

การเตรียมอิเล็กทรอนิกส์โทรมเมมเบรนชนิดคัดเลือกแอนไอออนจากปรากฏการณ์คอนเนนเฟลีย์  
เหนี่ยวนำโดยไอออนคอปเปอร์(II)



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บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)  
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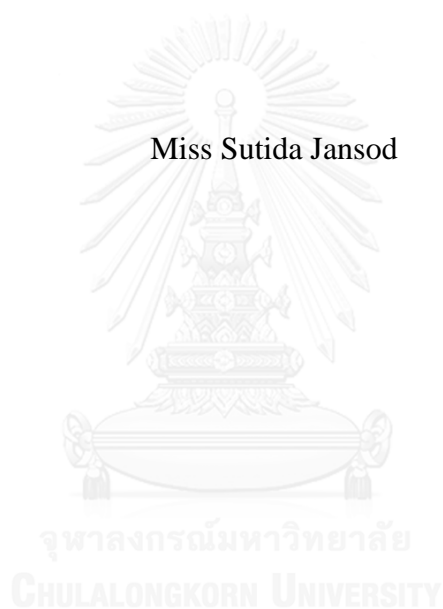
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2558

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

PREPARATION OF ANION SELECTIVE MEMBRANE ELECTRODES FROM  
DONNAN FAILURE PHENOMENON INDUCED BY COPPER(II) ION

Miss Sutida Jansod



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

Department of Chemistry

Faculty of Science

Chulalongkorn University

Academic Year 2015

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สุธิดา จันทรืสศ : การเตรียมอิเล็กโทรดเมมเบรนชนิดคัดเลือกแอนไอออนจากปรากฏการณ์คอนแนนเฟลีย์ร่เหนี่ยวนำโดยไอออนคอปเปอร์(II) (PREPARATION OF ANION SELECTIVE MEMBRANE ELECTRODES FROM DONNAN FAILURE PHENOMENON INDUCED BY COPPER(II) ION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ศ. ดร.ชวรัชช์ ต้นทุลานี, 47 หน้า.

สารประกอบเชิงซ้อนโลหะโมโนนิวเคลียร์และไดนิวเคลียร์ที่มีจำนวนแขนข้างและอะตอมคอนเนอร์ที่แตกต่างกันโดยมีฐานเป็นคาลิซ[4]เอรีนและแอนทราซีน ใช้เป็นไอโอโนฟอร์หรือตัวนำพาไอออนในการสร้างขั้วไฟฟ้าแบบเลือกจำเพาะต่อแอนไอออน เมมเบรนพอลิเมอร์ที่ประกอบด้วยไอโอโนฟอร์ L1 และโพแทสเซียมเตรดอะคิซพาราคลอโรฟีนิลโบเรต (KTPCIPB) ทำหน้าที่เป็นแคตไอออนเอกเซนเจอร์เกิดปรากฏการณ์คอนแนนเฟลีย์ร่ขึ้น เมื่อมีไอออนโลหะเป็นตัวกระตุ้น โดยไอโอโนฟอร์ L1 จับกับไอออนโลหะได้อย่างแข็งแรงมาก จึงเหนี่ยวนำให้เกิดการสักร่วมของแอนไอออนเข้ามาในเมมเบรนและเปลี่ยนการเลือกตรวจวัดของเมมเบรนเป็นแอนไอออน โดยพบการตอบสนองของศักย์ไฟฟ้าในทิศทางที่เป็นลบ ในการตรงกันข้ามขั้วไฟฟ้าเมมเบรนที่ประกอบด้วยไอโอโนฟอร์ L2 – L4 ให้ศักย์ไฟฟ้าที่เป็นบวกต่อเกลือของโลหะไอออนเป็นส่วนใหญ่ ขั้วไฟฟ้าที่ดีที่สุดที่จำเพาะต่อเปอร์คลอเรต ประกอบด้วยไอโอโนฟอร์ L1 และโพแทสเซียมเตรดอะคิซพาราคลอโรฟีนิลโบเรต (KTPCIPB) ปริมาณ 25 เปอร์เซ็นต์โมลสัมพัทธ์กับปริมาณของไอโอโนฟอร์ โดยผสมในเมมเบรนพอลิเมอร์ PVC ที่มี *o*-NPOE เป็นสารปรับสภาพความยืดหยุ่น และใช้คอปเปอร์(II) คลอไรด์เป็นตัวกระตุ้น ได้ค่าความชันของเนินสัต์เท่ากับ  $-55.80 \pm 0.36$  มิลลิโวลต์ต่อเดเคด ที่ช่วงความเข้มข้นในการตอบสนองของเปอร์คลอเรต ตั้งแต่  $10^{-5}$  ถึง  $10^{-2}$  โมลาร์ และมีขีดจำกัดการตรวจวัดที่ 2.84 ไมโครโมลาร์ นอกจากนี้ขั้วไฟฟ้าเมมเบรนที่ประดิษฐ์ขึ้นมา สามารถใช้ในช่วงพีเอชตั้งแต่ 3 – 9 มีการผันกลับที่ดีเยี่ยม และยังสามารถประยุกต์ใช้ในการตรวจวัดความเข้มข้นของเปอร์คลอเรตในน้ำประปาได้ผลอย่างน่าพอใจ

ภาควิชา เคมี

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ปีการศึกษา 2558

# # 5572149623 : MAJOR CHEMISTRY

KEYWORDS: ION SELECTIVE ELECTRODE / DONNAN EXCLUSION FAILURE / PERM-SELECTIVE MEMBRANE

SUTIDA JANSOD: PREPARATION OF ANION SELECTIVE MEMBRANE ELECTRODES FROM DONNAN FAILURE PHENOMENON INDUCED BY COPPER(II) ION. ADVISOR: PROF. THAWATCHAI TUNTULANI, Ph.D., 47 pp.

The fabrication of anion selective electrode using mono- and dinuclear metal complexes based on calix[4]arene and anthracene with different number of side-arms and donor atoms were used as ionophores or ion-carriers. The polymeric membrane containing the ionophore L1 and potassium tetrakis(*p*-chlorophenyl)borate (KTPCIPB) as a cation exchanger in the presence of metal ions as triggers showed the Donnan exclusion failure phenomenon. The ionophore L1 bound metal ions very tightly inducing the co-extraction of anions into the membrane and changed the permselectivity of the membrane to anions by the observation of negative EMF responses. However, the membranes containing L2 – L4 gave the positive EMF responses to most metal salts. The best perchlorate anion selective electrode was accomplished using ionophore L1 and 25 mol% of KTPCIPB related to the ionophore incorporated in the *o*-NPOE plasticized PVC membrane preconditioned in CuCl<sub>2</sub> with Nernstian slope of  $-55.80 \pm 0.36$  mV/decade, over the concentration range of  $10^{-5}$  –  $10^{-2}$  M and the limit of detection of 2.84  $\mu$ M. In addition, the fabricated membrane electrode could be used in the pH range of 3 – 9 with great reversibility and successfully applied to determine the concentration of perchlorate in tap water with satisfactory results.

Department: Chemistry

Student's Signature .....

Field of Study: Chemistry

Advisor's Signature .....

Academic Year: 2015

## ACKNOWLEDGEMENTS

Firstly, I would like to express my sincere appreciation to my advisor Prof. Dr. Thawatchai Tuntulani for the continuous support of my master degree studies and related research, for his patience, motivation, and immense knowledge. His instruction helped me during the time of the research and writing this thesis. He also gave me an opportunity to do the research abroad in order to extend my ideas and visions. I could not have imagined having a better advisor and mentor in my master degree study.

Besides my advisor, I would like to thank all of my thesis committee: Assoc. Prof. Dr. Vudhichai Parasuk, Asst. Prof. Dr. Soamwadee Chaianansutcharit, and Assoc. Prof. Dr. Wittaya Ngeontae for their insightful comments, encouragement and valuable recommendations as well as the motivation to broaden my research from different perspectives.

My sincere thanks also goes to Prof. Dr. Eric Bakker, who provided me an opportunity to join his team as intern to learn more about electrochemical sensors. It would not be possible to achieve my research abroad without his instruction. In addition, I would like to express my thanks to the Development and Promotion of Science and Technology Talents Project (DPST) for the financial support throughout my study.

In particular, I gratefully thank Asst. Prof. Dr. Wanlapa Aeungmaitrepirom for facilities and space in her lab. I sincerely thank Dr. Wanwisa Janrungroatsakul and Dr. Phetlada Kunthadee for teaching and giving me advices and meaningful discussion. I thank my friends and all members in the Supramolecular Chemistry Research Unit (SCRU) and Environmental Analysis Research Unit (EARU) for interesting discussions and friendship in the last three years.

Eventually, I would like to thank my family, my parents and sisters for support, love, advice, encouragement throughout my life.

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# CHAPTER I

## INTRODUCTION

Ion-selective electrodes (ISEs) based on polymer membrane matrixes are important analytical devices due to their advantages including simple instrumentation, fast response, low cost, ease of preparation and procedures, free of contamination, unaffected by color or turbidity, wide dynamic range and reasonable selectivity [1]. The ISEs are applied successfully for the determination of various ions in environmental and clinical as well as in industrial applications. However, traditional anion-selective electrodes demonstrate a Hofmeister selectivity sequence: perchlorate > thiocyanate > iodide ~ salicylate > nitrate > bromide > nitrite > chloride > sulfate. Generally, the membrane selectivity is controlled by the free energy of hydration of the ions involved [2]. For decades, researchers have focused on the electrodes using plasticized poly(vinyl chloride) (PVC) membranes incorporating different metal complexes as an anion carrier. The researchers have especially concentrated on the ion carriers with organometallic complexes via specific anion coordination with the central metal ion of the complexes [3-5]. The coordination structure of the complex formation would play crucial role in the selectivity characteristics of the ISEs.

Supramolecular chemistry of anions and artificial ion carriers has been widely explored for many decades [6, 7]. The design of synthetic carriers takes advantages of the different elements of the host-guest chemistry. The important part of the ion carrier-based ISE is the ion-sensitive solvent polymeric membrane, physically a water-immiscible liquid of high viscosity placed between the sample and the internal electrolyte solution [1]. Since the membrane components are typically dissolved in the organic polymer phase, Ionophores should be highly lipophilic. They are strongly retained within the organic phase to ensure a long lifetime of the sensor. This is particularly a challenge for macrocyclic ionophores due to their high lipophilicity. A good ionophore is most frequently achieved by incorporating ion receptors, for example, simple crown ethers, bis-crown, non-cyclic amide and thioamide as well as basket shaped calixarenes. Ionophores should have a polar moiety or a set of polar

functional groups responsible for the ion recognition process [8]. More than decades, the tripodal molecular platform, three arms with donor atoms, at which it can coordinate with the analyte is attached on the building blocks in order to accomplish an ion recognition unit [9].

