



Research Article

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Highly selective monohydrogen phosphate anion sensor for $[\text{CrL}](\text{NO}_3)_3$

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ABSTRACT

Spectroscopic studies of the interaction between Chromium Nitrate complex of the ligand, 3,4,5,13,14,15-hexamethyl-2,6,12,16,21,22-hexaazatricyclo [15.3. 1¹⁻¹⁷ 1⁷⁻¹¹]dicosane-1 (21),2,5,7,9,11(22),12,15,17,19-decaene shown in [figure 1] showed a selective interaction between complex and monohydrogen phosphate anion respect to the other anions tested. The sensor worked well with a wide working concentration of $1.0 \times 10^{-1} \text{ M} - 4.0 \times 10^{-7} \text{ M}$, detection limit of $2 \times 10^{-7} \text{ M}$ and a Nernstian slope of $-28.6 \pm 0.3 \text{ mV}$ per decade. The electrode had relatively short response time, less than 15s.

INTRODUCTION

The products containing phosphate are widely used in many areas of human activities such as fertilizers and detergents. Owing to phosphate leaching into lakes and rivers, phosphate levels in the environment have increased in the past 50 years [1]. The species containing phosphate in underground water reservoirs can contribute to eutrophication and make unsafety for human consumption. The need for an analytical procedure for the monitoring and routine analysis of phosphate is thus necessary.

Although the potential applications in environmental and biomedical research have led to great interest in the design and synthesis of abiotic ionophores for phosphates and their derivatives, it still remains a challenge to achieve a useful selectivity for very hydrophilic phosphate anions over hydrophobic anions. This is due to the difficulty in compensating large differences in Gibbs free energies of transfer between phosphates and interfering anions by selective complexation [2]. In recent decade some PVC membrane electrodes prepared with complex carriers have been developed [3-14] with Nernstian slope.

In this work, we describe $[\text{CrL}](\text{NO}_3)_3$ [Figure1] as a novel ionophore used in PVC polymeric phosphate selective electrodes.

EXPERIMENTAL SECTION

Reagents and Instruments

High molecular weight PVC and plasticizers such as benzyl acetate (BA), nitrobenzene (NB), dibutyl phthalate (DBP), acetophenone (AP), hexadecyltrimethylammonium chloride (HTAC), tetrahydrofuran (THF) were purchased from Fluka and used as received. Metallic salts used (all from Merck, Aldrich), were of the highest purity and used without any further purification except for vacuum drying over P_4O_{10} . Triply distilled water was thoroughly used.

Potentials were measured with digital potentiometer EQ-602 Equiptronics (accuracy, 0.001 V, India). The pH measurements were carried out on digital pH meter (Lab India pH Conmeter, India). Auto ranging Conductivity meter/TDS meter TCM-15 (Toshniwal Instruments Mfg. Pvt. Ltd Ajmer).

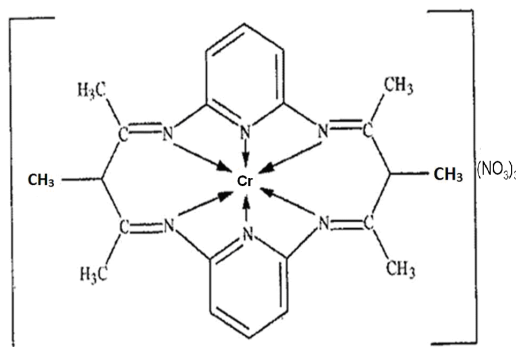


Figure1 Ionophore [CrL](NO₃)₃

Electrode preparation.

Different compositions of membrane ingredients, including ionophore, the plasticizers DBP, BA, AP, the additive HTAC and PVC (**Table1**), were thoroughly dissolved in 10 ml THF. The resulting solution was carefully cast in to a glass dish of 2 cm diameter for slow evaporation at room temperature to obtain membrane of about 0.3 mm thickness with optimum composition and behavior. The membrane was cut and pasted to the one end of pyrex tube with the help of araldite. The electrode was then filled with an internal solution of 1.0×10^{-2} M MHP. The prepared electrodes were finally conditioned by soaking in a 1.0×10^{-2} M MHP solution for 24 h.

Emf measurements

All emf measurements were carried out with the following assembly:

Hg|Hg₂Cl₂, KCl (satd.) ||sample solution | membrane | internal solution 1.0×10^{-2} mol L⁻¹ MHP| Ag-AgCl.

