concentration for the interfering ions in FIM was $10^{-2}$ M [45,46].

## 3. Results and discussion

### 3.1. Potentiometric response

In preliminary experiments, the potentiometric response of the plasticized PVC membrane electrode based on ionophore to various anions was measured. In the presence of the proposed carrier, the optimized membranes demonstrated Nernstian response and remarkable selectivity for nitrate anion over a wide variety of anions. The potentiometric response curves obtained for individual metal ions with ionophore under identical conditions are given in Fig. 2. Among these ions, except for nitrate ion, for all other ions the slope of all the corresponding potential vs. log[$M^{n-}$] plots is much different than the expected Nernstian slopes of 59.0, 29.5 mV/decade for the univalent and divalent anions respectively with very narrow linear range of concentration.

**Table 1**
Composition and response characteristics of the PVC-based membrane sensor for $NO_3^-$.

| Membrane no. | % Composition (w/w) of various components in membranes | | | | | | | Detection limit | Slope (mV/decade of activity) | Response time (s) |
|---|---|---|---|---|---|---|---|---|---|---|
| | I (%) | PVC | TBAB | DBP | DOP | DBBP | CN | | | |
| 1 | 1 | 99 | – | – | – | – | – | $1.0 \times 10^{-4} \pm 0.11$ | $45.0 \pm 0.6$ | 65 |
| 2 | 1 | 33 | 1 | 65 | – | – | – | $3.9 \times 10^{-5} \pm 0.07$ | $57.0 \pm 0.2$ | 20 |
| 3 | 1 | 33 | 1 | – | 65 | – | – | $5.0 \times 10^{-5} \pm 0.23$ | $54.0 \pm 0.7$ | 42 |
| 4 | 4 | 1 | 33 | 1 | – | 65 | | $7.6 \times 10^{-5} \pm 0.15$ | $65.0 \pm 0.4$ | 37 |
| 5 | 1 | 33 | 1 | – | – | – | 65 | $1.0 \times 10^{-4} \pm 0.09$ | $55.5 \pm 0.5$ | 54 |
| 6 | 1 | 34 | – | 65 | – | – | – | $9.7 \times 10^{-5} \pm 0.17$ | $53.0 \pm 0.8$ | 48 |
| 7 | 1 | 32 | 1 | 66 | – | – | – | $4.7 \times 10^{-5} \pm 0.08$ | $56.5 \pm 0.4$ | 26 |
| 8 | 1 | 34 | 1 | 64 | – | – | – | $5.2 \times 10^{-5} \pm 0.13$ | $55.3 \pm 0.9$ | 35 |
| 9 | 1 | 35 | 1 | 63 | – | – | – | $6.5 \times 10^{-5} \pm 0.32$ | $56.0 \pm 0.6$ | 40 |
| 10 | 1 | 36 | 1 | 62 | – | – | – | $6.8 \times 10^{-5} \pm 0.23$ | $55.8 \pm 0.4$ | 42 |

### *3.2. Performance characteristics of sensor*

The potentiometric response characteristics of nitrate ion sensor based on N,N-bis-succinamide-based dendritic molecule as electroactive material, with various plasticizers; DBP ($\varepsilon \sim 6.4$), DOP ($\varepsilon \sim 5.1$), DBBP ($\varepsilon \sim 4.6$), CN ($\varepsilon \sim 5$); in PVC matrix were measured in the concentration range of $1.0 \times 10^{-6}$ to $1.0 \times 10^{-1}$ M. A perusal of data presented in Table 1 shows that the sensor no.1 without plasticizer exhibited a high detection limit of $1.0 \times 10^{-4} \pm 0.11$ M with a slope $45.0 \pm 0.6$ mV/decade of activity (Fig. 3). Solvent mediators are frequently used to enhance the performance characteristics of plasticized membranes. It is well documented that the addition of the plasticizers not only improves the workability of the membranes but also contributes significantly towards the improvement in the working concentration, stability and shelf-life of the sensor [47,48]. Adequate plasticizer to be used in membranes should exhibit high lipophilicity, high molecular weight, low vapour pressure and high capacity to dissolve the substrate and other additives present in the membrane [49]. The addition of plasticizers to the membrane enhanced sensitivity of the sensors, as the membranes fabricated using DBP showed a linear and stable response for nitrate with detection limit of $3.9 \times 10^{-5} \pm 0.07$ M with a Nernstian slope of $57.0 \pm 0.2$ mV/decade (Fig. 3). The best performance of DBP among other plasticizers can be attributed to the polarity of DBP ($\varepsilon \sim 6.4$), which can be estimated from the interaction of charged species with a continuum of given dielectric constant. The DBP concentration was also examined. The membrane electrodes (Nos. 2 and 7) with 65 wt% and 66 wt% DBP show the better properties (slope and detection limit) than that of membrane electrodes with 62, 63, 64 wt% DBP. Thus, membrane composition with 65 wt% DBP was chosen for further experiments.