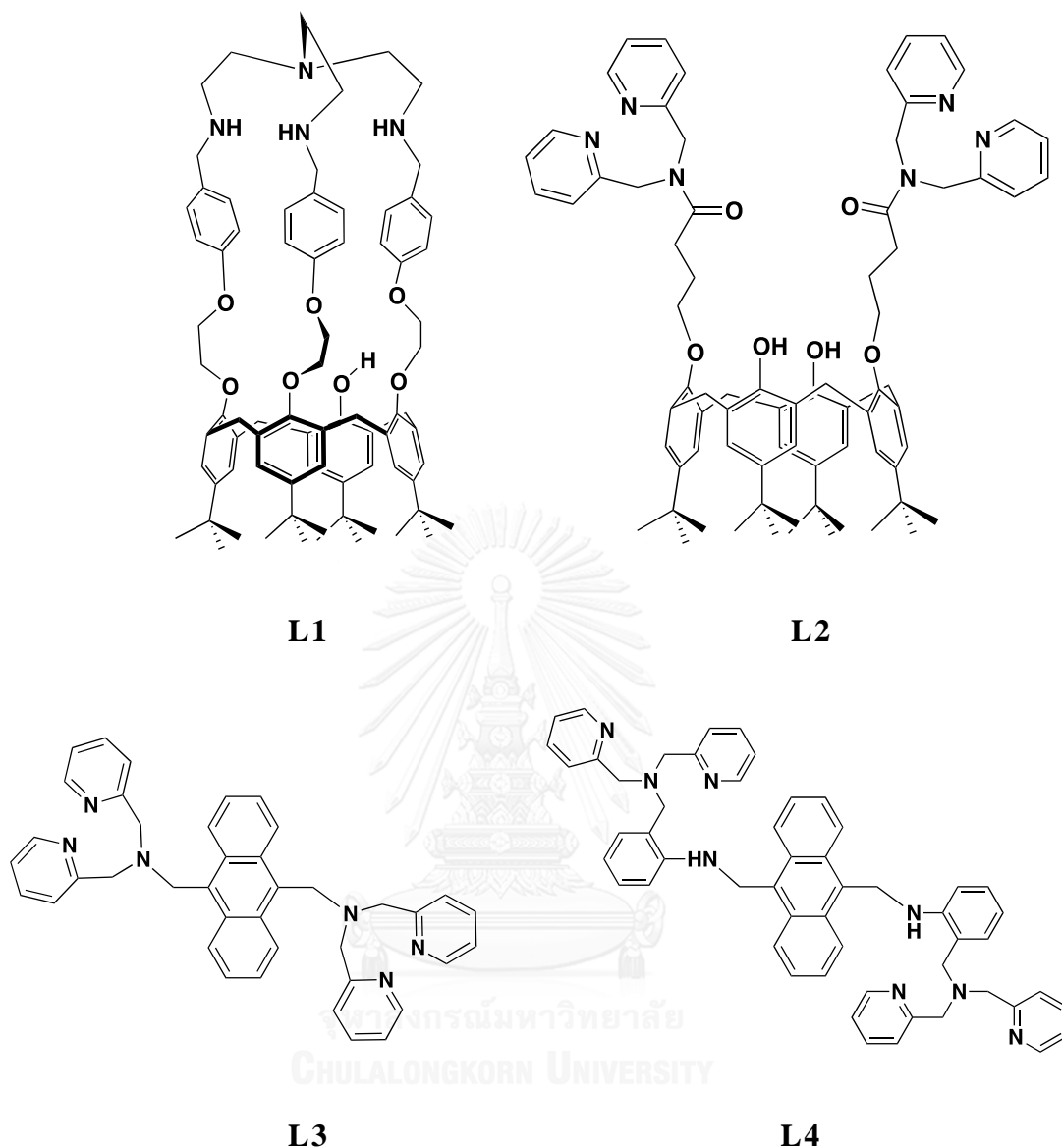
In this research, we have fabricated anion selective polymeric membrane electrodes using calix[4]arene and anthracene as the building blocks attached with different types of receptors, which are expected to enhance the molecular recognition properties using Cu(II) ion as binding center. However, the ionophore binds Cu(II) ion too tightly, the extraction of Cu(II) salt from aqueous phase increases  $a_{\text{Cu(II)}}$  in the organic phase and then leads to a breakdown of the permselectivity of the membrane from cationic to anionic response. This phenomenon is known as Donnan exclusion failure [1, 10-13].

### 1.1 Research Objective

The purpose of this research is to study the characteristics and fabrication of anion selective electrodes using ionophores processing calix[4]arene and anthracene building blocks containing amine receptors and various metal ions are tested as triggers to induce Donnan exclusion failure phenomenon.

### 1.2 Scope of the Research

There are four purposed ionophores, **L1 – L4**, based on calix[4]arene and anthracene with different topology ligands as shown in Figure 1.1, successfully incorporated into polymeric membrane-based ISEs. The proposed membrane electrodes are determined by a variety of metal ions. Since the ionophore employed binds very tightly to Cu(II) and non-reversible complexes with Cu(II), leading to Donnan exclusion failure. The polymeric membrane stores many positive charges from Cu(II) ion and leads to collapse the permselectivity of the membrane. To maintain electroneutrality, the membrane induces the co-extraction of anions from aqueous phase entirely into the membrane phase and then changes the cationic response to an anionic species.



**Figure 1.1** Structures of ionophores (**L1-L4**); (**L1**) tripodal aza crown ether calix[4]arene derivative, (**L2**) dipicolylamine calix[4]arene derivative, (**L3**) anthracene-based dipicolylamine, and (**L4**) anthracene-based tripodal tetramine

The membrane components, such as ionophore (**L1 – L4**), ionic additive (KTpCIPB) and plasticizer (*o*-NPOE/DOS), generally dissolved in the organic polymer phase. The polymeric membrane are prepared in the classical manner using a 1:2 mass ratio of PCV and plasticizer (1:2 w/w) mainly composed of the ionophores and various amount of the cation exchanger as well as the types of the plasticizer. A variety of metal salts such as transition, alkaline and alkaline earth metal ions are

utilized in order to investigate the interactions between the metal ions and the ionophores which one is suitable to use as the trigger. These components could play important roles in the membrane as they effect to the characteristics of the membrane electrodes towards anions.

### **1.3 Benefits of the Research**

The optimization of anion selective electrode (ISE) is expected to use for determining a specific anion in tap water with satisfying characteristics.



## CHAPTER II

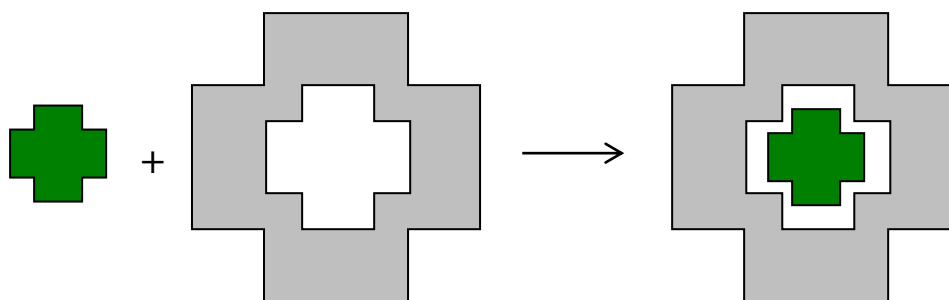
### THEORY AND LITERATURE REVIEWS

#### 2.1 Supramolecular based membrane sensors

Supramolecular chemistry, by the other names including host-guest chemistry and molecular recognition, is the chemistry of the intermolecular interaction of two or more species [6]. In 1873, Johannes Diderik van der Waals first supposed the existence of intermolecular bonds. Nevertheless, in 1894 a scientist named Hermann Emil Fisher developed supramolecular chemistry's fundamental principle of host-guest chemistry and discovered the lock-and-key model suggested that enzyme-substrate interactions take the form of a lock (enzyme) receives a key (substrate) [14]. The importance of supramolecular chemistry was constituted by the 1987 Nobel Prize for chemistry awarded to three of the pioneers namely Jean-Marie Lehn, Donald Cram and Charles Pedersen who took these concepts and applied them to synthetic molecules [15]. The development of selective host-guest complexes, in which a host molecule recognizes and selectively binds an exact guest, has been referred as an important achievement.

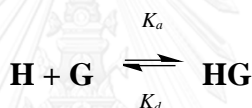
Host-guest chemistry, as mentioned above, explains complexes that are comprised of two or more molecules or ions that are held together by non-covalent bonds as shown in Figure 2.1. The non-covalent interactions are different from covalent bonds. The chemical energy released in the formation of non-covalent interactions is regularly weak forces and generally classified into 4 categories: electrostatic interactions, hydrogen bonds, van der Waals forces and hydrophobic effects [6, 16, 17].





**Figure 2.1** Host-guest chemistry according to Lehn [6]

In thermodynamic principles of host and guest interactions, there is an equilibrium between the uncomplexed state and the complexed state which may be clarified in terms of the dissociation constant ( $K_d$ ) and the association constant ( $K_a$ ), respectively [17].



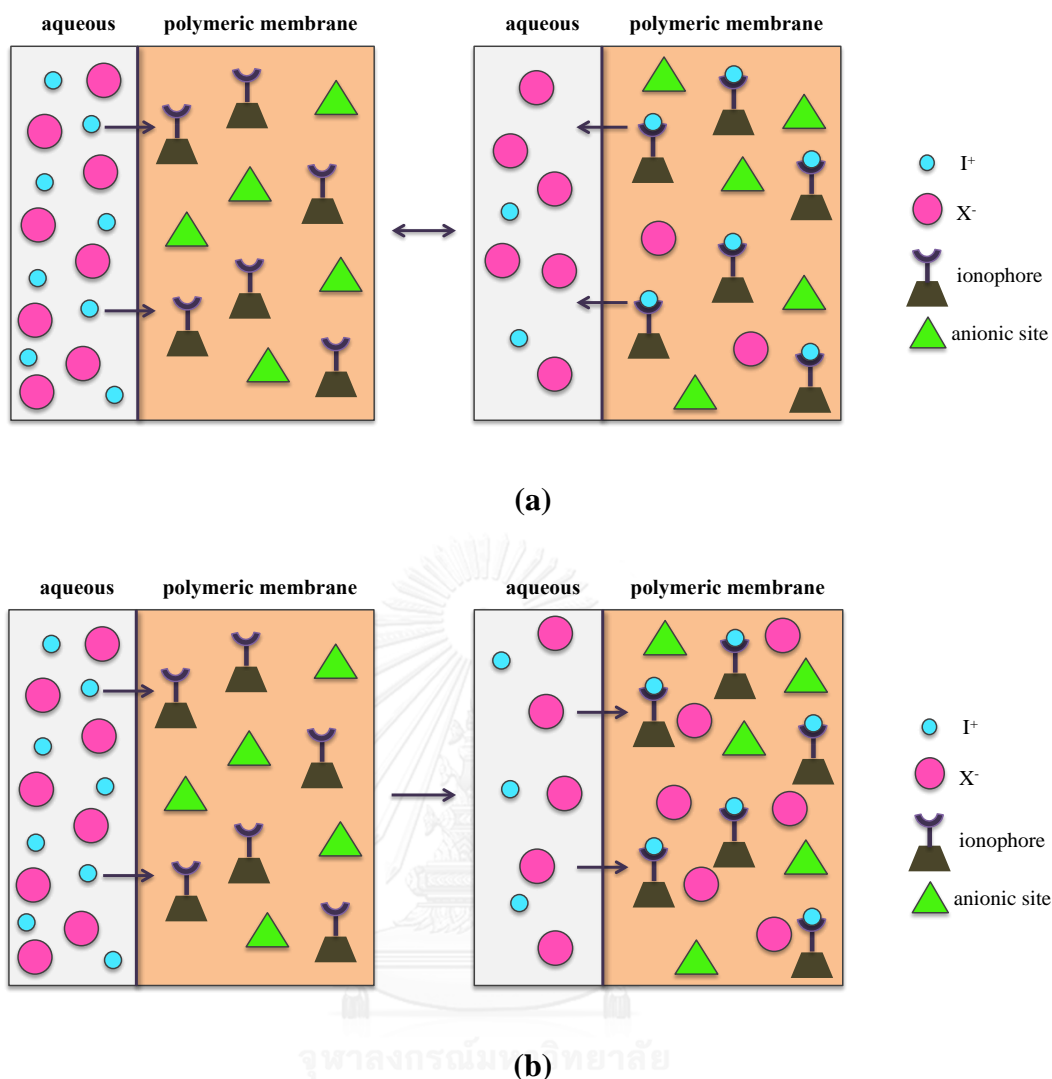
Where H = host, G = guest, HG = host–guest complex

The characteristics of the host and guest are crucial in supramolecular chemistry because the selective bonding between the host and the guest originates the information. This information is literally kept in the host and readout by the guest, which is controlled by the association and dissociation rates. This characteristic information can reveal the stability, selectivity, reactivity and transport of the complexes [18].

In addition, the molecular recognition and sensing of cations and anions have attracted a significant research attention with regard to their potential utilizations in various fields such as clinical diagnostics, industrial and environmental monitoring [7, 19-22]. In order to strengthen an artificial receptor that is selective towards a specific analyte, the interactions between host and guest must be considered.

## 2.2 Theory of Donnan failure and the literature reviews

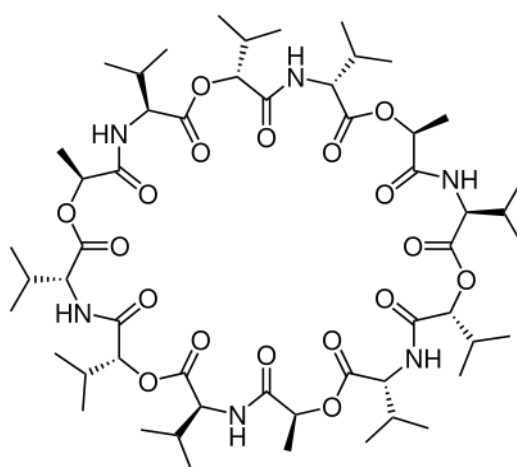
Generally, the composition of the surface layer of the membrane contacting the sample solution must be kept constant in order to obtain an exact Nernstian response of the electrode [1]. Phase transfer of aqueous ions in and out of an organic membrane is necessary for the classic behavior of ISEs [18]. The essential for gaining a theoretical response with ISE membranes is their permselectivity. The liquid membranes are routinely doped with a salt of a lipophilic ion. During the condition period the hydrophilic counterion of the ion-exchanger in the membrane is replaced with the analyte ion of interest (I) [1, 8, 23]. For example, potassium tetrakis(4-chlorophenyl) borate (KTpCIPB) for cation-selective electrodes and tridodecylmethyl ammonium chloride (TDMACl) for anion-selective electrodes. It suggests that the membrane, in the presence of ion exchanger, is permeable only for ion with the same charge sign of the ion of interest. As well as the ion exchanger can further prevent the coextraction of counterion from the sample solution [1, 8, 23]. This membrane characteristic is called permselectivity or Donnan exclusion as showed in Figure 2.2 (a) which gives the positive potentiometric slope in the case of cation-selective electrode. Nevertheless, if the ion carrier or ionophore in the membrane binds the cation ( $I^+$ ) too tightly and non-reversible complex with cation. The activity of the cations ( $a_I$ ) in the organic membrane is increased and converted from neutral ionophore to the positive charge ionophore inside the membrane [24, 25]. The permselectivity of the membrane then is changed to respond to anion ( $X^-$ ) from aqueous electrolyte indicating by a negative potentiometric slope, exhibited in Figure 2.2 (b). This effect is known as Donnan exclusion failure [1, 10-13].



