Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Highly Selective Detection of Titanium (III) in Industrial Waste Water Samples Using Meso-octamethylcalix[4]pyrrole-Doped PVC Membrane Ion-Selective Electrode

Saeid Ahmadzadeh[a,*], Majid Rezayi[b], Ehsan Faghih-Mirzaei[c], Mehdi Yoosefian[d], Anuar Kassim[e]

[a] Pharmaceutics Research Center, Institute of Neuropharmacology, Kerman University of Medical Sciences, Kerman, Iran
[b] Chemistry Department, Faculty of Science, University Malaya, 50603 Kuala Lumpur, Malaysia
[c] Department of Medicinal Chemistry, Faculty of Pharmacy, Kerman University of Medical Sciences, Kerman, Iran
[d] Department of Chemistry, Graduate University of Advanced Technology, Kerman, Iran
[e] Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

ABSTRACT

A novel Ti^{3+} selective membrane electrode based on meso-octamethylcalix[4]pyrrole (OMCP) as an ionophore was successfully fabricated. The developed sensor revealed high selectivity towards Ti^{3+} ion over alkali, alkaline earth and transition metal cations. Among all of the membranes examined, the membrane with a composition of 4:33:62.8:0.2 mg of I:PVC:DOP:NaTFPB showed the best Nernstian slope of 29.49 ± 0.16 (mV per decade of activity) over the pH range from 1 to 3 with a satisfactory concentration range of 1.0×10^{-6} M to 1.0×10^{-2} M and detection limit of 8.0×10^{-7} M. The effects of various parameters such as composition of the membrane, different cation interferences and concentration of internal solution were investigated. The developed sensor exhibited a good reproducibility over a useful life time of about 3 months with a fast response time of 25 seconds. It demonstrated good analytical performance for accurate determination of Ti^{3+} trace amount in the presence of considerable concentration of common interfering ions. The fabricated sensor was used successfully as an indicator electrode for potentiometric titration of a titanium solution with EDTA and moreover it applied for direct determination of Ti^{3+} content of industrial waste water samples. The obtained results from optimized membranes were evaluated by comparing them with the data received from instrumental methods such as UV–Vis, AAS, ICP and SEM. By using density functional theory (DFT) calculations, several special adsorption sites of $TiOH^{2+}$ close to OMCP are fully optimized and the best one selected. Furthermore, NBO and QTAIM analysis carried out to study the bonding strength in formed complex and deep understanding of the nature of interaction between $TiOH^{2+}$ and OMCP.

© 2015 Published by Elsevier Ltd.

1. Introduction

Ion selective electrodes (ISEs) allow the potentiometric sensing of the activity of specific ions in the presence of other ions in aqueous and non-aqueous solutions. They measure the activity rather than the concentration and are not affected by turbidity or sample colour. The ISEs' advantages of simple preparation, easy application, fast response time, comparative low cost, capability of miniaturization, wide dynamic range with significant low detection limit even to ppb and ppt levels, portability for *in situ* measurements and durability for continuous monitoring in environmental, agricultural, industrial and clinical fields, has encouraged the persistent development of this research area [1–4].

In order to obtain highly selective polymeric membrane ISEs, suitable ionophores must be doped into the fabricated PVC membranes. The used ionophore, meso-octamethylcalix[4]pyrrole (OMCP) is a bowel shaped supramolecular compound which can bind selectively to the target ion and acts as an ion carrier in the membrane (see Fig. 1).

In the present study, OMCP is used to fabricate a novel highly selective membrane sensor towards Ti^{3+} cation. Calixarenes chemistry includes the study of non-covalent intermolecular interactions, which are mostly weak and reversible in nature. Calixarene derivatives construct complex through coordination

* Corresponding author. Tel.: +98 3431325241; fax: +98 3431325215.
E-mail addresses: chem_ahmadzadeh@yahoo.com,
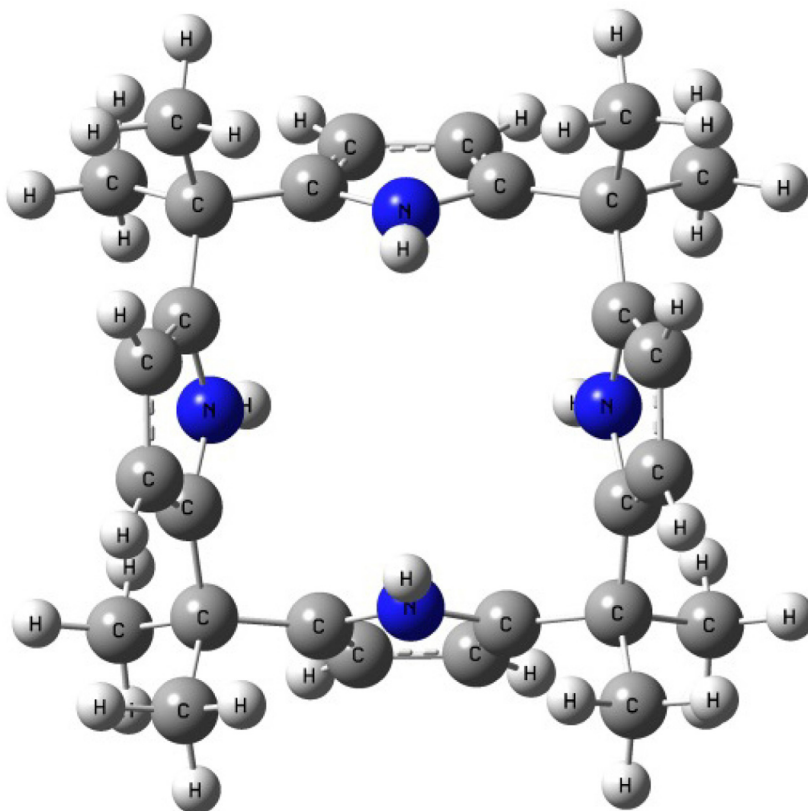saeid.ahmadzadeh@kmu.ac.ir (S. Ahmadzadeh).

Fig. 1. Chemical structure of meso-octamethylcalix[4]pyrrole.

bonds between the donor atoms such as oxygen, nitrogen or sulfur with the target cation, as well as π-coordination of the cation with the electron-rich aromatic rings [5–9]. Due to the ability of the calixpyrroles in binding to the cations through mentioned mechanism, OMCP is developed as a cation receptor in this study. So far only one report based on OMCP was found for thallium selective sensor [10], hence developing calixpyrroles as cation receptors can be regarded as a new and potential research area. The reported thallium electrode suffered from low selectivity and sensitivity as well as limited dynamic range and slow response time. Therefore, a new selective and sensitive electrode for Ti^{3+} which performs excellent electrode characteristics is developed in current study.

Titanium can be found abundantly in soils as it is a basic component of different types of rocks such as rutile, anatase, ilmenite, titanite and brookite. Owing to its distinctive characteristics, titanium has been highly commercialized in various sectors [11]. Generally, it is most demanded in aerospace industry since a lot of structural parts such as compressor case, turbine blades, discs, rings for jet engines and wing flap tracks are made by titanium [12]. As titanium has increasing industrial applications in different fields such as armor, automobile, biomedical and oil industries, it may lead to crucial environmental pollution if it is not removed effectively from waste water [13,14]. Hence, it demands more attention from scientists to develop an accurate method for selective determination of titanium concentration.

2. Experimental

2.1. Reagents and Materials

Meso-octamethylcalix[4]pyrrole (OMCP) as an ionophore and high molecular weight polyvinyl chloride (PVC) were purchased from Sigma–Aldrich. Four plasticizers, namely, dioctyl phthalate (DOP), dibutyl phthalate (DBP), 2-nitrophenyl octyl ether (o-NPOE), nitrobenzene (NB) and four lipophilic additives, namely, potassium tetrakis(4-chlorophenyl) borate (KTpClPB), sodium tetra phenyl borate (NaTPB), sodium tetrakis [3,5-bis (trifluoromethyl) phenyl] borate (NaTFPB) and tetradodecylammoniumtetrakis(4-chlorophenyl)-borate (TDATpClPB) were purchased from Sigma-Aldrich and Fluka. All nitrate and chloride salts with the highest available purity were purchased from Merck, Sigma–Aldrich, Fluka and Fisher Scientific. All reagents used in the current research were analytical reagent grade with the highest available purity and used without any further purification except for vacuum drying over P_2O_5. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) all from Merck were used for pH adjustments. In all cases, a 0.100 M stock solution of cationic salts was prepared by dissolving an appropriate and accurate amount of nitrate or chloride salts. All the pH of standard solutions were at 2.00 and all measurements for obtaining the calibration curve were carried out by pH adjustment in de-ionized water. Moreover, the solutions of cationic salts with concentration range from 1.0×10^{-6} M to 1.0×10^{-1} M were prepared daily by sequential dilution of the appropriate stock solution with de-ionized water.

