

*Full Paper*

## **All-Solid-State CNT Composite Calcium(II)-Selective Potentiometric Sensor Based on 4,7-Diaza-2,3,8,9-Dibenzo-15-Crown-5 Ionophore**

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**Abstract-** A composite of multi-walled Carbon nanotube (MWCN) and polyvinyl chloride (PVC) along with a synthesized neutral carrier 4,7-diaza-2,3,8,9-dibenzo-15-crown-5 (I) has been tried for its selective binding behavior for Ca(II) ions. Compound (I) works as an ionophore, exhibiting high selectivity for calcium ions, when taken with poly(vinyl chloride), sodium tetrphenylborate (NaTPB), MWCNT and tris(2-ethylhexyl) phosphate (TEP) in the ratio 10:100:3:3:50 (w/w). This composition was used to fabricate a solid contact calcium(II)-selective potentiometric sensor. The developed all solid-state sensor worked well in the concentration range of  $1.6 \times 10^{-7}$ - $1.0 \times 10^{-1}$  M, with a near Nernstian slope of  $28.8 \pm 1.0$  mV/decade of activity. The response time of this sensor was approximately 10 s. It exhibited a detection limit of  $9.1 \times 10^{-8}$  M. It worked satisfactorily in the pH range 3.5-7.0. The lifetime of the developed sensor was observed as six weeks and it exhibited good selectivity towards calcium ions over other cations. It was successfully used as an indicator electrode in the potentiometric titration of Ca(II) with EDTA. It produced comparable results for the determination of the activity of calcium ions in real samples.

**Keywords-** Ca<sup>2+</sup>-selective electrodes; Ion-selective electrodes; Potentiometric sensor; Crown ether; Multi-walled carbon nanotubes

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## 1. INTRODUCTION

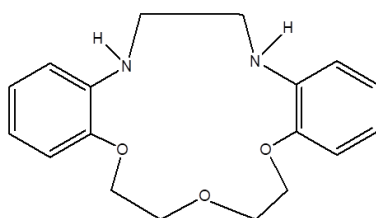
Calcium concentration monitoring finds its application in a number of areas of life. It includes science as well e.g. clinical chemistry, analytical chemistry, and environmental chemistry, etc. Calcium is necessary to provide energy to the nerves and it helps in the growth of hair. Its monitoring is important in organ transplants, hemodialysis, boilers, fertilizers, and soil [1-2]. It is the major constituent of bones and aids the maintenance of bones and teeth. It also helps to counteract fatigue, normal heart functioning, and for the kidney working [3-5]. On the other hand, an unusually high amount of  $\text{Ca}^{2+}$  in the blood may cause calcification of several internal organisms. Calcium is present mostly in the form of ions in body fluids. It works as a nucleation site for the deposition of cholesterol, which causes the formation of stones in the gall bladder and in the urinary tract [6]. Therefore, the monitoring of calcium in environmental, industrial as well as food samples is highly recommended.

Although there are many techniques available to determine the calcium ion concentrations, mostly spectroscopic methods electrochemical impedance spectroscopy, flame atomic absorption spectroscopy, and differential scanning calorimetry [7-9], yet these methods are complicated, destructive and remain unsuitable for online monitoring and feedback control. Automated flow analysis required highly skilled workers and expansive equipment. Also, all the above mentioned techniques need sophisticated infrastructure, instruments, and produce hazardous lab waste. On the other hand, ion sensors provide a highly selective, cheap but reliable, fast, and non-destructive method of analysis. Ion sensors take advantage of highly specific and selective electroactive materials, to selectively determine the concentration of any charged species. It is a sort of lock and key relation between electroactive material and the charged species.

