

คาลิกซ์[4]เอรีนที่มีควิโนลีนเป็นองค์ประกอบเพื่อเป็นไอออนอฟอร์
ในอิเล็กทรอนิกส์แบบเลือกจำเพาะต่อไอออน

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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CALIX[4]ARENE CONTAINING QUINOLINE AS IONOPHORE
IN ION SELECTIVE ELECTRODES

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry

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Chulalongkorn University

Academic Year 2013

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ชาตนิวัต สุขสำราญ : คาลิกซ์[4]เอรีนที่มีควิโนลีนเป็นองค์ประกอบเพื่อเป็นไอออนอพออร์รีโนลิเก็กโทรดแบบเลือกจำเพาะต่อไอออน. (CALIX[4]ARENE CONTAINING QUINOLINE AS IONOPHORE IN ION SELECTIVE ELECTRODES) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : ศ. ดร. ธวัชชัย ต้นทุลานี, 47 หน้า.

ได้เตรียมไอออนซีเล็คทีฟลิเก็กโทรดที่มีไอออนซีเล็คทีฟเมมเบรนชนิดใหม่ 2 ชนิด ไอออนซีเล็คทีฟ เมมเบรนนี้ประกอบด้วยไอออนอพออร์รีโนลิเก็กโทรด 2 ชนิด คือ QN-1 และ QN-2 ซึ่งมีพาราเทอร์เชียรีบิวทิลคาลิกซ์ [4]เอรีนเป็นโครงสร้างพื้นฐานทั้งสองชนิด และมีควิโนลีนหนึ่งหมู่และสองหมู่ตามลำดับเป็นรีเซปเตอร์ที่สามารถจับกับแคตไอออนของโลหะได้ มีพีวีซีเป็นพอลิเมอร์ มีโพแทสเซียมเตตราคิส(4-คลอโรเฟนิล)บอเรต (KTPCIPB) เป็นไอออนเอ็กซ์เชนเจอร์ มีออริโท -ไนโตรเฟนิลออกทิลอีเทอร์ (o-NPOE)) หรือไดออกทิล ซีบาแคต (DOS) เป็น พลาสติไซเซอร์ แล้วนำไปใช้ศึกษาความสามารถในการตอบสนองต่อแคตไอออนต่างๆ ได้แก่ Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ag^+ , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} และ Hg^{2+} และ พบว่า QN-1 ซึ่งเป็นไอออนอพออร์รีโนลิเก็กโทรดที่มีไนโตรเจนและออกซิเจนเป็นคอนเนกเตอร์อะตอมสามารถจับกับ Ag^+ ได้ดีเท่ากับ QN-2 ทั้ง QN-1 และ QN-2 มีความสามารถในการ แยกแยะความแตกต่างกับ Hg^{2+} ครอบคลุมได้ใกล้เคียงกัน แต่อย่างไรก็ตาม QN-2 มีความสามารถในการ แยกแยะ แคตไอออนรบกวนชนิดอื่น (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} และ Pb^{2+}) ได้ดีกว่า QN-1 จึงได้นำไอออนซีเล็คทีฟลิเก็กโทรดที่มี QN-2 เป็นไอออนอพออร์รีโนลิเก็กโทรดมาทำการศึกษาต่อไป พบว่าไอออนซีเล็คทีฟลิเก็กโทรดที่มีไดออกทิลซีบาแคตเป็นพลาสติไซเซอร์และมี QN-2 เป็นไอออนอพออร์รีโนลิเก็กโทรดตอบสนองต่อ Ag^+ ที่ใกล้เคียงกับแบบเนินสต์ ($53.3 \pm 1.0 \text{ mV decade}^{-1}$) มีช่วงในการตอบสนองคือ 10^{-5} ถึง 10^{-2} M และมีค่าความเข้มข้นต่ำที่สุด ที่สามารถตรวจวัดได้เท่ากับ 8.3×10^{-7} M และยังได้ศึกษาการตอบสนองแบบย้อนกลับโดยการวัด EMF ของสารละลาย Ag^+ สองความเข้มข้นคือ 10^{-4} และ 10^{-3} M สลับกัน พบว่าค่า EMF ที่วัดได้ในแต่ละความเข้มข้นมีค่าคงที่ ฉะนั้น ไอออนซีเล็คทีฟลิเก็กโทรดสามารถใช้วัดความเข้มข้นของ Ag^+ โดยมีการตอบสนองแบบย้อนกลับอย่างดีเยี่ยม นอกจากนี้ได้นำไอออนซีเล็คทีฟลิเก็กโทรดที่มี QN-2 เป็นไอออนอพออร์รีโนลิเก็กโทรดไปประยุกต์ใช้ในการตรวจวัด Ag^+ โดยเทคนิคอาร์เจนโตเมตริกไทเทรชันด้วย

ภาควิชา.....เคมี..... ลายมือชื่อนิสิต.....
 สาขาวิชา.....เคมี..... ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก.....
 ปีการศึกษา.....2556.....

5372226023: MAJOR CHEMISTRY

KEYWORDS: IONOPHORE / ION SELECTIVE ELECTRODE

CHARTNIWAT SUKSAMRARN: CALIX[4]ARENE CONTAINING QUINOLINE AS IONOPHORE IN ION SELECTIVE ELECTRODES. ADVISOR: PROF. DR. THAWATCHAI TUNTULANI, Ph.D., 47 pp.

Two ion selective electrodes (ISEs) containing two new ion selective membranes were prepared. The ion selective membranes consisted of two supermolecules, **QN-1** and **QN-2**, as ionophores. Both structures of ionophores were based on *p-tert*-butylcalix[4]arene. The structures of ionophores **QN-1** and **QN-2** comprised one and two quinoline units, respectively, as metal ion receptors. The ion selective membranes also consisted of PVC as a polymer, potassium tetrakis(4-chlorophenyl)borate (KTPClPB) as an ion exchanger, *o*-nitrophenyloctyl ether (*o*-NPOE) or dioctyl sebacate (DOS) as a plasticizer. The ability of the ISEs in response to Na⁺, K⁺, Ca²⁺, Mg²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, Pb²⁺ and Hg²⁺ was studied. **QN-1**, the ionophore containing one soft nitrogen and one hard oxygen donors, showed the same selectivity towards Ag⁺ as **QN-2**. Both **QN-1** and **QN-2** exhibited comparable discriminating abilities to interfering Hg²⁺. However, **QN-2** showed much improvement in discriminating abilities to other interfering cations (Na⁺, K⁺, Ca²⁺, Mg²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺) as compared to **QN-1**. The ISE containing **QN-2** as ionophore has, therefore, been selected for further studies. The DOS-plasticized membrane from **QN-2** exhibited a near-Nernstian response to silver ion (53.3 ± 1.0 mV decade⁻¹) and a linear range of 10⁻⁵ to 10⁻² M with a detection limit of 8.3×10^{-7} M. The electrode reversibility was performed by alternatively measuring EMF at two different concentrations, 10⁻⁴ and 10⁻³ M Ag⁺ and it was found that the EMF signals was restored at the same concentration of Ag⁺ in every cycle. Therefore, the electrode can be used to measure the Ag⁺ concentration with excellent reversibility. An application of the fabricated electrode **QN-2** in argentometric titration of chloride ion was achieved.

Department:Chemistry..... Student's Signature

Field of Study:Chemistry..... Advisor's Signature

Academic Year:2013.....

ACKNOWLEDGEMENTS

I would like to express my highest gratitude to Professor Dr. Thawatchai Tuntilani, my thesis advisor, for the opportunity he has given me to work in his group and also for his valuable guidance, understanding, support, patience and warm encouragement. My deepest thanks would be expressed to Dr. Wanwisa Janrungroatsakul for introducing me into the field of ion selective electrodes and her advices and caring throughout my thesis work. I would also give my deep thanks to Dr. Pannee Leeladee for her caring encouragement, useful comments and helpful advice.

I am grateful to Assistant Professor Dr. Boosayarat Tomapatanaget and Dr. Gamolwan Thumcharoen as thesis examiners for their valuable comments and suggestions.

I am also grateful to Assistant Professor Dr. Chomchai Suksai and Mr. Sarayut Watchasit for the synthesis of the inonophores QN-1 and QN-2, Assistant Professor Dr. Wanlapa Aeungmaitrepirom for providing facilities and space in the laboratory. I would like to give my appreciation to all members of Supramolecular Chemistry Research Unit (SCRU) and Environmental Analysis Research Unit (EARU) for their advice, friendship and supports.

I am indebted to the Junior Science Talent Project (JSTP) for the financial support throughout my study.

Finally, I would like to thank my grandmother, my father and my mother for their unfailing love, supports and encouragements throughout my life.

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LIST OF ABBREVIATIONS

Ag-ISE	Silver ion selective electrode
°C	Degree Celsius
DL	Detection limit
DOS	Diocetyl sebacate
EMF	Electromotive force
FIM	Fixed interference method
g	Gram
h	Hour
HDL	High detection limit
ISE	Ion selective electrode
KTpCIPB	Potassium tetrakis[4-chlorophenyl] borate
LDL	Low detection limit
M	Molar
MPM	Matched potential method
mL	Millilitre
mV	Millivolt
μL	Microlitre
<i>o</i> -NPOE	<i>o</i> -Nitrophenyl octyl ether
ppb	Part per billion
ppt	Part per billion
PVC	Poly(vinyl chloride)
R ⁻	Cation exchanger
SSM	Separate solution method
THF	Tetrahydrofuran
v/v	Volume by volume
wt.%	Percent by weight

CHAPTER I

INTRODUCTION

Methods for the determination of metals and metal ions are available, for example, atomic absorption spectrometry, and the use of an inductively coupled plasma in combination with atomic emission or mass spectrometry are recommended methods [1,2]. These and many other techniques often require quite extensive and time-consuming sample pretreatment, including preconcentration and matrix separation. Preconcentration is a process as a result of which the ratio of the concentration or the amount of microcomponents (trace constituents) and macrocomponents (matrix) increases. Frequently, preconcentration enables a relative detection limit to be improved by two to three orders of magnitude or more. The use of preconcentration may increase the accuracy and precision of determinations as a result of the elimination of interferences, but it also may decrease them owing to losses of components being determined or to contamination. This process has many drawbacks. In most cases, it lengthens the analysis and frequently complicates it; reagents of high purity are needed, especially when common elements are determined, sometimes in great amounts; in some cases, special equipment and mastering of specific working procedures are desirable. Preconcentration may be affected by losses of the elements being determined or by introduction of external contaminants [3]. The matrix includes the analyte and other constituents, which are termed concomitants. The analysis of real samples is complicated by the presence of the sample matrix. This matrix can contain species that have chemical properties similar to the analyte. Such species can react with the same reagents as the analyte or they can cause an instrument response that cannot be easily distinguished from the analyte. These effects interfere with the determination of the analyte. Matrix separation is therefore necessary in many cases to avoid interference of some cations [4].

