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A novel polymeric membrane sensor for determining titanium (III) in real samples: Experimental, molecular and regression modeling

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ABSTRACT

The construction of a potentiometric titanium(III)-selective electrode based on methylcalix[4]resorcinarene (CMCR) incorporated into a poly(vinyl chloride) (PVC) matrix is reported. The polymeric membrane incorporates 8.0 mg CMCR as an electroactive sensing material, 59.0 mg dioctylphthalate (DOP) as a plasticizer, 3.0 mg sodium tetraphenyl borate (NaTPB) as an anionic additive and 30 mg PVC as a neutral matrix exhibiting a Nernstain potential response of 30.38 ± 0.15 mV per decade in the concentration range from 1×10^{-6} to 1×10^{-2} M with a detection limit of 8.9×10^{-7} M and fast response time of 15 s. The proposed sensor was successfully applied to determine titanium cations in real samples and the obtained results were compared to those of spectroscopy methods such as AAS and ICP instruments. The structure of CMCR ligand and its complexation with some common cations were investigated using quantum mechanical DFT calculations where the titanium (III) cation showed prominent affinity for the CMCR carrier. The regression model was applied to obtain the membrane composition model of Ti(III)-ISE affecting the potential response of the polymeric sensor. The results show that the regression model can be used as a practical method for obtaining the Nernstian slope of the proposed sensor in this study.

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1. Introduction

Titanium is known as the ninth most plentiful element in the earth's crust. It is an important element as an alloying agent for some metals such as aluminum, manganese, molybdenum and iron [1]. The applications of these alloys have been extended due to their lightweight strength and are able to withstand high temperatures. Titanium is stronger and 45% lighter than steel, 60% heavier and two times stronger than aluminum [2]. These properties, in addition to its corrosion resistance, enables the use of titanium and its compositions in many industrial applications such as airplanes, jewellery, motors and heat exchange systems [3]. Moreover, they can be used in the medical industry as knee replacements, bone-plates and screws for bones fractures due to the non-toxic effect that titanium has on the human body [4]. Despite its advantages, the use of titanium in cosmetics, food, sunscreens and paint is a health hazard reagent [5]. As it has been reported before, children in the age group most exposed to titanium because of the use of sweets [6–8]. The effect of the huge usage of titanium compounds on the environment and health was the motivation to investigate methods for measuring titanium in environmental and industrial samples.

Titanium trichloride ($TiCl_3$) is commonly prepared by reduction of titanium tetrachloride ($TiCl_4$) as a coloring agent in molasses and Ziegler–Natta catalyst for polymerization of propylene. It is also used as a reagent in organic synthesis in the presence of some reducing agents such as zinc [9].

Several methods were reported for titanium determination, such as flame emission spectrophotometry, inductively coupled plasma with atomic emission spectrophotometer (ICP-AES) [10], adsorptive stripping voltammetry (AdSV) [11], kinetic methods (catalytic fluorimetric [12] and flow kinetic spectrophotometric method [13]), electrothermal atomic absorption spectrometry (ETAAS), gravimetric filter weight (G/FW) [14] and sensor devices [15,16].

X-ray fluorescence was applied to determine the trace amount of titanium in water samples by Blasius et al. [17]. According to the reported method, the titanium and cesium were detected with the sensitivities of the order of 0.4 and 30 μg/kg for metals in the ionic and particulate forms, respectively. Titanium level in the sea water was in the range of 1–9 μg/L [18]. Determining of trace elements includes titanium in water was done by Hamilton and Minski via applying the spark-source mass spectroscopy [19].

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Detection of titanium in the food samples such as fruits, vegetable and fish meat showed a little or no detectable amount [20]. In cheese samples, high concentration of titanium were due to the usage of titanium dioxide as a whitener aging in the manufacture of mozzarella cheeses [21]. The titanium also used for improving the quality of cheese [22]. The average levels of titanium in the plants were reported about 1 mg/kg and its levels were considered as indicators of soil contamination in herbage samples. Although potentiometric and photometric titration method show low sensitivity, they were frequently reported for determining of titanium in the environmental samples [23].

Among all the reported methods, sensor devices can be implemented in simple use and low-cost devices but provide low-level determination in comparison to those typically offered devices that incorporate much more expensive techniques [24–26]. Hence, more attention from researchers is needed to develop an accurate method for the selective determination of titanium concentration. Potentiometric ion selective polymeric membrane sensors including neutral-carrier as a key element to select the targeted ions have been employed for more than three decades to determine ions in industrial, clinical and environmental samples [27–29].

These kinds of sensors have more advantages compared to other sensor devices because of their easy usage, relatively fast response, suitable repeatability and reproducibility, cost and time efficiency, and reliability. In addition, non-destructive and on-line monitoring without any pretreatment were obtained by potentiometric ion selective sensors [30–33]. Therefore, due to the mentioned merits, a number of polymeric cation selective sensors have been reported [34–38]. In this current research work, the development of polymeric PVC membrane sensor based on a methylcalix[4]resorcinarene (CMCR) carrier for determining titanium (III) cations was introduced and its applicability in the potentiometric determination of titanium (III) cations in water samples was studied. To the best of our knowledge, the introduced electrode showed specific features such as selectivity to titanium(III) cations, Nernstian response, low detection limit, good repeatability and reproducibility, fast response and suitable life time.