**Figure 2.2** Schematic views of the permselectivity of the polymeric membrane-based ISEs; (a) Donnan exclusion in the case of cation-ISE, (b) Donnan exclusion failure

There have been several publications using the Donnan failure phenomenon for construction of anion-selective electrodes based on ISEs. In 1987, Buck studied the theory of Donnan exclusion failure in low anion site density membrane containing a neutral ionophore, valinomycin, as shown in Figure 2.3 [10]. A structure of valinomycin basically is an alternate link between amind and ester bridges, which is highly selective for  $K^+$  ions over sodium ions within the cell membrane [26]. However at high loading of activities of  $K^+$  salts, the Donnan exclusion failure occurred by producing fixed positive sites. The neutral carrier filled with  $K^+$  ( $K^+Val$ ) showed slightly greater concentration that could extract anions such as  $Br^-$ ,  $NO_3^-$ ,  $I^-$ ,  $Cl^-$ ,  $F^-$  and

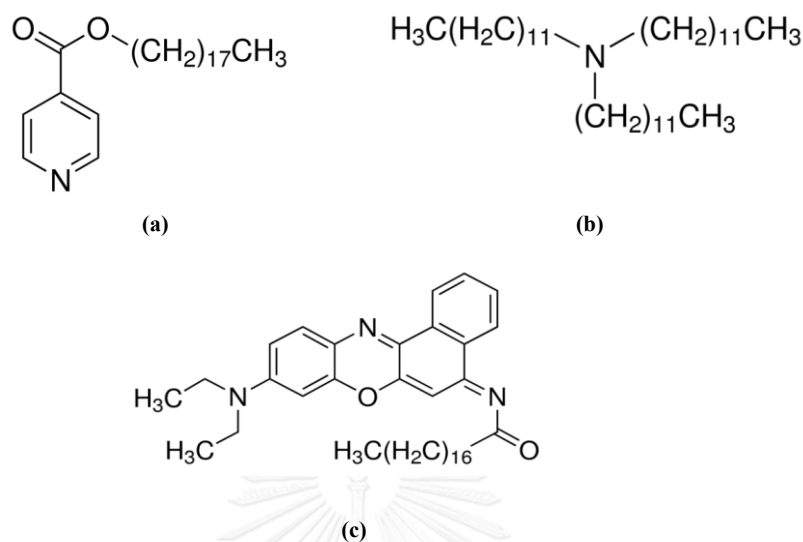
$\text{SCN}^-$  from bathing electrolyte into the membrane phase. Nevertheless,  $\text{K}^+$  ions responded only at very low bathing activities. This was typically occurred when ion exchanger of low capacity or low site density underwent Donnan failure which co-anions were admitted into the membrane. The membrane lost the permselectivity and then responded to anions. The phenomenon exhibited that the resistance of the membrane decreased after 4 days treatment in 0.1 M KSCN during the impedance measurements.



**Figure 2.3** Structure of valinomycin

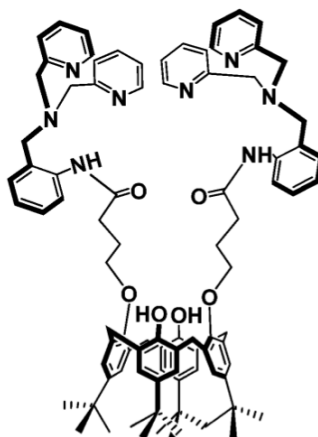
In 1993, Buck and coworkers studied anion effects on Donnan failure of aminated-poly(vinylchloride)-based and neutral carrier-based pH sensors [11]. At low pH bathing electrolyte, the overall partitioning of HX was dominated by binding of  $\text{H}^+$  to the neutral carrier (ETH-1778, TDDA, and ETH-5924, Figure 2.4) and the aminated PVC ( $\text{PVC-NH}_2$ ). Donnan failure produced fixed positive sites that created a nearly ideal anion sensor. The result showed the presence of significant anions ( $\text{X}^-$ ) in the membrane, owing to the differences in their lipophilicity such as  $\text{ClO}_4^-$ ,  $\text{SCN}^-$  and  $\text{Cl}^-$  in order to maintain the electroneutrality. Ideally, the pH-sensitive membrane electrodes should not have interfering anions when used in physiological pH. It implied that pH solutions were important in order to transport interfering anions into the membrane. The optimal condition showed that at higher pH values the anion interference ( $\text{Cl}^-$ ) disappeared or became more negligible in the presence of  $\text{SCN}^-$ . Therefore, the Donnan failure depends on the basicity of the carriers, the primary ion

activity ( $H^+$ ) and the hydrophobic of the anions. These effects should be considered for construction of the pH sensors.



**Figure 2.4** Structure of neutral carriers (a) ETH-1778 (hydrogen ionophore IV), (b) TDDA (tridodecylamine), and (c) ETH-5294 (chromoionophore I)

In 2013 our group reported the fabrication of thiocyanate anion-selective electrode from Donnan failure using a di-tripodal amine calix[4]arene as an neutral carrier (Figure 2.5) [12]. Only Cu(II) ions bound very tightly with the ionophore caused the membrane, containing ionophore and 75 mol%  $KTpClPB$ , losing its permselectivity by extraction of anions into the membrane and responding negatively in EMF measurement. This electrode also exhibited an elegant anti-Hofmeister that the membrane electrode was selective to  $SCN^-$  in the presence of other lipophilic anions.



**Figure 2.5** Structure of di-tripodal amine calix[4]arene

### 2.3 Ion-carriers for anion-selective electrodes (ISEs)

Potentiometric detection based on ion-selective electrodes, as a simple method, possesses many advantages, for example, simple method, fast response, low cost, ease of preparation and procedures, free of contamination, unaffected by color or turbidity, wide dynamic range and reasonable selectivity [1, 8]. These characteristics have led to sensors for several ionic species, and the list of available electrodes has grown increasingly.

Recently, the design and synthetic of sensory molecules for anion-selective electrodes has become a challenging task because anions play fundamental roles in an extensive range of medical, biological and environment processes. The response of the anion, in membrane-based anion-selective electrodes depends on the Hofmeister series, which is related with the energy necessary for carrying the anion from water to the membrane [27]. This means that higher lipophilic anions will cause larger responses based on the lipophilicity of the anions as illustrated in the Hofmeister series with the selectivity order  $\text{ClO}_4^- > \text{SCN}^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{NO}_2^- > \text{OAc}^- \sim \text{Cl}^- \sim \text{F}^- > \text{H}_2\text{PO}_4^- > \text{SO}_4^{2-}$  [1, 28, 29].

#### 2.3.1 Perchlorate-selective polymeric membrane electrodes

An increasing of the quantity of the perchlorate has come to serious concerns because the perchlorate can be found as a contaminant in food products, water, soil,

fertilizers and plants [30, 31]. Perchlorate is quite soluble, greatly mobile in aqueous solution and rather nonreactive with other ions in water [32]. It is typically known that the selective interaction of an anion and a metal complex as an ionophore within the membrane is necessary for fabrication of anion selective membranes. The anion selectivity is largely governed by specific interaction between the central metal of the ionophore and anion [33]. In the case of perchlorate ISEs, the potentiometric response is normally the result of the axial coordination of the perchlorate to the metal center [21, 34].

In this work we expected that our proposed ionophores (**L1** – **L4**) could show great characteristics of anion selective ionophores upon triggering by metal ions. The response characteristics of perchlorate selective electrodes of some previous publications based on metal complexes are summarized in Table 2.1 and their structures are demonstrated in Figure 2.6.

In 2000, Sanchez-Pedreno and coworkers reported a gold(I) complex of bri(tri-(*p*-methoxyphenyl) phosphine) (**I1**) as the ionophore without using the anion exchanger [35]. A Nernstian slope was found to be -56.77 mV/decade. The electrode could be interfered in the presence of a higher concentration of chlorate because the selectivity order strongly depended on the lipophilicity of anions. Even the electrode was good enough to use in the direct measurement without prior separation steps in tap water, human urine and cattle urine, the composition of the membrane should be improved in order to yield a better selectivity.

In 2006, Ganjali and his coworker [36] reported the  $\text{ClO}_4^-$  salt of Ni(II) complex of 1,3,5,8,10,13 hexaazacyclo tetradecane (**I2**) and hexadecyltrimethyl ammonium bromide (HTAB) as the anion exchanger exhibited a very good selectivity for  $\text{ClO}_4^-$  ions over a wide variety of anions which had the selectivity coefficients values lower than -2.0 except  $\text{MnO}_4^-$  (the selectivity coefficient was -1.0). It implied that  $\text{MnO}_4^-$  interfered the measurement. Nevertheless, the electrode showed good recoveries in cattle urine samples.

Later, Zanjanchi and his group [37] proposed that cobaloxime(III) complex of chlorobis(dimethylglyoximate) (triphenylphosphine) (**I3**) and cetyltrimethyl ammonium bromide (CTAB), the anion exchanger, could be successfully used as a perchlorate-selective PVC membrane electrode. The electrode showed excellent selectivity towards  $\text{ClO}_4^-$  ion even in the presence of much higher concentration of other anions because the selectivity coefficients of those common anions were lower than -2.0. Moreover, the electrode was greatly applied to measure  $\text{ClO}_4^-$  in tap water and human urine by direct potentiometry using standard addition method.

Perchlorate-selective PVC membrane electrode based on bis(dibenzoylmethanato) cobalt(II) complex (**I4**) was proposed as the neutral ionophore in 2009 by Rezaei and coworkers [38]. The membrane electrode based on Co(II) complex and methyltrioctylammonium chloride (MTOAC) as an anion exchanger was found to be selectively responsive to  $\text{ClO}_4^-$  over several anions except  $\text{SCN}^-$ ,  $\text{IO}_4^-$ ,  $\text{I}^-$  and  $\text{NO}_3^-$ . However, the electrode was applied to measure  $\text{ClO}_4^-$  from river, tap water and human urine samples with satisfactory results.

In 2011, Gholamian and coworkers [33] used Cu(II) complex of 1,9-dibenzyl-1,3,7,9,11,15 hexaazacyclohexadecane (**I5**) as the ionophore and trioctylmethyl ammonium chloride (TOMAC) as the anion exchanger incorporating in the PVC membrane electrode. The electrode was highly selective to  $\text{ClO}_4^-$  over a number of other anions. The interaction of  $\text{ClO}_4^-$  ion with the ionophore was stronger rather than other anions. The selectivity coefficients of other anions were lower than -2.2. This sensor successfully used in determining the concentration of  $\text{ClO}_4^-$  without the pretreatment steps in the tap water samples with good recoveries.

In 2014, Gupta et al. [27] suggested that the polymeric membrane electrode containing hexadecyltrimethylammonium bromide (HTAB) and zinc complex (**I6**) of 6,7;13,14-dibenzo-2,4,9,11-tetramethyl-1,5,8,12-tetramethylacrylate-1,5,8,12-tetraaza cyclotetradecane-6,13-diene demonstrated the highest formation constant with  $\text{ClO}_4^-$  ion over other anions and could be used to determine  $\text{ClO}_4^-$  in real samples with satisfactory results.

