

USE OF MODIFIED NaY ZEOLITE AS IONOPHORE FOR PERCHLORATE SELECTIVE
ELECTRODE



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การใช้ซีไอไลต์โซเดียมวายเป็นไอโคโนฟอร์สำหรับขั้วไฟฟ้าเลือกจำเพาะต่อเปอร์คลอเรต



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ซีโอไลต์โซเดียมวายเป็นสามารถนำมาใช้งานในด้านของตัวเร่งปฏิกิริยา ตัวดูดซับ และตัว
 แลกเปลี่ยนไอออน จากการใช้งานข้างต้น คุณสมบัติของการแลกเปลี่ยนไอออนถูกนำมาใช้งานใน
 เรื่องของขั้วไฟฟ้าเลือกจำเพาะต่อไอออน ซึ่งในงานวิจัยนี้จะนำเอาซีโอไลต์โซเดียมวายเป็นเชิงพาณิชย์
 มาดัดแปรด้วยซิติลไตรเมทิลแอมโมเนียมโบรไมด์ที่มีความเข้มข้นต่าง ๆ (100, 150 และ 200 มิลลิ
 โมลาร์) เรียกว่า 100, 150 และ 200 SMZ ผลการศึกษาด้วย XRD, FT-IR, SEM และ TGA/DTG
 แสดงให้เห็นว่าสารลดแรงตึงผิวถูกดูดซับอย่างสมบูรณ์บนพื้นผิวของซีโอไลต์ หลังจากนั้นมันถูก
 นำมาใช้ในการสร้างเมมเบรนพอลิเมอร์ด้วย polyvinyl chloride (PVC) พลาสติกไซซ์ด้วย o-
 nitrophenyl octyl ether (o-NPOE) การดำเนินงานของขั้วไฟฟ้าเลือกจำเพาะต่อไอออนที่ดีที่สุด
 เกิดขึ้นที่องค์ประกอบเมมเบรน คือ 200 SMZ : PVC : o-NPOE ในอัตราส่วน 16.30 : 30.03 :
 62.07 ค่าคงที่ความจำเพาะของขั้วไฟฟ้าต่อไอออนรบกวนอื่น ๆ ถูกวัดด้วยวิธี Separate
 Solution และผลการวัดพบว่าขั้วไฟฟ้านี้มีความจำเพาะต่อไอออนเปอร์คลอเรต ขั้วไฟฟ้านี้ทำงาน
 ได้ดีในช่วงความเข้มข้น 10 ไมโครโมลาร์ ถึง 10 มิลลิโมลาร์ ของไอออนเปอร์คลอเรต โดยได้ความ
 ชันของเนิร์นส์ที่ $-57.63 \pm 0.47 \text{ mV decade}^{-1}$ ด้วยข้อจำกัดการตรวจวัดต่ำสุดที่ 9.28 ไมโครโม
 ลาร์ เวลาที่ใช้ในการตอบสนองของขั้วไฟฟ้าเกิดขึ้นเร็วมาก (น้อยกว่าหรือเท่ากับ 10 วินาที) โดย
 สามารถใช้งานได้อย่างน้อย 1 เดือน และทำซ้ำได้ดี ขั้วไฟฟ้าเลือกจำเพาะต่อไอออนเปอร์คลอเร
 ตถูกนำมาใช้วิเคราะห์หาไอออนเปอร์คลอเรตในน้ำตัวอย่างจริงด้วยผลการวิเคราะห์ที่เป็นที่น่า
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Boonyakorn Srisassawatkul : USE OF MODIFIED NaY ZEOLITE AS
IONOPHORE FOR PERCHLORATE SELECTIVE ELECTRODE. Advisor: Prof.
THAWATCHAI TUNTULANI, Ph.D.

NaY zeolite is well deserved for being employed as a catalyst, adsorbent, and ion exchanger. Therefore, its ion exchange property is used in ion selective electrodes (ISEs). Commercial NaY zeolite was modified with cetyltrimethylammonium bromide (CTAB) in various concentrations (100, 150, and 200 mM), denoted them as 100, 150 and 200 SMZ, respectively. XRD, FT-IR, SEM and TGA/DTG showed good agreement of CTAB adsorption on zeolite surface. Then SMZ is used to fabricate polymeric membrane with polyvinyl chloride (PVC) plasticized with *o*-nitrophenyl octyl ether (*o*-NPOE). The best performance of ISE was exhibited at the membrane composition of 200 SMZ: PVC: NPOE in the ratio of 16.30: 30.03: 62.07. The selectivity coefficients of the proposed electrode towards various interfering ions were determined by separate solution method (SSM) and the result showed that our fabricated ISE is selective to perchlorate anion. This electrode worked well over wide concentration range from 1×10^{-5} to 1×10^{-2} M of with a Nernstian slope of -57.63 ± 0.47 mV decade⁻¹ with a low detection limit of 9.28 μ M. The response time of electrode is very fast (≤ 10 s) over a period of 1 month with good reproducibility. The fabricated ClO₄⁻ ISEs were used to analyze ClO₄⁻ in real water samples with satisfactory results.