2.2. EMF Apparatus

All EMF measurements were performed using presented assembly:

Ag/AgCl, KCl (3 mol L^{-1}) | sample solution | PVC membrane | internal solution of TiCl$_3$ (1×10^{-3} mol L^{-1}) | Ag/AgCl, KCl (satd.)

The potential and pH measurements carried out using Mettler Toledo combined pH electrode at room temperature (25 ± 1 °C) and Mettler Toledo Ion Meter (seven multi, Ion pH/mV/ORP).

A Perkin-Elmer Lambda spectrophotometer (model 1650PC Shimadzu) was used to obtain the optical absorption data which predicated on the complex reaction between ionophore and Ti^{3+} cation. A Perkin-Elmer emission spectrometer (model Optima 2000DV, sequential scanning inductively coupled plasma-atomic emission spectrometer ICP-AES) and a Thermo Scientific Atomic Absorption Spectrometry (AAS, model S Series, S_4) were used to validate the accuracy of the developed Ti^{3+} selective electrode by comparing the obtained data with the data acquired from AAS and ICP. Moreover, SEM studies of membrane morphology were performed using Jeol scanning electron microscope (Model JSM 6400 SEM).

Phase boundary model was employed to explain the mechanism of ISEs response and the modified Nicolsky–Eisenman equation was used to evaluate the response of the developed ISEs with any combination of target and interfering ion charge [15–17].

$$E = K_i + \frac{RT}{z_i F} \ln\left(a_{i,(ij)} + (K_{ij}^{Pot})^{\frac{z_i}{z_j}} a_{i,(ij)}^{1-\frac{z_i}{z_j}} a_{j,(ij)} \right) \tag{I}$$

Where a_i and a_j denote the activities of target ion (i) and interfering ion (j), respectively, in a mixed sample. z_i and z_j denote the charge of target ion (i) and interfering ions (j), respectively. T, R and F denote the absolute temperature in Kelvin, universal gas constant and Faraday's constant, respectively. The term K_{ij}^{Pot} represents the selectivity coefficient. And K_i represents all the constant potentials in the electrochemical cell measurement with such ISEs.

2.3. Membrane Preparation

The general procedure to prepare PVC membrane involved the thorough dissolving of 33.0 mg PVC as a polymeric matrix, 4.0 mg of OMCP as an ionophore, 62.8 mg of DOP as a plasticizer and 0.2 mg of NaTFPB as a lipophilic additive in 3 ml of fresh THF to acquire a homogenous solution. The solvent was evaporated slowly under inert atmosphere at room temperature, until an oily concentrated mixture was obtained. The dip-coating method was used to form the membrane. A Pyrex tube (with a tip diameter of 3 mm o.d) was dipped into the oily mixture for about 10 seconds. Then, the tube was pulled out from the mixture and kept at room temperature for ∼24 hours so that a non-transparent film of ∼0.3 mm thickness was formed. The tube was filled with the 1.0×10^{-3} M $TiCl_3$ internal solution. The electrode was finally conditioned for 24 hours by soaking in the same solution. Ag/AgCl reference electrode was used as the internal reference electrode.

3. Results and Discussion

3.1. Potentiometric Response Characteristics of Fabricated Ti (III) Selective Electrodes

In preliminary experiments, OMCP was used as an ion carrier to fabricate a number of PVC based membrane electrodes. The electrode was conditioned in 1.0×10^{-3} M solution of the corresponding cations for 24 hours. The potential responses of the fabricated electrode towards a extensive variety of metal ions including alkali, alkaline earth, transition metal ions over a wide concentration range of 1.0×10^{-6} M to 1.0×10^{-1} M were investigated and showed in Fig. 2. The obtained results reveals that titanium ion with the most sensitive response in compare to other cations was determined with the membrane electrode. Hence, OMCP was used as an ionophore for preparation of titanium-ISE for further studies.

Titanium exists in aqueous solution as $Ti(H_2O)_6^{3+}$ (pH < 1), $Ti(OH)(H_2O)_5^{2+}$ (1 < pH < 3), $Ti_2O(H_2O)_{10}^{4+}$ (pH = 3), $Ti(OH)_{3+x}$ (3 < pH) (x corresponding to the oxidation rate) and TiO_2 [11,18–20]. On
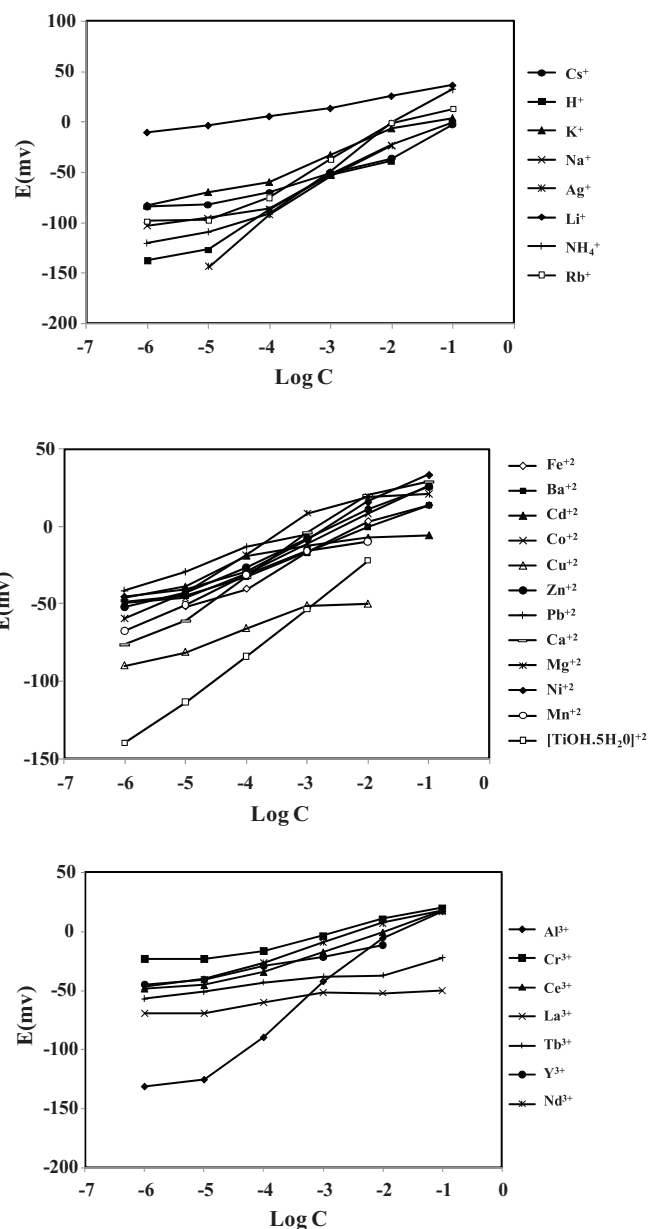

Fig. 2. The potential responses of the optimized PVC membrane sensor based on OMCP towards (a) monovalent, (b) divalent and (c) trivalent cations at 25 °C.

the other hand, Cassaignon et al. revealed that the process of dissolution and hydrolysis of titanium chloride (which was employed as a source of titanium in current study) is a multivariate process, in which the existence of each species relies on different variables such as pH, temperature and titanium concentration [11]. The obtained result confirmed that, in the pH range of 1 to 3, the main species of titanium in the solution is $Ti(OH)(H_2O)_5^{2+}$ which is in agreement with the Nernstian slope of 29.49 ± 0.16 (mV per decade of activity) for the double charged cationic species [21].

$$TiCl_3 + 6H_2O \leftrightarrow TiOH(H_2O)_5^{2+} + 2Cl^- + HCl$$
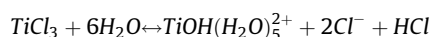
3.2. Optimization of Fabricated Selective PVC Membranes

Besides the importance of ionophore nature in constructing a selective membrane sensor, the sensitivity and selectivity of the fabricated selective PVC membranes are significantly affected by

Table 1
Optimization of the membrane composition to fabricate high Ti^{3+} selective electrode.