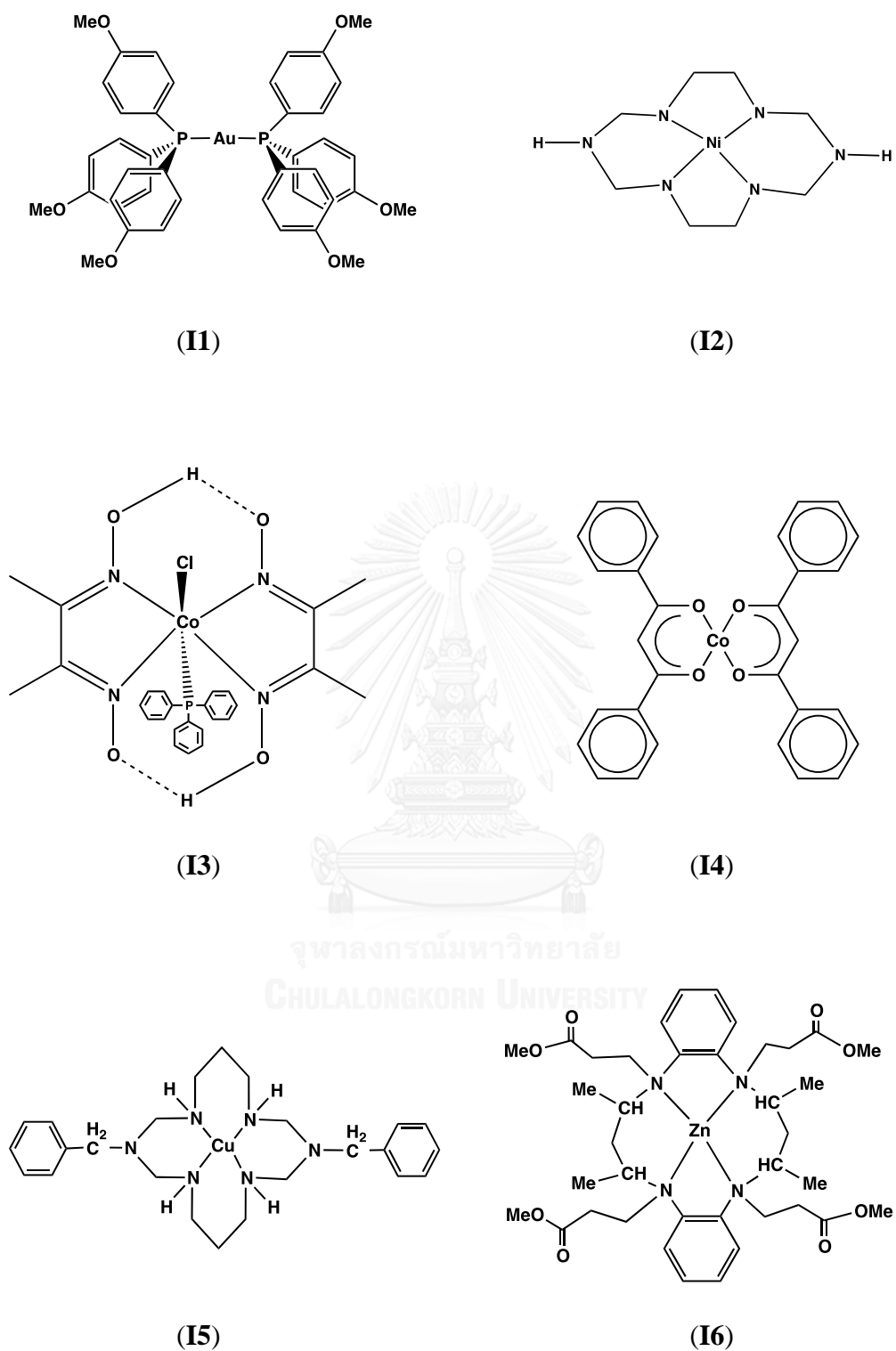


**Table 2.1** Response characteristics of perchlorate-ISEs in comparison to metal complexes as the ionophores (**I1** – **I6**)

Ionophore	Metal ion	Cationic additive	Plasticizer	Slope (mV/decade)	Linear range (M)	Detection limit (M)	Response time (s)	pH range
bis(tri-( <i>p</i> -methoxyphenyl) phosphine) gold(I) complex; ( <b>I1</b> )	Au(I)	-	<i>o</i> -NPOE	-56.77	5.0 x 10 <sup>-6</sup> - 1.0 x 10 <sup>-2</sup>	1.1 x 10 <sup>-6</sup>	≤ 14	2 – 12
1,3,5,8,10,13 hexaaza-cyclo tetradecane Ni(II) complex; ( <b>I2</b> )	Ni(II)	HTAB	BA	-59.5	9.0 x 10 <sup>-7</sup> - 1.0 x 10 <sup>-1</sup>	6.0 x 10 <sup>-7</sup>	< 10	3 – 11
chlorobis(dimethylglyoximeato)(triphenylphosphine) cobalt(III) ; ( <b>I3</b> )	Co(III)	CTAB	DBP	-56.8	1.0 x 10 <sup>-6</sup> - 1.0 x 10 <sup>-1</sup>	8.3 x 10 <sup>-7</sup>	< 15	3 – 10

Ionophore	Metal ion	Cationic additive	Plasticizer	Slope (mV/decade)	Linear range (M)	Detection limit (M)	Response time (s)	pH range
Bis(dibenzoylmethanato)cobalt(II) complex; <b>(14)</b>	Co(II)	MTOAC	DBP	-60.3	$8.0 \times 10^{-7}$ - $1.0 \times 10^{-1}$	$5.6 \times 10^{-7}$	$\leq 5$	2 – 9
(1,9-dibenzyl-1,3,7,9,11,15 hexaazacyclohexadecane) copper(II) complex; <b>(15)</b>	Cu(II)	TOMAC	DOP	-59.4	$1.0 \times 10^{-6}$ - $1.0 \times 10^{-1}$	$4.0 \times 10^{-7}$	7	3 – 10
Macrocyclic Zn(II) complex <sup>6</sup> ; <b>(16)</b>	Zn(II)	HTAB	BA	-58.7	$8.3 \times 10^{-7}$ - $1.0 \times 10^{-2}$	$5.4 \times 10^{-7}$	12	3 – 8

*a*: zinc(II) complex of 6,7:13,14-dibenzo-2,4,9,11-tetramethyl-1,5,8,12-tetramethylacrylate-1,5,8,12-tetraaza-cyclohexadecane-6,13-diene, BA: benzyl acetate, DBP: dibutyl phthalate, DOP: dioctyl phthalate, *o*-NPOE: *o*-nitrophenyl octyl ether



**Figure 2.6** Structures of ionophore **I1 – I6**

## CHAPTER III

### EXPERIMENTAL

#### 3.1 General procedures

##### 3.1.1 Reagents and materials and solutions

High molecular weight polyvinyl chloride (PVC), *o*-nitrophenyl octyl ether (*o*-NPOE), bis(2-ethylhexyl)sebacate (DOS), Potassium tetrakis(*p*-chlorophenyl)borate (KTPCIPB), dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), chloroform (CHCl<sub>3</sub>) and tetrahydrofuran (THF) were purchased with Selectophore® grade from Fluka. Nitrate salts of cations also sodium and potassium salts of anions of analytical grade were obtained from Merck, Carlo Erba, Fluka, Sigma-Aldrich, Reidel and BDH. The pH of the solution was adjusted by HNO<sub>3</sub> or NaOH. All experiments were performed with ultrapure water from Milli-Q (Bedford, MA, USA) water purification system (Millipore). Calix[4]arenes derivatives, **L1** and **L2** and anthracene derivatives for **L3** and **L4**, were prepared by the previously published procedures [39-42].

#### 3.2 Ion selective electrode studies

##### 3.2.1 Membrane preparation

The membrane cocktail composing of ionophore (**L1** – **L4**) 10 mmol kg<sup>-1</sup>, cation exchanger (KTPCIPB), 33 wt.% PVC and 66 wt.% plasticizer (total mass of 220 mg) were dissolved completely in 2.5 mL of THF. Some ionophores required to be dissolved in a small volume of other solvents due to their low solubility (Ionophore **L1** dissolved in CH<sub>2</sub>Cl<sub>2</sub>, ionophores **L3** and **L4** dissolved in CHCl<sub>3</sub>). The transparent cocktail was poured into a 30 mm-i.d. glass ring placed on a glass plate. The solvent at room temperature was evaporated slowly overnight. The prepared membrane was punched into small sizes of 7.5 mm-i.d. and preconditioned overnight in 10 mM of metal salt solution then conditioned several hours in 10 mM of anion salt solution before measuring the potentiometric anion responses by the potentiometric method.

### 3.2.2 Metal ions triggers in Donnan exclusion failure

The plasticized PVC membranes containing the ionophores (**L1 – L4**) and cation exchanger (KTpCIPB) were studied electrochemically in order to measure the cation responses by preconditioned the membranes overnight in 10 mM of metal nitrate solutions such as Cu(II), Zn(II), Ni(II), Co(II), Cd(II), Ag(I), Hg(II), Pb(II), Cr(III), Na(I), K(I), Mg(II), Ca(II), except metal chloride solution for Fe(III) ion. Those transition, alkaline and alkaline earth metal ions, which used as the triggers, displaced the  $K^+$  ions sitting on the cation exchanger by binding the ionophores in the membranes according to form the metal complexes. The preconditioned membrane was mounted into a working electrode body. The inner filling solution (IFS) used for determining the membrane response was 10 mM of its metal chloride solution. The EMF responses of the membranes, which gave near Nernstian slope of -59.2 mV/decade, were suitable to use as the triggers for investigating anion responses lead to the Donnan exclusion failure phenomenon.

### 3.2.3 Anions measurements

To determine the anion response after preconditioning membrane in metal salt solution, the membrane was conditioned in 10 mM of anion salt solution for several hours. A mixed solution of anion (10 mM) and NaCl (1 mM) was used as the inner filling solution. The prepared membrane was mounted into the electrode body for measuring the EMF response. The sodium or potassium salts of anions, which used to determine the anion responses, were  $ClO_4^-$ ,  $SCN^-$ ,  $I^-$ ,  $NO_3^-$ ,  $Br^-$ ,  $NO_2^-$ ,  $OAc^-$ ,  $Cl^-$ ,  $F^-$  and  $H_2PO_4^-$ . The EMF recorded by adding each anion salts from the concentration of  $10^{-7}$  to  $10^{-2}$  M. The Nernstian slopes were explored and recorded.

### 3.2.4 EMF measurements

The prepared membrane was attached into the electrode body filling with the inner filling solution as mentioned above. The potential difference between the reference electrode and the working electrode placed to the sample phase was measured in stirring solution at ambient temperature in the galvanic cell:

Ag,AgCl/3M KCl//1 M LiOAc//sample solution/membrane/IFS/AgCl,Ag.

The reference electrode Ag/AgCl with double junction was used (type 6.0726.100, Metroh AG, CH-9010 Herisau, Switzerland) with 1 M LiOAc as salt bridge electrolyte. The EMF measurements were carried out with a high impedance input 16-channel EMF monitor (Lawson Labs Inc., Malvern, PA 19355, USA) under zero current. Activity coefficients of anions in aqueous solutions were calculated according to the Debye-Hückel approximation [8, 43]. A Faraday cage was employed to protect the system from unpleasing noise.

### 3.2.5 Selectivity measurements

The selectivity coefficients were determined by separate solution method (SSM) and calculated analytically by the IUPAC commission and Nicolsky-Eisenman equation as shown in Eq. (1) [1, 8, 13].

$$\log K_{i,j}^{pot} = \frac{Z_i F \{E(j) - E(i)\}}{2.303 RT} + \log [a_i(i) / a_j(j)^{Z_i/Z_j}] \quad (1)$$

The prepared membranes were conditioned first in 10 mM of metal salt solution overnight and a few hours in interfering anion solution afterwards. The potential was recorded in two separation solutions, first creating a calibration curve of interfering anion (j) from the concentration of  $10^{-7}$  to  $10^{-2}$  M and another one of primary anion (i) at the same concentration range. The mixed solution of 10 mM and 1 mM of interfering anion and NaCl, respectively was used as inner filling solution. The measurement was done in triplicate (using new membrane for one replicate).

### 3.2.6 Effect of the solution pH

The reference electrode and pH electrode were immersed in solution and the solution was adjusted to pH 3 with 2% HCl and increased to pH 11 by adding 10 - 100 mM NaOH. Both pH and EMF values were read simultaneously. These measurements were carried out using the same electrode, but concentrations of the sample solution were varied from 1 mM to 10 mM.

### 3.2.7 Reversibility of the membrane potential

The membrane reversibility was determined by measuring the EMF values of  $\text{ClO}_4^-$ -ISE in a 1 mM  $\text{ClO}_4^-$  solution. Subsequently, the electrode was rinsed and again dipped into a 10 mM  $\text{ClO}_4^-$  solution. The cycle was repeated four times.