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CHAPTER I

INTRODUCTION

1.1 Background and significance of research

The development of perchlorate anion sensors has been paid attention due to its important roles in environmental¹⁻³ and human health risk reduction⁴⁻⁶. The toxicity of perchlorate is to inhibit iodine uptake to thyroid gland which results in reduce metabolism of thyroid hormone⁷. Hence, a large number of sensing techniques to detect perchlorate anion have been carried out using direct and indirect instrumental methods including ion chromatography⁸ (IC), liquid chromatography tandem mass spectrometry³ (LC-MS), stripping cyclic voltammetry⁹ (SCV) and UV-Visible spectrophotometry¹⁰. These methods are time consuming, require skilled-labor and use sophisticated instrumentation. There are tremendous approaches try to develop an easier-utilized device to detect perchlorate anion which break down limitations and drawbacks of previously mentioned methods.

Ion selective electrodes (ISEs) are one of powerful analytical tools for analysis of various ions in environmental and medical fields because they are simple, fast response, low cost and easily prepared. The content of ISE membrane composed of polymer as a membrane backbone, plasticizer as a polymer linkage, ion additive as a charge increment and a crucial content in ISEs is ionophore which has ion-exchange property that can allow target ions pass through inner filling solution by concentration gradient.

There are several reports about supramolecular-based ionophore for perchlorate-selective electrode¹¹⁻¹⁴, the advantage of using organic ionophores is the high solubility in organic solvent, homogeneity of membrane and ease of preparation. However, there are disadvantages that are taking tremendous efforts in synthesis process, using a large number of solvents. In this case, we are interested to use NaY zeolite as in ISEs.

NaY zeolite is a microporous aluminosilicate compound in the class of Faujasite (FAU) that is widely employed in several applications such as an adsorbent, a catalyst and an ion exchanger due to its large pore size, high Si/Al ratio, high surface area and ion-exchange property¹⁵. The ion exchange property is an important property to apply in ISEs due to immigration of metal ion balancer in the supercage. This ion-exchange property is similar to the function of ionophore in membrane electrode. Therefore, NaY zeolite is a good candidate ionophore for ISEs. Modification of NaY zeolite with surfactant solution concentration higher than Critical Micelle Concentration (CMC) can expel Na⁺ ion charge balancer and form bilayer on the zeolite surface^{16, 17}, hence it can reverse charge from negative to positive one. This characteristic plays a crucial role on adsorption behavior and can be adapted to use for potentiometric determination of anions¹⁸⁻²². To the best of our knowledge, surfactant modified NaY zeolite (SMZ) based anion selective electrodes have been rarely reported. Thus, utilizing SMZs as ionophores in ISEs is very interesting and challenging.

In this study, our goal is to use commercial NaY zeolite modified with cetyltrimethylammonium bromide, a cationic surfactant, as ionophores in polyvinyl chloride (PVC) plasticized with *o*-nitrophenyl octyl ether (*o*-NPOE) to fabricate perchlorate ISEs.

CHAPTER II

LITERATURE REVIEWS

2.1 Perchlorate, properties and toxicity

Perchlorate is an oxyanion consisted of tetrahedral array of oxygen atoms surrounded by central chlorine atom¹. It is both from natural and anthropogenic sources³. Perchlorate is mostly occurred in solid salts at ambient temperature, consists of white or clear crystal and also easy soluble in water. Perchlorate salts can be found in ammonium, potassium or sodium forms and perchloric acid²³. Perchlorate salts have low vapor pressure and cannot volatilize under ambient conditions¹. According to its high solubility in water, it is usually discovered in ground water, surface water and drinking water¹. Nowadays, apart from being found in water, it also can be found and accumulated in foodstuffs such as vegetables, meats, fruits and edible crops due to increase of global population in recent years^{2, 3}. Hence, as a water and food contaminant, it has become severe environmental issue and affected to human health³. Perchlorate has been classified as goitrogen (substance that inhibits iodine uptake by thyroid cells in thyroid organ), which disturbs the metabolism of thyroid hormone and consequently lead to serious health issue⁷.

Therefore, detection of perchlorate in real sample to prevent risk with direct and indirect methods take an important role. There are many instrumental methods including ion chromatography⁸ (IC), liquid chromatography tandem mass spectrometry³ (LC-MS), stripping cyclic voltammetry⁹ (SCV) and Ultraviolet-Visible spectrophotometry¹⁰ (UV-Vis). These methods have drawbacks that are time consuming, require skilled-labor and use sophisticated instrumentation. There are tremendous approaches to develop an easier-utilized device to detect perchlorate anion which break down limitations and drawbacks of previously mentioned methods. One of the techniques is Ion Selective Electrodes (ISEs).

2.2 Ion Selective Electrodes (ISEs)

Ion selective electrode (ISE) is a potentiometric chemical sensor composing of membrane whose potential demonstrates the activity of ion to be defined in a solution as analyte. Membranes of ISEs consist of either liquid-based or glassy or solid that have insignificant electron conductivity under condition of measurements. ISE technique has several undoubted advantages such as low cost, ease of preparation, portable and suitable for direct determination and ion sensing in solution²⁴.

The most essential advance in liquid membrane electrodes, occurred when it was exhibited the organic liquid of liquid membrane ISE could be immobilized into poly(vinyl) chloride (PVC) to make a polymer film with sensing property. These was possible because of preparation reagents were commonly, excellent plasticizer for PVC. The plasticizer help lowering the glass transition of PVC and fructify homogeneity and flexibility of films. PVC-based membrane electrodes contain all crucial reagents which selectively binds with interested ion. This reagent generally referred to ionophore or ion carrier²⁴.