Metals are utilized for a wide range of applications. This can be exemplified in the case of silver. This metal has been used in medicine, electronics, optics, photography, including the production of jewelry, coins, batteries, photovoltaic cells, bearings, and catalysts. Since silver salts and silver nanoparticles possess antibacterial properties, they are used for the disinfection of drinking water and the preparation of topical gels, specialty bandages, implantable prostheses, and catheters. Consequently, about 2,500 tons of silver are released into the environment annually, and approximately 80 tons end up in surface waters [5]. Although silver is not as toxic to humans as many other heavy metals, the U.S. Environmental Protection Agency (EPA) reported that a concentration higher than 1.6 nM is toxic to fish and microorganisms [6], and the maximum contaminant level for total silver in drinking water was 0.9 μM [7]. Though atomic absorption spectrometry including the use of an inductively coupled plasma together with atomic emission or mass spectrometry are the recommended methods, the sample preparation for analysis is time consuming as mentioned above, and this method is costly. Development of other more sensitive methods is therefore necessary.

Ion selective electrode (ISE) is an ion analysis technique that provides many unique characteristics. ISE is a valuable tool for measuring concentration of metal ions and this technique requires little sample preparation and manipulation while still permitting very wide ranges of linear response, low limits of detection, high selectivity, and the possibility to distinguish between the free metal ion and its complexes [8,9]. Advances in the understanding of ion fluxes across ISE membranes have made it possible for the measurements with ISEs in the ppb (parts-per-billion) and ppt (parts-per-trillion) level possible [10-12]. Potentiometry based on ion selective electrodes has widely been used for the determination metal ions for several decades [13] since ISEs offer several advantages, especially cheap and simple device.

Metal ion selective electrodes have been developed and successfully constructed from a diversity of ionophores (or carriers) [14-22]. Silver ion selective electrodes (Ag-ISEs) for monitoring and determination of silver ion have also been explored [23-35]. However, more sensitive and ion selective ISEs are needed.

Calixarene is a very popular molecular platform for ionophores since calixarene derivatives possessing different functional groups with various donor atoms [36,37] can offer different selectivity of ionophores towards metal ions, including Ag^+ ion [33,34,38-42].

In this research, two ionophores based on calix[4]arene containing quinoline as donor atoms were used to construct ISEs in order to find the best electrode which is most selective to metal ions, especially Ag^+ , and give excellent selectivity with low interference of other cations, particularly Hg^{2+} .

Research Objective

The research aims to fabricate new ISEs using calix[4]arene with quinoline unit as ionophores. Particular interest would be paid to the fabricated Ag-ISEs. The prepared ISEs would be compared in order to find the best one in term of selectivity, stability constant and lower detection limit. Membrane compositions would then be optimized to obtain the best ISE, which was examined the electrode characteristics such as selectivity, lower detection limit, response time and reversibility.

Scope of the Research

In this research, ISEs were prepared from two ionophores, **QN-1** and **QN-2**, which are calix[4]arene with one and two quinoline units as shown in Figure 1.1. These ionophores were then incorporated into a plasticized poly(vinyl chloride) (PVC) matrix with a lipophilic cation exchanger for preparation of a membrane electrode. The fabricated Ag-ISEs were compared in order to find the best ones in term of selectivity, stability constant and lower detection limit. Membrane compositions were optimized to obtain the best Ag-ISE, and electrode characteristics such as selectivity, lower detection limit, response time and reversibility were examined.

QN-1

QN-2

Figure 1.1 Structures of two selected ionophores (**QN-1** and **QN-2**).

Benefits of the Research

A novel ISE that could be used for the analysis of cations, in particular Ag^+ ion, with selectivity, stability constant and lower detection limit, should be obtained.

CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Ion Selective Electrodes (ISEs)

Ion selective electrodes (ISEs) are potentiometric chemical sensors since some selective chemistry takes place at the surface of the electrode producing an interfacial potential [36]. The output of membrane electrical potential is proportional to the activity (or concentration) of the analyte as the logarithmic value. The membrane must therefore contain a component that will react chemically and reversibly with the analyte. This component is a receptor unit or carrier-based ISE, which has different structure and type of coordinate atoms to provide a variety of electrodes selective towards particular analyte ion. The binding between carrier-based ISE and analyte ion uses the basis of host-guest interaction or coordination chemistry. The ion selective membranes are divided into many categories such as glass membranes, sparingly soluble inorganic salts membranes, polymer-immobilized ionophore membranes, gel-immobilized and chemically bonded enzyme membranes.

The advantages of ISEs over several analytical devices are their low cost and simple device that are compatible with miniaturization and they can be the excellent tools in biomedical, industrial and environmental applications. Works on the applications of ISEs in these areas are growing in importance. A new approach for the invention of glucose biosensor based on polymeric membrane Ag-ISE fabricated has been investigated [41]. Increasing interest in the applications of miniaturized ISEs for monitoring NADH [44], protein immunoassays [45] or DNA hybridization [46-48] in connection to Ag, CdS-nanocrystal labels, enzyme tags or liposomes has been noted.

2.1.1 Components of the polymeric ion selective electrodes

The ion-sensitive solvent polymeric membrane is physically water immiscible liquid of high viscosity consisting of the components as listed below.

1) Polymer matrix

The polymeric membranes in ISEs are commonly prepared with PVC in order to provide mechanical stability and elasticity to the membrane. In ideal cases it is inert and has no chemical interaction with the sensed ions.

2) Plasticizer

The plasticizer or membrane solvent must be compatible with all membrane components to provide a homogenous organic phase. It should have high lipophilicity, high molecular weight, low tendency for exudation from polymeric membrane, low vapor pressure with high capacity to dissolve membrane components present in the polymeric membrane [49]. Although the plasticizers have different dielectric constants, structures and lipophilicity characteristics, they are usually used in polymeric liquid membranes. The commonly used plasticizers are bis(2-ethylhexyl)sebacate (DOS, apolar) and *ortho*-nitrophenyl octyl ether (*o*-NPOE, polar) [50].

3) Ion exchanger

Lipophilic salts are cation or anion exchanger in ISE membranes to maintain membrane permselectivity [8] that is ability of the membrane to allow only ions of the same charge as primary ion to pass resulting in the theoretical Nernstian response. Ionic sites also reduce membrane resistance and interference from counter ions. Cation-selective membranes commonly used lipophilic tetraphenylborate salts while anion-selective systems employed tetraammonium derivatives.

4) Ionophore

Ionophore or ion carrier is the most important component for the selectivity of ISE membrane. The ionophore can form complex with analyte ion and reversible complex to free ionophore with very fast reaction. The structure of ionophore must contain lipophilic groups to prevent the ionophore leaching from membrane to the sample phase.

2.1.2 Response mechanism

The potentiometric measurement consists of an ISE, a reference electrode and a potential-measuring device (see Figure 2.1). A reference electrode is an electrochemical half-cell which maintains virtually constant potential with respect to a solution.

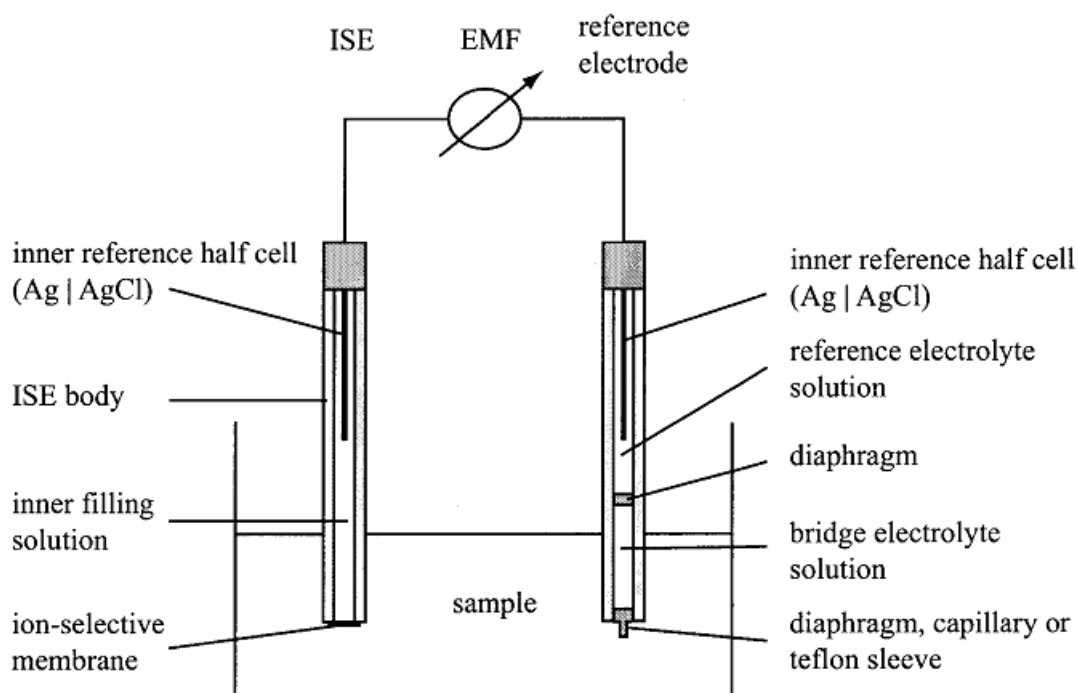


Figure 2.1 Diagram of a potentiometric cell with an ISE [51].

