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Electrochemical Anion Sensor for Monohydrogen Phosphate Based on Nano-composite Carbon Paste

P. Norouzi[1,*], *M. R. Ganjali*[1], *F. Faridbod*[1], *S. J. Shahtaheri*[2], *H. A. Zamani*[3]

[1] Center of Excellence in Electrochemistry, University of Tehran, Tehran, Iran
[2] Department of Occupational Health, School of Public Health, Center for Environmental Research, Tehran University of Medical Sciences, Tehran, Iran
[3]Department of Applied Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Iran
[*]E-mail: norouzi@khayam.ut.ac.ir

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Spectroscopic studies of the interaction between cerium acetylacetonate complex (CAA) and a number of inorganic anions showed a selective interaction between CAA and monohydrogen phosphate anion respect to the other anion tested. Therefore, CAA was used as a suitable ionophore (sensing element) in construction of a nano-composite carbon paste electrode. The nano-compoite paste was composed of 5% Multi-walled Carbon Nanotube (MWCNT), 65% graphite powder, 15% room temperature ionic liquid (RTIL) and 15% of CAA. The proposed electrode composition was selected after a series of experiments and optimizations. The sensor worked well with a Nernstian response of -29.3±0.4 mV decade^{-1} of HPO_4^{2-} anion in a wide dynamic concentration range of 1.0×10^{-6}-1.0×10^{-1} mol L^{-1}. The electrode had relatively short response time (20 s), and it was found to produce stable responses for more than two months. It was also used for monitoring of monohydrogen phosphate ion concentration in waste water samples.

Keywords: Monohydrogen phosphate, Multi-walled Carbon Nanotube, Ionic liquid, Sensor, Ion selective electrode, Potentiometry

1. INTRODUCTION

Monohydrogen phosphate is one of the anions which play important roles in biological, environmental and many industrial processes. Phosphate levels in water have increased in recent years because of leaching from agricultural soil after wide use of phosphate fertilizers, which may have a negative effect on water quality [1,2].

There are some analytical methods for measurement of monohydrogen phosphate ion at low concentrations including UV–Vis spectrophotometric methods such as molybdenum blue, complex of molybdophosphate with basic dye compounds [3].

An alternative method for determination of monohydrogen phosphate ion is potentiometry using a selective electrode. Such methods are simple, low cost, accurate and rapid, which is the reason behind the increasing interest in them [4-16]. Carbon paste electrodes are a class of ion selective electrodes with a high physical stability, long lifetime, the versatility of chemical modification, miniaturization, and rapid renewal of the electrode surface [17-24].

Multi-walled carbon nanotubes (MWCNTs) have been recently used in the compositions of carbon paste electrodes [20-26] due to their extraordinary physicochemical properties, such as ordered structures with high aspect ratios, ultra-light weight, high thermal conductivity, metallic or semi-metallic behavior, high surface area, high electrical conductivity and remarkable mechanical strength [27, 28].

Ionic liquids are also a good choice as binder in carbon paste electrodes due to their interesting properties, such as stability, low vapor pressure, low toxicity, low melting temperature, ion-exchange properties, extraction and catalytic activity, high ionic conductivity and good electrochemical and thermal stability [20,21]. Recently, room temperature ionic liquids (RTILs) have been widely used as efficient pasting binders instead of non-conductive organic binders in preparation of carbon composite electrodes.

Carbon paste electrode based on MWCNTs and RTILs types of electrodes show superior performance over traditional carbon paste electrodes.

Solution studies shows a selective interaction between CAA and monohydrogen phosphate respect to a number of anions tested, therefore, the complex was used as sensing material in construction of a HPO_4^{2-} nano-composite carbon paste sensor based on MWCNTs and RTILs.

2. EXPERIMENTAL SECTION

2.1. Equipments

A glass cell where the carbon paste electrode was used consisting of an R684 model Analion Ag/AgCl double junction electrode as a reference electrode. A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at 25.0±0.1 °C.