The typical PVC membrane-based-ISE was shown in Figure 2.1. The ion selective membrane, a crucial component in this work can be prepared by dissolving ionophore, polymer backbone, plasticizer, ion additive with organic solvent and so-called mixture is cocktail solution. The cocktail solution was casted via a cylindrical tube, dipped and waited to solvent slowly evaporated until membrane formation as a disc sticked onto the end of cylindrical tube surface. A suitable inner filling solution of desired ion was added into the tube. These were the configuration ordinary used in commercial polymer membrane electrodes. Even though some producers developed or modified electrode for easier usage.

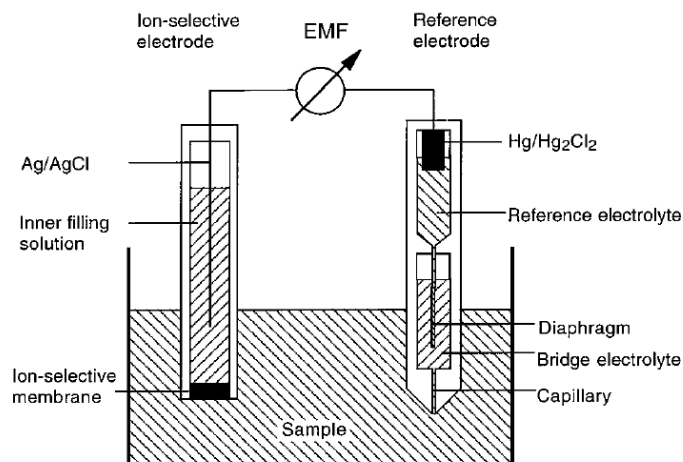


Figure 2.1 Schematic diagram of a membrane electrode measuring circuit and cell assembly²⁴

The potentiometry of ion selective electrode, it is usually the electromotive force (EMF) of cell of the following general type that is measured.²⁵

Reference electrode 1 || solution 1 | membrane | solution 2 || reference electrode 2

The solution 1 (the analyte) contained the ion to be measured. The actual potentiometric system consisted of internal reference electrode 2, inner filling of the ISE and polymeric membrane. The reference electrode, second kind of electrode (silver/silver chloride electrode, calomel electrode) were normally used.

The EMF responds to only one type of ions can be described by following Nernst's equation.

$$E_M = E^0 + 2.303 \left(\frac{RT}{z_I F} \right) \log \frac{a_I(aq)}{a_I(org)} \quad \dots (1)$$

Where E_M is membrane potential, E^0 incorporates all potential contributions of measuring cell that are constant for this measurement. While z_I , $a_I(aq)$ and $a_I(org)$ are charge and activity of measured ion in aqueous phase and organic

phase, respectively. Symbols R , T and F have their common values for universal gas constant, absolute temperature and Faraday constant in C/mol e^- unit, respectively.

The selectivity of polymeric membrane is obviously one of the most important characteristics for potentiometric sensor. It often defined as credible measurement in the analyte is probable. The theoretical selectivity describes the key parameters for developing the performance of potentiometric electrodes, for example, adjusted weighting parameters (i.e., absolute membrane concentrations) or chose different plasticizer.

The determination of selectivity coefficient can be derived from Nernst's equation (equation 1) into two different measuring methods defined as Nicolskii-Eisenman Formalism (shown in equation 2), one is so-called Separate Solution Method (SSM) and another is Fixed Interference Method (FIM). The Separate Solution Method (SSM) associated the measurement of two separate solutions, each contains only determined ion. Whereas Fixed Interference Method (FIM) focuses on primary ion that is determined in the constant background of interfering ions.

In this study, we use SSM as the Nicolskii selectivity coefficient calculation and calculating from two observed potential displayed in equation 3

$$E = E_I^0 + \frac{RT}{z_I F} \ln (a_I(I)) \quad \dots (2)$$

$$K_{I,J}^{pot} = \frac{a_I}{a_J^{z_I/z_J}} \exp \left\{ \frac{E_J - E_I}{RT} z_I F \right\} \quad \dots (3)$$

Where $a_I(I)$ is primary ion activity in the solution without interfering ion in the sample, $K_{I,J}^{pot}$ is the selectivity coefficient, E_I and E_J are potential response of primary and interfering ions, respectively, a_I and a_J are primary and interfering ion activities, respectively, z_I and z_J are the charge of primary and interfering ions, respectively. The determination of Nicolskii coefficient in SSM is shown in Figure 2.2.

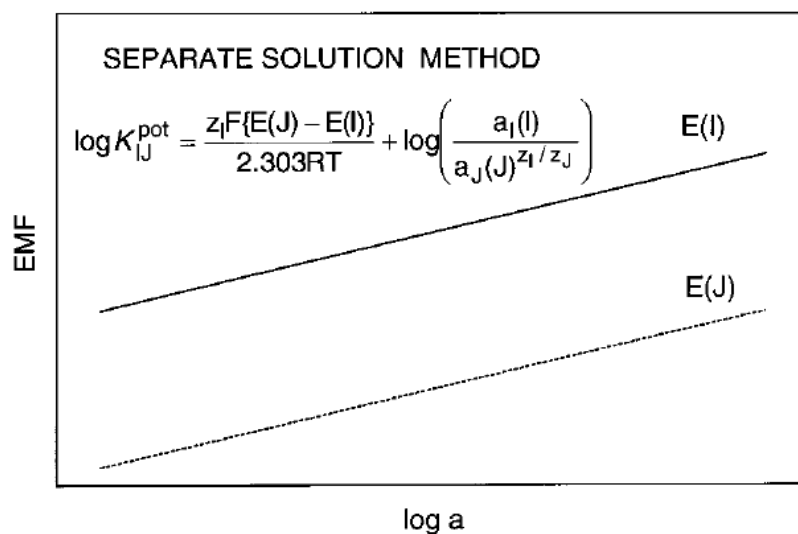


Figure 2.2 Determination of Nicolskii coefficient according to the separate solution method (SSM)²⁴