### *3.3. Effect of pH*

The influence of measuring solution pH on the potentiometric response of the membrane electrode was examined at $1 \times 10^{-4}$ and $1 \times 10^{-3}$ M $NO_3^-$ concentration. pH was adjusted by adding few drops of dilute sulphuric acid and sodium hydroxide solutions as required. The typical results for $1 \times 10^{-4}$ and $1 \times 10^{-3}$ M is shown in Fig. 4. The results show that the sensor is suitable for nitrate determination in the wide pH range of 2.8–9.6. The drift in potentials at higher pH (pH higher than 9.6) may be due to the competence of nitrate ions with $OH^-$ ions whereas in acidic media (pH lower than 2.8) the drift in potential may be due to the protonation of the nitrogen and oxygen sites present in the ionophore.

### *3.4. Response time and lifetime*

The practical response time of the sensor was calculated by measuring the time required to achieve 95% of the equilibrium potential from the moment of addition of $1.0 \times 10^{-5}$ M $NO_3^-$ solution. The practical response time was found to be 20 s. The practical reversibility required for the $NO_3^-$ sensor to reach a potential within ±1 mV of the final equilibrium value was measured by

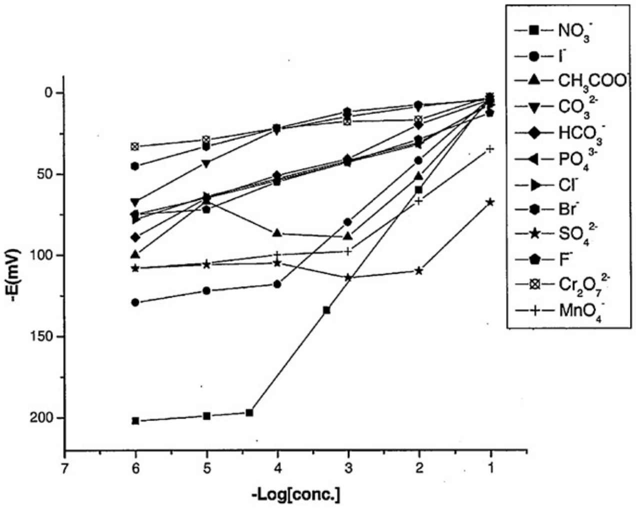

**Fig. 2.** Potentiometric response curves of PVC-based electrodes containing I as ionophore towards various metal I ions (electrode membrane composition: I/DBP/PVC/TBAB).