### 3.3 Application for determination of perchlorate in real sample

The proposed perchlorate anion-selective electrode was applied to determine the quantity of perchlorate in real water samples. The samples were spiked with known concentrations of the perchlorate anion ( $5.0 \times 10^{-5}$  and  $1.0 \times 10^{-4}$  M) and then calculated the percentage recoveries using the EMF recorded.



## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Design of ionophores

Four ionophores containing mono- and dinuclear metal complexes based on calix[4]arene and anthracene attached with different topology of ligands such as tripodal amine (**L1** and **L4**) and dipicolylamine (**L2** and **L3**) as receptor units were used to prepare PVC membrane ISEs. Particularly, the tripodal amine ionophores often bound metal ions very strongly led to the Donnan exclusion failure phenomenon, which later changed the permselectivity of membranes. From this phenomenon, we can fabricate anion-selective electrodes by the proposed ionophores incorporated in polymeric membranes-based ISEs. The properties of each ionophore were listed below.

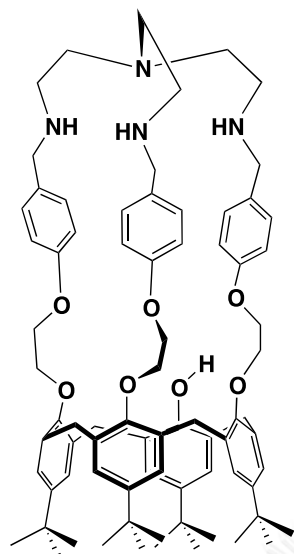
Ionophore **L1**: Tripodal aza crown ether calix[4]arene, containing four nitrogen donors was able to form complexes with transition metal ions such as Co(II), Ni(II), Cu(II) and Zn(II) and the stability of the complexes followed the sequence: Ni(II) < Co(II) <<Cu(II)>>Zn(II) [39].

Ionophore **L2**: Dipicolylamine calix[4]arene was synthesized and found that **L2** could be used to fabricate silver ion-selective electrode (Ag-ISE) as it was selective to Ag(I) in the presence of other metal ions [40].

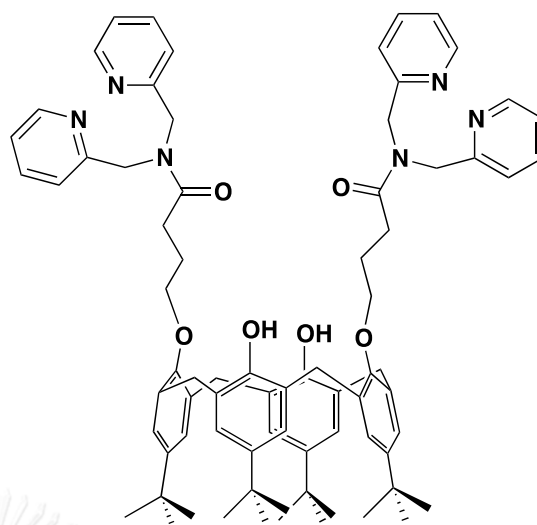
Ionophore **L3**: Anthracene-based dipicolylamine was reported that it selectively bound phosphorylated chemical species induced by Zn(II) ion and caused the florescent spectral change [41].

Ionophore **L4**: Anthracene-based tripodal tetramine induced by Zn(II) could be used to detect  $P_2O_7^{4-}$  or PPI selectively under indicator displacement assay using methylthymol blue (MTB) as the indicator [42].

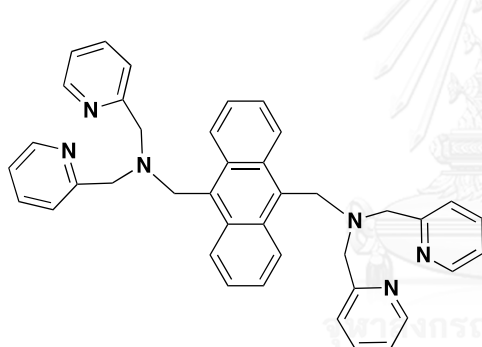




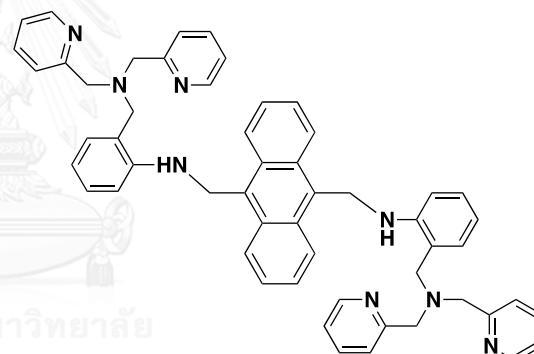
L1



L2



L3



L4

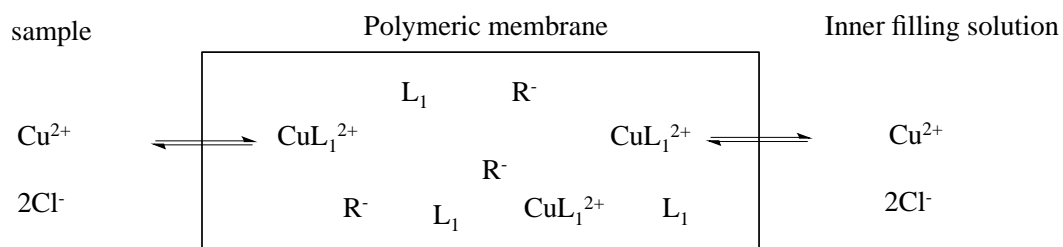
## 4.2 Fabrication of anion-selective electrodes

This is a great challenge to incorporate the proposed ionophores in polymeric membranes based ISEs in order to fabricate anion-selective electrodes by Donnan exclusion failure. Herein, the polymeric membranes in the total weight of 220 mg were prepared, containing ionophores (L1-L4), various amounts of cation exchanger (KTpCIPB) in a classical manner using the ratio of PVC and plasticizer (PVC, *o*-NPOE) at 1:2 w/w. These compositions of the membranes were intentionally studied the sensing characteristics including the selectivities, sensitivity, working concentration range, limit of detection, working pH range, reversibility also the

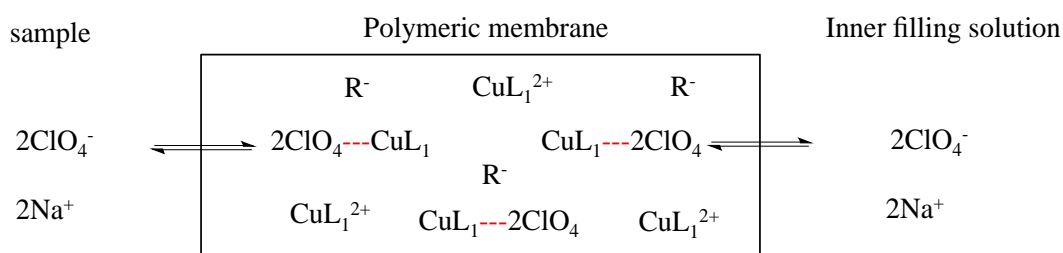
performance of the optimized membrane electrode for determining the quantity of anion of interest.

#### 4.2.1 Donnan exclusion failure phenomenon

According to the well-known Nernst equation, the composition of the surface layer of the membrane contacting the sample must be kept constant in order to obtain an exact Nernstian response of the electrode. The prerequisite for obtaining a theoretical response with ISE membranes is their permselectivity, which means that no significant amount of counterions may get in the membrane phase [1]. To accomplish this so-called Donnan exclusion as shown in Figure 4.1 (a) in the case of the neutral ionophore, the counterions limited to the membrane must be presented. If the ionophore **L1** binds Cu(II) ion too tightly and non-reversible complex with Cu(II), the extraction of CuCl<sub>2</sub> in aqueous phase increases the activity of the Cu(II) ion ( $a_{\text{Cu(II)}}$ ) in organic phase and leads to a breakdown of the permselectivity of the membrane, as known as Donnan exclusion failure. To maintain electroneutrality, the membrane induces the co-extraction of anions such as ClO<sub>4</sub><sup>-</sup> in sample solution into the membrane phase. The permselectivity of the membrane is converted to respond to anion as illustrated in Figure 4.1 (b) and later observed the negative potentiometric responses.



(a)

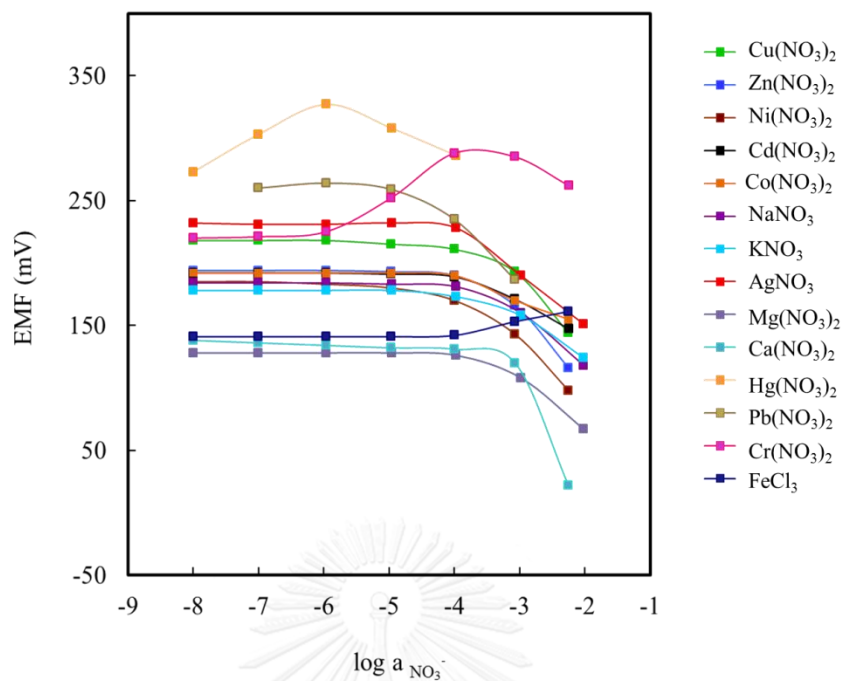


(b)

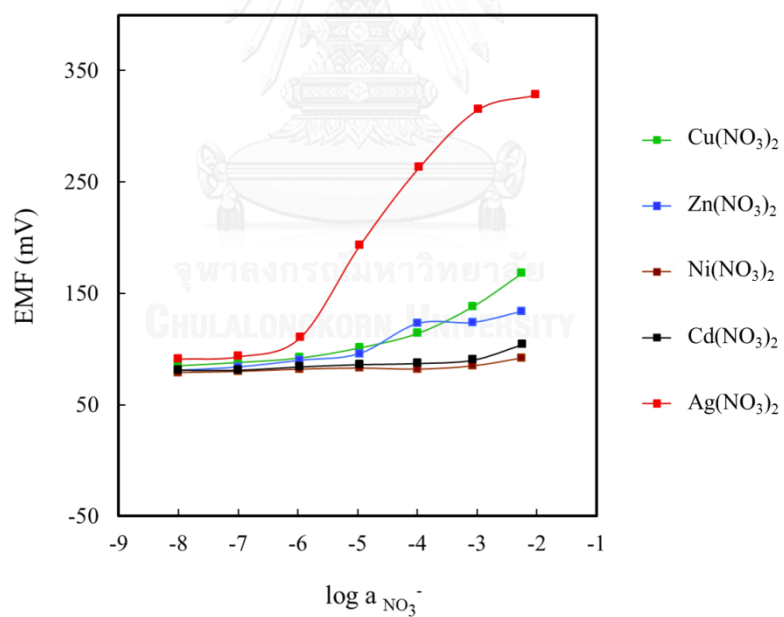
**Figure 4.1** Schematic views of the equilibria between sample and inner filling solution, (a) Donnan exclusion, (b) Donnan exclusion failure; anionic additive ( $\text{R}^-$ )

#### 4.2.2 Potentiometric anion responses

The polymeric membranes were prepared by controlling the ratio of PVC:*o*-NPOE at 1:2 w/w containing the concentration of ionophores, **L1-L4**, at ca. 10 mmol/kg with various amounts of cation exchanger or anionic additive, KTpClPB, (25, 50 and 75 mol% relative to the ionophore). These polymeric membranes were initially preconditioned in various metal salts overnight to form complexation with ionophores.



(a)



(b)

**Figure 4.2** The EMF responses of the *o*-NPOE plasticized PVC membrane in the presence of 50 mol% of the cation exchanger (KTpCIPB) preconditioned in a variety of metals salts; (a) membrane containing L1 and (b) membrane containing L2.