Sensor No.	I	PVC	Plasticizer				Lipophilic additive				Nernstian slope* (mV decade^{-1})	R^2	Response time (s)
			DOP	DBP	o-NPOE	NB	KTpClP	NaTFPB	TDATpClPB	NaTPB			
1	0	33.0	66.8	–	–	–	–	0.2	–	–	15.37 ± 0.36	0.996	N/A
2	3.0	33.0	63.8	–	–	–	–	0.2	–	–	28.79 ± 0.22	0.986	21
3	4.0	33.0	62.8	–	–	–	–	0.2	–	–	29.49 ± 0.16	0.999	15
4	5.0	33.0	61.8	–	–	–	–	0.2	–	–	33.42 ± 0.24	0.993	18
5	4.0	33.0	–	62.8	–	–	–	0.2	–	–	28.61 ± 0.36	0.990	17
6	4.0	33.0	–	–	62.8	–	–	0.2	–	–	32.67 ± 0.23	0.992	19
7	4.0	33.0	–	–	–	62.8	–	0.2	–	–	34.40 ± 0.27	0.991	16
8	4.0	33.0	62.0	–	–	–	–	1.0	–	–	38.31 ± 0.42	0.982	17
9	4.0	33.0	62.5	–	–	–	–	0.5	–	–	32.47 ± 0.29	0.998	18
10	4.0	33.0	63.0	–	–	–	–	0	–	–	26.90 ± 0.33	0.992	22
11	4.0	33.0	62.8	–	–	–	0.2	–	–	–	31.17 ± 0.23	0.999	17
12	4.0	33.0	62.8	–	–	–	–	–	0.2	–	26.48 ± 0.44	0.983	21
13	4.0	33.0	62.8	–	–	–	–	–	–	0.2	33.12 ± 0.26	0.991	19

*Average and standard deviation for triplet measurements.

the composition of membrane [22–24]. Therefore, effects of various parameters such as different amount of membrane ingredients as well as different type of plasticizers and lipophilic additives on the potential responses of fabricated selective electrodes were investigated.

As it is illustrated in Table 1, in order to optimize the characteristics performance of the fabricated electrode based on OMCP, membranes with different compositions were prepared and the potential responses of the electrodes towards Ti(OH)$^{2+}$ were obtained. The obtained results revealed that the sensitivity and selectivity of the fabricated electrode affected by the amount of ionophore in membrane [25,26]. The values of the slopes showed that the membranes with 4% of OMCP have the best Nernstian responses, with the slope and correlation coefficient of (29.49 mV per decade of activity, 0.999) towards Ti(OH)$^{2+}$ species. The membrane without ionophore did not have any significant potential response. On the other hand, optimized membranes with extra amount of ionophore are predicted to have super Nernstian responses.

The effects of different plasticizers on characteristics performance of the developed Ti^{3+} selective electrode were investigated and the obtained results were summarized in Table 1. It is noteworthy to mentioned that, the dielectric constant of membrane phase affected by the nature of used plasticizers and also the plasticizer has a very important role in optimizing the physical properties of PVC membrane as well as ensuring high mobility of ionophore and its complex in membrane [9,27]. DOP as a plasticizer provided the best electrochemical characteristics for the fabricated membrane with high selectivity and sensitivity towards Ti(OH)$^{2+}$ species.

The presence of lipophilic additive enhances the selectivity of the membrane by diminishing the anionic interference effects. It also improves the potential responses behavior of ISEs by reducing the response time and decreases the membrane ohmic resistance by increasing the cation extraction efficiency [6,27]. Therefore, in the current work the influence of the nature and amount of different lipophilic additives as an anion excluder on the potential responses of the fabricated electrodes were investigated. Among four different lipophilic additives which were applied, NaTFPB revealed better Nernstian response and linear dynamic range for Ti^{3+} selective electrode based on OMCP.

3.3. Characterization of the Fabricated Selective PVC Membrane

Scanning electron microscopy (SEM) techniques were used to investigate the surface morphology of the fabricated selective PVC membrane for distinguishing their surface characteristics such as

fouling and swelling [28]. As it is shown in Fig. 3, the fabricated membrane without OMCP reveals a physically tight structure (A), while the membrane with ionophore exhibited a physically permeable and loose structure that includes channels through which Ti(OH)$^{2+}$ species can diffuse (B) [15,16,28,29]. Furthermore, the physical appearance of the membrane shows swollen structure due to daily use over three months and stored in 1.0×10^{-3} M of TiCl$_3$ solution when not in use (C). Consequently, it causes a relative fluctuation in the Nernstian slope and detection limit of the electrode. The results obtained by SEM are in good agreement with the potentiometric response of electrodes.

The UV spectra absorption of OMCP with the concentration of 1.0×10^{-4} M, Ti^{3+} cation with the concentration of 1.0×10^{-3} M and their mixture (1:1) were recorded over 250 to 400 nm to investigate the strength of selective interaction between them. It is known that the ionic species which cause significantly change in spectrum result in higher potential responses and therefore have a better selectivity [30]. The absorption spectra as exhibited in Fig. 4 revealed that while Ti^{3+} shows a very wide absorption peak maximum in 260 nm, OMCP shows distinct absorption maximum at 219 nm. The presence of Ti^{3+} ions in the mixture leads to the decrease in intensity and shift of spectrum absorption to 211 nm. The obtained result confirmed the selective interaction between Ti^{3+} and OMCP in the fabricated selective PVC membrane.

3.4. Characterization of Fabricated ISE

The performance of Ti^{3+} selective electrode based on OMCP with respect to various parameters such as calibration graph, detection limit, repeatability, reproducibility, response time, life time and selectivity was characterized in details.

As it is illustrated in Fig. 5, the optimized electrode exhibited a linear potential response to the concentration of Ti(OH)$^{2+}$ species in the range of 1.0×10^{-6} M to 1.0×10^{-2} M with the Nernstian slope of 29.49 ± 0.16 mV per decade of activity. As it is clarified by the standard deviation value, the fabricated electrodes exhibited good stability and repeatability in potential responses with high accuracy and precision (see Table 2). By extrapolating the linear regions of the calibration graph to the base line potential, the values of 8.0×10^{-7} M and 2.0×10^{-2} M were obtained as lower and upper detection limit for fabricated electrode. Repeatability and reproducibility study of the fabricated electrodes were carried out over a wide concentration range of 1.0×10^{-6} M to 1.0×10^{-2} M of Ti^{3+} standard solutions. For repeatability studies, the same selective electrode were used for five times on the same day. The reproducibility studies were carried out by using five different
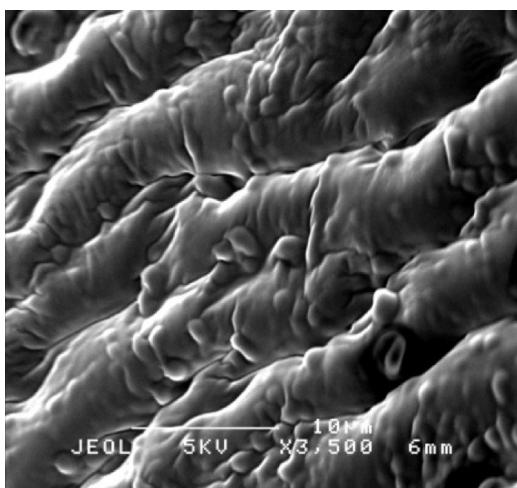
(A)
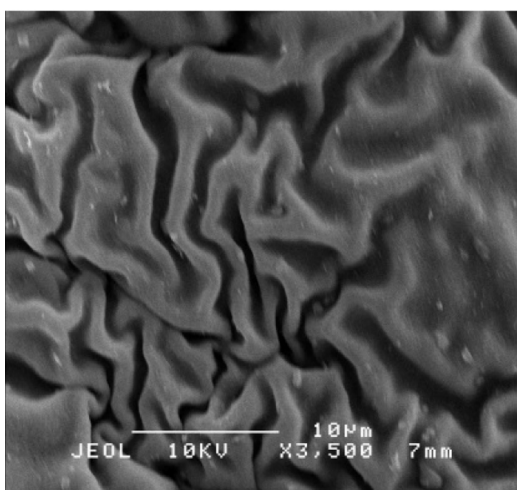
(B)
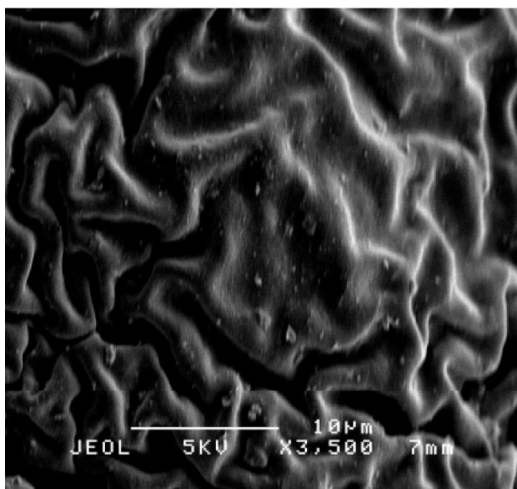
(C)