Macrocyclic compounds e.g. porphyrins, crown ethers, metal ligands, chelates, inclusion compounds, and calixarenes etc., which have varied cavity sizes and shapes, are interesting materials to fabricate poly (vinyl chloride) membrane electrodes for the selective determination of various metal ions [10,11]. These compounds are known to selectively bind with specific ions in a complex mixture. However, a number of calcium selective compounds have been reported in the literature. Crown ethers may work as highly selective complex forming agents for selective metal extraction processes, across membrane transport, phase transfer catalytic reactions. Due to the superiority of ion selective electrodes over other instrumental techniques, the development of ion sensors with high selectivity, sensitivity, and good reproducibility is always needed. We could develop ion sensors for a number of metal ions e.g.  $\text{Cr}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ , etc. [12-18], but the reported calcium ion sensors are less in number. These sensors have specific ion carriers e.g. bis-di[4-(1,1,3,3-tetramethylbutyl)phenyl phosphoric acid] [19,20], bis(dialkylphosphate) [21], ETH 129 [22-24], ETH 1001 [25-28], N-ethyl-N-(2-trimethylammoniummethyl)-N'-heptyl-N'-methyl-succinamide [29], dibenzo-18-crown-6 [30], 2-[(2-hydroxyphenyl)imino]-1,2-diphenylethanone [31], tetrone antibiotic [32] and

$\alpha$ -furildioxime [33] methacrylate functionalized poly(3,4-ethylenedioxythiophene) [34-36]. However, some of these sensors exhibit high response time and suffer interference in the presence of other metal ions. Therefore, a better performing calcium ion sensor is highly desirable.

Here, we report for the first time a calcium ion sensor, with a wide concentration range and better lifetime. The electrode is based on a macrocyclic ionophore namely 4,7-diaza-2,3,8,9-dibenzo-15-crown-5 (Figure 1). The determined selectivity coefficient value of this electrode suggested that it suffers no interference due to the presence of common cations such as  $\text{Cr}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Ag}^+$ , etc. Various parameters like membrane composition, time of contact with the equilibrating solution, etc. were carefully optimized to obtain reproducible results.



**Figure 1.** Structure of ionophore 4,7-diaza-2,3,8,9-dibenzo-15-crown-5

## 2. EXPERIMENTAL SECTION

### 2.1. Reagents and equipment

Analytical reagent grade chemicals were used for this study. 4,7-diaza-2,3,8,9-dibenzo-15-crown-5 was synthesized as described elsewhere [37]. Potassium (tetrakis-4-chlorophenyl) borate (KTPClPB), Nitrophenyl Octyl ether (NPOE), MWCNT were purchased from (Aldrich, USA). Anion excluder sodium tetrphenylborate (NaTPB) from (BDH, England), di-octyl sebacate (DOS), dibutyl butyl phosphonate (DBBP), 1-chloronaphthalene (CN), tris(2-ethylhexyl) phosphate (TEP), dibutyl phthalate (DBP), Tri-n-butyl phosphate (TBP), and dioctyl phthalate (DOP) from (E-Merck, Germany), and poly(vinyl chloride) high molecular weight (PVC) were purchased from Sigma Chemical Company. All these chemicals were used without further treatment. The solvent tetrahydrofuran (THF) and all the metal salts were obtained from Merck, India and their solutions were prepared with high-purity Millipore deionized water. PH5652 digital pH meter/ millivoltmeter (ECIL India) and CVM 30 (Century microvoltmeter, India) were used to determine the potentials.

### 2.2. Complexation Study

A complexation study was carried out to determine the best selective behavior of the ionophore towards any metal ion. Standard EDTA solution was first titrated with 20 mL 0.1 M

solution of a specific metal ion namely  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Ni}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cs}^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{La}^{3+}$  and  $\text{Al}^{3+}$ . Secondly, the standard EDTA solution was titrated with the same solution after keeping it in contact with approximately 0.2 g of ionophore for 24 h. The distribution coefficients were determined by using the following equation:

$$K_d = (I-F)/F V/W \quad (1)$$

where I is the volume of standard EDTA solution consumed before the interaction of metal ion solution with the ligand; F is the volume of standard EDTA solution, consumed by the metal ion solution after its interaction with the ionophore for 24 h. V is the initial volume of the metal ion solution, and W is the initial mass of the ionophore. The distribution coefficient value for  $\text{Ca}^{2+}$  was obtained as 38.7 while for all other metal ions it remained between 11.0 and 21.9. It shows that the ionophore is selective for  $\text{Ca}^{2+}$  ions, therefore, it was selected to develop a calcium ion sensor.