The performance of each electrode was investigated by measuring its potential of the primary ion solutions in the range of 1.0×10^{-1} M to 1.0×10^{-7} M. The solutions were stirred and potential readings were recorded when they reached steady state values. The data were plotted as observed potential versus the logarithm of the anions activity. The detection limit was determined according to IUPAC recommendations.

Calculation of the activity of the phosphate species in solution required values of the total phosphate concentration $[H_xPO_4^{(x-3)}]_{Tot}$, the solution pH, and ionic strength. Phosphate exists in the form of four species in solution: H₃PO₄, H₂PO₄⁻, HPO₄²⁻ and PO₄³⁻. The total phosphate concentration $[H_xPO_4^{(x-3)}]_{Tot}$ can be calculated as $[H_xPO_4^{(x-3)}]_{Tot} = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$

The fraction of each species can be determined by the pH values of the solution. The ionic strength can be estimated by the concentration of different species existing in a solution. The activity coefficients are then calculated by using the extended Debye-Huckel equation.

RESULTS AND DISCUSSION

Potential Response

The selectivity behaviour of a certain ion selective sensor is greatly dependent on the ionophore used [15-22]. According to the structural characteristics [CrL](NO₃)₃ [Figure1] was used as suitable active component in the fabrication of a number of PVC-membrane sensors for a wide variety of common inorganic anions including chloride, bromide, iodide, nitrate, sulfite, sulfate, carbonate, perchlorate, cyanide, thiocyanate, dihydrogen phosphate, tetrasodium pyrophosphate, and sodium tripoly phosphate ions, the potential responses of which are shown in [Figure 2]. As can be seen from [Figure 2], while the slopes of the linear parts of the potential responses of the sensors for all other anions tested, are much lower than those expected by the Nernst equation, the resulting MHP potential response shows a near-Nernstian behavior.

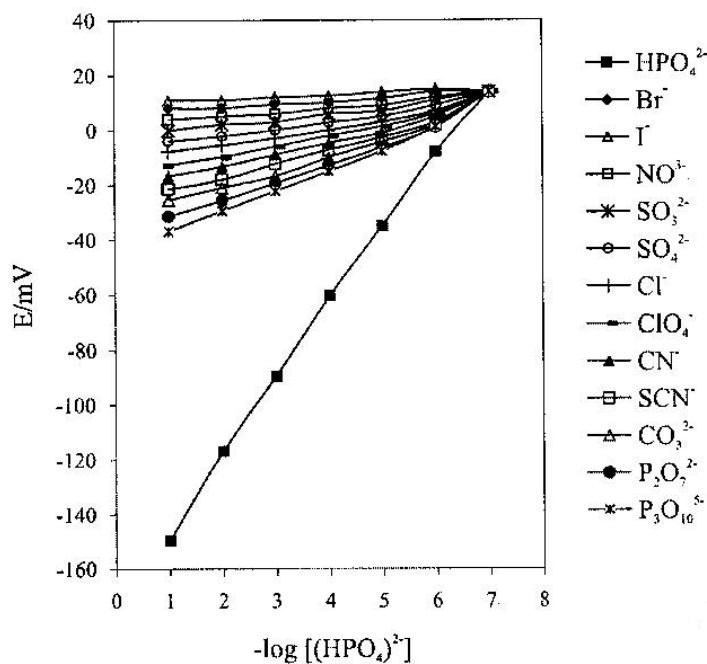


Figure 2 Potential response of different ion-selective electrodes based on $[\text{CrL}](\text{NO}_3)_3$.

UV-Vis study

The preferential response towards MHP is believed to be associated with the coordination of MHP with the central metal of the ion-carrier $[\text{CrL}](\text{NO}_3)_3$

UV-Vis spectra, of $1.0 \times 10^{-4} \text{ mol L}^{-1} [\text{CrL}](\text{NO}_3)_3$ in DMSO were obtained with and without the presence of $1.0 \times 10^{-4} \text{ mol L}^{-1} \text{HPO}_4^{2-}$ as illustrated in **Figure 3**, it was possible to distinguish the interactions between the central metal and MHP. The substantial increase in the absorbance at 214.2 nm after the contact of the carried solution with a monohydrate phosphate-containing phase suggested that the absorbing species had increased in size and axial coordination was thought to take place.