2.3 Ionophores for Anion Selective Electrode

Ionophores or ion carriers were crucial contents in the membrane electrode. They performed as complexing agent or chelating ligand by binding with transition metal like Cu(II), Zn(II), Ni(II), often composed of macrocyclic molecules or supramolecular structure and selectively bound to a primary analyte ion. Metal complexes composing of different ligands for example, uranyl¹², dioxaoctane²⁶, tetraphenylporphyrin²⁷, cobaloxime²⁸, phthalocyanine²⁹, salens³⁰, pyrrole³¹ have been reported to be good candidate for anions.

Mazloum-Ardakani *et al.*¹² synthesized uranyl complex (UO₂L) as ionophore used in PVC membrane-based potentiometric ion selective electrode which were selective to perchlorate anion in aqueous solution as shown in Figure 2.3 and lipophilic cationic additive (TOMACl) enhanced the response of perchlorate. Within the perchlorate concentration range of 1.0×10^{-6} to 1.0 mol L^{-1} , the electrode had a linear Nernstian response slope of $-60.6 \pm 1.0 \text{ mV decade}^{-1}$. The detection limit of this electrode was extrapolated linear section of $8.0 \times 10^{-7} \text{ mol L}^{-1}$ and selectivity order of the membrane was $\text{ClO}_4^- > \text{F}^- > \text{Cl}^- > \text{NO}_2^- = \text{HCO}_3^- > \text{CN}^- > \text{Br}^- = \text{I}^- = \text{citrate} = \text{NO}_3^- = \text{CH}_3\text{COO}^- > \text{SCN}^- > \text{Salicylate} > \text{C}_2\text{O}_4^{2-}$.

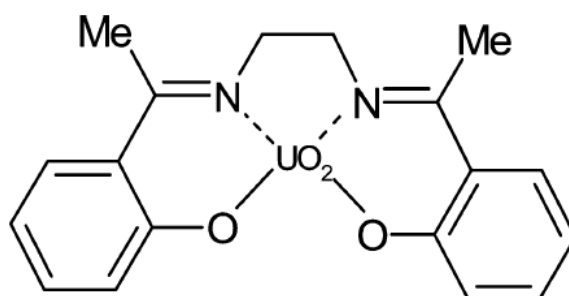


Figure 2.3 Structural representation of the compound 2,2'-(1,2-ethanediyl-bis(nitriloethylidene))-bis-phenolato uranyl (UO₂L) used as ionophore in the PVC membrane¹²

Mazloun-Ardakani *et al.*²⁶ synthesized Ni(II) dioxaoctane complex as ionophore used in PVC membrane-based potentiometric ion selective electrode which were bound selectively with salicylate anion and exhibited wide linear concentration range of 7.0×10^{-7} to 1.0×10^{-1} mol L⁻¹ salicylate. The detection limit of this ionophore was 5×10^{-8} mol L⁻¹. The selectivity order was $\text{Sal}^- > \text{N}_3^- > \text{SO}_4^{2-} > \text{IO}_4^- = \text{NO}_2^- = \text{CO}_3^{2-} > \text{BrO}_3^- > \text{HPO}_4^{2-} > \text{HCO}_3^- = m\text{-Sal}^- > \text{Cl}^- = \text{IO}_3^- = \text{ClO}_3^- > \text{F}^- = \text{Benz}^- > \text{S}_2\text{O}_3^{2-} > \text{SCN}^- > \text{NO}_3^- > \text{I}^- = \text{CH}_3\text{COO}^- > \text{ClO}_4^- = \text{C}_2\text{O}_4^{2-}$. It was successfully applied to measure salicylate ion in real sample

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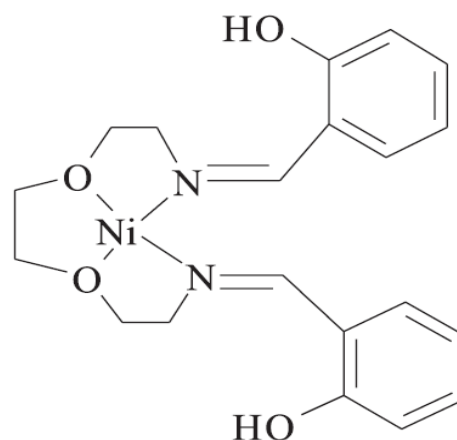


Figure 2.4 Structural representation of the compound 1,8-diamino-3,6-dioxaoctane nickel(II) [Ni(DADOO)] used as ionophore in the PVC membrane²⁶

Shamsipur *et al.*²⁷ synthesized phosphorus(V)-tetraphenylporphyrin complex with polymeric membrane electrode (PME) and coated glassy carbon electrode (CGCE). The electrode exhibited near Nernstian behavior over wide ClO_4^- concentration of 8.0×10^{-6} to 1.6×10^{-1} mol L⁻¹ for PME and 1.0×10^{-6} to 3.0×10^{-2} mol L⁻¹ for CGCE and detection limits were 5.0×10^{-6} mol L⁻¹ for PME and 7.0×10^{-7} mol L⁻¹ for CGCE.