Fig. 3. Scanning electron microphotographs of Ti^{3+} selective PVC membrane: (A) membrane without ionophore that conditioned for one day, (B) membrane with ionophore that conditioned for one day and (C) membrane that conditioned for three months and used daily over the mentioned period.
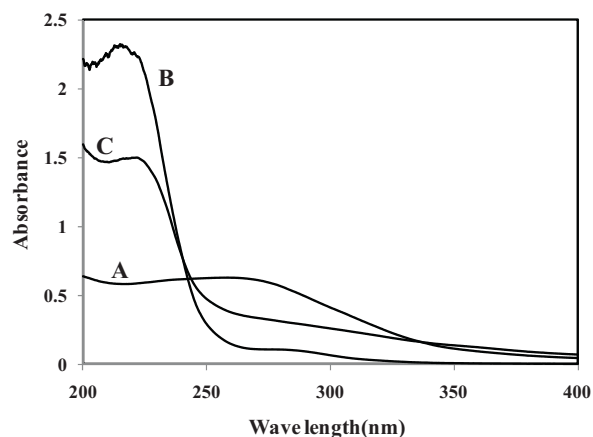

Fig. 4. UV–Vis absorption spectra: (A) 1.0×10^{-4} M Ti^{3+}, (B) 1.0×10^{-4} M OMCP and (C) mixture of ionophore and cation.
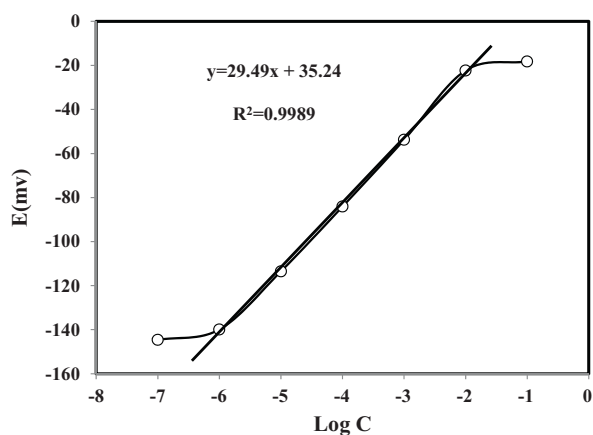

$y = 29.49x + 35.24$

$R^2 = 0.9989$

Fig. 5. Calibration graph of the Ti^{3+} selective electrode based on OMCP at 25 °C.

Table 2
The repeatability and reproducibility of the fabricated Ti^{3+} selective electrode at 25 °C.

Study	Nernstian slope (mV decade^{-1})	Average	Standard deviation	RSD
Repeatability	29.49, 29.38 29.44, 29.56 29.73	29.52	0.13	0.54
Reproducibility	28.69, 29.18 29.37, 29.49 29.81	29.31	0.41	1.43

electrodes where each electrode was used only once. The average and standard deviation of the Nernstian slopes were calculated and their values were 29.52 ± 0.13 and 29.31 ± 0.41 mV per decade of activity, respectively. The obtained values for relative standard deviation were much lower than 5% which can consider as an acceptable value for repeatability and reproducibility studies. Due to the difference in the thickness and morphology of the membranes at different locations, which result in fluctuation in extraction equilibrium of corresponding ions at the vicinity of the interface between the membrane and aqueous layer, the difference of Nernstian slope from one electrode to another could be vindicated. Consequently, the variation of the thickness can cause minor changes in Nernstian slope of the electrodes [30].

Rresponse time studies were carried out for several times by immediate and successive changing of target ion over the
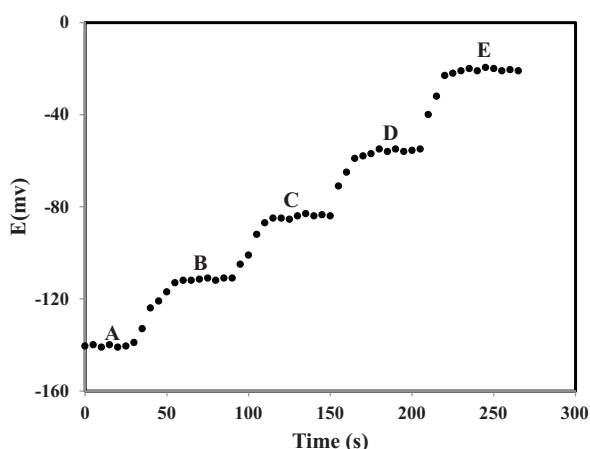
Fig. 6. Dynamic response time of the Ti^{3+} selective electrode for step changes in the concentration of the TiCl$_3$ solution: (A) 1.0×10^{-6} M, (B) 1.0×10^{-5} M, (C) 1.0×10^{-4} M, (D) 1.0×10^{-3} M and (E) 1.0×10^{-2} M at 25 °C.

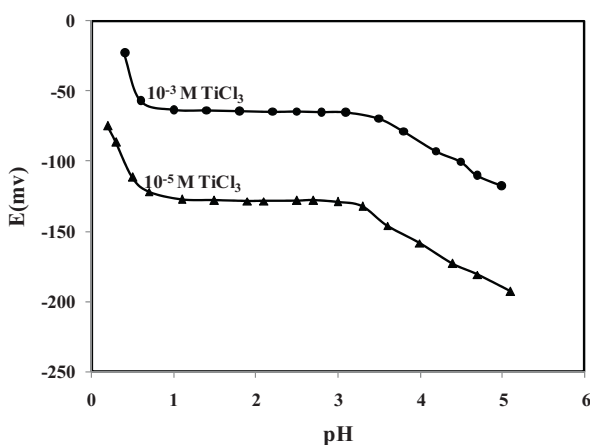**Fig. 7.** pH effect of the sample solutions on the potential response of Ti^{3+} selective electrode at 25 °C.

concentration range of 1.0×10^{-6} M to 1.0×10^{-2} M. The average time needed for the membrane electrode to reach a potential to the steady potential response within ± 1 mV of ultimate equilibrium value. As it can be seen from Fig. 6, the average of dynamic response time obtained for the fabricated electrode to reach to its equilibrium potential response in the whole linear concentration range was less than 25 seconds. This is probably due to the fast exchange kinetics of Ti(OH)$^{2+}$ species complexation-decomplex-ation with OMCP at the interface of PVC membrane with the test solution [31,32]. To investigate the stability and life time of the developed electrode, the characteristics performance of it with respect to Nernstian slope and detection limit was examined over a period of 15 weeks using four electrodes. Where, the electrodes were used daily over an extended time period (1 hour per day) and stored in 1.0×10^{-3} M TiCl$_3$ solution, when they were not in use. The obtained results demonstrated that after 10 weeks, only slight changes were observed in the slope and detection limit. The electrode showed changes in slope from 29.49 ± 0.16 mV per decade of activity to 28.42 ± 0.42 mV per decade of activity, whereas its detection limit changed from 8.0×10^{-7} M to 1.5×10^{-6} M of Ti^{3+} concentration. The limitation of life time might be due to the loss of membrane ingredients by leaching into the sample. According to the obtained results, fabricated Ti^{3+} selective electrode based on OMCP demonstrated comparatively long life time with high stability, which indicates that it can be

practically used for the determination of titanium concentrations in different fields such as environmental and industrial analysis.