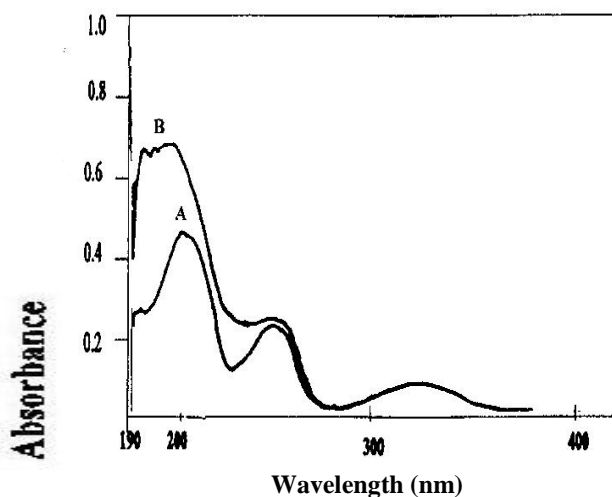


Figure 3 UV-Vis spectra of $1.0 \times 10^{-4} \text{ mol L}^{-1} [\text{CrL}](\text{NO}_3)_3$ in DMSO in the absence (A) and presence (B) of $1.0 \times 10^{-4} \text{ mol L}^{-1} \text{HPO}_4^{2-}$.

Effect of plasticizer

To compare the effect of the various plasticizers on response characteristics of the electrodes, the electrodes based on $[\text{CrL}](\text{NO}_3)_3$, prepared with DBP, AP, and BA were tested in HPO_4^{2-} solutions. **[Figure 4].**

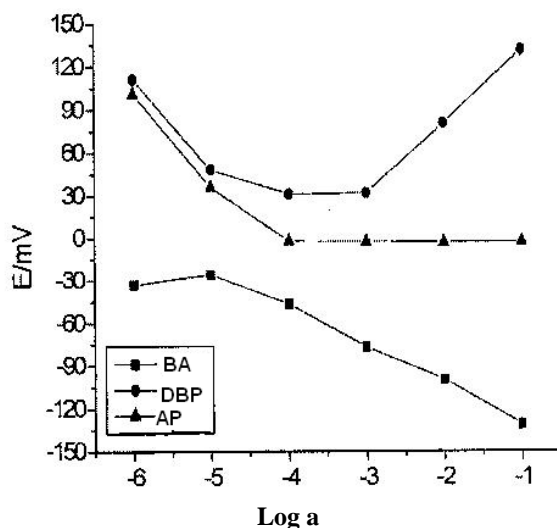


Figure 4 Potential response of HPO_4^{2-} ion-selective electrodes based on $[\text{CrL}](\text{NO}_3)_3$ in PVC membrane with different plasticizers.

The results in [Figure 4] show that the EMF responses to HPO_4^{2-} were strongly influenced by changes in the plasticizer. Membrane electrodes prepared with BA showed the widest linear range, Nernstian response and a very low detection limit. On the other hand, the use of AP and DBP as plasticizers led only to poor responses. The reason for these phenomena might be that the polarity of the plasticizer affects the response characteristics of the electrodes. The relatively non-polar AP and DBP result in a worse solvation of ionophore than BA.

Effect of membrane composition

It is well known that the sensitivity as well as selectivity and linearity of ISE are affected not only by the nature of ionophore but also significantly by membrane composition and nature of solvent mediator and lipophilic additive used [23-26, 50-55]. The composition of membranes with different proportional ingredients the performance and characteristics of the electrode are given in Table 1. Our experience on using several plasticizers including BA, AP and DBP for preparation of membrane showed that plasticizer BA perform best as it exhibits the widest working concentration range and near-Nernstian slope. Plasticizer influence both dielectric constant of membrane, mobility of ionophore enhance its interaction with HPO_4^{2-} ion. The effect of ionophore amount on the functioning of membrane was investigated. Membranes with different compositions were prepared and preliminary studies revealed that a membrane having a composition of 33:60:5:2 of PVC:BA:I:HTAC gave the best response characteristics (Table 1, membrane 6). Table 1 shows that if 2% of HTAC is present as a suitable additive, the slope of the proposed sensor increases from -15.3 (membrane 3) to -28.6 mV decade^{-1} (membrane 6).