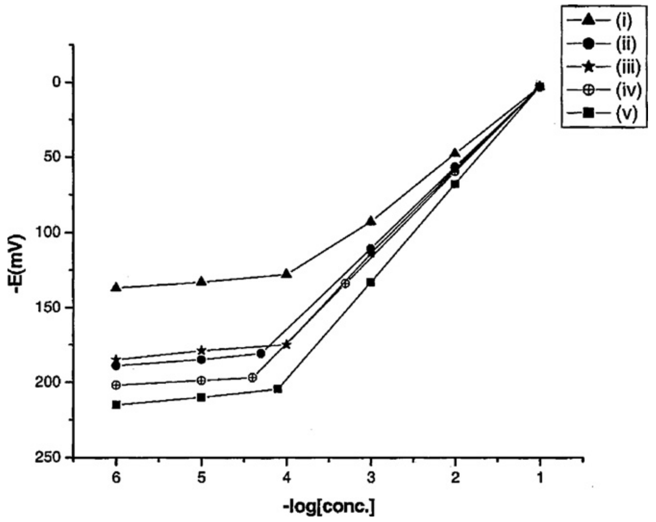

**Fig. 3.** Variation of cell potential with activity of $NO_3^-$ ions of PVC-based membranes of I with different plasticizers. (i) Without plasticizer; (ii) DOP; (iii) CN; (iv) DBP; and (v) DBBP.

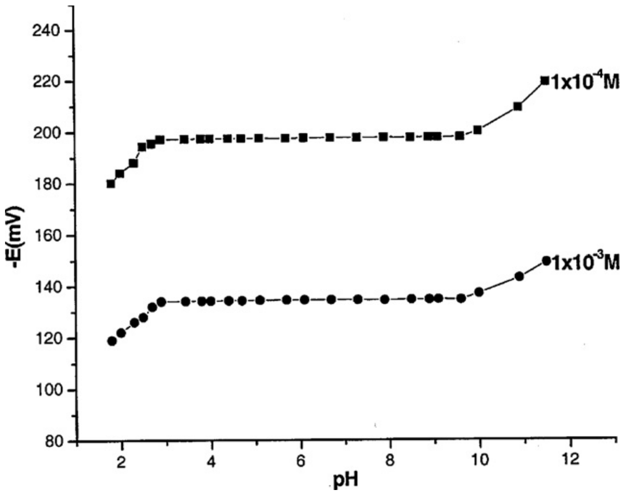

**Fig. 4.** Effect of pH on the potential response of the optimized $NO_3^-$ selective electrode.

successive immersion in a series of the nitrate ion solutions, each having a 10-fold difference in concentration. This dynamic response is plotted as EMF versus time and is shown as Fig. 5. The potentials remained constant for about 2 min. The sensing behavior of the membrane remained unchanged when potentials were recorded either from low to high concentrations or vice versa.

The membranes were used over a period of 45 days without significant change in potentials. Whenever a drift in potential was observed, membranes were re-equilibrated with 1.0 M $NO_3^-$ for 2–3 days. The membranes were stored in 0.1 M $NO_3^-$ solution when not in use.

### 3.5. Ionophore stability studies

The stability (chemical and structural) of an ionophore over a time under operational conditions is a very important characteristic and is very well studied using potentiometry [50,51]. The state of the ionophore directly influences the interfacial potential generated, due to the ability of the carrier to complex the target ion. Any signal drift, loss in sensitivity or selectivity is thus a measure of the ionophore's stability. Therefore, the sensitivity of the ISEs based on ionophore I using sensor no. 2 (Table 1) was monitored for 45 days (Table 2). During this test period, the ISEs showed good sensitivity with detection limit and the slope remaining almost unchanged for the entire test period. Between measurements, the ISEs were stored in an aqueous solution of 0.01 M $NaNO_3$.

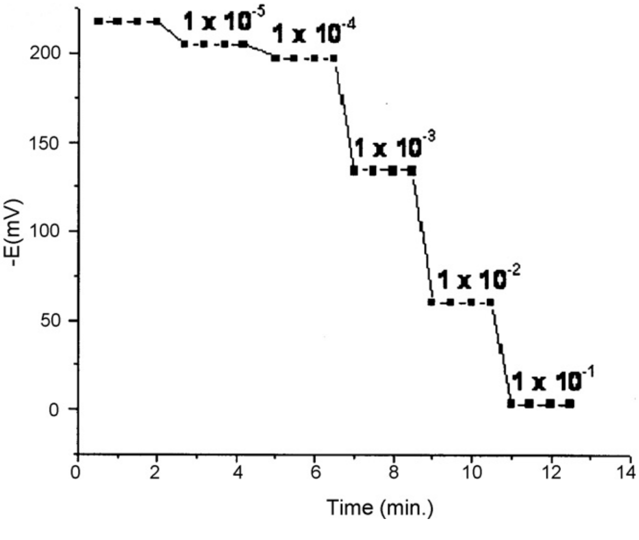

**Fig. 5.** Dynamic response time of the sensor for reversibility with step changes in concentration of $NO_3^-$ ($1 \times 10^{-5}$ to $1 \times 10^{-1}$ M).