The electromotive force (EMF) across the entire potentiometric cell is the sum of the individual potential contributions.

$$\text{EMF} = E_{\text{const}} + E_J + E_M \quad (2.1)$$

where E_M is membrane potential, E_J is liquid junction potential at the sample/bridge electrolyte interface which can be kept small and constant by using high concentration of bridge electrolyte (for example, 1 M KCl, NH_4OH or LiOAc) according to Henderson formalism [52,53] and E_{const} is a constant contribution. The membrane potential (E_M) contains three separate potential contributions, i.e., the phase boundary potential at the membrane/sample solution interface ($E_{\text{PB}'}$), the phase boundary potential at the membrane/inner filling solution interface ($E_{\text{PB}''}$) and the diffusion potential within the membrane (E_{diff}).

$$E_M = E_{\text{PB}' } + E_{\text{PB}''} + E_{\text{diff}} \quad (2.2)$$

The potential at the membrane/inner filling solution interface is usually independent of the sample. The diffusion potential within the membrane is negligible due to membranes that show a Nernstian response in most experiments.

$$E_M = E_{\text{const},1} + E_{\text{PB}' } \quad (2.3)$$

The potential thus depends only on the phase boundary potential at membrane/sample solution interface ($E_{\text{PB}'}$) arising from an unequal equilibrium distribution of ions between aqueous sample and organic membrane phases. For aqueous solution containing ion I in equilibrium with the membrane, the electrochemical potential, $\tilde{\mu}$, of the ion I aqueous phase is

$$\tilde{\mu}(\text{aq}) = \mu(\text{aq}) + zF\phi(\text{aq}) = \mu^0(\text{aq}) + RT \ln a_1(\text{aq}) + zF\phi(\text{aq}) \quad (2.4)$$

and for the contacting organic phase:

$$\tilde{\mu}(\text{org}) = \mu(\text{org}) + zF\phi(\text{org}) = \mu^0(\text{org}) + RT \ln a_1(\text{org}) + zF\phi(\text{org}) \quad (2.5)$$

in this case, μ is the chemical potential, μ^0 is chemical potential under standard conditions, z is the charge of the ion I, a_I is the activity of ion I, ϕ is the electrical potential, and R , T and F are the universal gas constant, the absolute temperature and the Faraday constant, respectively. Assuming that the interfacial ion transfer and complexation processes are relatively fast so that the equilibrium holds at the interface, the electrochemical potentials for both phases are equal [50]. This leads to a simple expression for the phase boundary potential [54] as follows

$$E_{PB} = \Delta\phi = -\frac{\mu^0(\text{org}) - \mu^0(\text{aq})}{zF} + \frac{RT}{zF} \ln \frac{a_I(\text{aq})}{a_I(\text{org})} \quad (2.6)$$

where $\Delta\phi = \phi(\text{org}) - \phi(\text{aq})$. If $a_I(\text{org})$ is constant, it could be combined with other sample-independent terms into $E_{\text{const},2}$ and equation (2.6) reduce to the form of Nernst equation.

$$E_{PB} = E_{\text{const},2} + \frac{RT}{z_1F} \ln a_I(\text{aq}) \quad (2.7)$$

Substitution of E_{PB} into equation (2.3) and (2.1) gives an equation describing the response of ISE towards ion I in aqueous solution.

$$E = E_I^0 + \frac{RT}{z_1F} \ln a_I(\text{aq}) \quad (2.8)$$

where E_I^0 is a new constant, including all sample-independent potential in a cell. The Nernstian slope of the response function is $2.303 RT/z_1F = 59.2 \text{ mV}/z_1$ for $z = 1$ at 298 K.

In order to obtain exact Nernstian response of electrode for the uncharged carriers, the ion-exchange mechanism between the organic and aqueous phases is controlled by lipophilic anionic additive to ensure permselectivity. This process is shown in Figure 2.2 for the neutral ionophores based on ISE.

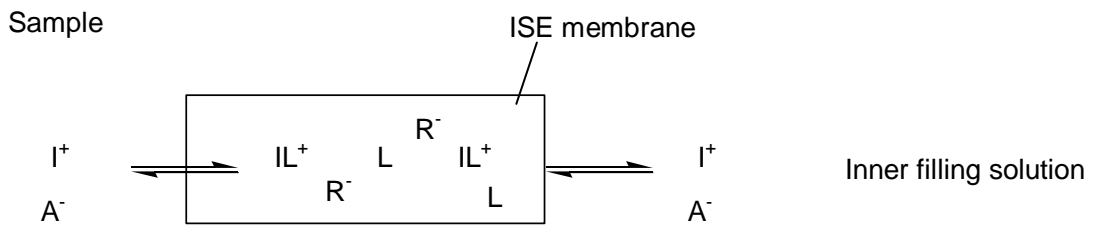


Figure 2.2 Neutral-carrier-based ion selective electrode (L, neutral carrier; R^- , negatively charged ionic sites, I^+ and A^- are sample ions). Square indicates species in the organic phase.

2.1.3 Electrode characteristics

2.1.3.1 Selectivity

Selectivity is one of the most important characteristics of an ISE and is defined as the degree of discrimination of an electrode to ions in solution other than the primary ion [55-57]. According to Nicolskii-Eisenman formalism [58,59], the activity term in the Nernst equation is replaced by a sum of selectivity-weighted activities.

$$E = E_1^0 + \frac{RT}{z_1 F} \ln (a_1(IJ) + K_{IJ}^{pot} a_J(IJ)^{z_1/z_J}) \quad (2.9)$$

where $a_1(IJ)$ and $a_J(IJ)$ are the activities of primary ion I and interfering ion J in the mixed sample. The Nicolskii coefficient, K_{IJ}^{pot} , is the potentiometric selectivity coefficient for I over J. If the coefficient value is small, it leads to good selectivity of the electrode. When K_{IJ}^{pot} is very small and $a_1(IJ)$ approaches the primary-ion activity $a_1(I)$ in a solution without interfering ions according to the equation:

$$a_1(I) = a_1(IJ) + K_{IJ}^{pot} a_J(IJ) \quad (2.10)$$

the meaning is that there is no interference. If interference is observed, a lower activity $a_i(IJ)$ of the mixed sample will give rise to the same response as the activity $a_i(I)$ of a solution containing no interfering ions.

For carrier-based ISEs, the selectivity is determined by composition of the membrane. The relationship between ion selectivity and the membrane composition of cation selective electrodes is explained in equation (2.11) considered from charge balance and mass balance [60].

$$K_{IJ}^{pot} = K_{IJ} \frac{(\beta_{ILnJ})^{z_I/z_J}}{\beta_{ILnI}} \frac{R_T^-}{z_I[L_T - n_I(R_T^-/z_I)]^{n_I}} \times \left(\frac{z_J[L_T - n_J(R_T^-/z_J)]^{n_J}}{R_T^-} \right)^{z_I/z_J} \quad (2.11)$$

where K_{IJ} is the equilibrium constant for the ion exchange between the uncomplexed primary and interfering ions between the sample and the membrane phase, L_T and R_T are the total concentrations of ionophore and anionic site, z_I and z_J the charge of the primary ion and interfering ion, respectively, whereas β is the complex formation constant of the ion-ionophore complex and n the complex stoichiometry.

Determination of selectivity of ion selective electrodes

1. Separate solution method (SSM)

Separate solution method (SSM) is used to determine the selectivity of an ISE as illustrated in Figure 2.3. The SSM concerns the measurement of two separate solutions, each containing the primary ion and interfering ion. The selectivity is calculated from the following equation:

$$\log K_{IJ}^{pot} = \frac{z_I F \{E(J) - E(I)\}}{2.303 RT} + \log \left(\frac{a_I(I)}{a_J(J)^{z_I/z_J}} \right) \quad (2.12)$$

where $E(J)$ and $E(I)$ are the recorded potentials in separate solutions for primary ion I and interfering ion J and $a_i(I)$ and $a_j(J)$ the activities of I and J in separate solutions. The selectivity coefficient values thus obtained are equal to the thermodynamically defined ones as long as the response slopes of all of the ions are Nernstian.

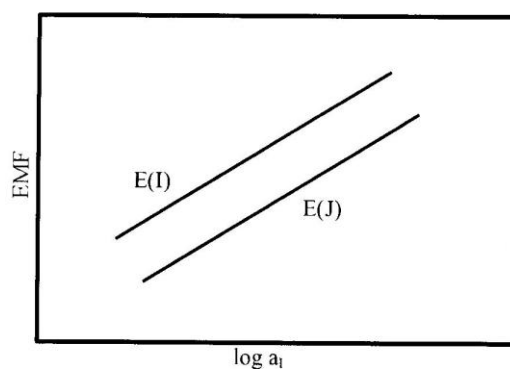


Figure 2.3 Schematic representation of ISE selectivity as determined by the separation solution method [61].

2. Fixed interference method (FIM) or Mixed interference method

In this method, an entire calibration curve for the primary ion is measured in the presence of an interfering ion which is fixed activity as the background (Figure 2.4). $a_J(\text{BG})$ is the activity of the constant interfering ion in the background. $a_I(\text{DL})$ is the low detection limit (LDL) of the Nernstian response curve of the electrode as a function of the primary ion activity. The selectivity of FIM is calculated from

$$\log K_{IJ}^{\text{pot}} = \log \left(\frac{a_I(\text{DL})}{a_J(\text{BG})^{z_I/z_J}} \right) \quad (2.13)$$

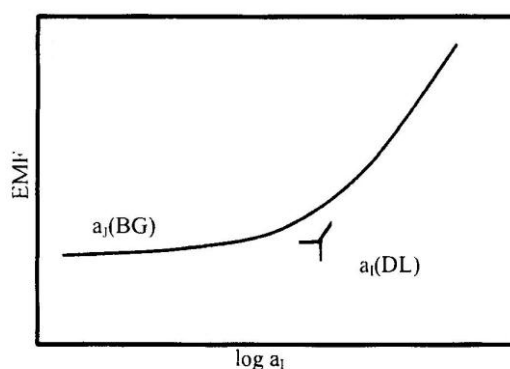


Figure 2.4 Schematic representation of ion selective electrode selectivity as determined by the fixed interference method [61].

The SSM and FIM require Nernstian response of both interfering ion and primary ion [8,56,57].

3. Matched potential method (MPM)

In the MPM, a known amount of primary ions is added to a reference solution and the potential is measured. Another experiment, interfering ions are gradually added to an identical reference solution until the membrane potential matches with the other one obtained from the primary ion. The selectivity is calculated from the following equation:

$$\log K_{IJ}^{\text{pot}} = \frac{\Delta a_I}{\Delta a_J} \quad (2.14)$$

The advantage of this approach is that it can be used when the response of the electrode is not Nernstian or even linear. However, the drawback is that the selectivity coefficient may change under different experimental conditions, particularly the concentrations at which the measurements were made. In most situations, the selectivity obtained from matched potential method cannot be directly compared to the values obtained from other methods.

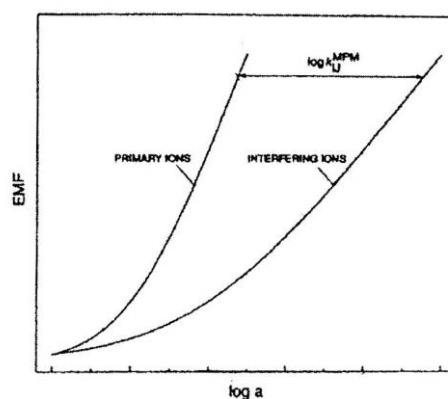


Figure 2.5 Schematic representation of ion selective electrode selectivity as determined by the matched potential method [61].

2.1.3.2 Detection limits

Deviations of the electrode function from the linear response are normally observed at high and low activities of the measuring ion. According to the IUPAC recommendation [55], the detection limits are defined by the cross-section of the two extrapolated linear calibration curves (see Figure 2.6).

The upper detection limit is caused by the coextraction process of primary ion and interfering counterion from the sample into the membrane resulting in a loss of membrane permselectivity. Activity of membrane phase increases with increasing the activity of sample but the EMF difference is smaller than expected by the Nernst equation.

