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A novel ionic liquid/polyoxomolybdate based sensor for ultra-high sensitive monitoring of Al(III): Optimization by Taguchi statistical design

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ABSTRACT

A novel ionic liquid electrostatically supported Nano-Cs-polyoxomolybdate modified carbon paste electrode (Nano-IL-PMo_{12}-CPE) has been developed by using 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ($Bmim.BF_4$) as a superconductive hydrophobic binder. The supramolecular gel (IL-PMo_{12}) exhibits an ordered structure, various physicochemical properties, and specifically as a result of its substantial reversible self-assembly, it can be used as an intelligent ion-exchange smart platform in the carbon paste bulk of the electrode. The provided materials were characterized by XRD, FT-IR, UV–vis, and elemental analyses. As expected, a significant linear correspondence was found between the sensor output signal (emf/mV) and logarithm of Al(III) ion activity with a Nernstian slope of 19.9 (± 0.2) mV decade^{-1} over a wide concentration range of 1.0×10^{-9} to 2.2×10^{-1} mol L^{-1} ($R^2 = 0.9997$). The sensor considered, exploits an astounding lower limit of detection and short response time of 7.94×10^{-10} mol L^{-1} and 8 s respectively within the working pH range of 2.0 to 5.0. A statistical design of experimental (Taguchi method with Qualitek-4 software and L_{16} orthogonal array robust design) was implemented in this work to optimize the process to achieve the least number of experimental runs as much as possible. Ultimately, practical capability of the sensor was investigated successfully by assessment of Al(III) ion quantity in some aqueous samples namely mineral water, Al-Mg syrup, black tea extract, and ore samples (Basalt and Andesite), in perfect agreement with flame atomic absorption spectroscopy (FAAS).

1. Introduction

Due to the important roles of Aluminum in the pathology of Parkinson's disease (PD), Alzheimer's disease and diseases of dialysis (dialysis encephalopathy or dialysis dementia), also it's toxicological effects on living system, especially on human beings and because of its utility as an aggregating agent in potable water treatment units [1–4], there is an increasing necessity for aluminum monitoring in real samples. So, sensitive, fast, and specific methods for the determination of this element in different biological and physiological matrices and in environmental and food samples are needed. Up to date, various methods comprising different sorts of spectrophotometry, spectrofluorimetry, and chromatography have been successfully applied for determination of aluminum ion quantity in trace levels [5]. In spite of their intrinsic assets, this method has some inherent shortcomings such as time-consuming, involving tedious pre-treatment procedures, or too expensive [3,5].

As an appropriate and reliable alternative, electrochemical methods utilizing chemically modified carbon paste electrodes (CMCPEs) are the most reliable methods for the determination of some biologically important molecules, medicines and toxic metal ions [3–6]. CPEs characterized of many properties such as low background current, easy renewal surface, rich surface chemistry, facile fabrication and modification with desired properties via incorporating different substances during the paste preparation, and above all, suitability for various sensing and detection applications [7–14].

Polyoxometalates (POMs) as mediators shuttling the redox equivalents between the substrate and the electrode for indirect electrochemical processes have garnered continuing attentions in recent years [15–18]. In particular, owing to the strong Brønsted acidity and special structural properties, Keggin-type POMs, as non-coordinating templates have attracted much attention. They especially have some very useful and interesting properties including; high stability, redox potentials tunability, and the possibility of their reversible multi-electron transfer

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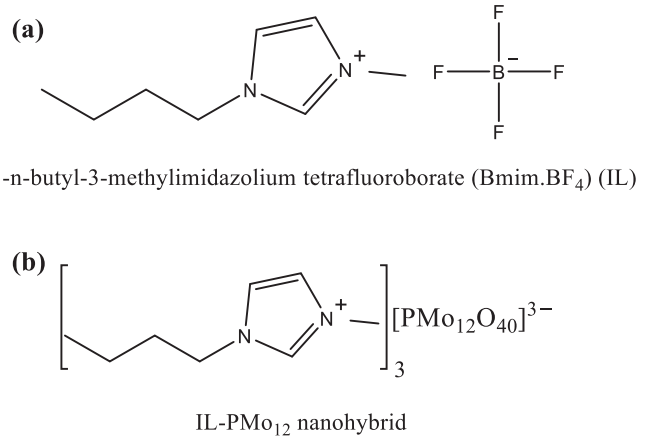

Fig. 1. a) Chemical structure of RTIL [Bmim].BF_4 as a carbon paste binder, b) Electrostatic coupling of imidazolium half of IL with $[PMo_{12}]^{3-}$ [22–24,26,33].

[18].

The unique properties of ionic liquids, including high thermal stability, tunability of their acidities, and excellent retention of polar or charged catalysts, make them appealing media for a broad range of catalytic applications [19]. Supported ionic liquid catalysis is a concept that combines the advantages of ionic liquids with those of heterogeneous support materials. The catalytically active polyoxometalate anion $[PMo_{12}O_{40}]^{3-}$ was immobilized onto the IL support by stoichiometric anion exchange via a very simple preparation procedure under relatively benign and easy-to-handle conditions (Fig. 1) [20–22]. Contrary to its bulk form, Nano-sized POMs possess some intrinsic preferences of high electrical conductivity, high specific surface area, low solubility in aqueous media (metal salt form), and in consequence high stability [23,24]. In this context, the combination of room temperature ionic liquid (RTIL) with Cs-Nano-PMo_{12} (IL-PMo_{12}) can be concluded to be a novel kind of supramolecular gel. The results indicate that it's properties (i.e., transformation points and conductivities) can be tuned by the design of the organic part. The features of unique Nano-sized space and functional surface of metal–organic frameworks, enable them to efficiently serve as host materials for various species (target species) [15,25–30].

