UNIVERSITI PUTRA MALAYSIA

POLYMERIC MEMBRANE SENSORS FOR DETECTION OF TITANIUM (III) IONS BASED ON TRIPODAL- OR CALIXARENE-LIGAND AND DETECTION OF CHROMIUM (VI) USING METALLO-SALEN IONOPHORES

MAJID REZAYI

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By

MAJID REZAYI

Thesis submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy

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Special dedication to my beloved parents

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Chair: Professor Anuar Kassim, PhD

Faculty: Science

Currently, despite of many developments in the field of ion selective electrodes (ISEs), it continues to evolve. The introduction of low detection limit ISEs may open a new opportunity to determine trace target ions. Improvements of detection limits, selectivities, understanding the response mechanism and developing new membrane materials are constantly being reported in the literatures. Moreover, the development of ISEs used in hospital and industrial setting as well as in clinical, environmental and physiological research has been opened new horizons in front of us. This research is focused on the fabrication of new PVC-membrane sensors based on tris(2pyridyl) methylamine, tpm and c-methylcalix[4]resorcinarene, CMCR as an cationic ionophores for detection of titanium (III) cation, and also N,N′Bis(salicylidene) ethylenediamino cobalt(II) ,Co(SALEN) as an anionic ionophore for determining the chromate (II) anion.

The complex reactions of Co(SALEN) with chromate (II) anion, tpm and CMCR with titanium (III) cation in water (H_2O), acetonitrile (AN) and their binary mixture solutions at different temperatures by using the conductometric method, are investigated. The characterization and evalution of materials are described. In addition, a variety of analytical methods, including UV-Vis spectroscopy, FT-IR spectroscopy, Scanning Electron Microscopy (SEM), are used to study these processes. Later on, the application and validation of proposed ISEs with the potentiometric titration, atomic absorption spectrometry (AAs) and inductively coupled plasma atomic emission spectrometry (ICP-AES) are studied. Based on conductometric measurement results, the stoichiometry of complex formation for all the cases of ion-ionophore is 1:1. Furthermore, the average of stability constant ($\log K_f$) obtained for tpm-$Ti(OH)(OH_2)_5^{2+}$, CMCR-$Ti(OH)(OH_2)_5^{2+}$ and Co(SALEN)-CrO_4^{2-} complexes at 25°C are 2.70, 3.13 and 3.02, respectively. Therefore, the mentioned ionophores can be used as sensing elements to fabricate ISE membranes for determination of titanium and chromate ions. These electroactive composite materials resulted in three new ionophore types which one based on selective ion–sensing membrane electrodes. They were fabricated for the determination of Ti (III) and CrO_4 (II) ions in solutions. The membrane sensors showed fast, stable and Nernstian response for the cation of titanium (III) and anion of chromate (II) over the concentration range from 1.0×10^{-6} to 1.0×10^{-2} M and 1.0×10^{-6} to 1.0×10^{-1} M at 25°C, over the pH range from 1 to 2.5 and 7 to 10 respectively. For titanium (III) cation, based on tpm and CMCR ionophores, the Nernstian slopes, detection limits and response times were 29.17±0.24 and 30.38±0.15 mV/decade of activity , 7.9×10^{-7} and 8.9×10^{-7} M, 20 and 15 s, respectively. For chromate (II)

anion, using Co(SALEN) ionophore, the Nernstian slope, detection limit and response time was -28.33±0.10 mV/decade of activity, 7.9×10^{-7} M and <10 s. The direct determination of 4 to 39 µg/ml of titanium (III) standard solution and 2 to 48.5 µg/ml of chromate (II) standard solution showed an average recovery of 94.60, 94.70 and 96.03 % and a mean relative standard deviation of 1.8, 2.2 and 1.6% at 100.0 µg/ml for tpm, CMCR and Co(SALEN) sensors, respectively. Finally, the utilizing of electrodes as the end point indicators for potentiometric titration with EDTA and $Pb(NO_3)_2$ solutions for titanium (III) and chromate (II) sensors were successfully carried out respectively.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SENSOR MEMBRAN POLIMERIK UNTUK PENGESANAN ION TITANIUM (III) BERDASARKAN TRIPODAL- ATAU KALIKSARENA- LIGAN DAN PENGESANAN KROMIUM (VI) MENGGUNAKAN IONOFOR METALLO-SALEN