**Table 2**
Lifetime behavior of nitrate ion-selective electrode based on ionophore (I).

| Time (days) | Slope (mV/decade) | Detection limit |
|---|---|---|
| 1 | 57.0 ± 0.2 | $3.9 \times 10^{-5} \pm 0.07$ |
| 7 | 57.0 ± 0.2 | $3.9 \times 10^{-5} \pm 0.07$ |
| 14 | 57.0 ± 0.2 | $3.9 \times 10^{-5} \pm 0.07$ |
| 21 | 57.0 ± 0.2 | $3.9 \times 10^{-5} \pm 0.07$ |
| 35 | 56.8 ± 0.5 | $4.0 \times 10^{-5} \pm 0.08$ |
| 40 | 56.4 ± 0.6 | $4.2 \times 10^{-5} \pm 0.08$ |
| 45 | 56.1 ± 0.5 | $4.8 \times 10^{-5} \pm 0.09$ |

### 3.6. Potentiometric selectivity

The most important characteristic of any anion selective electrode are its response for the primary ion in the presence of other anions. The selectivity is defined in terms of potentiometric selectivity coefficient, defines the ability of an ion-selective electrode to distinguish between different ions in the same solution. The potentiometric selectivity coefficient ($K^{\mathrm{Pot}}_{\mathrm{A,B}}$) has been evaluated using fixed interference method at $1 \times 10^{-2}$ M concentration of interfering ions. Potentiometric selectivity coefficient data of the sensor for several anions relative to nitrate ion are listed in Table 3. As evident from the data, the electrode based on ionophore I has high selectivity towards $NO_3^-$ relative to anions, such carbonate, bicarbonate, bromide, chloride, iodide, fluoride acetate, oxalate, sulphate, sulphite, acetate, phosphate, nitrite, dichromate, permanganate, etc.

The order of selectivity coefficient values has been found to be:

$$I^- > MnO_4^- > Br^- > SO_3^{2-} > CH_3COO^- > F^- > CO_3^{2-}$$
$$> SO_4^{2-} > Cl^- > HCO_3^- > NO_2^- > PO_4^{3-} > Cr_2O_7^{2-}$$

The selectivity pattern clearly shows a deviation from conventional Hofmeister anion response pattern for highly lipophilic anions. The deviation from the Hofmeister series resulted from the unique interactions between the ionophore and anions, rather than hydration free energy of the anions. Most of the interfering ions showed low values of selectivity coefficients (~$10^{-2}$, $10^{-3}$), indicating no or minimum interference in the performance of the electrode assembly.

In Table 4, the selectivity coefficients for the proposed sensor are compared with selectivity coefficients of previously reported PVC-membrane nitrate-selective electrodes based on different carriers along with their other performance characteristics. As seen,

**Table 3**
Selectivity coefficient values for nitrate-selective membrane electrode for various interfering ions (B) using the fixed interference method (FIM).