Ionophore **L1** with a shorten cavity was a cage of tripodal amine shape containing four nitrogen donor atoms supporting to bind metal ion strongly and non-reversible between **L1** and metal ions in the membrane. The membranes then responded to  $\text{NO}_3^-$  (from metal nitrate) by observation of negative EMF responses in Figure 4.2 (a). The EMF responses of ionophore **L1** and the Nernstian slopes when varied the metal salts were summarized in Table 4.1. In contrast ionophore **L2** was an opened dinuclear complex could not able to bind strongly to metal ions which gave the positive EMF responses to most of metal ions as exhibited in Figure 4.2 (b). It implied that dipicolylamine containing three nitrogen atoms in ionophore **L2** was improper to host metal ions tightly. In addition, the ionophores based on anthracene (**L3-L4**), leached from the organic phase into the aqueous phase very fast. They were also inappropriate for studying electrochemically because they had no responses to the EMF measurement (data was in Appendix A).

In summary, the ionophore **L1** was the best ion-carrier caused the Donnan exclusion failure phenomenon in order to fabrication of anion-selective electrodes. However, ionophore **L2** was inappropriate because it was not able to extract anions of interest into the membrane phase.

#### 4.2.3 Metal ion and membrane solvent effects to perchlorate selectivities

The ionophore **L1** bound the metal ions very tightly and non-reversible between the ionophore and metal ions in the membrane. The membranes were then converted the permselectivity from cation to anion indicating by the negative potentiometric responses of  $\text{NO}_3^-$  ions, except Fe(III) ion which gave the positive EMF response, as summarized in Table 4.1. These results supported us to fabricate anion-selective electrodes using the ionophore **L1** as the ion carrier.

Moreover, the EMF responses of membranes containing **L1** in Table 4.1 gave near Nernstian responses (-59.2 mV/decade for monovalent anion) when using the transition metal ions such as Cu(II), Zn(II) and Ni(II) ions. These metal ions were used as the triggers in the following experiments.

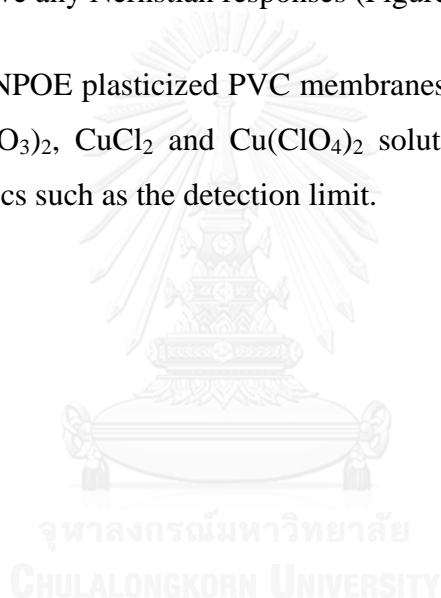
**Table 4.1** The potentiometric responses of ionophore **L1** towards metal ions

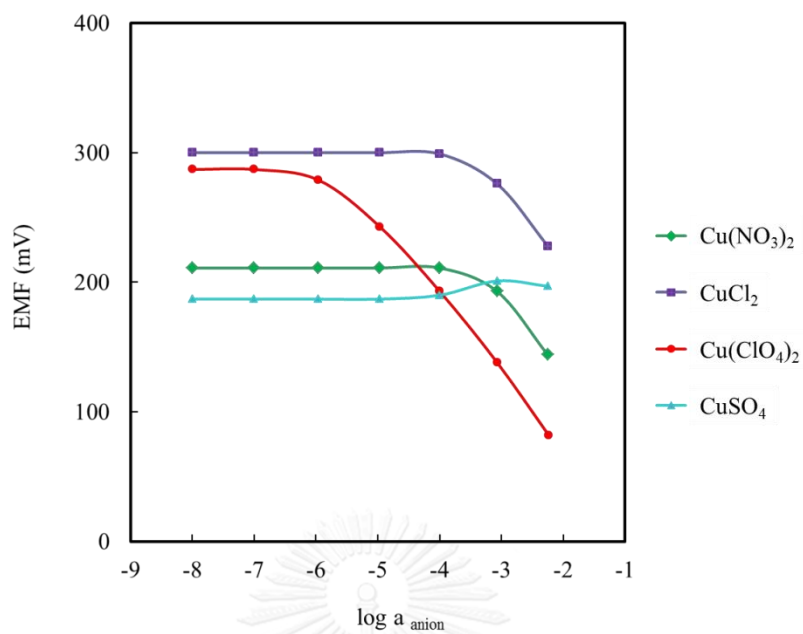
Samples	Conditioning solution (10 mM)	IFS (10 mM)	Linear range (M)	Slope (mV/decade)
Cu(NO <sub>3</sub> ) <sub>2</sub>	Cu(NO <sub>3</sub> ) <sub>2</sub>	CuCl <sub>2</sub>	10 <sup>-3</sup> -10 <sup>-2</sup>	-59.77 ±1.22
Zn(NO <sub>3</sub> ) <sub>2</sub>	Zn(NO <sub>3</sub> ) <sub>2</sub>	ZnCl <sub>2</sub>	10 <sup>-3</sup> -10 <sup>-2</sup>	-61.52 ±0.86
Ni(NO <sub>3</sub> ) <sub>2</sub>	Ni(NO <sub>3</sub> ) <sub>2</sub>	NiCl <sub>2</sub>	10 <sup>-3</sup> -10 <sup>-2</sup>	-54.01 ±1.41
Co(NO <sub>3</sub> ) <sub>2</sub>	Co(NO <sub>3</sub> ) <sub>2</sub>	CoCl <sub>2</sub>	10 <sup>-4</sup> -10 <sup>-2</sup>	-20.92 ±0.45
Cd(NO <sub>3</sub> ) <sub>2</sub>	Cd(NO <sub>3</sub> ) <sub>2</sub>	CdCl <sub>2</sub>	10 <sup>-3</sup> -10 <sup>-2</sup>	-31.26 ±2.21
AgNO <sub>3</sub>	AgNO <sub>3</sub>	AgNO <sub>3</sub>	10 <sup>-4</sup> -10 <sup>-3</sup>	-53.64 ±2.86
Hg(NO <sub>3</sub> ) <sub>2</sub>	Hg(NO <sub>3</sub> ) <sub>2</sub>	HgCl <sub>2</sub>	10 <sup>-5</sup> -10 <sup>-4</sup>	-22.83 ±0.58
Pb(NO <sub>3</sub> ) <sub>2</sub>	Pb(NO <sub>3</sub> ) <sub>2</sub>	PbCl <sub>2</sub>	10 <sup>-4</sup> -10 <sup>-3</sup>	-51.47 ±0.77
Cr(NO <sub>3</sub> ) <sub>3</sub>	Cr(NO <sub>3</sub> ) <sub>3</sub>	CrCl <sub>3</sub>	10 <sup>-3</sup> -10 <sup>-2</sup>	-26.10 ±2.58
FeCl <sub>3</sub>	FeCl <sub>3</sub>	FeCl <sub>3</sub>	10 <sup>-4</sup> -10 <sup>-2</sup>	+11.31 ±2.92
NaNO <sub>3</sub>	NaNO <sub>3</sub>	NaCl	10 <sup>-3</sup> -10 <sup>-2</sup>	-41.79 ±1.58
KNO <sub>3</sub>	KNO <sub>3</sub>	KCl	10 <sup>-3</sup> -10 <sup>-2</sup>	-35.64 ±1.59
Mg(NO <sub>3</sub> ) <sub>2</sub>	Mg(NO <sub>3</sub> ) <sub>2</sub>	MgCl <sub>2</sub>	10 <sup>-3</sup> -10 <sup>-2</sup>	-45.68 ±3.14
Ca(NO <sub>3</sub> ) <sub>2</sub>	Ca(NO <sub>3</sub> ) <sub>2</sub>	CaCl <sub>2</sub>	10 <sup>-4</sup> -10 <sup>-3</sup>	-6.73 ±0.54

IFS: inner filling solution

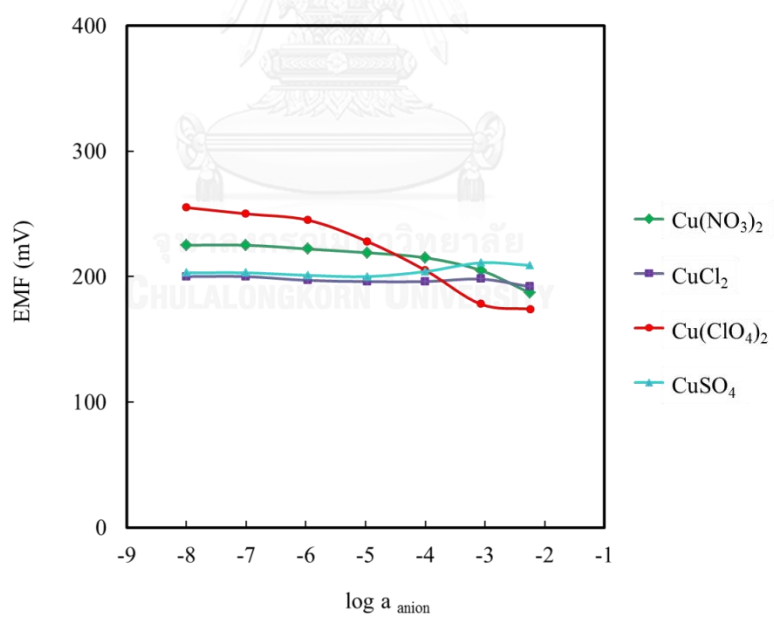
Furthermore, we also examined the EMF responses of various Cu(II) salts and membrane solvents or plasticizers which were strongly affected the co-extraction of anions and the permselectivity of the membranes. The *o*-NPOE (polar plasticizer) and DOS (apolar plasticizer) plasticized membranes were then preconditioned in different types of Cu(II) salts. The results showed in Figure 4.3 (a) that *o*-NPOE – plasticized PVC membranes preconditioned in Cu(NO<sub>3</sub>)<sub>2</sub>, CuCl<sub>2</sub>, Cu(ClO<sub>4</sub>)<sub>2</sub> gave the negative EMF responses nearest to the Nernstian responses of -59.77, -58.55 and -58.75 mV/decade, respectively whereas in CuSO<sub>4</sub> the response was not close to the Nernstian slope (-4.88 mV/decade). On the other hand, DOS – plasticized PVC membranes did not give any Nernstian responses (Figure 4.3 (b)) at all.

Hence, the *o*-NPOE plasticized PVC membranes were further constructed and conditioned in Cu(NO<sub>3</sub>)<sub>2</sub>, CuCl<sub>2</sub> and Cu(ClO<sub>4</sub>)<sub>2</sub> solutions in order to study their electrode characteristics such as the detection limit.





(a)



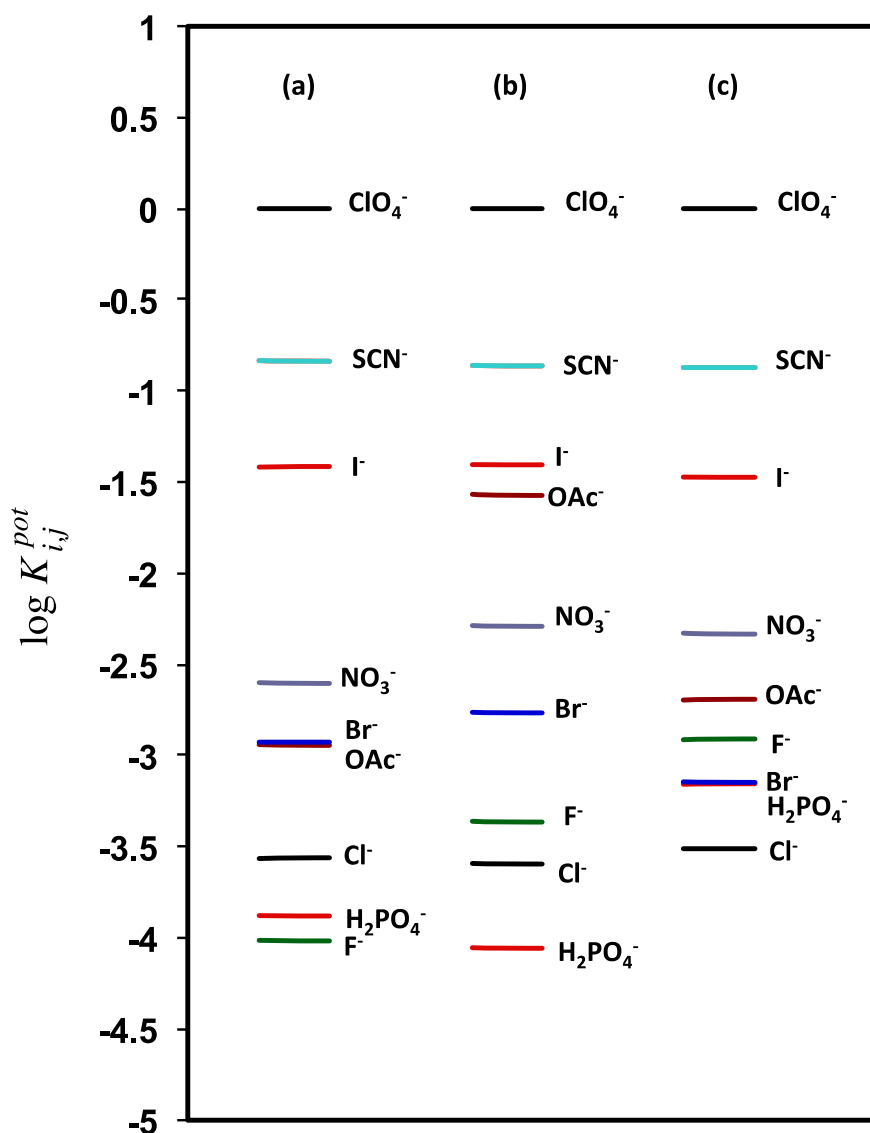
(b)