The pH independence of Ti^{3+} selective electrode was investigated in two concentrations, i.e. 1.0×10^{-3} M and 1.0×10^{-5} M of TiCl$_3$ solution. As it is demonstrated in Fig. 7, the obtained result revealed that the fabricated electrode can be used to determine Ti^{3+} concentration in the pH range of 1 to 3. As it is mentioned before, in the pH range of 1 to 3, the main species of titanium in solution is Ti(OH)$^{2+}$ which is in agreement with the Nernstian slope of 29.49 ± 0.16 mV per decade for the double charged cationic species. The drift in the potential response of Ti^{3+} selective electrode at lower pH could be due to the protonation of ionophore as well as response of the electrode to Ti(H$_2$O)$_6$$^{3+}$ complexes in the solution, which resulted in an increase in the potential response of electrode. However, at higher pH, the observed drift in potential response could be attributed to the formation of some more hydroxide complexes of titanium in the solution such as Ti$_2$O(H$_2$O)$_{10}$$^{4+}$ [11].

3.5. Selectivity Coefficient of Fabricated ISE

Selectivity of the developed ISEs towards ion of interest is one the most important characteristics which can prove the ability of the fabricated membrane sensors to distinguish between target ion and other ions in the solution. High selectivity of the fabricated electrodes provides an accurate and precise determination of target ion activity. According to the IUPAC technical report related to the recommended methods for determining K_{ij}^{Pot} value, the selectivity coefficient based on Separate Solution Method (SSM) can be evaluated by determining the potential responses of the electrochemical cell which consist of fabricated ISE and a reference electrode in pure solution of each target ion and interfering ion, separately [33–35].

In this study, the selectivity coefficients of the developed ISEs towards their target ions with respect to a wide range of interfering ions were determined. For selectivity evaluation of the fabricated titanium selective electrodes, the concentration of 1.0×10^{-2} M was used for both target ion and interfering ions. As it can be

Table 3
Selectivity coefficient of the developed Ti^{3+} selective electrode based on Separate Solution Method (SSM) at 25 °C.

Examined Cation	Log$K_{Ti,M}^{Pot}$	$K_{Ti,M}^{Pot}$
Cs$^+$	−4.68	2.11×10^{-5}
K$^+$	−4.51	3.06×10^{-5}
Na$^+$	−4.23	5.89×10^{-5}
Li$^+$	−4.21	6.23×10^{-5}
Rb$^+$	−4.55	2.83×10^{-5}
Zn^{2+}	−2.94	1.15×10^{-3}
NH$_4$$^+$	−4.58	2.64×10^{-5}
Ni^{2+}	−3.04	9.12×10^{-4}
Ba^{2+}	−3.79	1.62×10^{-4}
Cd^{2+}	−4.78	1.65×10^{-5}
Co^{2+}	−2.97	1.07×10^{-3}
Cu^{2+}	−2.87	1.35×10^{-3}
Mn^{2+}	−3.51	3.09×10^{-4}
Pb^{2+}	−2.67	2.14×10^{-3}
Mg^{2+}	−3.14	7.24×10^{-4}
Fe^{2+}	−2.84	1.45×10^{-3}
H$^+$	−3.18	6.61×10^{-4}
Al^{3+}	−3.24	5.75×10^{-4}
Ca^{2+}	−3.11	7.76×10^{-4}
Nd^{3+}	−3.34	4.57×10^{-4}
Fe^{3+}	−3.75	1.78×10^{-4}
La^{3+}	−3.28	5.25×10^{-4}
Cr^{3+}	−3.41	3.89×10^{-4}
Ce^{3+}	−3.49	3.24×10^{-4}
Y^{3+}	−4.10	7.94×10^{-5}
Tb^{3+}	−3.72	1.91×10^{-4}

Table 4
Ti^{3+} ion concentration in industrial waste water samples.

Sample No.	Concentration of Ti^{3+} ions (ppm)		
	ISE method[*]	AAS method[*]	ICP method[*]
1	18.26 ± 0.51	18.29 ± 0.08	18.35 ± 0.17
2	6.42 ± 0.33	6.47 ± 0.15	6.50 ± 0.11
3	27.14 ± 0.29	27.20 ± 0.13	27.19 ± 0.19
4	41.32 ± 0.21	41.38 ± 0.17	41.42 ± 0.15

[*]Average and standard deviation for triplet measurements.

Table 5
Ti^{3+} ion concentration in tab water samples.

Amount added (ppm)	Found Concentration of Ti^{3+} ions (ppm)			Recovery (%)
	ISE method[*]	AAS method[*]	ICP method[*]	
0.00	ND	0.00	0.00	0.0
10.00	10.23 ± 0.27	10.08 ± 0.35	10.01 ± 0.25	102.3
25.00	24.92 ± 0.26	24.76 ± 0.32	24.66 ± 0.29	99.7
50.00	50.82 ± 0.35	50.70 ± 0.24	50.58 ± 0.23	101.6
75.00	74.48 ± 0.36	74.34 ± 0.29	74.21 ± 0.30	99.3
100.00	100.51 ± 0.41	100.38 ± 0.27	100.33 ± 0.37	100.5

[*]Average and standard deviation for triplet measurements.

concluded from Table 3, it is obvious that the fabricated electrode exhibited high selectivity towards Ti^{3+} metal ions in compare to a variety of investigated interfering cations. The selectivity coefficient data indicates that $K_{Ti,j}^{Pot}$ values are of the order of 10^{-3} to 10^{-5} for mono, bi and tri-valent interfering cations. Moreover, Table 3 revealed that the selectivity behaviour of the developed electrode shows a considerable improvement compared to the previously reported Ti^{3+}- selective electrode[36].

3.6. Validation and Application of Fabricated ISE

The data obtained via developed Ti^{3+} selective electrode was validated with the data obtained by independent spectrophotometric method such as atomic absorption spectrometry (AAS) and inductively coupled plasma technique (ICP). It can be concluded that current work provides an alternative device for quantitative determination of Ti^{3+} trace amount of the real industrial and biological samples according to the procedure described by Zamani et al. [37].

The fabricated electrode was applied for direct Ti^{3+} monitoring in industrial waste water samples. Four diluted waste water samples were prepared using 10.0 ml of buffer hydrochloric acid / potassium chloride (pH = 2.0) and de-ionized water in a 100 ml volumetric flask. Then, according the obtained potential responses of the fabricated electrode, the concentration of Ti^{3+} in each sample were determined and compared with the results obtained using AAS and ICP methods..

On the other hand, tab water samples were analysed by the fabricated electrode, AAS and ICP method to detect Ti^{3+} concentration via the spiked samples[38]. Standard addition technique was used by adding known amounts of Ti^{3+} to tab water and the potentials of the solutions were measured via fabricated electrode.

As it can be concluded from both Tables 4 and 5, there is a satisfactory agreement between the results obtained by fabricated electrode with those obtained by certified AAS and ICP methods. Hence, it confirmed the accuracy and precision of fabricated Ti^{3+}-selective electrode in successful determination of Ti^{3+} trace amount in real environmental and industrial samples.

The practical utility of the fabricated electrode was examined by its use as an indicator electrode in potentiometric titration of 25 mL of 1.0×10^{-4} M $TiCl_3$ solution with 1.0×10^{-2} M of standard
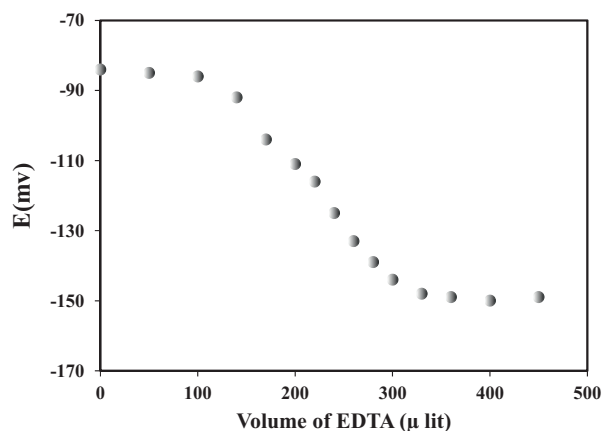

Fig. 8. Potentiometric titration curve of Ti^{3+} ion against standard EDTA.