The lower detection limit can be dictated by two processes:

(a) the interference of a competing ion present in the sample. In this case the detection limit $a_I(\text{DL})$ is related to the Nikolsky equation (2.9) and is given by:

$$a_I(\text{DL}) = K_{IJ}^{\text{pot}} a_J^{z_I/z_J} \quad (2.15)$$

(b) the leaching of primary ions from the membrane phase into the sample.

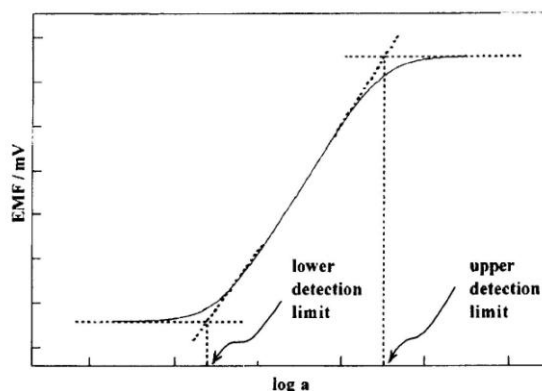


Figure 2.6 The detection limits of an ion selective electrode are defined according to the IUPAC recommendations [55] by the cross-section of the two extrapolated linear segments of the calibration curve.

2.1.3.3 Response time

The response time is another important characteristic of the ISE. According to IUPAC [62], response time ($\Delta E/\Delta t$) is the length of time which elapses between the instant when an ISE and the reference electrode are brought into contact with a sample solution (or at which the activity of the ion of interest in a solution is changed) and the first instant at which the EMF/time slope ($\Delta E/\Delta t$) becomes equal to its steady-state value within 1 mV. The stirring rate and the composition of solution should be controlled in all experiments.

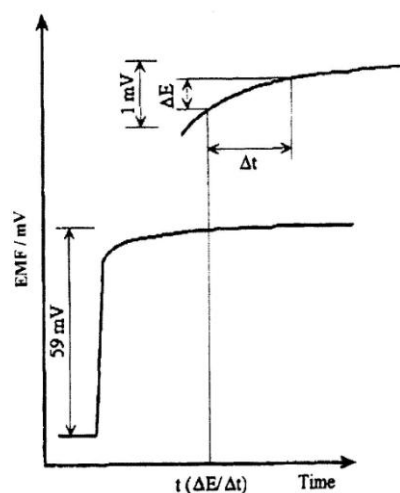
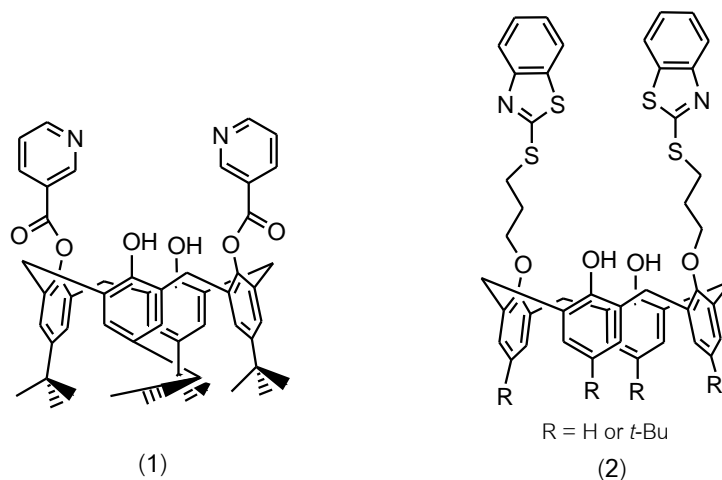


Figure 2.7 Definition and determination of response time $t(\Delta E/\Delta t)$ [62].

2.2 Ionophore for Ion Selective Electrodes

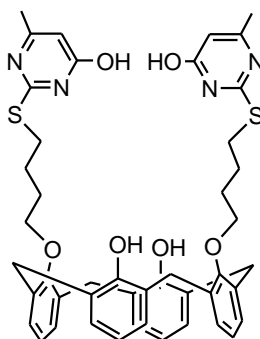
Ionophores that have been used in ion selective electrodes have been referred to as references in Chapter I [14–22]. Ionophores with calyx[4]arene-based for Ag^+ ion selective electrodes have been investigated [23–35] including the following examples. Calixarene derivative containing nitrogen atom as a neutral carrier for silver polymeric membrane electrode and in metal ions transport by bulk liquid membrane has been investigated by Chen and co-workers in 2000 [63]. The faster transport rates were found by the soft heavy metal ions such as Ag^+ , Hg^{2+} in the bulk

liquid membrane system. The silver ion-selective electrode based on the synthesized calixarene derivative **1** gave a good Nernstian response of 57 mV per decade for silver in the activity range 5×10^{-6} – 1×10^{-2} M, with the limit of detection of $10^{-5.3}$ M. The electrode exhibited high selectivity towards alkali, alkaline earth and transition metal ions. The electrode was used as the indicator electrode in titrations of Br^- and Cl^- with Ag^+ ion. In the same year, Chen and co-workers [64] prepared silver ion-selective electrodes with polymeric membranes based on nitrogen containing calixarene derivatives. The electrodes gave good Nernstian response of 49-53 mV per decade for silver in the activity range 5×10^{-6} – 5×10^{-2} M. The limit of detection was up to $10^{-5.6}$ M and the electrode exhibited high selectivity towards alkali, alkaline earth and transition metal ions. The electrode was used as indicator electrode in titrations of Ag^+ with Cl^- ions. In 2001 Chen and co-workers [65] prepared the silver ion-selective electrodes by incorporating calix[4]arene derivatives substituted by benzothiazolyl units as the neutral carrier into the plasticized polymeric membranes. The construction, response characteristic and application of silver ISEs were investigated. The better results were obtained with membranes containing bis(2-benzothiazolyl) groups (ionophore **2**) with dibutyl phosphate (DBP) as a plasticizer. The electrodes show good Nernstian response to Ag^+ over a wide concentration range (5×10^{-6} – 1×10^{-1} M) for electrodes based on calix[4]arene derivatives containing benzothiazolyl groups and very good selectivity against alkali, alkaline earth and some transition metal ions. The electrode has been used as indicator electrode in titration of Ag^+ with Cl^- ions.



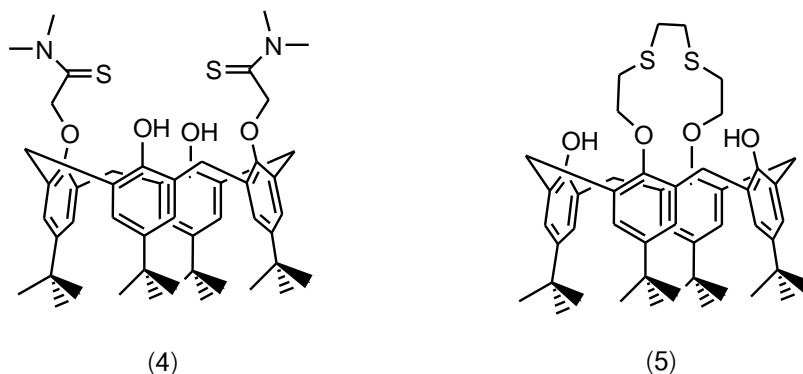
A new silver solid-state ion-selective electrode by directly coating the surface of a glassy carbon electrode with THF solution containing PVC, 25,27-dihydroxy-

26,28-bis[5-(4-methyl-6-hydroxypurimidine)thiaamyloxy] calix[4]arene (**3**), dioctyl phthalate and sodium tetraphenyl borate has been prepared by Lu and co-workers [66]. It was found that the response of the electrode was linear with a good Nernstian slope of 61.4 mV per decade over an Ag^+ ion concentration range of $5 \times 10^{-8} - 1 \times 10^{-1}$ M with a detection limit of 1×10^{-8} M. The response time to achieve a 95% steady potential for Ag^+ concentrations ranging from $1 \times 10^{-1} - 1 \times 10^{-6}$ M was between 5 and 10 s. The electrode was suitable for use within the pH range of 3–7. The selectivity relative to several alkali, alkaline earth, transition and heavy metal ions was good. The electrode could be used for at least one month without a considerable alteration in its potential.

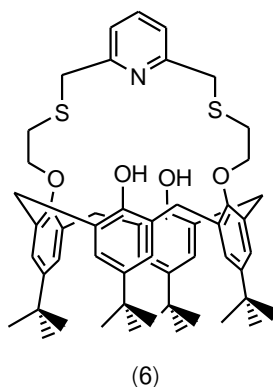


(3)

Direct potentiometric detectability of Ca^{2+} , Pb^{2+} and Ag^+ ions in very low amounts at 100 picomolar concentrations without any preconcentration, analyte recycling, or electrocatalytic signal enhancement has been explored by Malon and co-workers in 2006 [67]. The ionophore used was of the structure **4**. In the same year Demirel and co-workers [68] prepared a new PVC membrane potentiometric sensor for Ag^+ ion based on a recently synthesized calix[4]arene compound of 5,11,17,23-tetra-*tert*-butyl-25,27-dihydroxy-calix[4]arene-thiacrown-4 (**5**). The electrode exhibits a Nernstian response for Ag^+ ion over a wide concentration range ($1.0 \times 10^{-2} - 1.0 \times 10^{-6}$ M) with a slope of 53.8 ± 1.6 mV per decade. It has a relatively fast response time (5 – 10 s) and can be used for at least 2 months without any considerable divergence in potentials. The proposed electrode shows high selectivity towards Ag^+ ions over Pb^{2+} , Cd^{2+} , Co^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} , Sr^{2+} , Mg^{2+} , Ca^{2+} , Li^+ , K^+ , Na^+ , NH_4^+ ions and can be used in a pH range of 2 – 6. However, the interference of Hg^{2+} is present. It could be used as an indicator electrode in potentiometric titration of a mixture of chloride, bromide and iodide ions.

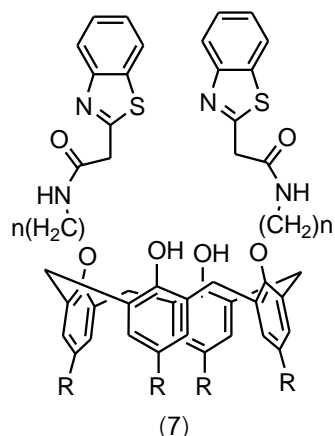


Thiacalix[4]arene ionophores comprised of cyclic or linear O,S,N ligating and/or π -coordinate groups on the lower rim (e.g., compound **6**) have been synthesized by Csokai and co-workers in 2006 [69] and their Ag^+ binding was studied by ^1H NMR methods in comparison with the known and new calix[4]arene counterparts. It was found that calix[4](O,S,N)crowns were stronger binders than the π -coordinate molecules and in general thiacalixarene ionophores were superior to calixarenes. The finding has made it possible to develop silver ion-selective electrodes working in the subnanomolar region.