2.2. Reagents

Graphite powder with a <50 μm particle size (Merck), and 2.2 g/cm^3 density; along with the paraffin oil (Aldrich) of the highest purity, and 1-n-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF_4, were used for the preparation of the carbon pastes. The multi-walled carbon nanotubes (MWCNTs) with 10-40 nm diameters, 1-25 μm length, core diameter: 5-10 nm, SBET: 40-600 m^2/g, V_{total}: 0.9 cm^3/g, bulk density 0.1 g/cm^3, true density 2.1 g/cm^3 and with 95% purity were purchased from a local company (Iran). The sensing element, cerium acetylacetonate complex (CAA), $Ce(CH_3COCH_2COCH_3)_3$, was purchased from Aldrich. The monohydrogen phosphate solution was prepared by solving K_2HPO_4 in distilled water and adjusting the pH of the solution at first is about 9.5 and by using some amount of phosphoric acid to the solution the pH adjusted to 8.

2.3. Fabrication of nano-composite based monohydrogen phosphate sensor

Various amounts of CAA, graphite powder, 1-n-butyl-3-methylimidazolium tetrafluoroborate $[bmim]BF_4$ or paraffin, and MWCNTs were thoroughly mixed. The resulting mixtures were transferred into a glass tube. The electrode body was fabricated from a glass tube of 5 mm i.d. and a height of 3 cm. After the mixture was homogenized, the paste was carefully packed into the tube tip to avoid possible air gaps, often enhancing the electrode resistance. A copper wire was inserted into the opposite end to establish electrical contact [20-26]. The external electrode surface was smoothed with soft abrasive paper to produce a new surface and replacing the carbon paste. The electrode was finally conditioned for 48 h by soaking in a 1.0×10^{-3} M K_2HPO_4 solution.

2.4. Emf measurements

The electrochemical cell can be represented as follows:

Ag, AgCl(s), KCl (3 M) || sample solution | nano-composite carbon paste electrode

Calibration graph was drawn by plotting the potential, E, versus the logarithm of HPO_4^{2-} ion concentration.

3. RESULTS AND DISCUSSIONS

The selectivity behavior of a certain ion selective sensor is greatly dependant on the ionophore used [29-35]. Due to the affinity of CAA toward monohydrogen phosphate ion according to the solution study, the compound was taken to be a suitable ionophore in construction of a number of sensors with different composition and modification. There are some reports on monohydrogen phosphate in the literatures which are all potentiometric sensors based on PVC membrane electrodes. The proposed sensor in this work is a carbon paste electrode. It is superior to the best previously reported monohydrogen phosphate ion selective membrane electrodes in the case of lifetime, mechanical stability, and selectivity [36-38]. Also, the selectophore used here is a commercial one which is easily available. In addition working and preparation of a carbon paste electrode is more easily than PVC membrane electrodes. By polishing the surface of the electrode, a new electrode can be produced.

3.1. Electrode composition and modification

To assess the performance of the electrode, different compositions were made according to Table 1. As it can be seen, paste composition no. 3 revealed that the optimum amount of CAA should be 15%. In this case the traditional carbon paste electrode showed a near Nernstian slope of about -19.7 mV decade^{-1} in the absence of any modifier.

Replacement of paraffin oil, an organic binder, with RTIL, improved the sensitivity of the sensor to a near-Nernstian slope (no. 7). Enhancement of the electrochemical behavior of RTIL based electrodes can be related to its enhanced conductivity. Because of the good solubility and high viscosity, the IL can form a layer on the carbon particles and can fill in the empty spaces between carbon particles, so the conductivity of the IL-based electrodes was greatly enhanced compared to the traditional CPE. Also, RTIL can be a better solvent and extract the analyte from the solution to the electrode surface.

Because of the high conductivity of MWCNT, its addition to the composition of the carbon paste was expected to increase the dynamic working range and response time of the sensor. Addition of 5% of MWCNT to the composition was found to increase the response to a Nernstian slope of about -27.1 mV decade^{-1} (no. 11).