EDTA solution. As can be seen from Fig. 8, the addition of EDTA causes a decrease in potential as a result of decrease in free Ti^{3+} ion concentration due to its complexation with EDTA. The obtained plot has a standard sigmoidal shape with sharp break point which indicates that the fabricated electrode is selective towards Ti^{3+} ions. Moreover, the end point of the plots corresponds to 1:1 stoichiometry of EDTA-Ti^{3+} ions complex. As a result, it is possible to determine the amount of Ti^{3+} ions in solution accurately by the fabricated electrode.

4. Theoretical analysis

In this section the comprehensive theoretical study on adsorption process of $Ti(OH)^{2+}$ cationic species by OMCP was investigated based on the DFT/B3LYP computational level with the 6-31G (d, p) basis set by using Gaussian 03 program package [39]. Fig. 9 presents the geometry full optimized structure of title complex.

Adsorption energy (E_{ads}) between OMCP and $Ti(OH)^{2+}$ was defined as follow:

$$E_{ads} = E\ (complex) - E\ (OMCP) - E\ (Ti(OH)^{2+}) \qquad (II)$$

Where E (complex) is the total energy of the OMCP with $Ti(OH)^{2+}$ cationic species, E (OMCP) and E ($Ti(OH)^{2+}$) are the total energy of OMCP and $Ti(OH)^{2+}$, respectively.

The large negative adsorption energy value (E_{ads}) is -10.22 eV that indicates the stable formed complex. Molecular electrical transport properties can be determined by the energy gap between the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO) frontier molecular orbitals. Fig. 10 shows the HOMO-LUMO diagrams and energies of OMCP and the formed complex. The HOMO-LUMO energy gap for the complex is 3.24 eV which reveals the electron conductivity (the eventual charge transfer interactions) and a measure of the structural stability properties.

To investigate the nature of intermolecular interactions, the value of the natural bond orbital (NBO) calculated at the same level of theory. The results of our NBO analysis i.e. most important donor-acceptor interactions and their second-order perturbation stabilization energies $E^{(2)}$ are provided in Table 6. The charge transfer between lone pairs of Ti as donor and $\sigma^*_{(N-Ti)}$ as acceptor and $\sigma_{(N-C)}$, $\sigma_{(N-H)}$, $\sigma_{(C-C)}$ as donor and LP^* (Ti) as acceptor participate as the adsorption feature. The obtained results revealed that titanium prefer to contribute in the formed complex as an acceptor while N and aromatic rings act as donors via coordination bands.

Additionally, the Quantum Theory of "Atoms in Molecules" (QTAIM) of Bader [40] has been also applied here in order to find the topological parameters such as critical points (bond critical
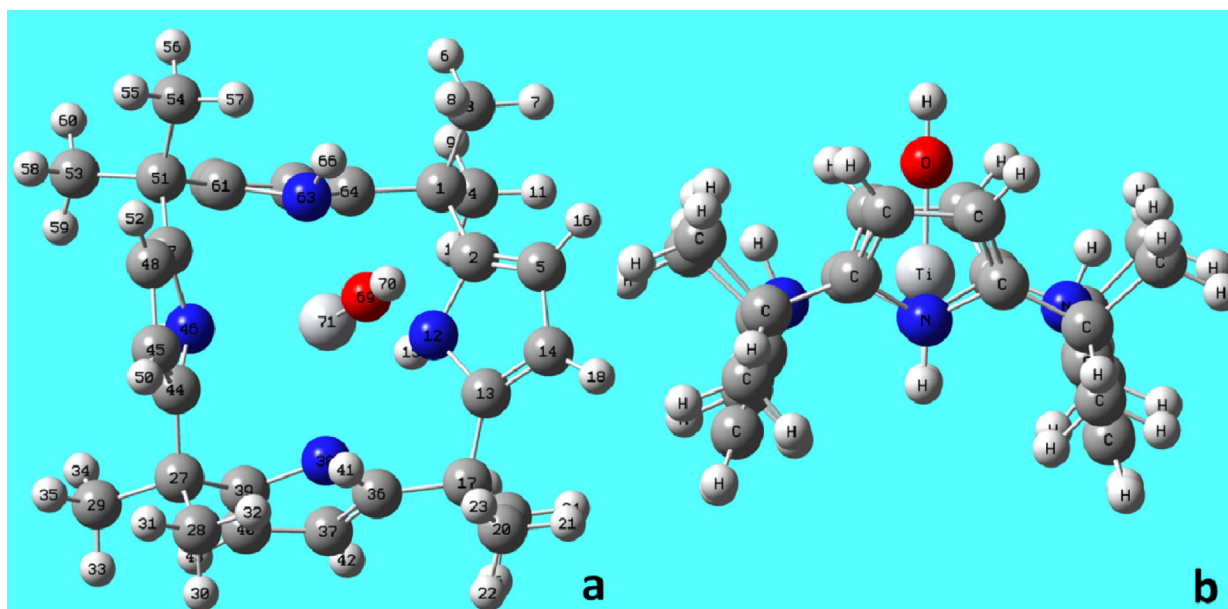
Fig. 9. Optimized structure of title complex from (a) top view and (b) side view.

points (BCPs), ring critical points (RCPs), and analyzing them in terms of electron densities (ρ's) and their Laplacians ($\nabla^2\rho$'s). The optimized geometries were employed to obtain suitable wave function files to be used with AIM 2000 suiting the programs [41] and applied to perform the AIM calculations. As shown in Fig. 11, the charge density (ρ) and Laplacian function of charge density

($\nabla^2\rho$) were calculated to discover more details about intermolecular interaction between the Ti(OH)$^{2+}$ cation and OMCP.

Topological parameters and geometries for selected bonds are given in Table 7 with respect to the sign of Laplacian function of charge density andthe type of bond can be recognized. So, if $\nabla^2\rho>0$, the bond is closed-shell interaction, such as ionic and Van der
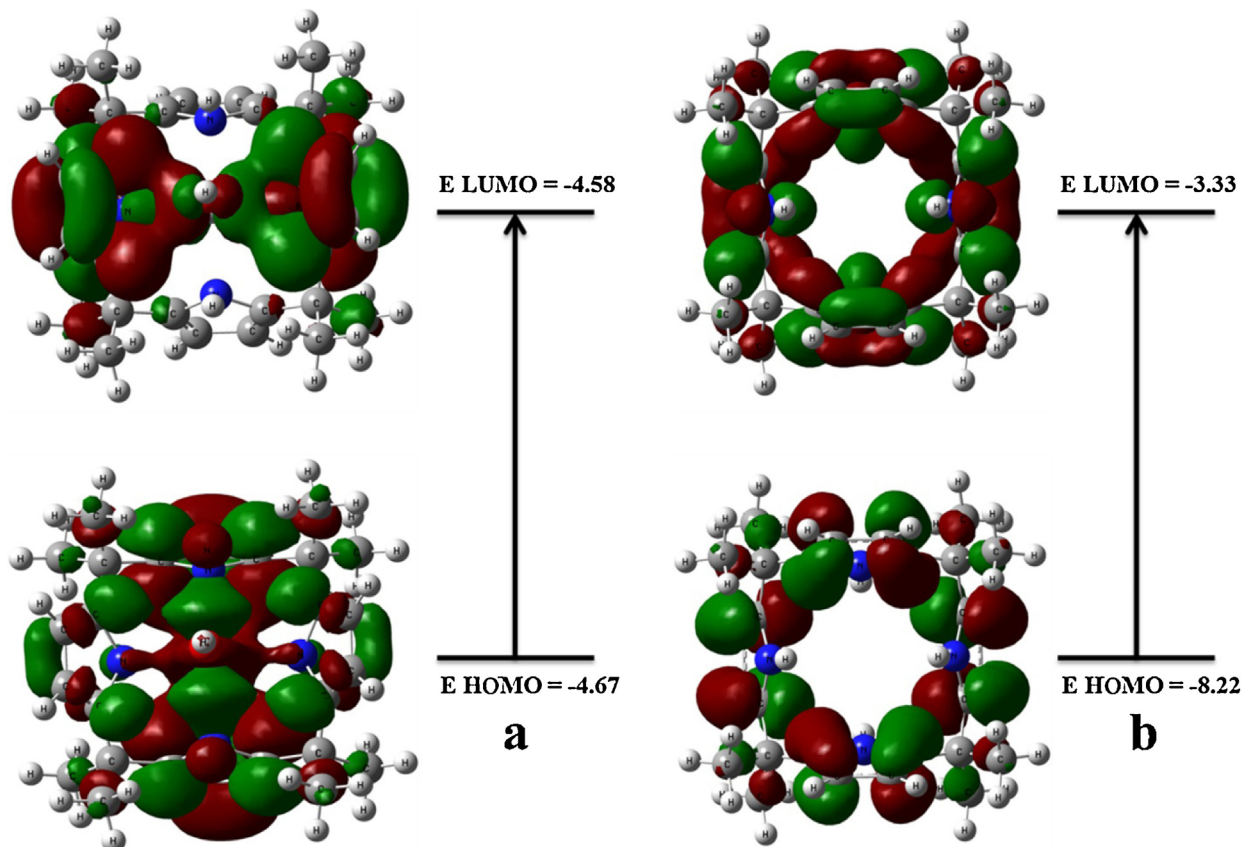

Fig. 10. HOMO and LUMO compositions of the frontier orbital for (a) formed complex and (b) OMCP.