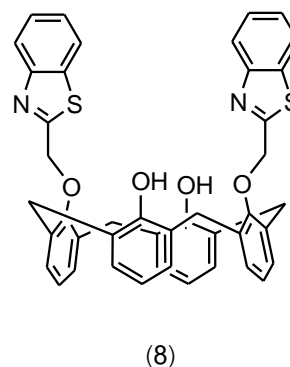


New Ag^+ receptors for use as ionophores in Ag^+ -selective electrodes have been developed in 2008 by Morakot and co-workers [39]. The ionophores **7** consisting of benzothiazolylacetamidoalkoxy calix[4]arenes were synthesized. PVC-based ion selective membrane electrodes employing the ionophores **7** were prepared using a membrane composition of 1.0 : 65.5 : 33.0 : 0.5 (ligand : *o*-NPOE : PVC : *KTpCIPB* in weight percent) to determine the potentiometric response for Ag^+ . PVC membrane electrodes incorporating such ionophores exhibited high selectivity and sensitivity towards Ag^+ . The studies showed that among calix[4]arene derivative-

ionophores, both *tert*-butyl substituents and the length of the pendant on the narrow rim affected the selectivity and sensitivity of the membranes in which the absence of *tert*-butyl group and shorter length of the pendant groups gave a better membrane electrode. In the same year, Ngeontae and co-workers [40] synthesized a new calix[4]arene (**8**) containing benzothiazolyl pendants and this compound has been used as an ionophore to fabricate macro- and micro- Ag^+ selective membrane electrodes. PVC has been used as membrane and NPOE as plasticizer to provide better selectivity coefficient towards Ag^+ than those plasticized with DOS. The selectivity coefficients for macro- and microelectrode were, respectively, -2.8 and -2.5 for Hg^{2+} and lower than -4.0 and -3.5 for other cations tested. The electrodes could be used in a wide pH range of 2 – 8 with a response time of less than 5 s. The electrodes exhibited near theoretical Nernstian slope (59.7 ± 0.8 mV per decade for macroelectrode and 59.8 ± 1.0 mV per decade for microelectrode) with low detection limits (ca. 5.0×10^{-7} M) and wide linear working range (10^{-6} to 10^{-2} M). The electrodes were used as an indicator electrode for the argentometric titration of the mixture of Cl^- and Br^- . The fabricated electrodes were also used in speciation analysis of Ag nanoparticles with good accuracy and precision. This Ag-ISE should be beneficial to research related to Ag nanoparticles. In 2009, Ngeontae and co-workers [41] investigated a new approach in glucose biosensor based on polymeric membrane Ag-ISE fabricated from the benzothiazole calix[4]arene **8**. Silver nanoparticles (AgNPs) were synthesized and demonstrated for the first time that it could be used as a potentiometric redox marker in a glucose biosensor. The linear relationship between logarithmic of H_2O_2 concentration and activity of free Ag^+ releasing from AgNPs was observed by direct potentiometry. The enzyme-substrate reaction between β -D-glucose and glucose oxidase produced H_2O_2 as a product. The generated H_2O_2 was able to oxidize AgNPs to free Ag^+ ions. The amount of Ag^+ ions corresponded to the concentration of glucose could be directly monitored using the Ag-ISE. The working linear range was 0.1 – 3 mM in 10 mM magnesium acetate buffer at pH 6.0. The lower detection limit was 1.0×10^{-5} M. The sensor provided a double selective function and could be used to determine glucose in beverages with good accuracy and precision.

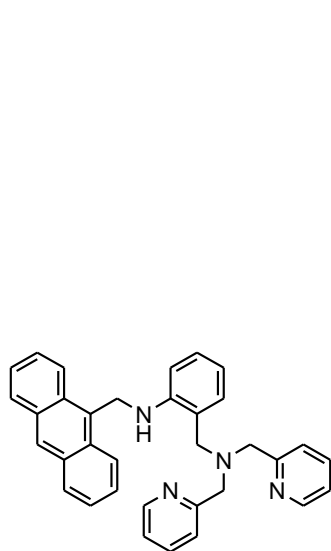


a, R = *t*-Bu, n = 4; b, R = H, n = 4
 c, R = *t*-Bu, n = 2; d, R = H, n = 2

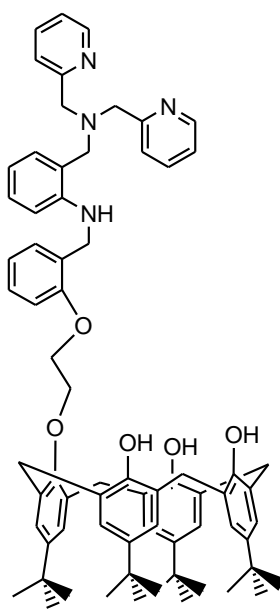


Apart from Ag-ISEs, ionophores for other cation detection have been investigated. For example, fabrication of PVC membrane electrodes incorporating selective neutral carriers for Cd^{2+} ion has been reported [42]. The ionophores were designed to have different topologies, donor atoms and lipophilicity by attaching tripodal amine (TPA) units to the lipophilic anthracene (ionophore **9**) and *p*-*tert*-butylcalix[4]arene (ionophores **10**, **11** and **12**). The synthesized ionophores were incorporated to the plasticized PVC membranes to prepare Cd^{2+} ion selective electrodes. The membrane electrodes were optimized by changing types and amounts of ionic sites and plasticizers. The selectivity of the membranes fabricated from the synthesized ionophores was evaluated and the relationship between structures of ionophores and membrane characteristics were explored. The ionophore **12** which composed of two opposites TPA units on the calix[4]arene platform showed the best selectivity toward Cd^{2+} . The best membrane electrode was fabricated from ionophore **12** (10.2 mmol per kg) with potassium tetrakis(*p*-chlorophenyl)borate (50.1 mol% related to the ionophore) as an ion exchanger incorporated in the DOS plasticized PVC membrane (PVC : DOS was 1 : 2). The Cd-ISE fabricated from ionophore **12** exhibited good properties with a Nernstian response of 29.4 ± 0.6 mV per decade of activity for Cd^{2+} ions and a working concentration range of $1.6 \times 10^{-6} - 1.0 \times 10^{-2}$ M. The sensor has a fast response time of 10 s and can be used for at least 1 week without any divergence in potential. The electrode can be used in the pH range of 6.0 – 9.0. The proposed electrodes using ionophores **11** and **12** were employed as a probe for

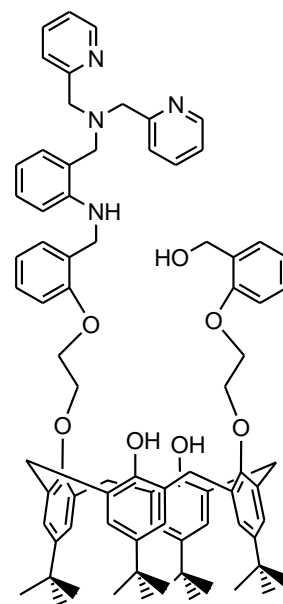
determining Cd^{2+} from the oxidation of CdS quantum dots solution and the real treatment waste water sample with excellent results.



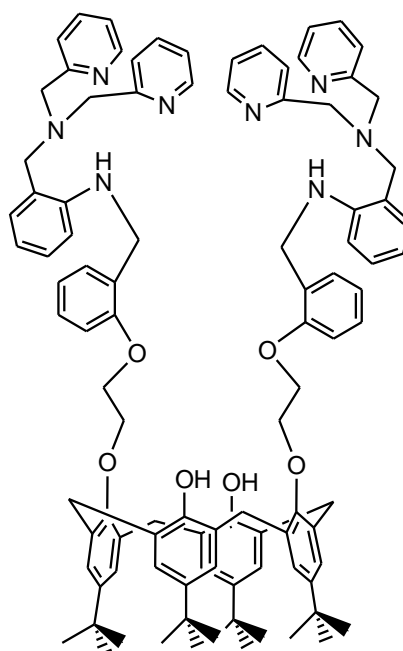
(9)



(10)



(11)



(12)

CHAPTER III

EXPERIMENTAL

3.1 General Procedures

3.1.1 Apparatus

EMF measurements were recorded by a 16-channel electrode monitor (Lawson Labs Inc., Malvern, PA 19355, USA). Ag/AgCl reference electrode (Metrohm 6.0726.100) with 1 M LiOAc as salt bridge electrolyte was used to determine pH values by using an Orion 2-Star Benchtop pH meter (Thermo Fisher Scientific).

3.1.2 Materials

Standard analytical grade materials and reagents were used without further purification. Chemicals, *KTpCIPB*, DOS, *o*-NPOE, PVC and THF, used for membrane preparation were purchased in selectophore® grade from Fluka. In ISE experiments, all solutions used were prepared with Milli-Q (Bedford, MA, USA) water using Nanopure Millipore water purification system.

3.2 Ion Selective Electrode Studies

3.2.1 Preparation of the electrode

The membrane (220 mg total mass) was prepared by dissolving ionophore (10 mmol kg⁻¹), potassium tetrakis[4-chlorophenyl] borate (*KTpCIPB*), 33 wt.% PVC and 66 wt.% plasticizer (*o*-NPOE or DOS) in 2.5 mL of THF and poured into a glass ring (30 mm i.d.) fixed on a glass plate, followed by evaporation of solvent at room temperature overnight. A transparent membrane of about 200 μm in thickness was obtained. The membrane was cut into small size (7.5 mm i.d.) and mounted with a

PVC/THF slurry on the top of PVC tube and connected to micropipette tip as an electrode body.

The above PVC tube contained an internal filling solution containing 0.01 M AgNO_3 and a AgCl-coated silver wire. This PVC tube was connected to micropipette tip. The 0.01 M AgNO_3 solution was used to soak the prepared membrane electrode overnight before use.

3.2.2 The EMF measurements

A 16-channel electrode monitor (Lawson Labs Inc., Malvern, PA 19355, USA) were used for measuring all potential at ambient temperature. The external reference electrode was a double junction type Ag/AgCl glass electrode (type 6.0726.100, Metrohm AG, CH-9010 Herisau, Switzerland) with 1 M LiOAc as a salt bridge electrolyte. The electrochemical cell for the EMF measurements was Ag, AgCl/3 M KCl//1 M LiOAc//sample solution/ISE membrane/IFS/AgCl, Ag. EMF measurements for the ISEs versus reference electrode were performed in stirred solution in the concentration range from 10^{-8} M to 10^{-2} M. The Debye-Hückel approximation [70] was used for calculation of the activities of metal ions in sample solutions. The determination of the detection limit was made according to IUPAC recommendations.