Table 1. The optimization of the carbon paste ingredients

CPE No.	binder	CAA	Graphite Powder	MWCNTs	Slope (mVdecade^{-1})	Linear Range (M)	R^2
1	Paraffin-15%	5%	80%	-	-15.8±0.4	1.0×10^{-5}-1.0×10^{-2}	0.912
2	Paraffin-15%	10%	75%	-	-16.3±0.3	1.0×10^{-5}-5.0×10^{-2}	0.933
3	Paraffin-15%	15%	70%	-	-19.7±0.3	5.0×10^{-6}-1.0×10^{-2}	0.952
4	Paraffin-15%	20%	65%	-	-19.6±0.3	5.0×10^{-6}-1.0×10^{-2}	0.947
5	Paraffin-20%	15%	65%	-	-16.0±0.5	2.0×10^{-5}-1.0×10^{-2}	0.887
6	Paraffin-10%	15%	75%	-	-10.7±0.6	5.0×10^{-5}-5.0×10^{-3}	0.792
7	RTIL-15%	15%	70%	-	-24.8±0.3	1.0×10^{-6}-5.0×10^{-2}	0.976
8	RTIL-20%	15%	65%	-	-23.6±0.4	1.0×10^{-6}-1.0×10^{-2}	0.968
9	RTIL-10%	15%	75%	-	-20.8±0.3	5.0×10^{-6}-5.0×10^{-3}	0.921
10	RTIL-15%	15%	67%	3%	-27.5±0.4	1.0×10^{-6}-5.0×10^{-1}	0.984
11	RTIL-15%	15%	65%	5%	-29.3±0.4	1.0×10^{-6}-1.0×10^{-1}	0.998
12	RTIL-15%	15%	63%	7%	-28.7±0.5	3.0×10^{-6}-1.0×10^{-1}	0.989
13	RTIL-15%	-	80%	5%	-3.8±0.6	5.0×10^{-4}-1.0×10^{-3}	0.554

Therefore, the composition containing 15% CAA, 5% MWCNT, 15% RTIL and 65% graphite showed the best performance with a Nernstian slope of -29.3 mV decade^{-1} (no. 11). According to Table 1, the electrode having the best composition but lacking the ionophore (no.13) showed a very low potential response.

3.2. Calibration curve

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 [39-43]. The applicable measuring range of the modified sensor as shown in Fig. 1 was found to be between 1.0×10^{-6}-1.0×10^{-1} M. By extrapolating the linear parts of the ion selective calibration curve, the detection limit of an ion selective electrode can be calculated. In this work the detection limit of the sensor is 7.9×10^{-7} M which was calculated by the extrapolating of the two segment of the calibration curve in Fig. 1.

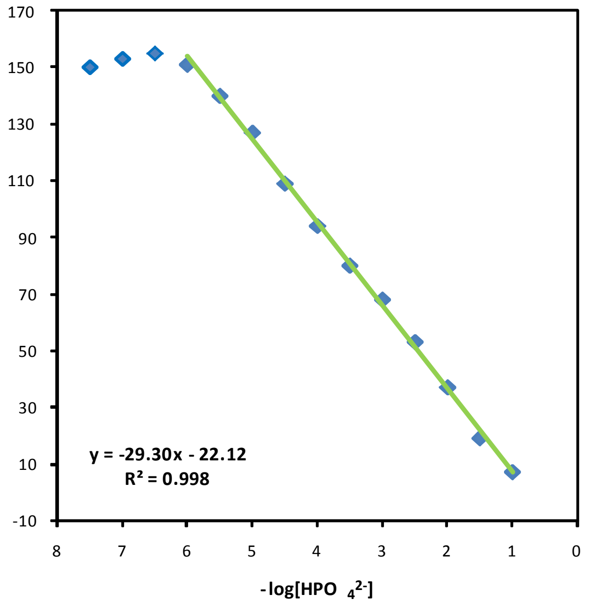

Figure 1. The calibration curve of the HPO_4^{2-} nano composite based sensor with the sensor no. 11

3.3. pH effect on the electrode response

In order to investigate the effect pH on the potential response of the sensor, the potentials were measured at a fixed concentration of HPO_4^{2-} ion (1.0×10^{-4} M) having different pH values. The pH was altered from 3-12 by adding HNO_3 or NaOH. The variations of the potential response of the best sensor as a function of pH showed the potential of electrode is constant between pH values of 8.0-9.5. Thus, the electrode works satisfactorily in this pH range, and no interference from H^+ or OH^- is observed in the range. In this pH the dominant species of phosphate ion is hydrogen monophosphate ion. The fluctuations above pH value of 9.5 might be due to the sensor response to OH^- ions in the solution. And the fluctuations below the pH value of 6.5, is most probably due to the formation of other form of phosphate ions.