Design of experiments (DOE) using Taguchi approach can economically satisfy the needs of problem solving and product/process design optimization complex projects to scrutinize the effect of multiple factors (i.e. variables, parameters, ingredients, etc.) simultaneously [31–33]. To complete planning of experiments and evaluation criteria before conducting experiments, steps for analysis are standardized (main effect, ANOVA and Optimum), using Taguchi statistical method (TSM) executed by Qualitek-4 (QT-4) software. A L_{16} orthogonal array type of QT-4 possessing four factors of control at four levels has been employed at the present study. The analysis of variance (ANOVA) of the mean electrode response and signal-to-noise ratio showed the great influence of PMo_{12}/GP weigh percentage ratio on the electrode potentiometric response. On the contrary, the other factors revealed low or no significant effect.

PMo_{12} is a Keggin type of anionic complex that has several applications in fuel cells, catalysis, molecular materials, electrochromism, super capacitors, medicine and some antibacterial activity against *Escherichia coli* and *Bacillus subtilis* [34]. The main objective of this research is to highlight the synthesis and characterization of a hybrid molecular salt based on 1-butyl 3-methyl imidazolium cation and polyoxometalate anion. As a unique class of metal oxide nanoclusters, Keggin-type $[PMo_{12}O_{40}]^{3-}$ (PMo_{12}) would represents as an IL supported building block to play key role of size-matching selective nanoporous agent on the CPE assemblies. Due to its synergetic physicochemical properties, IL impregnated Nano-PMo_{12}, gives a substantial

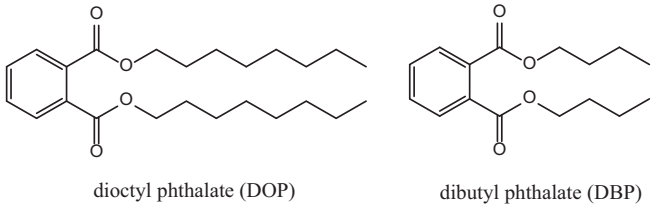

Fig. 2. Chemical structure of DOP and DBP as nonconductive pasting agent.

stability and sensitivity to the modified sensor. After optimization of critical parameters by QT-4 run of TSM, the IL-PMo_{12} modified CPE was satisfactorily used as a renewable probe electrode to investigate the Al (III) ion quantity in ultrahigh trace level included in the pharmaceutical and soil matrices, and aqueous samples.

2. Material and methods

2.1. Reagents and materials

Analytical reagent grade chemicals and doubly distilled water were used for preparing all aqueous solutions. Al(III) nitrate was obtained from Merck. Carbon graphite powder (1–2 μm), paraffin oil (PO), dioctyl phthalate (DOP) and dibutyl phthalate (DBP) (Fig. 2) were supplied from Aldrich and Fluka. 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (Bmim. BF_4), Na_2HPO_4, Na_2MoO_4, and CsCl were purchased from Merck chemical company (Germany). The $Cs_3[PMo_{12}O_{40}]$ nanocluster was provided at the Inorganic Chemistry Laboratory using a reverse micelles based nanoreactor inspired by reference [34]. Nitrate and chloride salts of metals (all from Merck) were of the highest purity available and used without any further purification. All other chemicals used were of the analytical reagent grade (from Merck, Aldrich, or Fluka). All glassware used in the experiments were washed with freshly prepared aqua regia ($HCl:HNO_3$, 3:1 v/v), rinsed thoroughly first with tap water and then deionized water before use.

2.2. Apparatus

The potential was measured under constant stirring of the test solution with respect to a double-junction silver/silver chloride reference electrode (Azar electrode, Urmia, Iran) in conjunction with chemically modified carbon paste indicator electrode. All potentiometric measurements and pH adjustments were accomplished with a digital pH/mV meter (Metrohm-827, Switzerland). Some solutions were homogenized by ultrasonic homogenizer (Bandelin UW 3200, Germany) whenever it was required. UV–vis absorption spectra were recorded with a Perkin-Elmer, Lambda 25 (USA) spectrophotometer. Melting points were also determined with a Barnstead Electrothermal model 9200 apparatus. X-ray diffraction (XRD) analyses were performed with MPD 3000 (Ital structure, Italy). FT-IR spectra were recorded on Perkin–Elmer Spectrum RXI (USA) using KBr pellets ranging from 400 to 4000 cm^{-1}. All measurements were carried out at laboratory ambient temperature. The ^1H NMR analysis was implemented using BRUKER AVANCE DPX 300 MHz apparatus. Elemental analyses were performed by Perkin Elmer 2400 series II CHN-O-Rapid and Perkin Elmer Avio 500 ICP-AES (USA) elemental analyzers.

2.3. Preparations

2.3.1. Synthesis of α-Keggin phosphomolybdic acid ($H_3[PMo_{12}O_{40}]$), Cs-Nano-PMo_{12} ($Cs_3[PMo_{12}O_{40}]$), and $[Bmim]_3[PMo_{12}O_{40}]$ nanohybrid

α-Keggin bulk form of phosphomolybdic acid (PMA) ($H_3[PMo_{12}O_{40}]$) was prepared by a self-assembly process, typically in an acidic aqueous solution according to the following procedure. Succinctly, 2.42 g of Na_2MoO_4 was firstly added to a 5 mL of aqueous