3.2.3 Selectivity measurements

Determination of the potentiometric selectivity coefficients were done by the separate solution method (SSM) [8]. The solution of interfering metal ions (nitrate salt) was used to condition membranes overnight. The measurement of the response of the electrode against the interfering metal ions (10^{-7} to 10^{-2} M) was first made by using 0.01 M the same interfering cations (chloride salt) as inner filling solution. The response of silver nitrate solutions was measured by electrode. Determination of selectivity coefficients for each metal ion was performed three times (changing new membrane each time). In this study, Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} and Hg^{2+} were used as interfering ions. The pH of solution was adjusted to 2 and 4,

respectively with HNO_3 to avoid precipitation in the determination of the selectivity coefficients of Hg^{2+} and Pb^{2+} . Calculation of the selectivity coefficients from mean value of three experiments with standard deviation.

3.2.4 Reversibility

Study of the membrane reversibility was done by measuring the EMF of Ag-ISE in a 10^{-4} M Ag^+ solution. The electrode was then rinsed and dipped into a 10^{-3} M Ag^+ solution; the cycle was repeated for three times.

3.3 Applications of Fabricated Ag-ISE from QN-2

3.3.1 Application as the indicator electrodes for argentometric titration

To determine the concentration of Cl^- , the Ag-ISE was used as an indicator electrode in potentiometric titrations. Preparation of sample solutions were performed by adding 25 μL of 1 M KCl into 25 mL ultra pure water, which was stirred and titrated with 0.01 M AgNO_3 .

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Design and Synthesis of Ionophores QN-1 and QN-2

The design and synthesis of calix[4]arene derivatives by attaching different functional groups to obtain different topology with various donor atoms for binding Ag^+ have been undertaken. In this study, **QN-1** and **QN-2** were synthesized and characterized by Assistant Professor Dr. Chomchai Suksai and Mr. Sarayut Watchasit and have been used as ionophores. The structure of ionophore **QN-1** contains a unit of calix[4]arene, a quinoline and a butylene linker. The ionophore **QN-2** contains a unit of calix[4]arene, two quinoline moieties and two butylene linkers as shown in Figure 4.1. The presence of one soft nitrogen and one oxygen atoms in **QN-1** and two nitrogen and two oxygen atoms in **QN-2** have been used as donor atoms for metal binding. According to Pearson, Hg^{2+} was generally a major interference for Ag-ISEs because soft metal ions, Ag^+ , Hg^{2+} and Pb^{2+} preferred to coordinate with soft donor atoms such as sulfur and nitrogen [71].

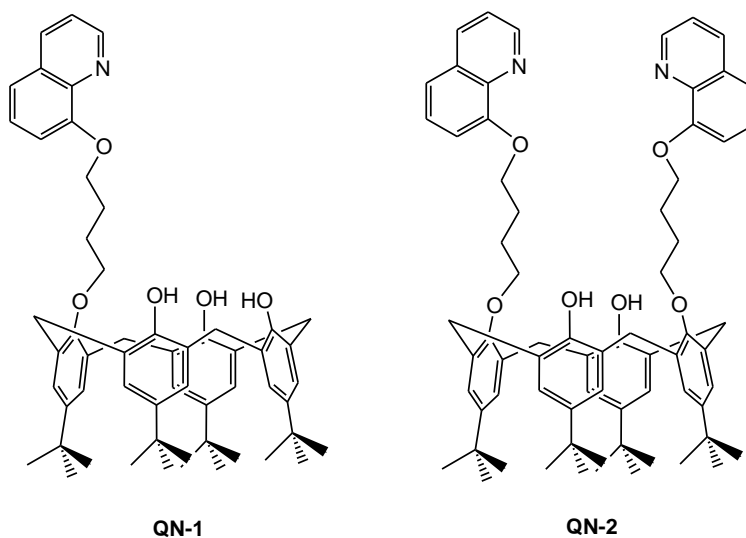


Figure 4.1 Structures of ionophores **QN-1** and **QN-2**.

4.2 EMF Response of Di-quinoline Units Compared to Mono-quinoline Unit of Calix[4]arene

The ionophores **QN-1** and **QN-2** which contained mono- and di-quinoline units, respectively, on the phenolic group of calix[4]arene showed similar features of EMF response. For both ionophores, Ag^+ was the cation that exhibited the most EMF response followed by Hg^{2+} (see Figures 4.2 and 4.3). In contrast, the remaining cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+}) showed low EMF response.

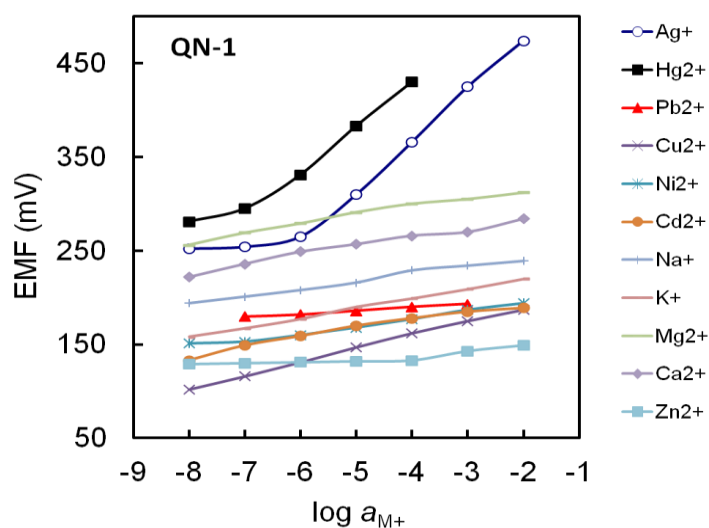


Figure 4.2 EMF response of ionophore **QN-1** on different cations.

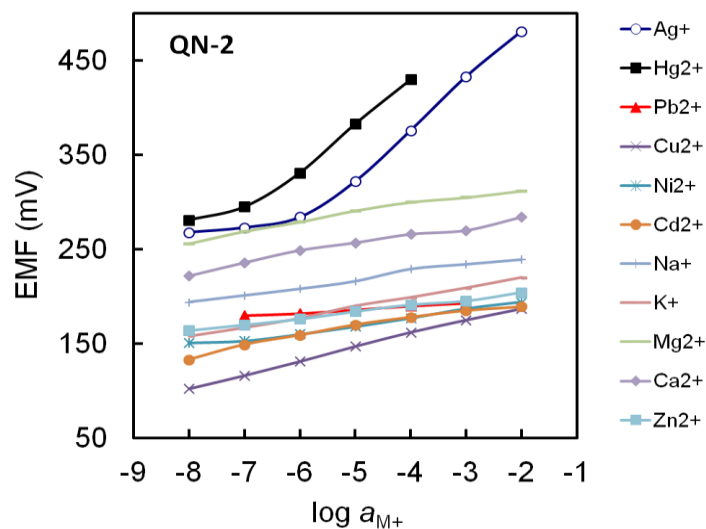


Figure 4.3 EMF response of ionophore **QN-2** on different cations.

4.3 Effect of Di-quinoline Units Compared to Mono-quinoline Unit of Calix[4]arene on Selectivity

It has been mentioned in the section 2.1.3.1 of Chapter II, Theory and Literature Reviews, that selectivity is one of the most important characteristics of an ISE and is the degree of discrimination of an electrode to ions in solution other than the primary ion [55–57], the selectivity of ion selective electrodes was determined by the separate solution method (SSM). The selectivity coefficients ($\log K_{Ag,j}^{pot}$) of **QN1** and **QN2** were determined and the results are presented in Table 4.1.

Table 4.1 Selectivity coefficients of **QN-1** and **QN-2**.

Interfering ion	$\log K_{Ag^+,j}^{pot}$	
	QN-1	QN-2
Na ⁺	-2.64	-4.11
K ⁺	-2.82	-3.90
Mg ²⁺	-4.26	-5.03
Ca ²⁺	-1.30	-4.46
Ni ²⁺	-2.65	-4.78
Cu ²⁺	-2.19	-4.11
Zn ²⁺	-2.24	-4.75
Cd ²⁺	-2.69	-4.41
Pb ²⁺	-0.79	-0.64
Hg ²⁺	-1.12	-4.02

Figure 4.4 displayed the ion selectivity features of electrodes for the ionophores **QN-1** and **QN-2** which contained mono- and di-quinoline units, respectively, on the phenolic group of calix[4]arene. **QN-1**, which contained one soft nitrogen and one hard oxygen donors, showed the same selectivity towards Ag⁺ as **QN-2**, which contained two nitrogen and two oxygen donors from di-quinoline. This suggested that more donor atoms in **QN-2** showed no preference in coordinating to Ag⁺ effectively compared to **QN-1**. Both **QN-1** and **QN-2** showed comparable discriminating abilities to interfering Hg²⁺. However, **QN-2** exhibited much higher discriminating abilities to other interfering cations (Na⁺, K⁺, Ca²⁺, Mg²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺ and Pb²⁺) than **QN-1**. In addition, the increment of lipophilicity from two butylene linkers may prevent ionophore from leaching from the membrane electrodes.

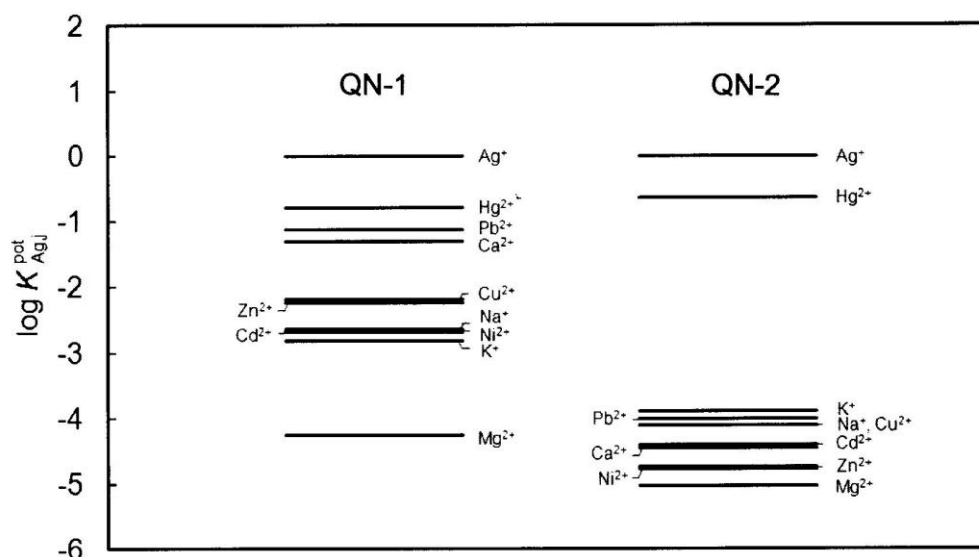


Figure 4.4 Comparison of selectivity coefficient ($\log K_{Ag,j}^{pot}$) of ionophores **QN-1** and **QN-2**.