Table 1. Composition of membrane ingredients.

| No. | Composition (%) | | | Ionophore | Slope No. |
|-----|-----------------|-------------|------|-----------|-----------------|
| | PVC | Plasticizer | HTAC | | |
| 1 | 33 | BA, 62 | -- | 5 | -12.9 ± 0.3 |
| 2 | 33 | BA, 63 | -- | 4 | -14.2 ± 0.3 |
| 3 | 33 | BA, 64 | -- | 3 | -15.3 ± 0.3 |
| 4 | 33 | BA, 62 | -- | 6 | -14.8 ± 0.3 |
| 5 | 33 | BA, 59 | 1 | 5 | -24.9 ± 0.3 |
| 6 | 33 | BA, 60 | 2 | 5 | -28.6 ± 0.3 |
| 7 | 33 | BA, 58 | 2 | 7 | -25.6 ± 0.3 |
| 8 | 33 | DBP, 58 | 2 | 7 | -26.2 ± 0.3 |
| 9 | 33 | AP, 58 | 2 | 7 | -25.8 ± 0.3 |
| 10 | 33 | BA, 65 | 2 | -- | -3.6 ± 0.30 |

Working concentration range and slope

The measuring range of ion selective electrodes refers to the linear part of the calibration graph. According to IUPAC definition, the measuring range of an ion selective electrode is defined as the activity range between the upper and lower detection limits [27-46]. The potential response of the membranes as a function of MHP activity is

shown in [Figure 5]. It is seen that membrane 6 shows a wide working concentration range (1.0×10^{-1} - 4.0×10^{-7} mol L⁻¹) with a detection limit of 2×10^{-7} mol L⁻¹ (~ 20 mg mL⁻¹), and a Nernstian slope of -28.6 ± 0.3 mV per decade of activity.

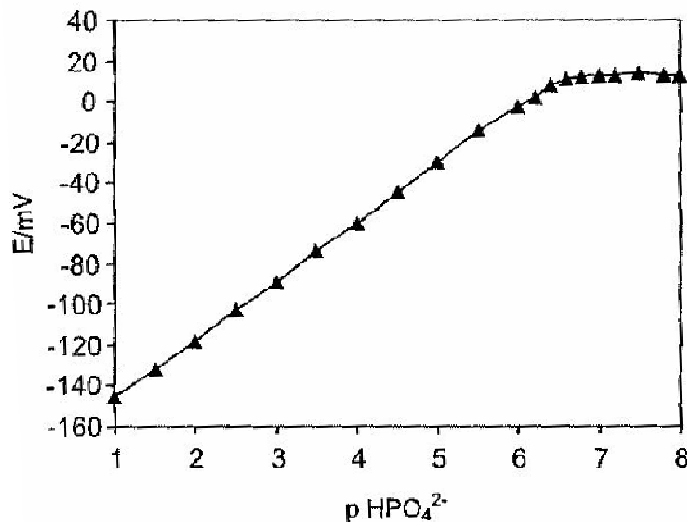


Figure 5 Calibration curves of MHP electrode based on [CrL](NO₃)₃ Optimization of pH.

The pH dependence of the membrane electrode prepared with membranes containing ionophore [CrL](NO₃)₃ was tested over the pH range of 1-12 in a 1.0×10^{-4} M HPO₄²⁻ solution. The results are shown in [Figure 6]. The results show that the potentials remain constant within a pH range of approximately 3.0 to 7.0 for sensor. Variation of the potential at pH < 3 could be related to protonation of HPO₄²⁻ in the solution and ionophore in the membrane phase, which results in a loss of its ability HPO₄²⁻ to interact with the ionophore. At higher pH > 7, the potential drop may be due to interference of hydroxide ions and formation of phosphate species.

