UNIVERSITI PUTRA MALAYSIA

POLYMERIC MEMBRANE SENSORS FOR DETECTION OF CESIU (I), CHROMIUM (III) AND TITANIUM (III) IONS BASED ON CALIXARENE IONOPHORES

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By

SAEID AHMADZADEH

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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To my beloved parents for their encouragement, support and faith in me.

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

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. ISEs are invaluable tools for continuous monitoring and can be used in environmental, agricultural, industrial and clinical fields. They measure the activity rather than the concentration and are not affected by turbidity or sample color. In order to obtain highly selective polymeric membrane ISEs, suitable ionophores must be doped into the fabricated PVC membranes. Ionophores used namely p-Isopropylcalix[6]arene (L_1), 4-Isopropylcalix[4]arene (L_2) and meso-octamethyl-calix[4]pyrrole (L_3) are group of calixarenes that is bowel shaped super molecular compounds which can bind selectively to the target ion and act as an ion carrier in the membrane. Three novel high selective membrane sensors were fabricated for selective and sensitive determination of trace amount of three very significant

cations, cesium (I), chromium (III) and titanium (III) using (L_1), (L_2) and (L_3) as the ion sensing reagents, respectively. A novel cesium selective membrane electrode based on p-Isopropylcalix[6]arene as an ionophore was fabricated. The amounts of ionophore (5 mg), PVC (30 mg), dioctyl phthalate (DOP) as a plasticizer (62 mg) and potassium tetrakis (4-chloro-phenyl)borate (KTpClPB) as a lipophilic additive (3 mg) were optimized in the preparation of the membrane. The sensors exhibited significantly enhanced response towards cesium ions over the concentration range of 1.0×10^{-6}M to 1.0×10^{-1}M at pH 2.0 to 11.0 with a lower detection limit of 8.0×10^{-7}M and Nernstian slope of 57.29±0.31 (mV per decade of activity). It has a fast response time within 10 seconds over the entire concentration range and can be used for at least 3 months without any divergence in potentials. Moreover, a novel chromium selective membrane electrode based on 4-Isopropylcalix[4]arene as an ionophore was fabricated. The amounts of ionophore (5 mg), PVC (33 mg), 2-nitrophenyl octyl ether (o-NPOE) as a plasticizer (61.5 mg) and sodium tetra phenyl borate (NaTPB) as a lipophilic additive (0.5 mg) were optimized in the preparation of the membrane. The chromium selective sensor exhibited a linear response with a Nernstian slope of 19.45±0.21 (mV per decade of activity) over a wide concentration range of 1.0×10^{-6}M to 1.0×10^{-1}M with a lower detection limit of 9.0×10^{-7}M. The potentiometric response of the developed electrode is independent of the solution pH in the range of 3.0 to 6.5 and exhibited good reproducibility over a useful lifetime of 3 months with a fast response time of 8 seconds. Lastly, a novel titanium selective membrane electrode based on meso-octamethylcalix[4]pyrrole as an ionophore was fabricated. The amounts of ionophore (4 mg), PVC (33 mg), dioctyl phthalate (DOP) as a plasticizer (62.8 mg) and sodium tetrakis [3,5-bis (trifluoromethyl) phenyl]-

borate (NaTFPB) as a lipophilic additive (0.5 mg) were optimized in the preparation of the membrane. The developed sensor exhibited a Nernstian slope of 29.49±0.16 (mV per decade of activity) over a pH range from 1.0 to 3.0 with a satisfactory concentration range of 1.0×10^{-6}M to 1.0×10^{-1}M. It showed good reproducibility over a period of about 3 months with a fast response time of 15 seconds. The results obtained from ISEs studies were evaluated by comparing them with the data received from instrumental methods such as UV-Vis, FT-IR, AAS, ICP and SEM. The complex reactions of p-Isopropylcalix[6]arene with cesium (I) cation in dimethyl sulfoxide (DMSO), acetonitrile (AN), 4-Isopropylcalix[4]arene with chromium (III) cation in dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) and meso-octamethylcalix[4]pyrrole with titanium (III) cation in ethanol (EtOH), acetonitrile (AN) and their binary mixture solutions at different temperatures by using the conductometric method, are investigated. 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 (p-Isopropylcalix[6]arene.$Cs)^{+}$, (4-Isopropyl-calix[4]arene.$Cr)^{3+}$ and (meso-octamethylcalix[4]pyrrole.$[Ti(OH)\text{-}(H_2O)_5])^{2+}$complexes at 25°C are 2.97, 2.90 and 2.97, respectively.

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

SENSOR MEMBRAN POLIMERIK UNTUK PENGESANAN ION CESIUM (I), KROMIUM (III) DAN TITANIUM (III) BERDASARKAN IONOFOR KALIKSARENA

Oleh

SAEID AHMADZADEH

Mei 2011

Pengerusi: Profesor Anuar Kassim, PhD

Fakulti: Sains

Elektrod-elektrod pemilihan ion (ISEs) membenarkan pengesanan aktiviti ion tertentu secara potentiometrik dalam pelarut akueus dan bukan akueus. ISEs merupakan alat penting yang dapat berfungsi secara berterusan, di mana ia sesuai diaplikasikan dalam bidang persekitaran, pertanian, industri dan klinikal. Ia mengukur aktiviti ion bukannya kepekatan ion dan tidak akan dipengaruhi oleh kekeruhan dan warna sampel. Bagi mencapai sifat pemilihan tinggi untuk membran polimerik ISEs, ionofor-ionofor yang sesuai perlu didopkan ke dalam membran PVC yang difabrikasi. Ionofor-ionofor yang digunakan iaitu p-Isopropylcalix[6]arene (L_1), 4-Isopropylcalix[4]arene (L_2) dan meso-octamethylcalix[4]pyrrole (L_3) merupakan sebatian supramolekul yang berbentuk ‘bowel’ daripada kumpulan calixarenes. Sebatian-sebatian tersebut dapat mengikat ion secara terpilih dan berfungsi sebagai pembawa ion dalam membran. Tiga penderia membran novel yang bersifat pemihan