4.4 Complex Formation Constants of QN-1 and QN-2 with Ag⁺

The basic concept of host-guest interactions or coordination chemistry can be used to explain the complexation between ionophores and Ag⁺. The lone pair electrons of donor atoms in ionophores (**QN-1** and **QN-2**) interacted with Ag⁺ using ion-dipole interactions. Ag⁺ (d¹⁰) prefers to form complexes with a linear shape because of its filled d-orbitals, though it can form 2 – 6 coordinated complexes [72]. The slopes of calibration curves for two synthesized ionophores **QN-1** and **QN-2** were close to theoretical Nernstian slope for monovalent cation Ag⁺ (z = 1), except in the case of **QN-2** with membrane composition of 5.27 and 7.47 mmol kg⁻¹ KTpCIPB in *o*-NPOE, as depicted in Tables 4.2 and 4.3, indicating 1:1 ion-ionophore complexes. From these two Tables, in the case of **QN-1**, the detection limit when *o*-NPOE was used as the plasticizer was generally better than that of DOS. However, in the case of **QN-2**, the detection limit when DOS was used as the plasticizer was better than that of *o*-NPOE. The reason for this contradictory observation could possibly be due to the polarity of the ionophores **QN-1** and **QN-2**, as compared to the plasticizers *o*-NPOE

Table 4.2 Membrane compositions and response properties based on ionophore **QN-1**.

Ionophore	Membrane composition (wt.%)				Slope ^a (mV decade ⁻¹)	Linear range (M)	Detection limit (M)
	Ionophore, L_T (mmol kg ⁻¹)	KTpCIPB, R_T (mmol kg ⁻¹)	PVC	Plasticizer			
QN-1	0.85 (10.00)	0.11 (2.27)	32.92	<i>o</i> -NPOE, 66.12	51.8 ± 0.5	10 ⁻⁵ to 10 ⁻²	6.9 × 10 ⁻⁷
	0.85 (10.02)	0.24 (4.92)	33.01	<i>o</i> -NPOE, 65.90	52.4 ± 1.0	10 ⁻⁵ to 10 ⁻²	8.1 × 10 ⁻⁷
	0.85 (10.06)	0.37 (7.46)	33.11	<i>o</i> -NPOE, 65.67	55.5 ± 0.6	10 ⁻⁵ to 10 ⁻²	7.0 × 10 ⁻⁷
	0.86 (10.18)	0.12 (2.38)	33.01	DOS, 66.00	53.9 ± 0.4	10 ⁻⁵ to 10 ⁻²	6.4 × 10 ⁻⁷
	0.85 (10.09)	0.25 (5.11)	32.91	DOS, 65.98	53.2 ± 0.2	10 ⁻⁵ to 10 ⁻²	2.1 × 10 ⁻⁶
	0.85 (10.07)	0.37 (7.47)	33.05	DOS, 65.73	52.6 ± 0.9	10 ⁻⁵ to 10 ⁻²	1.9 × 10 ⁻⁶

^a Standard deviations in triplicate experiments.

Table 4.3 Membrane compositions, response properties based on ionophores **QN-2**.

Ionophore	Membrane composition (wt.%)				Slope ^a (mV decade ⁻¹)	Linear range (M)	Detection limit (M)
	Ionophore, L_T (mmol kg ⁻¹)	KTpCIPB, R_T (mmol kg ⁻¹)	PVC	Plasticizer			
QN-2	1.03 (9.87)	0.13 (2.63)	32.87	<i>o</i> -NPOE, 65.97	46.8 ± 1.6	10 ⁻⁵ to 10 ⁻³	2.6 × 10 ⁻⁶
	1.09 (10.38)	0.26 (5.27)	32.69	<i>o</i> -NPOE, 65.96	48.7 ± 1.4	10 ⁻⁵ to 10 ⁻³	2.0 × 10 ⁻⁶
	1.04 (9.89)	0.37 (7.47)	32.75	<i>o</i> -NPOE, 65.84	52.0 ± 1.2	10 ⁻⁵ to 10 ⁻³	2.5 × 10 ⁻⁶
	1.04 (9.89)	0.13 (2.55)	32.82	DOS, 66.01	53.3 ± 1.0	10 ⁻⁵ to 10 ⁻²	8.3 × 10 ⁻⁷
	1.07 (10.24)	0.25 (5.11)	32.93	DOS, 65.75	53.7 ± 1.0	10 ⁻⁵ to 10 ⁻²	6.9 × 10 ⁻⁷
	1.05 (9.99)	0.36 (7.33)	32.68	DOS, 65.91	53.7 ± 0.7	10 ⁻⁵ to 10 ⁻²	7.0 × 10 ⁻⁷

^a Standard deviations in triplicate experiments.

and DOS. Since **QN-1** is more polar than **QN-2**, and *o*-NPOE is more polar than DOS, the complex formation of cation, or Ag^+ in this case, to **QN-1** should be in preference to the more polar matrix of *o*-NPOE. For the less polar **QN-2**, complex formation in the less polar matrix of DOS is preferred.

4.5 Fabrication of Ag-ISEs from QN-1 and QN-2

4.5.1 Optimization of the membrane composition from QN-1 and QN-2

The type and percentage of each composition in PVC membrane electrode are critical parameters that could affect the sensing characteristics of the fabricated electrode such as the working concentration range, lifetime, selectivity and sensitivity. It has been reported that the optimized 1:2 ratio by weight between PVC and plasticizer provided the best component [73]. The DOS and *o*-NPOE plasticizers were used and the responses of their corresponding ISE's were compared as shown in Figure 4.5. The response characteristic of *o*-NPOE membrane was highly dependent on the amount of the ion exchanger as shown in Figure 4.5 (a). In the presence of 25 mol% of *KTpClPB* (relative to ionophore) the membrane did not give the expected EMF changed while the concentrations of Ag^+ were increased. However, increasing of the ion exchanger to 50 and 75 mol%, a slope of 48.7 ± 8.4 and 52.0 ± 1.2 mV decade⁻¹, respectively, were obtained from the membrane response. The response characteristic of the membrane plasticized with DOS, as shown in Figure 4.5 (b), was independent on the amount of the ion exchanger added. Furthermore, the slopes obtained from DOS membranes were close to the theoretical Nernstian slope as summarized in Tables 4.2 and 4.3. The results can be explained that complexation between the ionophore **QN-2** and Ag^+ increased in a less polar matrix, DOS.

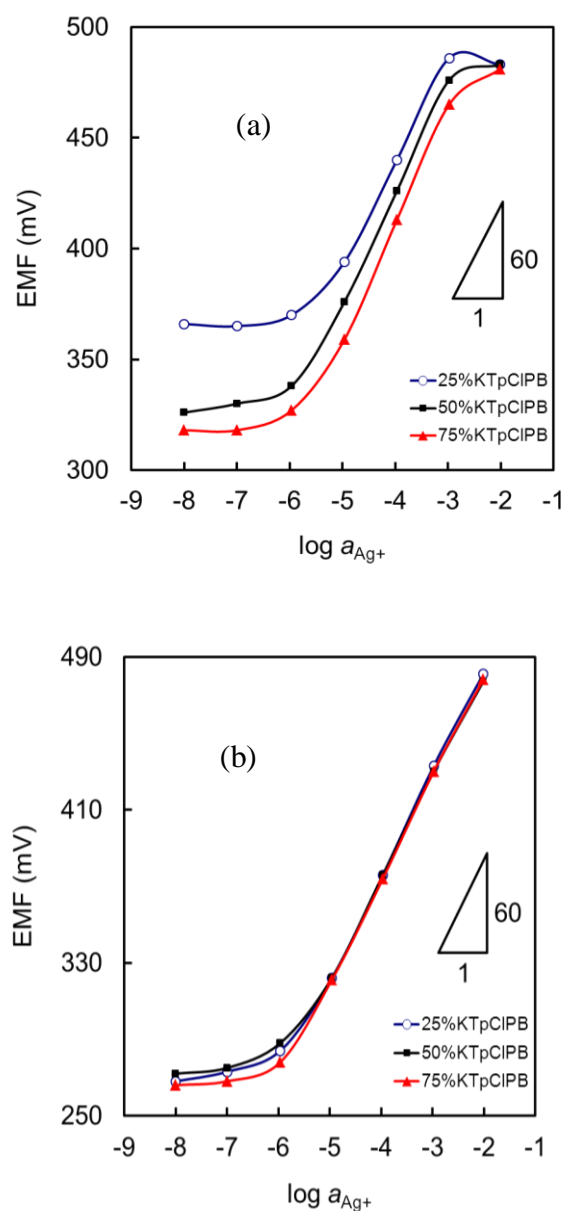


Figure 4.5 Effect of % ion exchanger (relative to the ionophore **QN-2**) to the membrane response in different plasticizer (a) *o*-NPOE and (b) DOS.

The lower detection limits of the membrane plasticized with DOS which containing 25%, 50% and 75% KTpCIPB, respectively, were found to be 8.3×10^{-7} , 6.9×10^{-7} and 7.0×10^{-7} M (Table 4.3). The lower detection limits in membrane plasticized with *o*-NPOE which containing 25%, 50% and 75% KTpCIPB, respectively, were found to be 2.6×10^{-6} , 2.0×10^{-6} and 2.5×10^{-6} M (Table 4.3).

4.5.2 Response characteristics

In order to study the response characteristics of the sensors, the optimized membrane compositions for ionophore **QN-2** was used. For the response of ISE, on the increment of the Ag^+ concentration, the EMF also increased with very stable potentials as shown in Figure 4.6. The electrode showed very fast response time to reach a stable EMF value. A minute signal fluctuation (of the traces) was observed when the EMF signals reach the plateau at a given concentration level. For the membrane plasticized with *o*-NPOE and DOS, the corresponding calibration curves gave Nernstian slope of 52.0 ± 1.2 and 53.3 ± 0.7 mV decade⁻¹ and lower detection limit of 2.5×10^{-6} and 8.3×10^{-7} M, respectively. The membranes plasticized with both *o*-NPOE and DOS could be used in a wide concentration range of Ag^+ (10^{-5} – 10^{-2} M) which indicated that the membrane electrode performed as a very good Ag^+ sensor.