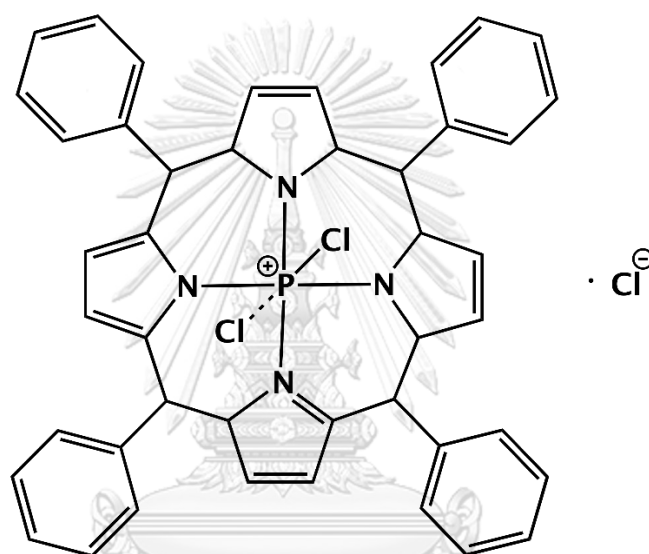


Figure 2.5 Schematic illustration of phosphorus(V)-tetraphenylporphyrin complex²⁷

Zanjanchi *et al.*²⁸ synthesized a supramolecule cobaloxime (Figure 2.6) named [(chlorobis(dimethylglyoximateo)(triphenylphosphine)) cobalt(III) complex as a suitable carrier for perchlorate selective polymeric membrane. It had Nernstian response slope of -56.8 ± 0.7 mV decade⁻¹ with linear range of determination of 1.0×10^{-6} to 1×10^{-1} mol L⁻¹. This electrode showed outstanding selectivity towards perchlorate over many common anions and was used as measurement method for perchlorate in water and human urine.

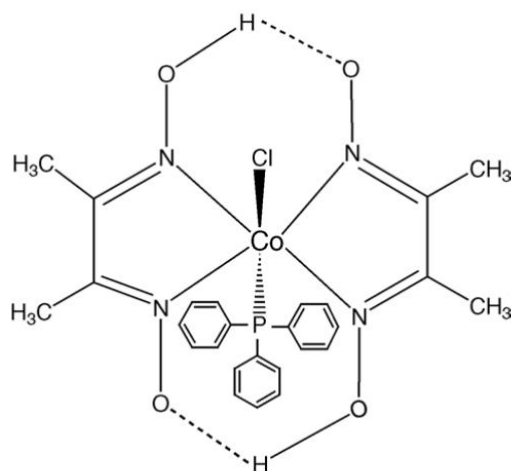


Figure 2.6 Structural representation of the cobaloxime used as ionophore in the perchlorate selective electrode²⁸

Xu *et al.*²⁹ studied a novel zinc-phthalocyanine complex as neutral carrier for thiocyanate PVC-based ion selective electrode. Its determined concentration was ranging from 1.0×10^{-6} to 1.0×10^{-1} mol L⁻¹ with a lower detection limit of 7.5×10^{-7} mol L⁻¹. This electrode selectivity displayed anti-Hofmeister series in the sequence of $\text{SCN}^- > \text{Sal}^- > \text{I}^- > \text{ClO}_4^- > \text{Br}^- > \text{Cl}^- > \text{NO}_3^- > \text{NO}_2^- > \text{H}_2\text{PO}_4^- > \text{SO}_4^{2-}$.

According to utilize supramolecular complex as ionophore for anion selective electrode, there are many advantages such as highly soluble in organic solvent, homogeneity of membrane. However, there are also disadvantages, the authors have to take tremendous effort for synthesize complex and use large amount of solvent and reagent for synthesize. Therefore, to reduce the previously mentioned drawbacks, inorganic ionophore like zeolite is a good choice to be used as ionophore due to its easy modification, inexpensive and excellent ion exchange property.

2.4 Zeolites

Zeolite is inorganic solid that is composed of elementary structure of aluminosilicate framework which consists of tetrahedral of silicon cation (Si^{4+}) and aluminium cation (Al^{3+}) that are encompassed by 4 oxygen anions (O^{2-})¹⁵. Each oxygen in Si-O and Al-O are connected with 2 cations and shared electron together. Figure 2.7 showed 2D structure of AlO_4^{5-} and SiO_4^{4-} . These result in macromolecular

structure of SiO_2 and AlO_2 tetrahedral building blocks. Thus, Si or Al cations in silicate tetrahedra has Si:O ratio of 1:2.