### 2.3. Membrane preparation

4,7-diaza-2,3,8,9-dibenzo-15-crown-5 as ionophore and high-density PVC were mixed in different weight ratios and transferred in 5 ml of THF solvent. This solution was transferred in an airtight tube and shaken for about 3 hours in a shaker until a homogeneous solution was obtained. To prepare the sensor membrane, firstly, the surface of the graphite electrode was thoroughly cleaned, polished with micro-sized silica gel, and sonicated to get rid of any deposited impurity. About 10  $\mu\text{L}$  of the membrane solution cocktail was dropped with the help of a micropipette on the surface of the cleaned graphite electrode. Then it was allowed to evaporate for about 24 hours in an isolated compartment at room temperature. Many such membranes having varied compositions were prepared and equilibrated in metal ion solutions with constant activity. Each of the membranes was tested for its response characteristics. The weight ratio of membrane ingredients was varied to provide the membranes, which exhibited reproducible results, quick and stable potential values. An optimum equilibration was obtained using 0.1 M metal ion solutions for about 24 hours. Plasticizers improve the response characteristics of the membranes by providing smoothness on the surface, increasing homogeneity and dielectric constant. Anion excluders were added as these compounds are well known to suppress the activity of anions and ensure permselectivity. Multi-walled carbon nanotubes were added to increase the sensitivity of the membranes as these are better ion-to-electron transducers. Therefore, eight plasticizers i.e. NPOE, DBP, DOP, DBBP, DOS, TBP, CN, and TEP; along with anion excluder NaTPB were tried as membrane ingredients. In the case of MWCNT addition, the mixture was ultrasonicated to ensure homogeneous dispersion of MWCNT throughout the mixture. Optimum equilibration with 0.1 M  $\text{CaCl}_2$  was achieved in 24 h. Initially, a membrane was equilibrated in a specific metal ion solution namely  $\text{Co}^{2+}$ ,

Cu<sup>2+</sup>, Zn<sup>2+</sup>, Hg<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ag<sup>+</sup>, Mg<sup>2+</sup>, Cr<sup>3+</sup>, Ca<sup>2+</sup>, La<sup>3+</sup>, Gd<sup>3+</sup> and Ni<sup>2+</sup> solutions, one at a time.

#### 2.4. Potential measurements

Graphite sensor/Test solution/(Ag-AgCl) External reference electrode, electrode set up was used to determine the potential gradient values. The metal ion activity in the test solution was varied from  $1.0 \times 10^{-8}$  to  $1.0 \times 10^{-1}$  M. Standard metal ion solutions were prepared by diluting  $1.0 \times 10^{-1}$  M stock solution. The metal ions solution activities were activity coefficients based which were calculated using the modified Debye-Huckel equation. These observed potential values were plotted against negative log values of metal ion activity to obtain the standard calibration curve. Atomic absorption spectrophotometer was used to confirm the concentrations of the standard solutions.