3.4. Response time

The response time of an ion-selective electrode is also an important factor for any analytical application. The average response time of the electrodes, defined as the required time for the electrodes to reach a cell potential of 90% of the final equilibrium values, after successive immersions in a series of solutions, each having a 10-fold concentration difference [39-44] was found to be 20 seconds The resulting potential–time responses for the mentioned electrode were obtained by changing HPO_4^{2-} concentration from 0.000001 to 0.1 M (by fast injection of μL-amounts of a concentrated solution of HPO_4^{2-}). Results in Fig. 2 showed that the potentiometric response time of the electrode was about 20 s in whole concentration range.

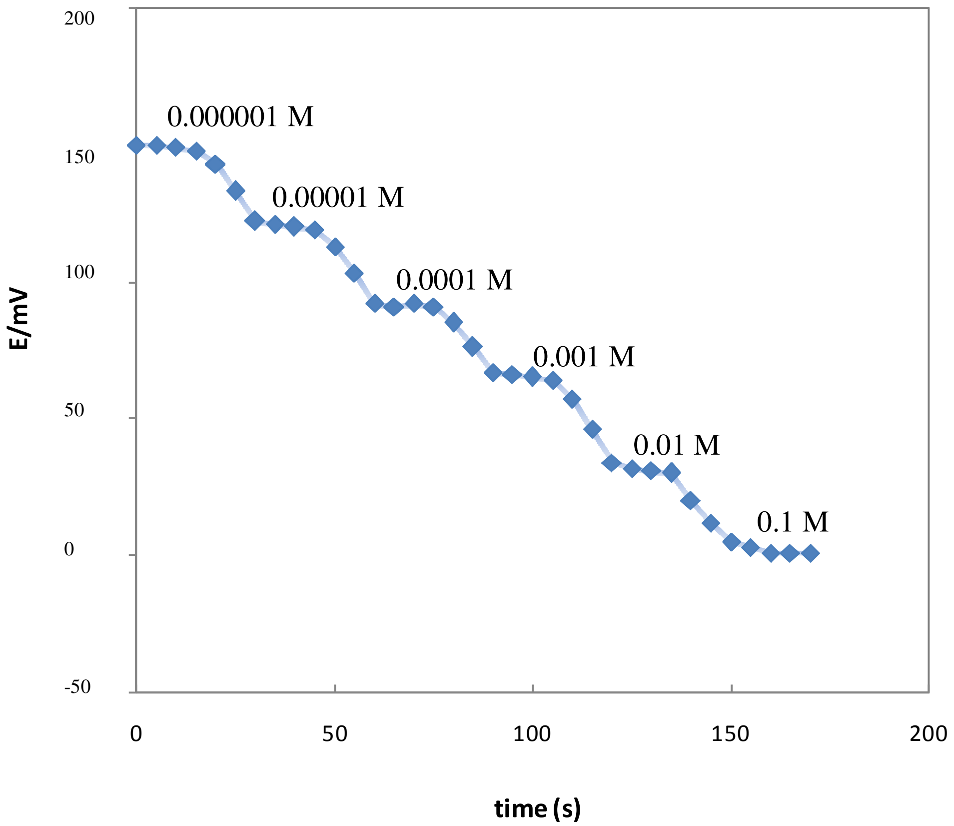

Figure 2. Dynamic response time of the HPO_4^{2-} nano composite based sensor with the sensor no. 11

3.5. Interference studies

Potentiometric selectivity coefficients, describing the preference of the suggested electrode for an interfering ion, X, with reference to the monohydrogen phosphate ion, HPO_4^{2-}, were determined by the matched potential method (MPM) [45-49]. The MPM is recommended by IUPAC to overcome the difficulties associated with the methods based on the Nicolsky–Eisenman equation.