**Figure 4.3** The EMF responses of membrane containing **L1** in the presence of 50 mol% of *KTpCIPB* in different types of Cu(II) salts 10mM; (a) *o*-NPOE plasticizer, (b) DOS plasticizer



According to Table 4.1, the EMF responses of membranes containing **L1** using Cu(II), Zn(II) and Ni(II) ions gave Nernstian (-59.77 mV/decade), super-Nernstian (-61.52 mV/decade) and sub-Nernstian slopes (-54.01 mV/decade), respectively. Those metal ions were used as the triggers in experiments. We preconditioned the membranes in those metal chloride salts because we found in the previous work [12] that chloride salts gave the lowest resistance of the membrane, which allowed anions entered the membranes easily. For measurement of the selectivity coefficients, the membranes were preconditioned overnight in CuCl<sub>2</sub>, ZnCl<sub>2</sub> and NiCl<sub>2</sub>.

In addition, we compared the selectivities of these membranes when preconditioned in those metal chloride salts (Figure 4.4). The selectivity of ISEs is described by the ion exchange constants depending on the standard free energies of the specific ions in the aqueous and organic phases [1, 8]. The selectivities coefficients of these anions were determined and calculated by using separate solution method (SSM) and the Nicolsky-Eisenman equation, respectively. The prepared membranes were later condition in lipophilic anion salts (i.e., ClO<sub>4</sub><sup>-</sup>, SCN<sup>-</sup>, I<sup>-</sup>), and more hydrophilic anion salts (i.e., NO<sub>3</sub><sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, F<sup>-</sup>, OAc<sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) for several hours before examining the selectivity coefficients which used those chosen metal ions as the triggers. It should be noted that the traditional anion selective electrodes exhibited theoretically a Hofmeister selectivity sequence: ClO<sub>4</sub><sup>-</sup> > SCN<sup>-</sup> > I<sup>-</sup> > NO<sub>3</sub><sup>-</sup> > Br<sup>-</sup> > NO<sub>2</sub><sup>-</sup> > OAc<sup>-</sup> ~ Cl<sup>-</sup> ~ F<sup>-</sup> > H<sub>2</sub>PO<sub>4</sub><sup>-</sup> > SO<sub>4</sub><sup>2-</sup> [1, 28, 29].



**Figure 4.4** A comparison of the selectivity coefficients of anions in the polymeric membrane containing **L1** and 25 mol% of *KTpCIPB* conditioned in different metal salts; (a)  $\text{CuCl}_2$ , (b)  $\text{ZnCl}_2$ , and (c)  $\text{NiCl}_2$

The results in Figure 4.4 demonstrated that the membranes preconditioning in  $\text{CuCl}_2$ ,  $\text{ZnCl}_2$  and  $\text{NiCl}_2$  exhibited the highest selective towards  $\text{ClO}_4^-$ . The electrode from **L1** preconditioning in  $\text{CuCl}_2$  showed the Hofmeister sequence,  $\text{ClO}_4^- > \text{SCN}^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- \sim \text{OAc}^- > \text{Cl}^- > \text{H}_2\text{PO}_4^- > \text{F}^-$  as illustrated in Figure 4.4 (a). We found that the membrane using  $\text{Cu(II)}$  ion as the trigger gave the best selectivity towards  $\text{ClO}_4^-$ . Because the logarithm of the selectivity coefficients of hydrophilic anions such as

$\text{NO}_3^-$ ,  $\text{OAc}^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$  and  $\text{H}_2\text{PO}_4^-$  were between -2.5 to -4.0. It implied that these hydrophilic anions were not able to obstruct the  $\text{ClO}_4^-$  when used Cu(II) ion as the trigger for fabrication of perchlorate-anion selective electrode.

Nevertheless, we discovered that metal ions caused the different orders of anions in Hofmeister series, which may stem from different coordination of the metal complexes and anions. The membrane using Zn(II) ion as the trigger was selective to  $\text{ClO}_4^-$  and demonstrated the Hofmeister sequence:  $\text{ClO}_4^- > \text{SCN}^- > \text{I}^- \sim \text{OAc}^- > \text{NO}_3^- > \text{Br}^- > \text{F}^- > \text{Cl}^- > \text{H}_2\text{PO}_4^-$  as shown in Figure 4.4 (b). However, the selectivity coefficients of the hydrophilic anions were between -2.3 to -4.0 except  $\text{OAc}^-$ , selectivity coefficient was -1.57. It can easily interfere  $\text{ClO}_4^-$  ion if the concentration of  $\text{OAc}^-$  was very high.

In addition, the membrane using Ni(II) as the trigger also selective to  $\text{ClO}_4^-$  and exhibited the Hofmeister sequence:  $\text{ClO}_4^- > \text{SCN}^- > \text{I}^- > \text{NO}_3^- > \text{OAc}^- > \text{F}^- > \text{Br}^- \sim \text{H}_2\text{PO}_4^- > \text{Cl}^-$  (Figure 4.4 (c)). The selectivity coefficients of the hydrophilic anions were between -2.0 to -3.5. They were worse than using Cu(II) ion as the trigger which suggested that those hydrophilic anions could disturb the membrane sensor.

In consequence, the membranes preconditioning in Zn(II) and Ni(II) ions were improper for determining the quantity of  $\text{ClO}_4^-$  in real samples because the membranes were interfered easily by other hydrophilic anions. For this reason, the membrane containing **L1** and preconditioning in  $\text{CuCl}_2$  was suitable for the construction of the perchlorate-anion selective electrode.

Furthermore, the electrodes properties containing the different amounts of cation exchanger (KTpCIPB) and Cu(II) salts as the preconditioning solutions, which were incorporated in the *o*-NPOE plasticized PVC membrane, were summarized in Table 4.2. The results showed that high amounts of anionic additive exhibited worse Nernstian responses and detection limits because there was a possible repulsion between charges of the primary anion ( $\text{ClO}_4^-$ ), which were extracted from aqueous phase, and the anionic sites (KTpCIPB) filled in the membrane phase. Therefore, it was found that the *o*-NPOE plasticized PVC membrane employing ionophore **L1** in

the presence of 25 mol% of  $KTpCIPB$  preconditioning in  $CuCl_2$  was the most suitable that could be used as an optimal condition for determination of the quantity of perchlorate in the presence of other lipophilic and hydrophilic anions with a sub-Nernstian slope of  $-55.80$  mV/decade and a detection limit of  $2.84$   $\mu M$ .



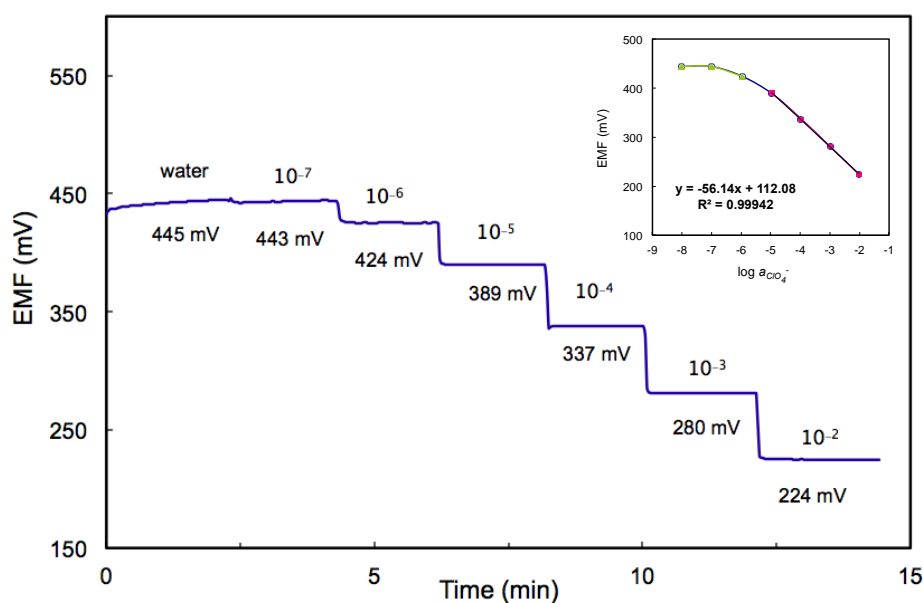
**Table 4.2** Membrane composition and electrode response properties of **L1** towards perchlorate in order of using Cu(II) as an trigger

Preconditioning solution	Membrane composition		Slope (mV/decade)	Linear range	Detection limit
	L1 (mg(mmol kg <sup>-1</sup> ))	KTpCIPB (mg (mol%))			
(10 mM) Cu(ClO <sub>4</sub> ) <sub>2</sub>	2.61 (10.0)	0.27 (24.7)	-56.19 ±0.40	10 <sup>-5</sup> – 10 <sup>-2</sup>	3.09
	2.62 (10.0)	0.55 (50.0)	-55.06 ±1.05	10 <sup>-5</sup> – 10 <sup>-2</sup>	3.70
	2.61 (10.0)	0.82 (75.1)	-48.10 ±0.82	10 <sup>-5</sup> – 10 <sup>-2</sup>	5.38
CuCl <sub>2</sub>	2.61 (10.0)	0.27 (24.7)	-55.80 ±0.36	10 <sup>-5</sup> – 10 <sup>-2</sup>	2.84
	2.61 (10.0)	0.55 (50.0)	-56.11 ±0.36	10 <sup>-5</sup> – 10 <sup>-2</sup>	2.88
	2.62 (10.0)	0.82 (75.1)	-51.19 ±0.38	10 <sup>-5</sup> – 10 <sup>-2</sup>	3.35
Cu(NO <sub>3</sub> ) <sub>2</sub>	2.61 (10.0)	0.27 (24.7)	-55.12 ±0.31	10 <sup>-5</sup> – 10 <sup>-2</sup>	2.86
	2.62 (10.0)	0.55 (50.0)	-53.76 ±0.66	10 <sup>-5</sup> – 10 <sup>-2</sup>	3.33
	2.61 (10.0)	0.82 (75.1)	-50.40 ±1.73	10 <sup>-5</sup> – 10 <sup>-2</sup>	4.14

The ratio of PVC: *o*-NPOE at 1:2 w/w

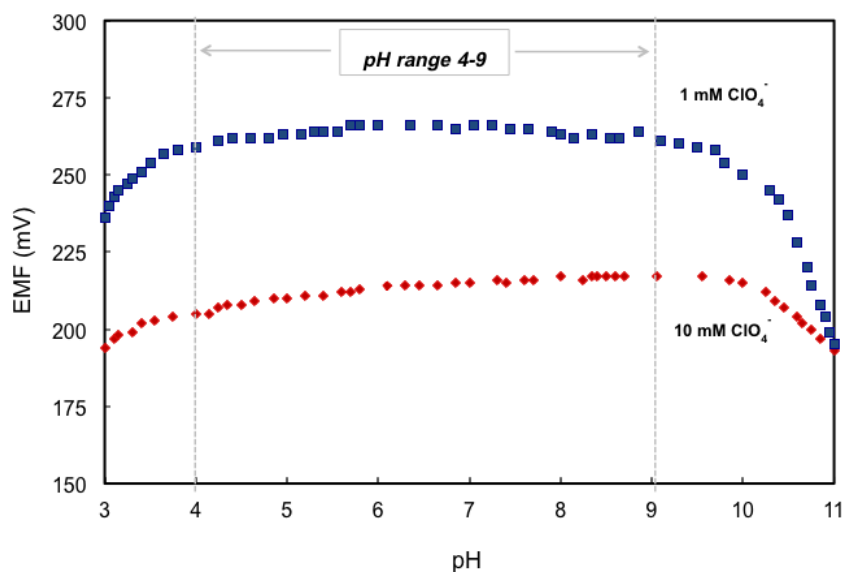
#### 4.2.4 Response time, working pH range and reversibility of the optimized electrode

The response time is one of the most important characteristics of ISEs. The optimal perchlorate-ISE containing L1 and 25 mol% of KTpCIPB conditioned in  $\text{CuCl}_2$  incorporated in *o*-NPOE plasticized PVC membrane demonstrated a fast response time of less than 5 seconds before reaching its steady-state EMF value as shown in Figure 4.5. Besides, the potential signal was stable and smooth after changing the concentration of perchlorate that presented a good characteristic of ISE.