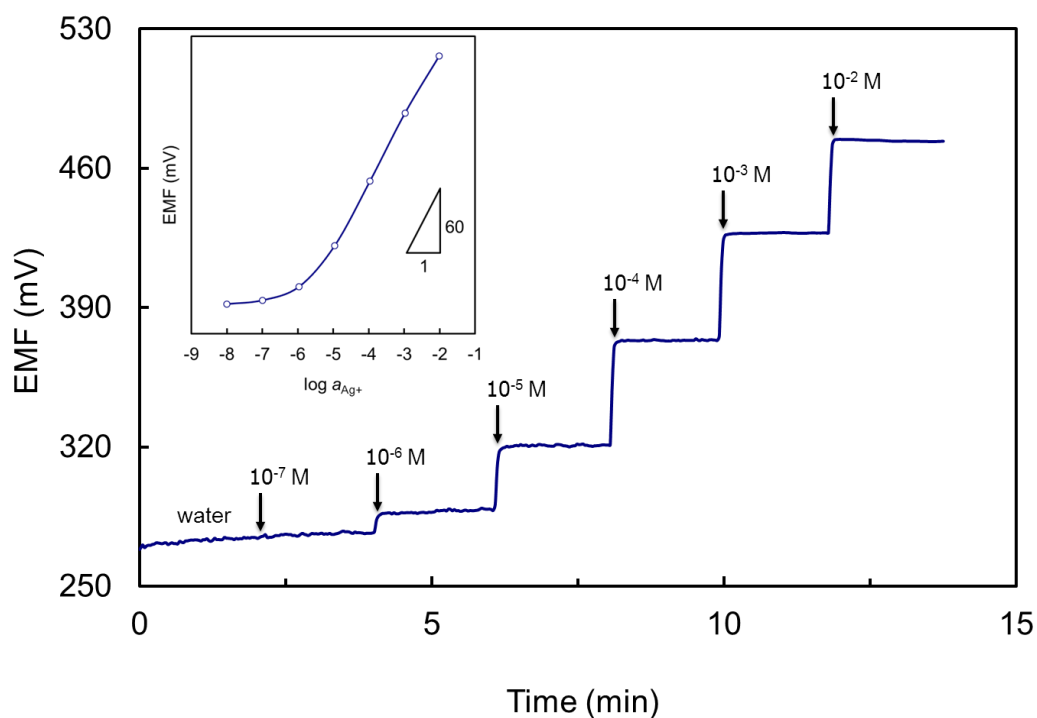


Figure 4.6 Time trace line observation of Ag-ISE after adding Ag^+ to the solution.

4.5.3 Reversibility of the fabricated electrodes

The evaluation of the electrode reversibility was performed by alternatively measured EMF's of two different concentrations, 10^{-4} and 10^{-3} M Ag^+ . The precision of the detection can be represented by the electrode reversibility from Figure 4.5, it was found that the EMF signals was restored at the same concentration of Ag^+ in every cycle. Therefore, the electrode can be used to measure the Ag^+ concentration with excellent reversibility.

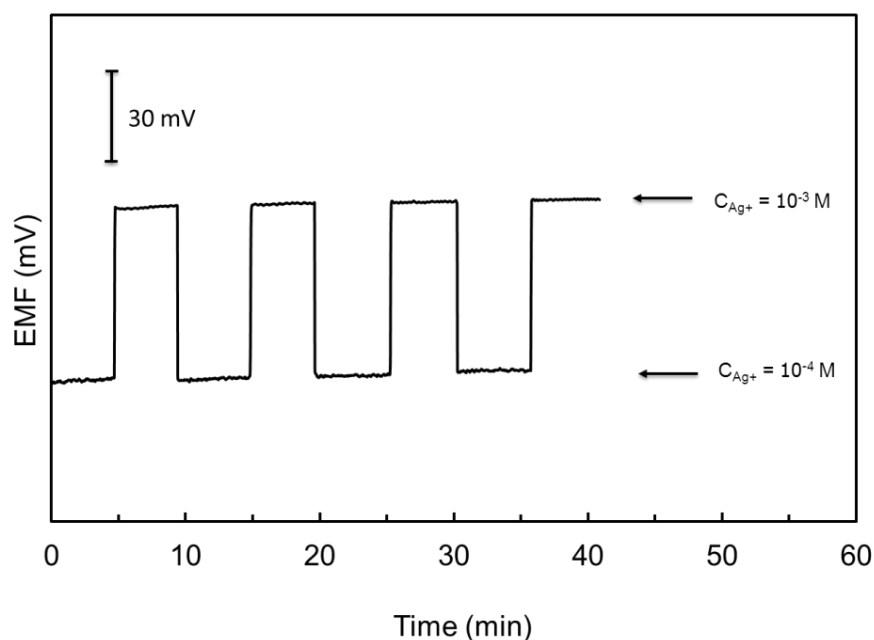


Figure 4.7 Reversibility of Ag-ISE containing QN-2 at concentration between 10^{-4} and 10^{-3} M.

4.6 Analytical Applications of Ag-ISE from QN-2 : Determination of Cl^-

Precipitation titrimetry, which is based on reactions that yield ionic compounds of limited solubility, is one of the oldest analytical techniques. Because of the slow rate of formation of most precipitates, there are only a few precipitating

agents that can be used in titrimetry. The most widely used and most important precipitating reagent is silver nitrate, which is used for the determination of the halides, the halide-like anions (SCN^- , CN^- , CNO^-), mercaptans and several divalent and trivalent inorganic anions. Titrimetric methods based on silver nitrate are sometimes called argentometric methods. The most common method of determining the halide ion concentration of aqueous solutions is titration with a standard solution of silver nitrate. The reaction product is solid silver halide. A titration curve for this method usually consists of a plot of pAg versus volume of silver nitrate added. Two general types of titration curves (and thus two general types of end points) are encountered in titrimetric methods. In the first types, called a sigmoidal curve, important observations are confined to a small region surrounding the equivalence point. A sigmoidal curve, in which the p-function of analyte (or sometimes the reagent) is plotted as a function of reagent volume. In the second type of curve, called a linear segment curve, measurements are made on both sides of, but well away from, the equivalence point [74].

Application of the fabricated electrode **QN-2** in potentiometric titrations of the chloride ion was performed. Figure 4.8 shows titration curve of 25 μL of 1.0 M KCl with 0.01 M AgNO_3 which appears as a sigmoidal curve. The end point corresponds to the quantity of Cl^- .

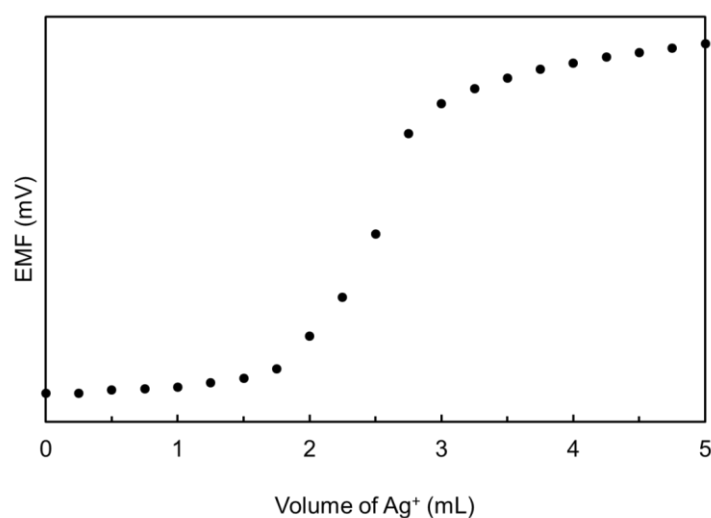


Figure 4.8 Potentiometric titration curve of 1.0 M (25 μL) NaCl with 0.01 M AgNO_3 .

CHAPTER V

CONCLUSIONS

The present work deals with the preparation of ion selective electrodes (ISEs) with calyx[4]arene containing quinoline as ionophore. Two ISEs incorporating two new ion selective membranes were prepared. The ion selective membranes consisted of two supermolecules, **QN-1** and **QN-2** as ionophores. Both structures of ionophores based on *p*-tert-butylcalix[4]arene. The structures of ionophore **QN-1** and **QN-2** comprise one and two quinolone units, respectively, as metal ion receptors. The ion selective membranes also consisted of PVC as a polymer, potassium tetrakis(4-chlorophenyl)borate as an ion exchanger, *o*-nitrophenyloctyl ether (*o*-NPOE) or dioctyl sebacate (DOS) as a plasticizer. The ability of the ISEs in response to Na⁺, K⁺, Mg²⁺, Ca²⁺, Ag⁺, Cu²⁺, Cd²⁺, Pb²⁺, Hg²⁺, Ni²⁺ and Zn²⁺ was studied. The complex formation between ionophores and metal ions resulted from interactions between donor quinolone nitrogen atoms and donor oxygen atoms of the quinoline units. The optimum condition for ion detection was ionophore : ion exchanger is 1 : 2 by weight and the working range was 10⁻⁵ to 10⁻² M.

The studies have revealed that both **QN-1** and **QN-2** ion selective electrodes exhibited highest selectivity towards Ag⁺. **QN-1**, the ionophore containing one soft nitrogen and one hard oxygen donors, showed the same selectivity towards Ag⁺ as **QN-2**. The finding suggested that more donor atoms in **QN-2** showed no preference in participation and coordination with Ag⁺ effectively as compared to **QN-1**. Both **QN-1** and **QN-2** exhibited comparable decrease in the interference from Hg²⁺. However, **QN-2** showed much decrease in the interference from the cations K⁺, Pb²⁺, Na⁺, Cu²⁺, Cd²⁺, Ca²⁺, Zn²⁺, Ni²⁺ and Mg²⁺ than **QN-1**.

The results have led to the selection of ISE with **QN-2** as ionophore for further study. This included the evaluation of the electrode reversibility by alternatively measured EMF at two different concentrations, 10⁻⁴ and 10⁻³ M Ag⁺ and it was found that the EMF signals was restored at the same concentration of Ag⁺ in every cycle. Therefore, the electrode can be used to measure the Ag⁺ concentration with excellent

reversibility. Application of the fabricated electrode **QN-2** in potentiometric titration of the chloride ion was performed and it was found that the determination of chloride ion by this method was successful.

In summary, PVC membranes based on ionophores **QN-1** and **QN-2** which contained mono- and di-quinoline derivatives of calix[4]arene, respectively could be used as potentiometric sensors for Ag^+ . Compared to **QN-1**, the membrane **QN-2** displayed very good selectivity to Ag^+ ions over alkali, alkaline earth and other metal ions. The Ag-ISE fabricated from **QN-2** exhibited a near-Nernstian response to silver ions ($53.7 \pm 0.7 \text{ mV decade}^{-1}$) and a linear range of 10^{-6} to 10^{-2} M with a detection limit of 8.3×10^{-7} and good reversibility. The Ag-ISE fabricated from **QN-2** can, therefore, be employed as an indicator electrode in argentometric titrations.

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Publications

Suksamrarn, C., Janrungroatsakul, W., Suksai, C., Watchasit, S., and Tuntulani, T., Calix[4]arene containing quinoline as ionophore in ion selective electrodes. 39th Congress on Science and Technology of Thailand, BITEC, Bangkok, October 2013.