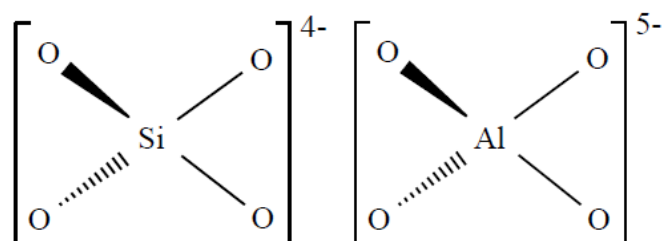


Figure 2.7 Tetrahedral arrangement of SiO_4^{4-} and AlO_4^{5-} molecules forming unit blocks of a zeolite¹⁵

Some Si^{4+} ions can be substituted by Al^{3+} ions in holes, will result in net negative charge in tectosilicate framework (Figure 2.8). This negative charge results from different valency between AlO_4^{5-} and SiO_4^{4-} tetrahedrons. Therefore, it is balanced of charge by alkali or alkali earth metal cations i.e., Na^+ , K^+ , Ca^{2+} etc. These metal balancers are found on external zeolite surface and bound with weaker electrostatic bond.

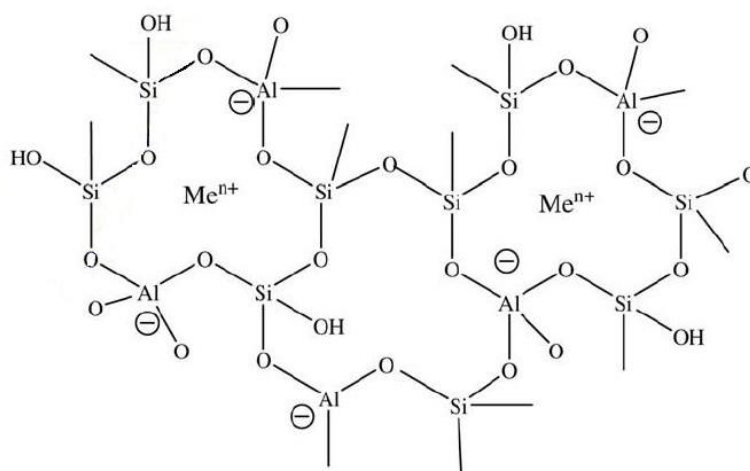


Figure 2.8 A two-dimensional representation of the framework structure of zeolites.

Me^{n+} signify extraframework cations¹⁵

There are various kinds of zeolite, one of our most interested is NaY zeolite. NaY zeolite belongs to class of Faujasite (FAU) which serves good characteristics. It is widely used as adsorbents, catalyst and ion exchanger due to metal ion balancer on the surface. Zeolite Y has higher Si/Al ratio rather than zeolite X. An important content in zeolite NaY is it composes of 6 sodalite cages (24-tetrahedracuboctahedral units, like fullerene) and connects each other by 6 hexagonal prisms (double 6-rings)³².

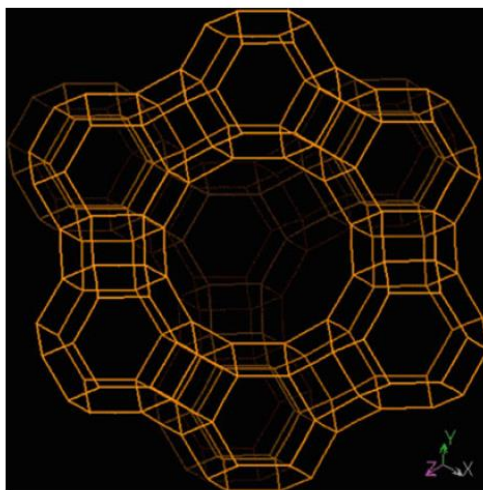


Figure 2.9 The FAU type zeolite supercage view along [111] direction page 2061³²

Rongchapo *et al.*³³ studied the Paraquat adsorption property of 2 types of zeolite (NaY and NaX) and found that NaY zeolite has higher Si/Al ratio than NaX zeolite which results in increase of herbicide adsorption via cation exchange in micropore. Figure 2.10 showed XRD patterns of bare zeolites and adsorbents.

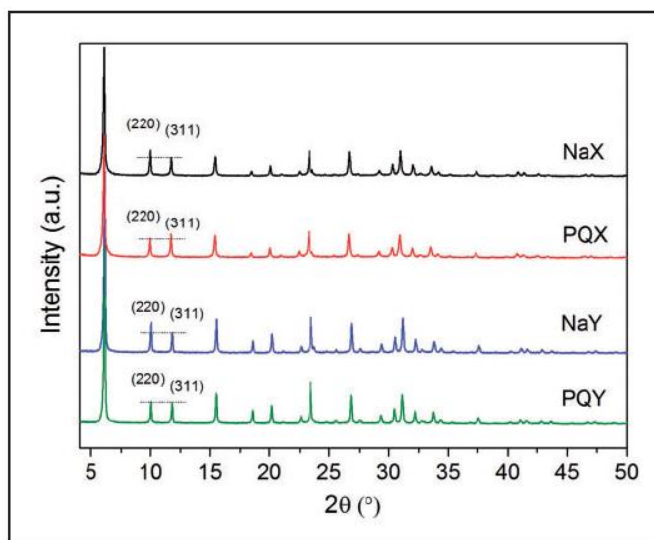


Figure 2.10 XRD patterns of bare zeolites (NaX and NaY) and paraquat-adsorbed zeolites (PQX and PQY)³³

Tamiji *et al.*³⁴ reported voltammetric determination of bromate by ion exchange property of Sn(II)-clinoptilolite modified carbon paste electrode. The modified clinoptilolite showed decrease peak current when added bromate ion into solution of sulfuric acid electrolyte. The chemical equation displayed example of ion exchange process via cyclic voltammetry (CV).