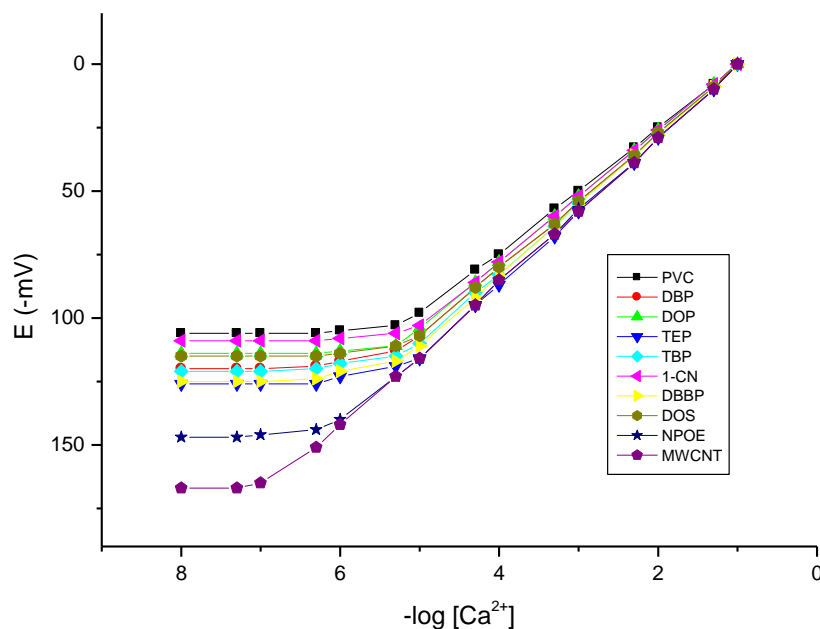
### 3. RESULTS AND DISCUSSION

#### 3.1. Optimization of membrane ingredients

Although complexation studies suggested that the ionophore is most selective towards calcium ions yet the selectivity of this ionophore was further checked for a number of cations. For these preliminary experiments, a number of electrodes were fabricated with PVC membranes containing the ionophore and were conditioned in a specific metal ion solution. The results of this experiment suggested that the best potential gradient was generated for calcium ions. Therefore, it may be concluded that the ionophore shows the best interaction with the ionophore and rapid exchange kinetics for the metal ion–ligand complex. This makes it a suitable neutral carrier in PVC membranes for selective quantification of calcium ions in various samples. As the potential characteristics of the membranes depend heavily on the weight ratio of the ionophore material and the binder i.e. PVC membranes, various combinations of these ingredients were prepared and tested for their performance. The studies exhibited that the membrane with a composition I: PVC (10:100) showed the best potential behavior. Anion excluders addition further improved the potential response of the membranes by suppressing the interference due to the anions and lowering the membrane resistance. The effect of solvent mediators has also been explored as these compounds are known to improve the dielectric constant and hence, improve the performance of the membranes, if compatible with the ionophore. Therefore, the effect of anion excluders namely sodium tetrphenylborate and potassium (tetrakis-4-chlorophenyl) borate; as well as the solvent mediators namely, NPOE, DBP, TEP, DOS, DBBP, DOP, TBP, CN, was also studied (Figure 2) and the results of these studies are compiled in Table 1.

**Table 1.** Compositions and response characteristics of PVC-based membranes having 4,7-diaza-2,3,8,9-dibenzo-15-crown-5 as an electroactive material

| S. No | (I) | DBP | DOP | NPOE | TBP | CN  | DBBP | DOS | TEP | MWCNT | NaTPB | PVC | Slope (mV/decade of activity) | Response time (s) | Working concentration range (M)                |
|-------|-----|-----|-----|------|-----|-----|------|-----|-----|-------|-------|-----|-------------------------------|-------------------|--|
| 1     | 10  |     |     |      |     |     |      |     |     |       |       | 100 | 25.0                          | ~150              | $9.4 \times 10^{-6}$ -<br>$1.0 \times 10^{-1}$ |
| 2     | 7   | 100 |     |      |     |     |      |     |     |       | 2.0   | 100 | 27.0                          | 70                | $6.2 \times 10^{-6}$ -<br>$1.0 \times 10^{-1}$ |
| 3     | 10  |     | 100 |      |     |     |      |     |     |       | 3.0   | 150 | 26.0                          | 70                | $7.0 \times 10^{-6}$ -<br>$1.0 \times 10^{-1}$ |
| 4     | 8   |     |     | 100  |     |     |      |     |     |       | 2.0   | 120 | 29.0                          | 30                | $8.5 \times 10^{-6}$ -<br>$1.0 \times 10^{-1}$ |
| 5     | 10  |     |     |      | 100 |     |      |     |     |       | 3.0   | 120 | 27.8                          | 20                | $5.0 \times 10^{-6}$ -<br>$1.0 \times 10^{-1}$ |
| 6     | 10  |     |     |      |     | 100 |      |     |     |       | 0     | 150 | 26.0                          | 100               | $9.0 \times 10^{-6}$ -<br>$1.0 \times 10^{-1}$ |
| 7     | 10  |     |     |      |     |     | 100  |     |     |       | 4.0   | 120 | 28.0                          | 20                | $4.0 \times 10^{-6}$ -<br>$1.0 \times 10^{-1}$ |
| 8     | 8   |     |     |      |     |     |      | 100 |     |       | 2.0   | 100 | 27.0                          | 25                | $6.0 \times 10^{-6}$ -<br>$1.0 \times 10^{-1}$ |
| 9     | 10  |     |     |      |     |     |      |     | 50  |       | 3.0   | 100 | 28.8                          | 18                | $1.8 \times 10^{-6}$ -<br>$1.0 \times 10^{-1}$ |
| 10    | 10  |     |     |      |     |     |      |     | 50  | 3.0   | 3.0   | 100 | 28.8                          | 10                | $1.6 \times 10^{-7}$ -<br>$1.0 \times 10^{-1}$ |
| 11    | 10  |     |     |      |     |     |      |     | 50  | 2.7   | 3.0   | 100 | 28.8                          | 10                | $4.8 \times 10^{-7}$ -<br>$1.0 \times 10^{-1}$ |
| 12    | 10  |     |     |      |     |     |      |     | 50  | 3.2   | 3.0   | 100 | 28.8                          | 10                | $1.6 \times 10^{-7}$ -<br>$1.0 \times 10^{-1}$ |