Oleh

MAJID REZAYI

Mei 2011

Pengerusi: Profesor Anuar Kassim, PhD

Fakulti: Sains

Pada masa kini, perkembangan dalam bidang elektrod pemilih-ion (ISE) masih berterusan. Pengenalan ISEs dengan had pengesanan rendah ini membuka peluang baru untuk menentukan ion sasaran surih. Peningkatan had pengesanan, selektiviti, pemahaman mekanisma tindak balas dan perkembangan bahan membran baru secara berterusan telah dilaporkan di dalam banyak penerbitan literatur. Selain itu, pembangunan ISE untuk digunakan dalam hospital dan industri seperti dalam kajian klinikal, persekitaran dan fisiologi telah membuka era baru dalam bidang ini. Kajian ini difokuskan kepada pembuatan/fabrikasi deria (sensor)PVC-membran baru berdasarkan pada bahan tris(2piridil) metilamina, tpm dan c-metilcalix[4]resorcinarena, CMCR sebagai ionofor kationik untuk mengesan kation titanium (III), dan juga

N,N'Bis(salicilidena) etilenadiamino kobalt (II), Co(SALEN) sebagai ionofor anionik untuk menentukan anion kromat (II). Kompleks tindakbalas Co(SALEN) dengan anion kromat (II), tpm dan CMCR dengan kation titanium (III) dalam air (H_2O), asetonitril (AN) dan larutan campuran binari kepada suhu yang berbeza dengan menggunakan kaedah konduktometri telah dikaji. Pencirian dan penilaian bahan dibincangkan. Selain itu, pelbagai kaedah analisis, termasuk serapan UV-Vis, spektroskopi FT-IR, Imbasan Mikroskop Elektron (SEM), digunakan dalam kajian proses ini. Seterusnya, aplikasi dan pengesahan untuk ISE yang dicadangkan, dikaji dengan pentitratan potentiometri, serapan atom (AA) dan induktif kupel plasma (ICP) spektrometri. Berdasarkan hasil pengukuran konduktometri, stoikiometri pembentukan kompleks untuk semua kes ion-ionofor adalah 1:1. Selain itu, pemalar kestabilan ($\log K_f$) purata yang diperolehi, untuk tpm-$Ti(OH)(OH_2)_5^{2+}$, CMCR-$Ti(OH)(OH_2)_5^{2+}$ dan Co(SALEN)-CrO_4^{2-} kompleks pada suhu 25°C adalah 2.70, 3.13 dan 3.02, masing-masing. Oleh kerana itu, ionofor tersebut boleh digunakan sebagai penderiaan unsur untuk membuat membran ISE bagi menentukan ion titanium dan kromat. Bahan komposit elektroaktif ini menghasilkan tiga jenis ionofor baru yang berdasarkan kepada membran pemilih ion-deria elektrod. Ionofor ini disediakan untuk penentuan Ti (III) dan CrO_4 (II) ion dalam larutan. Sensor membran menunjukkan tindakbalas cepat, stabil dan rangsangan Nernstian untuk kation titanium (III) dan anion kromat (II) dalam lingkungan kepekatan dari 1.0×10^{-6} hingga 1.0×10^{-2} M dan 1.0×10^{-6} hingga 1.0×10^{-1} M pada 25°C, pada lingkungan pH 1 hingga 2.5 dan 7 hingga 10 masing-masing. Untuk kation titanium (III), berdasarkan ionofor tpm dan CMCR, kecerunan Nernst, had pengesanan dan masa tindakbalas adalah 29.17±0.24 dan 30.38±0.15 mV/dekad aktiviti, $7.9\times10^{-}$

^{7} dan 8.9×10^{-7} M, 20 dan 15 s, masing-masing. Untuk anion kromat (II), yang menggunakan Co(SALEN) ionofor, kecerunan Nernst, had pengesanan dan masa tindakbalas adalah -28.33±0.10 mV /dekad aktiviti, 7.9 × 10^{-7} M dan <10 s. Penentuan langsung bagi 4 hingga 39 µg/ml titanium (III) larutan piawai dan 2 hingga 48.5 µg/ml kromat (II) larutan piawai menunjukkan perolehan semula purata 94.60, 94.70 dan 96.03% dengan sisihan piawai purata relatif 1.8, 2.2 dan 1.6% pada 100.0 µg/ml untuk tpm, CMCR dan Co(SALEN) sensor, masing-masing. Akhirnya, pengunaan elektrod sebagai penunjuk untuk titratan potensiometri dengan larutan EDTA dan $Pb(NO_3)_2$ menggunakan elektrod sensor titanium (III) dan kromat (II) masing-masing telah berjaya dilakukan.

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In the name of Allah, the most merciful, the most compassionate:

My God! Let me out of the darkness of illusion, and let me be honourable by the light of understanding. My God, open to us the doors of thy compassion and uncover to us the treasures of the knowledge by thy compassion, the most compassionate of the compassionate ones.

This thesis is not an individual product; it is the result of much support for others.

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I certify that a Thesis Examination Committee has met on 03 MAY 2011 to conduct the final examination of Majid Rezayi on his thesis entitled **"**Polymeric membrane sensors for detection of titanium (III) ions based on tripodal- or calixarene-ligand and detection of chromium (VI) using metallo-salen ionophores" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institutions.

MAJID REZAYI

Date: 03 May 2011

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