2.5 Surfactant Modified Zeolites (SMZs)

According to ion exchange property of zeolites, it can be applied or modified with surfactant or metal ion solution to enhance positively charged character. There are many reports studied about modification of zeolites with surfactant solutions.

Niknezhadi *et al.*¹⁶ converted natural clinoptilolite into nanosized-particles (CNP) by planetary ball mill and modified with hexadecyltrimethylammonium bromide (HDTMABr) solution of 0.15 mol L⁻¹ and agitated in dithizone solution of 5 mmol L⁻¹ as an active species for voltammetric determination of Sn (II). Interestingly, they suggested about using mix solvent (80:20 %v/v water: ethanol) for dissolving HDTMABr due to its low solubility. Figure 2.11 showed cationic surfactant bilayer

formation illustrated by electrostatic force and complex formation between dithizone and Sn(II) ion

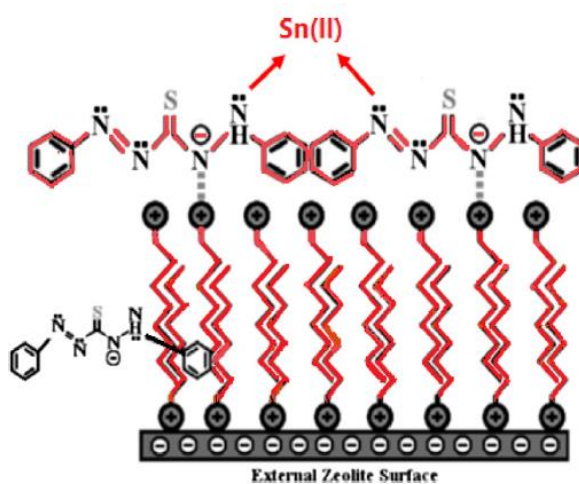


Figure 2.11 Graphical abstract revealed bilayer formation of HDTMA onto zeolite surface¹⁶

Anari-Anaraki *et al.*¹⁷ converted natural clinoptilolite into nanoparticles and micronized particles and then added them into HDTMA solution of 0.1 mol L^{-1} and agitated in dithizone solution of 1 mmol L^{-1} . Figure 2.12 showed surfactant bilayer and complex formation with Pb(II) cations by dithizone.

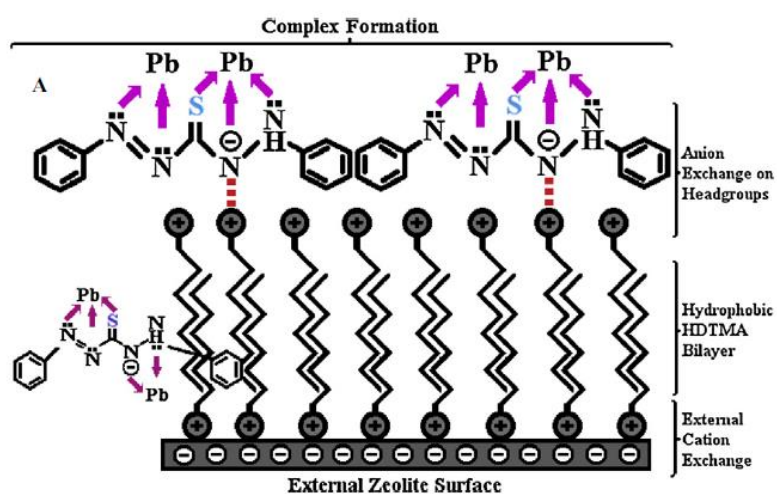


Figure 2.12 Typical model diagram for modification of zeolite surface by surfactant and dithizone and complex formation with Pb(II) cations¹⁷

Hasheminejad *et al.*²⁰ has modified natural clinoptilolite mechanically by crushing in agate mortar and received nanoparticles. They mixed clinoptilolite nanoparticles (CNP) with HDTMA solution of 100 mmol L⁻¹ and stirred for 24 hr. on magnetic stirrer and centrifuged at 6,000 rpm for 20 min. They repeated the same procedure for 50 and 200 mmol L⁻¹ of HDTMA solutions. Their electrodes were fabricated with mixing SMZ to PVC and plasticized with dioctylphthalate (DOP). Their ionophores manifested a Nernstian slope of -29.9 ± 0.2 mV decade⁻¹ for citrate anion and obtained good linear concentration range of 5.0×10^{-5} to 5.0×10^{-2} mol L⁻¹ citrate. The low detection limit of this nanosized particle electrode was 1.3×10^{-5} mol L⁻¹. The selectivity of ionophore was in order: Citrate \gg CN⁻ $>$ I⁻ $>$ CH₃COO⁻ $>$ Cl⁻ $>$ C₂O₄²⁻ $>$ CO₃²⁻ $>$ ClO₄⁻ $>$ NO₃⁻.