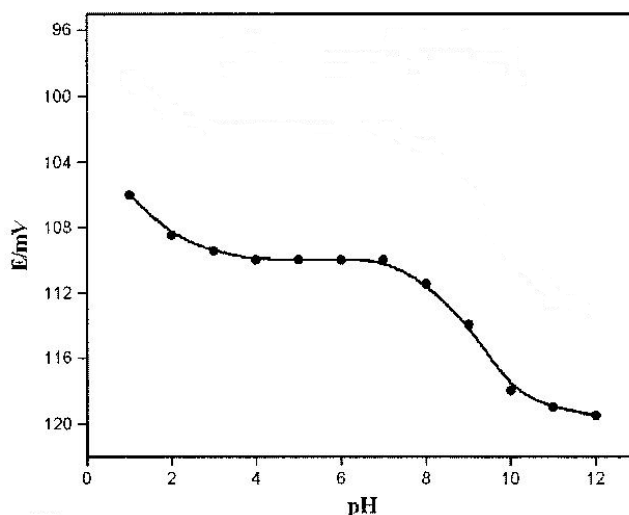


Figure 6 Effect of pH on the potential response of [CrL](NO₃)₃ at 1.0×10^{-4} M concentration of HPO₄²⁻ ion.

Lifetime and reproducibility of the sensor

The membranes were used over a period of eight weeks without showing any significant changes in the slope and detection limit of the sensor. During usage, the membranes were stored in 0.01 mol L⁻¹ MHP solution and were reequilibrated with 0.1 mol L⁻¹ MHP solution whenever any drift in potentials was observed (Table 2). Repeated monitoring of potentials (20 measurements) at 1.0×10^{-3} mol L⁻¹ concentration gave a standard deviation of 0.4 mV.

| Period(weeks) | Slope(mV decade ⁻¹) | Detection Limit |
|---------------|---------------------------------|------------------------|
| 1 | -28.6 ±0.2 | 2.0 × 10 ⁻⁷ |
| 2 | -28.6 ±0.1 | 2.0 × 10 ⁻⁷ |
| 3 | -28.5 ±0.5 | 3.0 × 10 ⁻⁷ |
| 4 | -28.3 ±0.4 | 4.0 × 10 ⁻⁷ |
| 5 | -28.2 ±0.3 | 4.0 × 10 ⁻⁷ |
| 6 | -28.2 ±0.3 | 6.5 × 10 ⁻⁷ |
| 7 | -28.1 ±0.2 | 8.0 × 10 ⁻⁷ |
| 8 | -27.9 ±0.5 | 9.0 × 10 ⁻⁷ |
| 9 | -28.8 ±0.4 | 2.0 × 10 ⁻⁶ |
| 10 | -28.4 ±0.3 | 3.0 × 10 ⁻⁶ |

Dynamic response time

Dynamic response time is one of the important factors for any ion-selective electrode [44-49]. In this study, the practical response time was recorded by changing the MHP concentration in solution; over a concentration range $1.0 \times 10^{-1} \text{ mol L}^{-1}$ to $1.0 \times 10^{-6} \text{ mol L}^{-1}$. The actual potential versus time traces is shown in [Figure 7]. As can be seen from [Figure 7], in the whole concentration range, the electrode reaches its equilibrium response in a very short time (<15 s). This is most probably, due to the fast exchange kinetics of complexation-decomplexation of MHP ion with the $[\text{CrL}](\text{NO}_3)_3$, at the test solution-membrane interface.

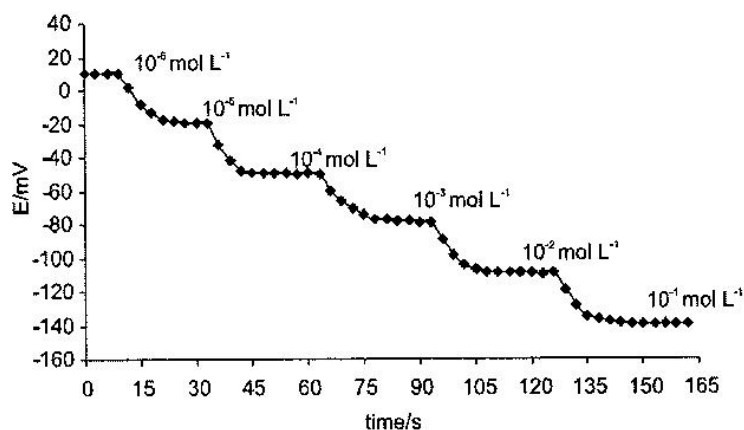


Figure 7 Dynamic response time of the potentiometric sensor for different concentration of monohydrogen phosphate.