tinggi telah difabrikasikan untuk penentuan tiga kation yang amat penting iaitu cesium (I), kromium (III) dan titanium (III) pada kepekatan rendah dengan menggunakan (L_1), (L_2) dan (L_3) sebagai reagen pengesanan ion masing-masing. Suatu elektrod membran pemilihan cesium baru yang berasakan ionofor p-Isopropylcalix[6]arene telah difabrikasikan. 5 mg ionofor, 30 mg PVC, 62 mg dioktil ftalat (DOP) sebagai 'plasticizer' dan 3 mg potassium tetrakis (4-chloro-phenyl)borate (KTpClPB) sebagai penambah lipofilik telah dioptimasikan dalam penyediaan membran. Penderia mempamerkan rangsangan (respons) yang diperkuatkan secara signifikasi terhadap ion cesium dalam julat kepekatan 1.0×10^{-6}M hingga 1.0×10^{-1}M, julat pH 2.0 hingga 11.0 dengan had pengesanan yang lebih rendah iaitu 8.0×10^{-7}M dan kecerunan Nernstian yang bernilai 57.29±0.31 (mV per aktiviti). Ia mempunyai masa rangsangan (respons) yang cepat dalam 10 saat untuk julat kepekatan keseluruhan dan boleh digunakan selama 3 bulan tanpa mengalami perubahan dalam potential. Selain itu, satu elektrod membran pemilihan kromium baru yang berasakan ionofor 4-Isopropylcalix[4]arene telah difabrikasikan. 5 mg ionofor, 33 mg PVC, 61.5 mg 2-nitrophenyl octyl ether (o-NPOE) sebagai 'plasticizer' dan 0.5 mg sodium tetra phenyl borate (NaTPB) sebagai penambah lipofilik telah dioptimasikan dalam penyediaan membran. Penderia pemilihan kromium menunjukkan rangsangan (respons) linear dengan kecerunan Nernstian yang bernilai 19.45±0.21 (mV per aktiviti) dan had pengesanan yang lebih rendah iaitu 9.0×10^{-7}M dalam julat kepekatan 1.0×10^{-6}M hingga 1.0×10^{-1}M. Rangsangan (respons) potentiometrik bagi elektrod tersebut adalah bebas daripada gangguan pH dalam julat 3.0 hingga 6.5 dan menunjukkan kebolehhasilan yang baik dalam jangka hayat 3 bulan dengan masa rangsangan (respons) yang secepat 8 saat. Akhir sekali,

satu elektrod membran pemilihan titanium baru yang berasakan ionofor meso-octamethylcalix[4]pyrrole telah difabrikasikan. 4 mg ionofor, 33 mg PVC, 62.8 mg dioktil ftalat (DOP) sebagai 'plasticizer' dan 0.5 mg sodium tetrakis [3,5-bis(trifluoromethyl)phenyl] borate (NaTFPB) sebagai penambah lipofilik additive telah dioptimasikan dalam penyediaan membran. Penderia tersebut mempamerkan kecerunan Nernstian yang bernilai 29.49±0.16 (mV per aktiviti) dalam julat pH 1.0 hingga 3.0 dengan julat kepekatan yang memuaskan iaitu dari 1.0×10^{-6}M hingga 1.0×10^{-1}M. Ia menunjukkan kebolehhasilan yang baik dalam jangka hayat 3 bulan dengan masa rangsangan (respons) yang secepat 15 saat. Keputusan hasil daripada kajian ISEs dinilai dengan membandingkannya dengan data yang diterima daripada kaedah instrumentasi seperti UV-Vis, FT-IR, AAS, ICP dan SEM. Kompleks tindakbalas p-Isopropylcalix[6]arene dengan kation cesium (I) dalam dimetil sulfoksida (DMSO), asetonitril (AN), 4-Isopropylcalix[4]arene dengan kation kromium (III) dalam dimetil sulfoksida (DMSO), tetrahidrofuran (THF) dan meso-octamethylcalix[4]pyrrole dengan kation titanium (III) dalam etanol (EtOH), asetonitril (AN) dan larutan campuran binari pada suhu yang berbeza dengan menggunakan kaedah konduktometri telah dikaji. 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 (p-Isopropylcalix[6]arene.Cs)$^{+}$, (4-Isopropyl-calix[4]arene.Cr)$^{3+}$ and (meso octamethylcalix[4]pyrrole.[Ti(OH)-$(H_2O)_5$])$^{2+}$ kompleks pada suhu 25°C adalah 2.97, 2.90 dan 2.97, masing-masing.

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"Our Lord, do not let our hearts falter once You have guided us;
grant us mercy from Your presence, for You are the Bountiful!"

The holy Quran, Aleomran, 8.

I certify that a Thesis Examination Committee has met on 05 May 2011 to conduct the final examination of Saeid Ahmadzadeh on his thesis entitled **"**Polymeric Membrane Sensors for Detection of Cesium (I), Chromium (III) and Titanium (III) Ions Based on Calixarene Ionophore**s"** 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.

Members of the Thesis Examination Committee were as follows:

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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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.

SAEID AHMADZADEH

Date: 5 May 2011

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