2. Materials

The ion-selective poly(vinyl chloride) (PVC) membranes were prepared from methylcalix[4]resorcinarene (CMCR) (Fluka, USA) as a carrier and high molecular weight PVC powder (Aldrich, USA). Sodium tetrakis(4-flurophenyl)borate dehydrate (NaTFPB) (Fluka, USA), sodium tetraphenyl borate (NaTPB) (Merck, Germany), tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500) (Fluka, USA) and potassium tetrakis(4-chlorophenyl)borate (KTK) (Fluka, USA) were used as lipophilic additives. Dibutyl phatalate (DBP) (Merck, Germany), dioctylphthalate (DOP) (Merck, Germany), 2-nitrophenyl octyl ether (oNPOE) (Fluka, USA), nitrobenzene (NB) (Fluka, USA), and benzyl acetate (BA) (Aldrich, USA) were used as plasticizers.

Double distilled-deionized water (DI-water) was used throughout the experiments. Ethylenediaminetetraacetic acid disodium salt (EDTA) (Sigma–Aldrich, Germany) was used for potentiometric titration. The stock solution (10^{-2} M) was prepared by dissolving $TiCl_3$ (Merck, Germany) in DI water. Other diluted solutions were prepared from this stock solution. All the used HCl, HNO_3 and NaOH (Merck, Germany) were analytical in grade and used to adjust the pH of the solution. All of the cationic salts were made from nitrate and chloride salts and used without any further purification except for vacuum drying over P_2O_5.

3. Apparatus

The EMF measurements were applied using Thermo Scientific Orion VersaStar. The pH of the sample solutions was simultaneously monitored using a pH-meter (DKK-TOA, HM-7J) and a conventional glass pH electrode. The Perkin-Elmer Lambda spectrophotometer 1650 pc (SHIMADZU) was used to get the spectra of ligand, titanium(III) cation and the resulted complex, respectively. Mercury/mercury chloride (Hg/Hg_2Cl_2, 3 M KCl) and silver/silver chloride (Ag/AgCl, 3 M KCl), RE-5B (7.5 cm length × 6 mm OD) were used as the internal and external reference electrodes from BASi, respectively. The Thermo Scientific atomic absorption spectrometer (AAS) (model S SEIES) and the Perkin-Elmer optical emission spectrometer (model Optima 2000 DV) were applied for analysis of tap water samples as an inductively coupled plasma (ICP) with Ar and N_2 high quality gases.

4. Methodology

The membrane was constructed via a dip-coating method based on our previous works with a composition consisting of 30% (W/W) high molecular poly(vinyl chloride), 8% of CMCR ionophore, 3% NaTFPB as an anion excluder and 59% DOP plasticizer in 3 mL THF. Nontransparent PVC membranes were formed on the lid of a Pyrex tube (3 mm OD) by dipping it into a oily mixture solution for about 10 s. The electrode is then left to dry at room temperature overnight, filled with an internal solution (1.0×10^{-3} M $TiCl_3$) and then soaked in a 1.0×10^{-3} M $TiCl_3$ solution for 24 h before applying the electrode in a $TiCl_3$ solution with the concentration range from 1×10^{-7} to 1×10^{-1} M. A SCE was used as the internal reference electrode (Scheme 1). The electrochemical schematic cell was:

$$\text{SCE}\ \left|\text{Internal solution}\,(1.0\times10^{-3}\ \text{M}\ \text{TiCl}_3)\right|\ \text{PVC membrane}\ \left|\text{sample test}\right|\ \text{Ag}\ \left|\text{AgCl},\ \text{KCl}\,(3\ \text{M})\right|$$

To investigate membrane electrode selectivity, its potential response was monitored in the presence of various interfering cations with the aid of the matched potential method (MPM) [39]. This method is independent of the Nicolsky-Eisenman equation. Here, the selectivity coefficient is defined as the activity ratio of the primary and interfering ions that give the same potential difference under identical conditions. In this method, the known activity of the primary ion (a'_I) and the interfering ion (a_J) are independently added to the reference solution of the primary ion with the fixed activity (a_I), and the corresponding potential changes (ΔE) for both solutions are recorded in the fixed background of the primary ion solution. Consequently, the following equation will give us the value of the selectivity coefficient:

$$K_{IJ}^{pot} = \frac{a'_I - a_I}{a_J} \qquad (1)$$

In this study, MPM was used to characterize the Ti (III)-ISE in 1.00×10^{-6} M titanium(III) chloride solution. Interfering solutions with a concentration of 1.00×10^{-1} M were added to the fixed primary ion solution (Table S2).

Statistical analyses were performed using SPSS 17 software (SPSS, Chicago, IL, USA) to statistically assess the data. For the data evaluation, significant difference between membranes was tested via one-way parametric ANOVA (level of significance is 0.05).

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