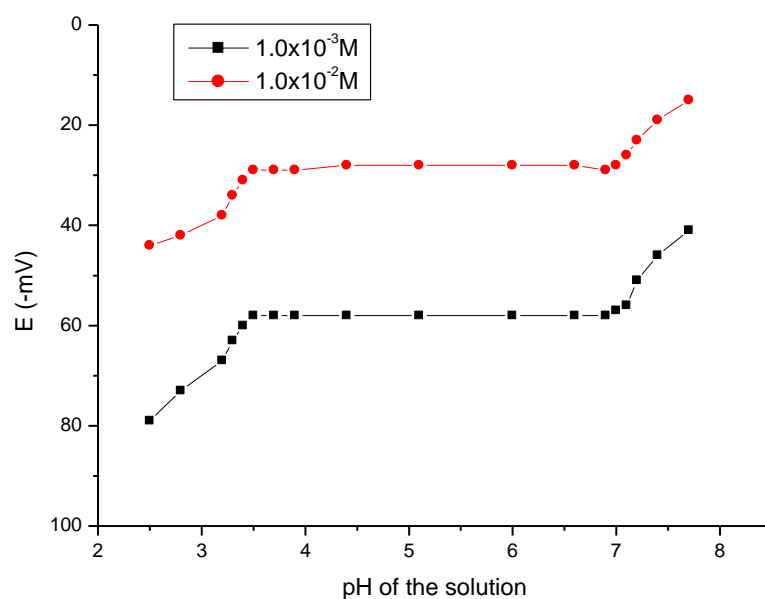
**Figure 2.** Potentiometric response of the PVC membrane sensor based on 4,7-diaza-2,3,8,9-dibenzo-15-crown-5