| | |
|--------------------------------|---|
| Linear range / M | $1.0 \times 10^{-1} \text{ M} - 4.0 \times 10^{-7} \text{ M}$ |
| Slope / mVdecade ⁻¹ | -28.6 ± 0.3 mV decade ⁻¹ |
| pH range | 3.0-7.0 |
| Detection limit/M | $2 \times 10^{-7} \text{ mol L}^{-1}$ |
| Life time/month | > 2 |
| Response time/s | <15s |

Selectivity of the Electrodes

The most important characteristic of an ISE is its selectivity against the interested analyte ion over other ions in solution. The selectivity coefficients of an ISE can be measured by several experimental methods such as the fixed interference (FIM) and the separate solution (SSM) methods. Both of these methods are recommended for ions having the same charge as the primary ion [18] because coefficients calculated by these methods are either deceptively large or small depending on whether the ion of higher charge is considered as the primary or interfering species. In this study, potentiometric selectivity coefficients of the proposed sensor was determined by the modified fixed interference (FIM) [19].

In the FIM, the selectivity coefficients are commonly calculated using Nicolsky –Eisenman equation

$$K^{\text{pot}}_{A:B} = aA / (aB)^{Z_A/Z_B}$$

where aA is the activity of the primary ion and aB the activity of the interfering ion and Z_A and Z_B are the charges of the primary and the interfering ion, respectively. However, this equation is valid only if the charges on the primary ions aA and interfering ions aB are the same. So in this paper, the selectivity coefficients are calculated by the modified

Nicolsky –Eisenman equation proposed by Sa 'ez de Viteri *et al.* [20].

$$K^{\text{pot}}_{A:B} = aA / aB$$

In this method, the concentration of the interfering ion was kept at 1.0×10^{-3} M. The resulting values obtained are listed in **Table 4**

It can be noticed that the electrodes are highly selective for HPO_4^{2-} over Cl^- , Br^- , Ac^- , NO_3^- , NO_2^- and SO_4^{2-} . The selectivity pattern for the electrodes is not consistent with the Hofmeister series. In addition, in most practical applications, interference by Cl^- seems to be the most important factor. From the corresponding selectivity coefficient, it can be seen that both of our electrodes response better to monohydrogenphosphate than to Cl^- .

| Table 4. Selectivity coefficients ($\log K^{\text{pot}}_{\text{MHP};B}$) for the HPO_4^{2-} ion-selective electrode. | |
|---|---------------------------|
| Interfering anion | Fixed Interference Method |
| | L |
| Cl^- | -1.25 |
| NO_3^- | -1.5 |
| Ac^- | -1.96 |
| SO_4^{2-} | -1.71 |
| Br^- | -1.34 |
| I^- | -0.44 |
| NO_2^- | -1.5 |
| CO_3^{2-} | -0.12 |
| SCN^- | 0.2 |
| ClO_4^- | 0.24 |

Analytical application

The membrane sensor was successfully used in the potentiometric titration of MHP with Ba^{2+} solutions. A 25.0 mL (1.0×10^{-4} mol L^{-1}) solution of MHP was titrated with 1.0×10^{-2} mol L^{-1} solution of Ba^{2+} [Figure 8]. As it is obvious from [Figure 8], the sharp break point corresponds to the stoichiometry of the MHP- Ba^{2+} precipitate (BaHPO_4). The equivalent volume is 250 μL .

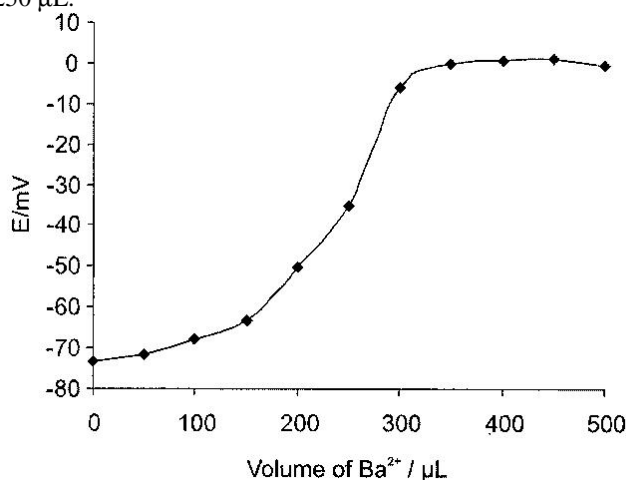


Figure 8

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