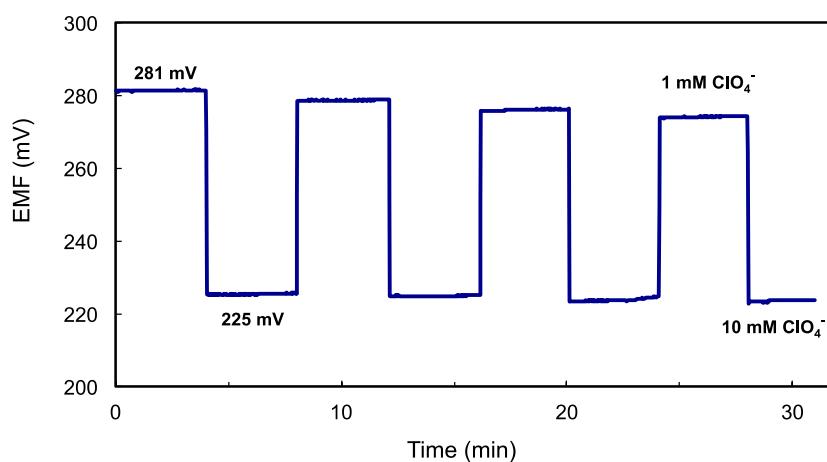
**Figure 4.5** Time-dependent response of the optimized electrode towards perchlorate concentration range from  $10^{-7}$  –  $10^{-2}$  M

Furthermore, the working pH range of the optimal perchlorate anion-selective electrode was explored over the pH range of 3.0-11.0 examining in 1 mM and 10 mM of the perchlorate concentration. The pH was adjusted by adding a small drop of 2% HCl to reach pH 3 and followed by 1-100 mM of NaOH. As we expected, the pH working range of this electrode showed a stable wide range of environmental conditions from pH 4.0-9.0 as presented in Figure 4.6.



**Figure 4.6** pH working range of the optimized electrode in different concentration towards 1mM and 10 mM of concentration of perchlorate

A prerequisite for the validity of the Nernst equation is a thermodynamic equilibrium between the adjacent aqueous and organic phases [1]. Thus, the reversibility of the optimal electrode is also a significant characteristic. As seen in Figure 4.7, the observed reversibility at ambient temperature was great as shown by cycles of potential signals when altered the concentration of perchlorate between 1 – 10 mM.



**Figure 4.7** Reversibility of the optimized electrode between 1mM and 10 mM of concentration of perchlorate

### 4.3 Applications of the optimized perchlorate electrode in samples

The proposed perchlorate fabricated from ionophore **L1** was used to determine the  $\text{ClO}_4^-$  concentration in water samples as presented in Table 4.5. After spiking standard perchlorate solution into the water samples at the concentration of  $5.0 \times 10^{-5}$  and  $1.0 \times 10^{-4}$  M, the results showed that the %recovery acquired from 109 to 113. These achieved recoveries exhibited the acceptable values with %RSD values less than 2.1 for 3 measurements. This proposed perchlorate anion-selective electrode further provided a great, which could be applied successfully to determine the quantity of  $\text{ClO}_4^-$  in real sample.

**Table 4.3** Determination of the quantity of perchlorate in water sample (n=3) using the fabricated perchlorate-selective electrode containing **L1** and 25 mol% *KTpCIPB* conditioned in 10 mM  $\text{CuCl}_2$

$\text{ClO}_4^-$ added ( $\times 10^{-5}$ M)	$\text{ClO}_4^-$ found ( $\times 10^{-5}$ M $\pm$ SD)	Recovery (% $\pm$ SD)	RSD (%)
-	n.d.	-	-
5	$5.43 \pm 0.11$	$109 \pm 2.20$	2.0
10	$11.34 \pm 0.22$	$113.4 \pm 2.19$	1.9

n.d. = not detectable

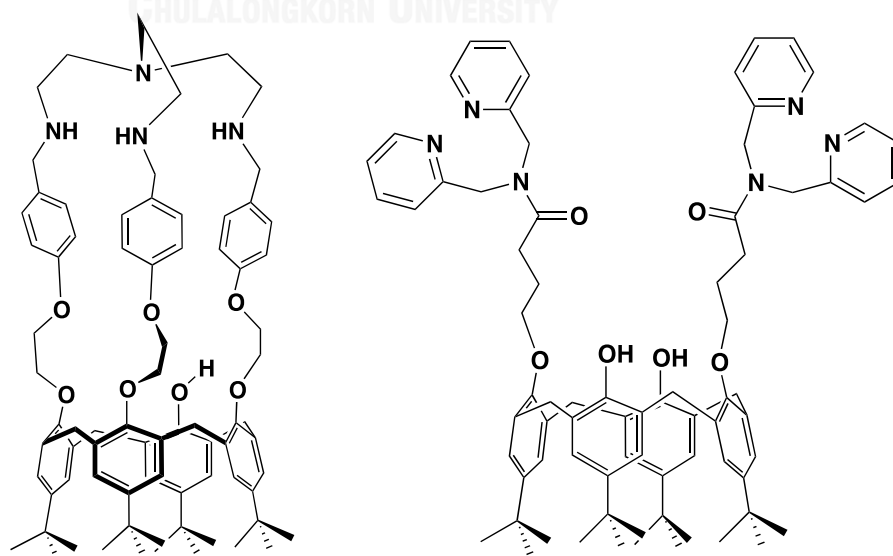


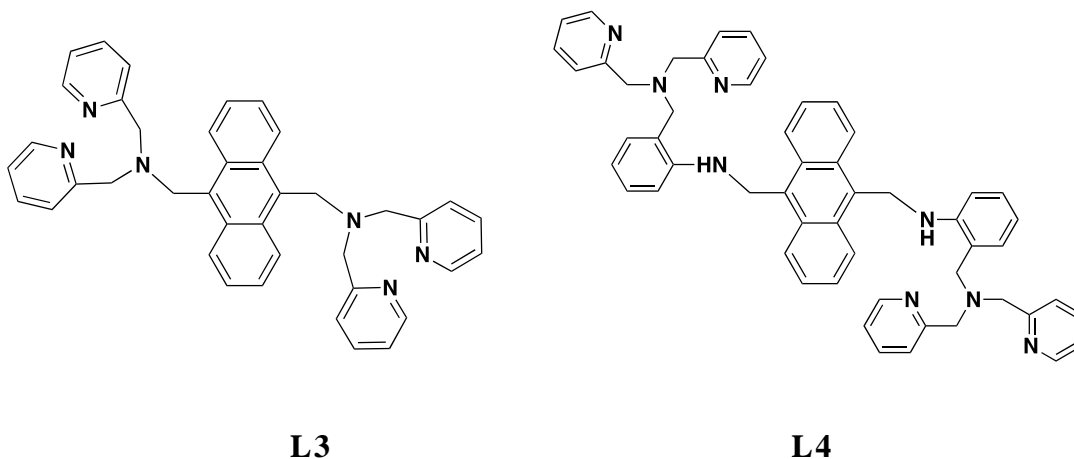
## CHAPTER V

### CONCLUSION

For fabrication of perchlorate anion-selective electrodes, the PVC-membrane containing **L1** and KTpCIPB showed Donnan exclusion failure in the presence of metal ions by extraction of anions into the membrane and giving negative EMF responses. However the membranes containing **L2** – **L4** were improper for the construction of anion-selective electrodes because **L2** gave the positive EMF change, preferred to cation response and **L3** – **L4** were not responded to the EMF measurement due to their less lipophilicity.

We found that an *o*-NPOE plasticized PVC membrane carrying **L1** and 25 mol% KTpCIPB conditioned in CuCl<sub>2</sub> solution was the best perchlorate anion-selective electrode. This electrode exhibited good characteristics with a Nernstian response of  $-55.80 \pm 0.36$  mV/decade of activity for ClO<sub>4</sub><sup>-</sup> ions and a detection limit of 2.84 μM. This anionic sensor was further employed to determine the quantity of perchlorate in real water samples with satisfying recoveries in a wide pH range of 4 – 9.

**L1****L2**



### Suggestion for future work

In this research, the electrodes did not show the anti-Hofmeister series distinctively. Ionophore **L1** was a closed mono-tripodal aza crown ether calix[4]arene. It was probably difficult to alter the coordination sphere of the metal center to accommodate anions, while di-tripodal amine calix[4]arene reported previously [12] was an opened ionophore with two dinuclear receptors that properly bound Cu(II) ions and demonstrated the anti-Hofmeister to selectively detect thiocyanate ions.

The author suggested that the ionophores should have more multiple binding sites containing different types of functional groups, arms and donor atoms. Their structures must allow the adjustment to match the shape of anions and coordination sphere of the metal center.

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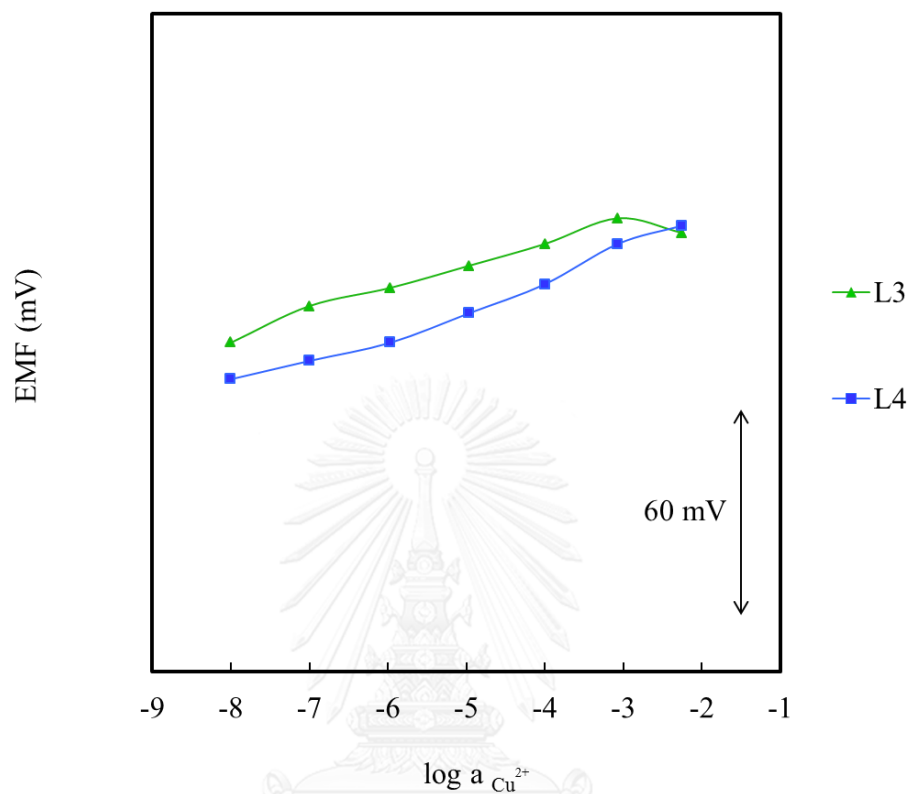
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## APPENDIX A



**Figure A1** Potentiometric responses towards  $\text{Cu}(\text{NO}_3)_2$  of the *o*-NPOE plasticized PVC membranes containing ionophores **L3** and **L4** in the presence of 50 mol% *KTpCIPB*

## VITA

Miss Sutida Jansod was born on March 18, 1990 in Nakhonphanom, Thailand. She received her Bachelor's degree in Chemistry from Khon Kaen University in 2012. She has got a fellowship from the Development and Promotion of Science and Technology Talents Project (DPST). She had opportunities to do researches abroad in Liverpool John Moores University in the United Kingdom in 2011, Japan Advanced Institute of Science and Technology (JAIST) in Japan in 2012, and University of Geneva in Switzerland in 2015. She has been a graduate student in the Department of Chemistry, Faculty of Science, Chulalongkorn University and become a member of Supramolecular Chemistry Research Unit (SCRU) and worked under the supervision of Professor Dr. Thawatchai Tuntulani since 2012.