### 3.2. Determination of working concentration range (WCR) and slope

The membranes containing the ionophore and the PVC matrix were prepared by varying the ratio of both the ingredients and their potential responses were observed. The best response was shown by the membrane, containing the ionophore and PVC in the ratio 10:100 (w/w). The electrode, fabricated using this membrane, showed a linear potential response over a concentration range of  $9.4 \times 10^{-6}$ - $1.0 \times 10^{-1}$  M with a slope of 25.0 mV/decade of activity. Sensor's response, especially response time and slope were significantly improved on the addition of anion excluder (NaTPB or KTpCIPB) and the solvent mediators i.e. NPOE, DBP, DOP, TEP, TBP, 1-CB, DBBP, or DOS. The best performing membranes having different plasticizers along with their optimum compositions were; 7:100:2:100 (I:PVC:NaTPB:DBP) with a working concentration range (WCR)  $6.2 \times 10^{-6}$ - $1.0 \times 10^{-1}$  M and slope 27 mV/decade of activity; and 7:100:3:120 (I:PVC:NaTPB:TBP) with a WCR  $5.0 \times 10^{-6}$ - $1.0 \times 10^{-1}$  M and slope 27.8 mV/decade of activity. The response curves of these compositions are summarized in Table 1. The optimized weight ratio of the ingredients of the best performing membrane was 10:100:3:50 (I:PVC:NaTPB:NPOE). This sensor exhibited a near Nernstian potential response with a slope of  $28.8 \pm 1.0$  mV/decade of activity and linearity in potential response over concentrations range of  $1.8 \times 10^{-6}$ - $1.0 \times 10^{-1}$  M. Addition of MWCNT further improved the WCR to  $1.6 \times 10^{-7}$ - $1.0 \times 10^{-1}$  M with a slope of  $28.8 \pm 1.0$  mV/decade of activity and with a detection limit of  $9.1 \times 10^{-8}$  M. The best performing composition was 10:100:3:3:50 (I:PVC:NaTPB:MWCNT:TEP). Repeated determination of potential (15 measurements) on the same test sample, exhibited a standard deviation of potential response 1.8 mV, for slope 1.0-1.5 mV, which suggests good reproducibility of the results. An adverse effect was observed on the sensor's response, on reducing the ratio of ionophore below the optimum ratio. On the other hand, there was no significant improvement in the response of the sensor if the weight ratio of the ionophore was increased than its optimum weight ratio.

### 3.3. Effect of pH

The effect of pH variation on the electrode potential was studied by observing the potential change over a pH range of 2-10, using  $10^{-3}$  and  $10^{-2}$  M calcium chloride solutions. Dilute solutions of sodium hydroxide and hydrochloric acid were added dropwise to these solutions for pH adjustment. Figure 3 exhibits that a pH change does not have any significant effect on the potential gradient values in pH range from 3.5 to 7.0. The drift at higher, as well as lower pH values, could be due to the formation of hydroxyl complexes of calcium ion in solution, and the protonation of the ionosphere respectively.



**Figure 3.** Effect of pH on the cell potential of an electrode in  $10^{-2}$  M  $\text{Ca}^{2+}$  ions

### 3.4. Non-aqueous effect

Sensor no. 10 was also tested for the effect of partially non-aqueous solvent on its potential response. Acetone-water, methanol-water, and ethanol-water mediums were used for this experiment (Table 2).

**Table 2.** Effect of partially non-aqueous medium on the working of  $\text{Ca}^{2+}$  ions

| % of non-aqueous content (v/v) | Slope (mV/decade of activity) | Working concentration range (M)             |
|--------------------------------|-------------------------------|---|
| 0                              | 28.8                          | $1.6 \times 10^{-7}$ - $1.0 \times 10^{-1}$ |
| Methanol                       |                               |   |
| 5                              | 28.8                          | $1.6 \times 10^{-7}$ - $1.0 \times 10^{-1}$ |
| 10                             | 28.5                          | $1.9 \times 10^{-7}$ - $1.0 \times 10^{-1}$ |
| 15                             | 25.8                          | $8.7 \times 10^{-7}$ - $1.0 \times 10^{-1}$ |
| Acetone                        |                               |   |
| 5                              | 28.6                          | $1.6 \times 10^{-7}$ - $1.0 \times 10^{-1}$ |
| 10                             | 27.2                          | $1.8 \times 10^{-7}$ - $1.0 \times 10^{-1}$ |
| 15                             | 25.0                          | $7.4 \times 10^{-7}$ - $1.0 \times 10^{-1}$ |
| Ethanol                        |                               |   |
| 5                              | 28.2                          | $1.6 \times 10^{-7}$ - $1.0 \times 10^{-1}$ |
| 10                             | 26.6                          | $1.8 \times 10^{-7}$ - $1.0 \times 10^{-1}$ |
| 15                             | 25.0                          | $7.2 \times 10^{-7}$ - $1.0 \times 10^{-1}$ |



The results clearly display that this sensor works satisfactorily when the non-aqueous solvent is present only up to 10% (v/v). Above this ratio of nonaqueous content, the WCR and the slope value of the sensor reduce sharply.