Table 6
NBO analysis of some important orbital interactions for studied complex.

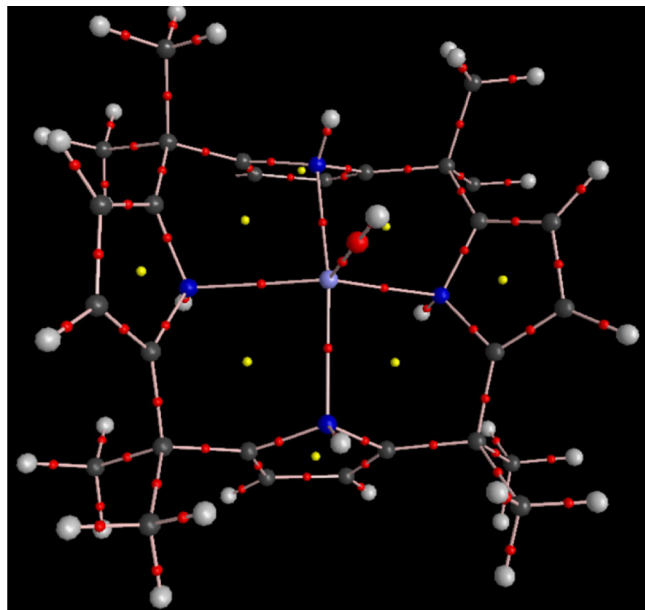| Donor NBO	Acceptor NBO	$E^{(2)}$kJ/mol
σC2-C7	LP*(3)Ti	6.44
σN12-C13	LP*(3)Ti	6.52
σN12-H15	LP*(3)Ti	5.31
σN46-C47	LP*(3)Ti	6.52
LP*(1)Ti	σ*(1)N12-Ti	6.98
LP*(1)Ti	σ*(1)N38-Ti	7.06
LP*(1)Ti	σ*(1)N46-Ti	6.98
LP*(1)Ti	σ*(1)N63-Ti	7.02
σ*N12-Ti	LP*(3)Ti	22.20
σ*N46-Ti	LP*(3)Ti	22.20

Fig. 11. The molecular graph of formed complex, the large circles represent attractors attributed to atomic nuclei and the small circles show the critical points (bond critical points and ring critical points). Solid lines represent the bond paths.

Table 7
The geometrical and topological parameters for selected bonds in formed complex.

Bond	Distance (A°)	ρ	$\nabla^2\rho$
N63-Ti	2.304	0.04754	0.21784
N46-Ti	2.297	0.04819	0.21959
N38-Ti	2.304	0.04755	0.21792
N12-Ti	2.297	0.04818	0.21951
Ti-O	1.753	0.14246	0.91222
O-H70	0.968	0.32413	−1.61744

Waals interaction and if $\nabla^2\rho < 0$, it is attributed to covalent interactions [42–46]. The obtained results were shown that there is very strong interaction between Ti atom and N atoms. Also, the sign of Laplacian for Ti . . . N in studied structures was positive which is indicating the bonds were closed-shell interaction such as ionic and Van der Waals interaction.

5. Conclusion

A fabricated PVC-based membrane electrode based on OMCP was demonstrated a good analytical performance for selective determination of trace amount of Ti^{3+} ions in the presence of interfering ions. The Ti^{3+} selective electrode exhibited a good reproducibility with a superior response time less than 25 seconds and can be operated over the pH range from 1 to 3 with a satisfactory concentration range of 1.0×10^{-6} M to 1.0×10^{-2} M. The proposed sensor was successfully applied for accurate and precise determination of Ti^{3+} ions in tab water and industrial waste water samples. However, the proposed electrode has a narrow pH range which is limited the applicability of it in the real samples. Moreover, the life time of the fabricated Ti^{3+} selective electrode is limited to almost 3 months which might be due to the loss of membrane ingredients by leaching into the sample.

Moreover, the density functional theory was employed to investigate the TiOH^{2+} interaction with OMPC. The obtained data demonstrated the preferred coordination of TiOH^{2+} cationic species by OMPC and confirmed their strong and selective interaction.

References

[1] A. Ceresa, E. Bakker, B. Hattendorf, D. Günther, E. Pretsch, Potentiometric polymeric membrane electrodes for measurement of environmental samples at trace levels: New requirements for selectivities and measuring protocols, and comparison with ICPMS, Anal. Chem 73 (2001) 343–351.
[2] A.C. Ion, E. Bakker, E. Pretsch, Potentiometric Cd^{2+}-selective electrode with a detection limit in the low ppt range, Analytica Chimica Acta 440 (2001) 71–79.
[3] A. Kassim, M. Rezayi, S. Ahmad Zadeh, W.T. Tan, N.A. Yusof, Y.H. Lee, Fabrication of a highly selective and sensitive CrO$_4$ sensor based on a N, N'Bis (salicylidene) ethylenediaminocobolt (II) hydrate, Malaysian Journal of Chemistry 11 (2009) 19–25.
[4] A. Kassim, M., Rezayi, S., Ahmadzadeh, G., Rounaghi, M., Mohajeri, N.A., Yusof, T.W., Tee, L.Y., Heng, A.H. Abdullah, A Novel ion selective polymeric membrane sensor for determining thallium (I) with high selectivity, IOP Conference Series: Materials Science and Engineering, IOP Publishing, 2011, pp. 012010.
[5] R. Bereczki, V. Csokai, A. Grun, I. Bitter, K. Toth, Crown bridged thiacalix[4] arenes as cesium-selective ionophores in solvent polymeric membrane electrodes, Analytica Chimica Acta 569 (2006) 42–49.
[6] Y. Choi, H. Kim, J.K. Lee, S.H. Lee, H.B. Lim, J.S. Kim, Cesium ion-selective electrodes based on 1, 3-alternate thiacalix [4] biscrown-6, 6, Talanta 64 (2004) 975–980.
[7] D. Couton, M. Mocerino, C. Rapley, C. Kitamura, A. Yoneda, M. Ouchi, Silver and thallium ion complexation with allyloxycalix[4] arenes, Australian Journal of Chemistry 52 (1999) 227–229.
[8] K. Kimura, K. Tatsumi, M. Yokoyama, M. Ouchi, M. Mocerino, Remarkable thallium(I) selectivity for ion sensors based on π-coordination of calix[4]arene neutral carriers, Analytical Communications 36 (1999) 229–230.
[9] K.S. Park, S.O. Jung, I. Yoon, K.M. Park, S.S. Lee, J.S. Kim, Structural Selectivity of Calix [m] pyrroles [n] furans (m + n = 4) as Ionophores in Ag (I) Ion-Selective Electrodes, Journal of Inclusion Phenomena and Macrocyclic Chemistry 39 (2001) 295–301.
[10] K.S. Park, S.O. Jung, S.S. Lee, J.S. Kim, Thallium (I)-Selective Electrodes Based on Calix [4] pyrroles, Bulletin-Korean Chemical Society 21 (2000) 909–912.
[11] S. Cassaignon, M. Koelsch, J.P. Jolivet, From TiCl3 to TiO2 nanoparticles (anatase, brookite and rutile): Thermohydrolysis and oxidation in aqueous medium, journal of physics and chemistry of solids 68 (2007) 695–700.
[12] E. Abele, B. Fröhlich, High speed milling of titanium alloys, Advances in Production Engineering and Management 3 (2008) 131–140.
[13] J. Gambogi, Titanium Industry Overview, USGS Technical Brief, (2001).
[14] J. Gambogi, S.J., Gerdemann, Titanium metal: extraction to application, Albany Research Center (ARC), Albany, OR, 2002.
[15] E. Bakker, P. Buhlmann, E. Pretsch, Carrier-based ion-selective electrodes and bulk optodes. 1. General characteristics, Chemical Reviews 97 (1997) 3083–3132.
[16] E. Bakker, P. Buhlmann, E. Pretsch, The phase-boundary potential model, Talanta 62 (2004) 843–860.
[17] M. Nagele, E. Bakker, Pretsch, General description of the simultaneous response of potentiometric ionophore-based sensors to ions of different charge, Analytical Chemistry 71 (1999) 1041–1048.
[18] R.L. Pecsok, A.N. Fletcher, Hydrolysis of titanium (III), Inorganic Chemistry 1 (1962) 155–159.
[19] R.J.H. Clark, The Chemistry of Titanium and Vanadium, Elsevier, Amsterdam, 1968.