| Interfering ions (B) | Selectivity coefficient ($K^{\mathrm{Pot}}_{\mathrm{A,B}}$) | log $K^{\mathrm{Pot}}_{\mathrm{A,B}}$ |
|---|---|---|
| $I^-$ | $1.9 \times 10^{-1}$ | −0.72 |
| $HCO_3^-$ | $3.1 \times 10^{-2}$ | −1.50 |
| $Cl^-$ | $3.4 \times 10^{-2}$ | −1.46 |
| $SO_4^{2-}$ | $3.7 \times 10^{-2}$ | −1.43 |
| $F^-$ | $5.2 \times 10^{-2}$ | −1.28 |
| $Br^-$ | $8.1 \times 10^{-2}$ | −1.09 |
| $NO_2^-$ | $2.3 \times 10^{-2}$ | −1.63 |
| $CO_3^{2-}$ | $4.5 \times 10^{-2}$ | −1.34 |
| $CH_3COO^-$ | $6.2 \times 10^{-2}$ | −1.20 |
| $SO_3^{2-}$ | $7.2 \times 10^{-2}$ | −1.14 |
| $MnO_4^-$ | $8.7 \times 10^{-2}$ | −1.06 |
| $Cr_2O_7^{2-}$ | $2.0 \times 10^{-3}$ | −2.69 |
| $PO_4^{3-}$ | $1.2 \times 10^{-3}$ | −2.9 |

**Table 4**
Comparison of the reported electrodes with the proposed $NO_3^-$ sensor.

| No. | Working concentration range | pH range | Slope (mV/decade) | Potentiometric selectivity coefficients log $K^{\mathrm{Pot}}_{NO_3^-,B}$ | | | | | Method of selectivity | References |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $Cl^-$ | $I^-$ | $F^-$ | $Br^-$ | $NO_2$ | | |
| 1 | $10^{-6}$ to $10^{-1}$ | 4–12 | −59.6 | −2.23 | −0.69 | −4.2 | −1.63 | −2.00 | FIM | [30] |
| 2 | $10^{-6}$ to 1.0 | 2.0–9.5 | −58.5 ± 1.0 | −3.60 | −1.20 | −3.50 | −1.80 | NM | FIM | [31] |
| 3 | $10^{-5}$ to $10^{-1}$ | 2.2–9.4 | −57.8 ± 1.0 | −4.30 | −1.10 | −5.50 | −3.10 | −4.50 | FIM | [51] |
| 4 | $10^{-5}$ to $10^{-1}$ | 5.0–8.0 | −57.4 | NM | −1.86 | NM | −1.86 | −1.53 | MPM | [50] |
| 5 | $10^{-5}$ to $10^{-1}$ | 2.8–9. 6 | 57.0 ± 0.2 | −1.46 | −0.72 | −1.28 | −1.09 | −1.63 | FIM | Proposed electrode |

**Table 5**
Determination of nitrate in industrial waste water samples using spectrophotometric method and developed nitrate sensor.

| Sample no. | Proposed ISE (ppm) | Spectrophotometry (ppm) |
|---|---|---|
| 1 | 16.1 ± 0.2 | 14.1 ± 0.1 |
| 2 | 13.1 ± 0.3 | 12.1 ± 0.2 |
| 3 | 14.7 ± 0.2 | 15.3 ± 0.2 |

the proposed electrode shows somewhat similar values in some cases and superior in most cases.

## 4. Analytical applications

The developed nitrate sensor has also been used for determination of nitrate in several water samples. The determination of nitrate ion is important in water industry as more and more water supplies are becoming polluted with it. This nitrate comes from various anthropogenic sources of which industrial wastes related to agricultural fertilizers, food processing, munitions are very common. Also the disposal from septic tanks, oxidation of ammonia in sewage works contributes to the high level of nitrates in water. Three samples from local industrial wastes were collected, filtered and stored without any further pretreatment. The analyses were performed by direct potentiometry using calibration plot and the results showed the nitrate content in the waste water obtained from triplicate measurements with the sensor was found to be in agreement with that determined spectrometry (Table 5).

## 5. Conclusions

The results demonstrate the usefulness of the N,N-bis-succinamide-based dendritic molecule as selective ionophore for the quantification of nitrate ion through ion-sensors. The electrode is more selective towards nitrate in contrast to several commercial and a number of the recently reported electrodes. The electrode can be used over a wide pH range, 2.8–9.6, which makes it useful for measurements in different samples and also in certain alkaline conditions. The electrode shows good response characteristics (sensitivity, stability, life time and response time).

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