According to this method, the specified activity (concentration) of the primary ion is added to a reference solution (0.000001 M HPO_4^{2-} ion, in this case) and the potential is measured.

In a separate experiment, interfering ions (X) are successively added to an identical reference solution, until the measured potential matched that obtained before the addition of the primary ions. The matched potential method selectivity coefficient, $k_{A,X}^{MPM}$ is then given by the resulting primary ion to the interfering ion activity (concentration) ratio, $k_{A,X}^{MPM} = \Delta a_{HPO4}{}^{2-}/a_X$.

The resulting values for HPO_4^{2-} sensor are listed in Table 2. As it can be seen from Table 2, anions tested have not significance interfere in the monitoring of monohydrogen phosphate ion.

Table 2. Selectivity coefficients of various interfering anions for the electrode no. 11

Interference (x)	$k_{A,X}^{MPM}$
Cl^-	3.2×10^{-4}
Br^-	4.0×10^{-4}
I^-	3.4×10^{-4}
NO_2^-	6.3×10^{-4}
NO_3^-	2.3×10^{-4}
SO_4^{2-}	5.5×10^{-4}
ClO_4^-	1.7×10^{-4}
ClO_3^-	2.4×10^{-4}
CH_3COO^-	7.6×10^{-4}
$C_2O_4^{2-}$	6.5×10^{-4}
SCN^-	3.0×10^{-4}
PO_4^{3-}	1.2×10^{-3}
$H_2PO_4^-$	5.4×10^{-3}
CrO_4^{2-}	3.8×10^{-4}
S^{2-}	1.0×10^{-4}

3.6. Lifetime

Lifetime of the nano-composite electrode was studied by periodically recalibrating and using the electrode to measure its potentiometric response to HPO_4^{2-} ion in standard monohydrogen phosphate ion solutions in a period of time. After the conditioning step the electrodes were repeatedly calibrated three times a day during a period of two months (the electrode worked one hour a day). Before eight weeks no significant change in the performance of the electrode was observed. This shows that the lifetime of the proposed electrode was about 8 weeks.

3.7. Monohydrogen phosphate ion analysis in water samples

The proposed nano-composite based monohydrogen phosphate sensor was applied for monitoring of monohydrogen phosphate ion concentration in waste water samples. The monohydrogen phosphate sensor was used for the direct monitoring of phosphate ions in the waste-water samples of monocalcium phosphate industry (Iran). Two milliliters of each sample was taken and dissolved in distilled water in a 100-ml volumetric flask. To this solution 5.0 ml of 0.1M EDTA (pH of 10.0) was added to the flask and diluted to the mark with distilled water. The concentration of each sample was measured by the monohydrogen phosphate sensor, using the calibration method. The results obtained by the direct potentiometry and spectrophotometry (colorimetry molybdenum blue) are depicted in Table 3. As can be seen, there is a good correlation between the both methods.

Table 3. Determination of HPO_4^{2-} ion in waste water samples; the results are based on triplicates measurements.

Sample	HPO_4^{2-} ion concentration CPE	Spectrophotometry
1	65.2±0.4 ppm	64.7±0.3 ppm
2	56.4±0.3 ppm	55.8±0.3 ppm
3	53.3±0.4 ppm	3.4 52.6±0.2 ppm
4	63.5±0.3 ppm	3.4 62.3±0.3 ppm
5	61.6±0.5 ppm	61.4±0.3 ppm

4. CONCLUSION

A new HPO_4^{2-} nano-composite carbon paste electrode was introduced. The electrode based on cerium β-diketon complex, MWCNT and RTIL exhibits linear response over a wide concentration range with a Nernstian slope, and a short response time of about 20 s. The present sensor can be used over the pH range of 8.0-9.5. Also it was successfully used in monohydrogen phosphate ion analysis in waste water samples. The results obtained by the direct potentiometry and spectrophotometry are in a good agreement.

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