[20] P.I. Premović, P.R. West, Electron Spin Resonance Studies in Aqueous Solution: Titanium (III) in the pH Region 1. 0-3.5, Canadian Journal of Chemistry 52 (1974) 2919–2922.

[21] M. Rezayi, R. Karazhian, Y. Abdollahi, L. Narimani, S.B.T. Sany, S. Ahmadzadeh, Y. Alias, Titanium (III) cation selective electrode based on synthesized tris (2pyridyl) methylamine ionophore and its application in water samples, Scientific reports 4 (2014) 0000–0025.

[22] V.K. Gupta, S. Jain, S. Chandra, Chemical sensor for lanthanum (III) determination using aza-crown as ionophore in poly (vinyl chloride) matrix, Analytica Chimica Acta 486 (2003) 199–207.

[23] S.K. Mittal, S.K. Kumar, H.K. Sharma, PVC-based dicyclohexano-18-crown-6 sensor for La (III) ions, Talanta 62 (2004) 801–805.

[24] M. Shamsipur, M. Yousefi, M. Hosseini, M.R. Ganjali, Lanthanum (III) PVC membrane electrodes based on 1, 3, 5-trithiacyclohexane, Anal. Chem 74 (2002) 5538–5543.

[25] M.R. Ganjali, R. Kiani-Anbouhi, M. Shamsipur, T. Poursaberi, M. Salavati-Niasari, Z. Talebpour, M. Emami, Novel potentiometric PVC-membrane and coated graphite sensors for lanthanum (III), Electroanalysis 16 (2004) 1002–1008.

[26] M. Javanbakht, A. Shabani-Kia, M.R. Darvich, M.R. Ganjali, M. Shamsipur, Cadmium (II)-selective membrane electrode based on a synthesized tetrol compound, Analytica Chimica Acta 408 (2000) 75–81.

[27] E. Bakker, P. Buhlmann, E. Pretsch, Carrier-based ion-selective electrodes and bulk optodes. 1. General characteristics, Chem. Rev 97 (1997) 3083–3132.

[28] E. Bakker, D. Diamond, A. Lewenstam, E. Pretsch, Ion sensors: current limits and new trends, Analytica Chimica Acta 393 (1999) 11–18.

[29] Y.W. Choi, N. Minoura, S.H. Moon, Potentiometric Cr (VI) selective electrode based on novel ionophore-immobilized PVC membranes, Talanta 66 (2005) 1254–1263.

[30] A.K. Singh, V.K. Gupta, B. Gupta, Chromium (III) selective membrane sensors based on Schiff bases as chelating ionophores, Analytica chimica acta 585 (2007) 171–178.

[31] S. Ahmadzadeh, A. Kassim, M. Rezayi, Y. Abdollahi, G. Hossein, A conductometric study of complexation reaction between meso-octamethylcalix [4] pyrrole with titanium cation in acetonitrile-ethanol binary mixtures, Int. J. Electrochem. Sci 6 (2011) 4749–4759.

[32] M. Rezayi, A. Kassim, S. Ahmadzadeh, A. Naji, H. Ahangar, Conductometric determination of formation constants of tris (2-pyridyl) methylamine and titanium (III) in water-acetonitryl mixture, Int J Electrochem Sci 6 (2011) 4378–4387.

[33] Y. Umezawa, P. Bühlmann, K. Umezawa, K. Tohda, S. Amemiya, Potentiometric selectivity coefficients of ion-selective electrodes. Part I. Inorganic cations (technical report), Pure and applied chemistry 72 (2000) 1851–2082.

[34] Y. Umezawa, K. Umezawa, P. Buhlmann, N. Hamada, H. Aoki, J. Nakanishi, M. Sato, K.P. Xiao, Y. Nishimura, Potentiometric selectivity coefficients of ion-selective electrodes. Part II. Inorganic anions (IUPAC Technical Report), Pure and applied chemistry 74 (2002) 923–994.

[35] Y. Umezawa, K. Umezawa, H. Sato, Selectivity coefficients for ion-selective electrodes-recommended methods for reporting KA, B (POT) values-(technical report), Pure Appl. Chem. 67 (1995) .

[36] M. Rezayi, R. Karazhian, Y. Abdollahi, L. Narimani, S.B.T. Sany, S. Ahmadzadeh, Y. Alias, Titanium (III) cation selective electrode based on synthesized tris (2pyridyl) methylamine ionophore and its application in water samples, Scientific reports 4 (2015) 4664–4671.

[37] H.A. Zamani, G. Rajabzadeh, M. Masrornia, A. Dejbord, M.R. Ganjali, N. Seifi, Determination of Cr^{3+} ions in biological and environmental samples by a chromium (III) membrane sensor based on 5-amino-1-phenyl-1H-pyrazole-4-carboxamide, Desalination 249 (2009) 560–565.

[38] S. Zhuiykov, Solid-state sensors monitoring parameters of water quality for the next generation of wireless sensor networks, Sensors and Actuators B: Chemical 161 (2012) 1–20.

[39] M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, J. Montgomery Jr, T. Vreven, K. Kudin, J. Burant, Gussian 03, Gaussian, Inc., Pittsburgh, PA, 2003.

[40] R.F. Bader, A. Streitwieser, A. Neuhaus, K.E. Laidig, P. Speers, Electron delocalization and the Fermi hole, Journal of the American Chemical Society 118 (1996) 4959–4965.

[41] F. Biegler-Konig, J., Schonbohm, D., Bayles, Software news and updates-AIM2000-A program to analyze and visualize atoms in molecules, John Wiley & Sons Inc 605 Third Ave, New York, NY 10158-0012 USA, 2001, pp. 545–559.

[42] H. Raissi, A. Jalbout, M. Nasseria, M. Yoosefian, H. Ghiassi, A. Hameed, The effect of substitution on the intramolecular hydrogen bonding in 3-hydroxy-propenethial, International Journal of Quantum Chemistry 108 (2008) 1444–1451.

[43] H. Raissi, M. Yoosefian, F. Mollania, Comprehensive study of the interaction between hydrogen halides and methanol derivatives, International Journal of Quantum Chemistry 112 (2012) 2782–2786.

[44] M. Yoosefian, Z. Barzgari, J. Yoosefian, Ab initio study of Pd-decorated single-walled carbon nanotube with C-vacancy as CO sensor, Structural Chemistry 25 (2014) 9–19.

[45] M. Yoosefian, Z.J. Chermahini, H. Raissi, A. Mola, M. Sadeghi, A theoretical study on the structure of 2-amino-1, 3, 4-thiadiazole and its 5-substituted derivatives in the gas phase, water, THF and DMSO solutions, Journal of Molecular Liquids 203 (2015) 137–142.

[46] M. Yoosefian, H. Raissi, E.S. Nadim, F. Farzad, M. Fazli, E. Karimzade, A. Nowroozi, Substituent effect on structure, electron density, and intramolecular hydrogen bonding in nitroso-oxime methane, International Journal of Quantum Chemistry 111 (2011) 3505–3516.