**Table 3.**  $K_{\text{pot}}^{\text{A,B}}$  values observed for sensor no. 10

| Interfering ion  | Fixed interference method | Matched potential method |
|------------------|---------------------------|--------------------------|
| $\text{NH}_4^+$  | $7.2 \times 10^{-3}$      | 0.15                     |
| $\text{Li}^+$    | $1.5 \times 10^{-2}$      | 0.11                     |
| $\text{K}^+$     | $2.7 \times 10^{-2}$      | 0.23                     |
| $\text{Ag}^+$    | $3.1 \times 10^{-2}$      | 0.27                     |
| $\text{Na}^+$    | $3.6 \times 10^{-2}$      | 0.14                     |
| $\text{Ni}^{2+}$ | $1.1 \times 10^{-2}$      | 0.16                     |
| $\text{Hg}^{2+}$ | $9.0 \times 10^{-3}$      | 0.10                     |
| $\text{Cu}^{2+}$ | $3.8 \times 10^{-2}$      | 0.12                     |
| $\text{Co}^{2+}$ | $5.6 \times 10^{-3}$      | 0.11                     |
| $\text{Cd}^{2+}$ | $3.0 \times 10^{-1}$      | 0.49                     |
| $\text{Mg}^{2+}$ | $3.2 \times 10^{-2}$      | 0.23                     |
| $\text{Pb}^{2+}$ | $8.4 \times 10^{-3}$      | 0.21                     |
| $\text{Zn}^{2+}$ | $3.0 \times 10^{-2}$      | 0.12                     |
| $\text{Ba}^{2+}$ | $6.0 \times 10^{-2}$      | 0.17                     |
| $\text{Sr}^{2+}$ | $2.9 \times 10^{-2}$      | 0.20                     |
| $\text{Fe}^{3+}$ | $7.1 \times 10^{-3}$      | 0.08                     |
| $\text{Cr}^{3+}$ | $9.5 \times 10^{-3}$      | 0.12                     |
| $\text{Ce}^{3+}$ | $6.8 \times 10^{-2}$      | 0.21                     |
| $\text{Al}^{3+}$ | $3.5 \times 10^{-2}$      | 0.22                     |

### 3.5. Lifetime and response time

By definition, the time required to achieve the 95% of the final potential value after the immersion of the sensor into the solution. The response time of the membranes containing only ionophore and PVC, was about 100 s at higher concentrations i.e.  $1.0 \times 10^{-2}$  M, while about 200 s at lower concentrations, i.e. below  $1.0 \times 10^{-5}$  M. Plasticizers' addition improved the response time remarkably. The best response time of 10 s was observed over the entire WCR on adding TEP as a plasticizer as a membrane ingredient.

This sensor was satisfactorily performed over a time period of six weeks without any considerable deterioration in the response characteristics. A drift in potential values was observed after this period. The sensor could be used for about one more week if it was re-equilibrated with 1.0 M calcium chloride solution for 12h. The sensor was stored in 0.1M  $\text{Ca}^{2+}$  solution when not in use to avoid cracking or drying of the membrane.

### 3.6. Potentiometric selectivity coefficient

Potentiometric selectivity coefficient values indicate the extent of interference due to the presence of other ions present in the test solution. These values were calculated using two

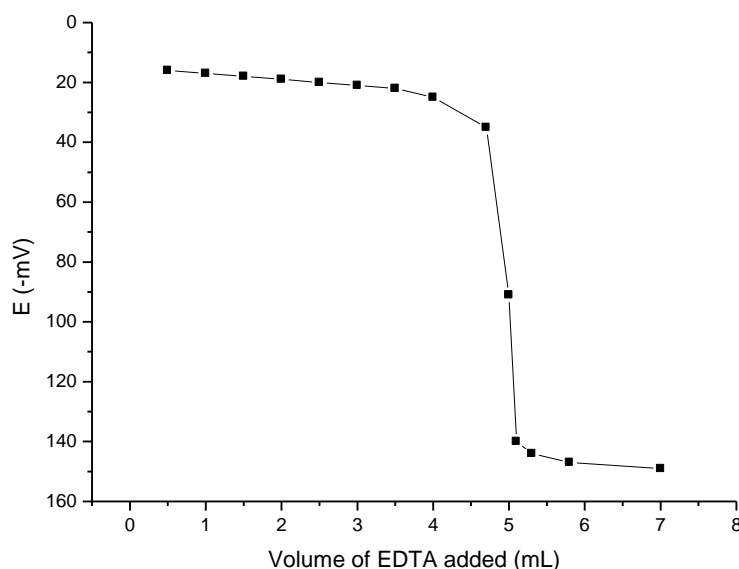
different methods namely the fixed interference method and the matched potential method [12-18]. The potential response of sensor no. 10 was determined for solutions having constant activity of the interfering ion,  $a_B$ , and varied activity of the primary ion,  $a_A$ . The observed emf values were plotted against the negative log values of the activity of the primary ion.  $a_A$  values were calculated by the intersection of the extrapolated linear portions and used for calculating  $K_{\text{pot}}^{A,B}$  using the equation:

$$K_{\text{pot}}^{A,B} = a_A / (a_B)^{z_A/z_B} \quad (2)$$

$K_{\text{pot}}^{A,B}$  values are presented in Table 3, which suggests that the proposed sensor exhibits a selective behavior for  $\text{Ca}^{2+}$  over a number of mentioned cations except for  $\text{Cd}^{2+}$  ions, as the selectivity coefficient values for  $\text{Cd}^{2+}$  ions are comparatively higher. However, even  $\text{Cd}^{2+}$  ions do not interfere if present in lower concentrations.

### 3.7. Applications of the proposed sensor

a. Potentiometric titration: This sensor was successfully used as an indicator electrode in the potentiometric titration of calcium ions with standard EDTA solution. A sigmoid curve was obtained when 25 ml of  $\text{Ca}^{2+}$  ion solution ( $0.2 \times 10^{-2}$  M) was titrated with  $1.0 \times 10^{-3}$  M standard EDTA solution and the negative potential values were plotted against the added volume of EDTA solution (Figure 4). The graph indicates the high sensitivity of the sensor towards calcium ions. The inflection point indicates 1:1 stoichiometry of the  $\text{Ca}^{2+}$ -EDTA complex.



**Figure 4.** Potentiometric titration curve of standard EDTA solution against  $10^{-2}$  M  $\text{Ca}^{2+}$  ions

b. Real sample analysis was conducted to determine the  $\text{Ca}^{2+}$  ion activity in the samples of horticulture drain water. The results are presented in Table 4. In parallel, the same samples were also tested by employing atomic absorption spectroscopy (AAS) so that the values could

be compared. The experiments were run five times and the values have been reported. A perusal of data suggests that the results are in good agreement. Therefore, the proposed sensor can be used to determine  $\text{Ca}^{2+}$  ion activity in real samples.

**Table 4.** Water sample analysis results for the potentiometric determination of calcium ions

| S. No. | $\text{Ca}^{2+}$ ion activity (ppm) using Sensor no. 10 | AAS results (ppm) |
|--------|---|-------------------|
| 1      | 14.832±0.04   | 15.67±0.02        |
| 2      | 23.97±0.06  | 24.82±0.01        |
| 3      | 36.56±0.03  | 39.66±0.01        |
| 4      | 11.84±0.04  | 12.43±0.02        |

#### 4. CONCLUSION

An all-solid-state sensor incorporating 4,7-diaza-2,3,8,9-dibenzo-15-crown-5 as a neutral carrier, TEP as a solvent mediator, NaTPB anion excluder, and MWCNT in PVC [10:50:3:3:100] w/w, was developed to determine  $\text{Ca}^{2+}$  ions. This sensor exhibits a concentration range of  $1.6 \times 10^{-7}$ - $1.0 \times 10^{-1}$  M with a detection limit of  $9.1 \times 10^{-8}$  M. The working pH range is 3.5-7.0 and it don't suffer with interference caused by other metal ions, in the estimation of calcium ions. The response time is 10 s while the lifetime of this sensor is six weeks in aqueous as well as in partially non-aqueous medium. It worked well as an indicator electrode in the potentiometric titration of  $\text{Ca}^{2+}$  ions against EDTA solution. In addition, it was successfully used in the real sample analysis and the obtained results were confirmed with AAS.

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