Esmailian *et al.*¹⁹ studied the carbon paste electrode (CPE) response of HDTMA surfactant modified with 13X zeolite (sub-class of NaX zeolite) within 3 concentrations (10, 50 and 100 mmol L⁻¹) using graphite powder mixed with nujol oil as oil binder and casted slurry mixture onto electrode body surface. Their potentiometric results revealed that zeolite 13X modified with 50 mmol L⁻¹ HDTMA had a good Nernstian behavior for sulfate anion with -29.8 ± 0.8 mV decade⁻¹. This CPE exhibited linear concentration range of sulfate species for 2.0×10^{-6} to 3.1×10^{-3} mol L⁻¹ with lower detection limit of 2.0×10^{-6} mol L⁻¹. The selectivity of electrode towards sulfate in order of SO₄²⁻ $>$ HPO₄²⁻ $>$ C₂O₄²⁻ $>$ CrO₄²⁻ $>$ Cr₂O₇²⁻ \gg Cl⁻ = NO₃⁻ $>$ Br⁻ = I⁻ $>$ CN⁻ \gg ClO₄⁻ \gg SCN⁻.

Masoudipour *et al.*²² fabricated SMZ modified CPE using NaY zeolite agitated into HDTMA in various concentrations (50, 100 and 200 mmol L⁻¹). They mixed SMZ in appropriate amount of SMZ (5-25 wt% with respect to graphite powder) and added nujol oil. Then casted the paste onto electrode body and measured the potentiometric responses. The results showed that the electrode containing 20 wt% of 100 mmol L⁻¹ SMZ responded to hydrogen phosphate ion (HPO₄²⁻) with Nernstian slope of -29.9 ± 0.9 mV decade⁻¹ in the linear concentration range of 1.58×10^{-5} to

$1.00 \times 10^{-2} \text{ mol L}^{-1}$ of and low detection limit of $1.28 \times 10^{-5} \text{ mol L}^{-1}$. Its selectivity arranged in order of $\text{HPO}_4^{2-} > \text{AsO}_4^{3-} > \text{SO}_4^{2-} \approx \text{Cr}_2\text{O}_7^{2-} > \text{I}^- \approx \text{Cl}^- > \text{NO}_3^- > \text{Br}^-$

It could be applied to real sample analysis for fertilizer compared to standard measuring instrument including UV-Visible spectroscopy and external standard and standard addition of analytical chemistry.

Mirzaeyan *et al.*²¹ synthesized NaA zeolite from waste porcelain (obtained from Esfahan glass factory, Iran) and then modified with 3 concentrations (50, 100 and 200 mmol L⁻¹) of hexadecylpyridinium bromide (HDPBr) solutions in 3 separate polyethylene bottles and received SMZs. All varied amounts of SMZs are proposed polymeric membrane with PVC plasticized by dioctylphthalate (DOP) as plasticizer. The potentiometric sensor containing 10 wt% SMZ, 30 wt% PVC and 60 wt% DOP displayed the best Nernstian slope of $-29.5 \pm 0.8 \text{ mV decade}^{-1}$ with suitable concentration range of 8.0×10^{-7} to $1.0 \times 10^{-1} \text{ mol L}^{-1}$ of sulfite (SO_3^{2-}) species and lower detection limit of $5.0 \times 10^{-7} \text{ mol L}^{-1}$. The selectivity pattern of this electrode for these interfering anions goes along with order: $\text{SO}_3^{2-} > \text{Cl}^- \approx \text{NO}_3^- > \text{I}^- > \text{SCN}^- > \text{ClO}_4^- > \text{PO}_4^{3-} > \text{C}_2\text{O}_4^{2-} > \text{SO}_4^{2-} > \text{ClO}_3^- > \text{Br}^-$.

Badri *et al.*³⁵ synthesized NaY zeolite from gel composition of $4.16\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 10\text{SiO}_2 : 205\text{H}_2\text{O}$ by mixing silica, sodium aluminate, sodium hydroxide and distilled water together to become sodium aluminosilicate (NaAlSiO_4) which could be the source of zeolite crystallization. After obtaining as synthesized NaY zeolite, they modified with 3 concentrations of HDTMA solutions (50, 100 and 200 mmol L⁻¹) denoted as 50 SMZ, 100 SMZ and 200 SMZ, respectively. All resulting SMZs mixed with PVC, plasticized with DOP and dissolved with THF. The indicator electrode responded dominantly to perchlorate anion with Nernstian slope of $-59.7 \pm 0.9 \text{ mV decade}^{-1}$ and lower detection limit of $4.07 \times 10^{-7} \text{ mol L}^{-1}$. The selectivity order of electrode was $\text{ClO}_4^- > \text{I}^- > \text{SCN}^- > \text{IO}_4^- > \text{NO}_3^- > \text{CO}_3^{2-} = \text{CN}^- > \text{Br}^- > \text{ClO}_3^- = \text{C}_2\text{O}_4^{2-} > \text{BrO}_3^- > \text{IO}_3^- > \text{Sal}^- > \text{CH}_3\text{COO}^-$.

Danesh-Khorasgani *et al.*³⁶ crushed natural clinoptilolite with mortar and planetary ball mill into nanoparticles and modified nanosized clinoptilolite with surfactant solution name tetradecyltrimethylammonium bromide (TDTMA-Br, C₁₄) in 3 various concentrations (50, 100 and 200 mmol L⁻¹) prepared in water : ethanol 80:20 %v/v. The preliminary results showed that this electrode responded to sulfate ion with a good Nernstian slope of -29.9 ± 1.2 mV decade⁻¹ for 100 mmol L⁻¹ SMZ within 4 wt% of SMZ combined with PVC 32 wt% and DOP 64 wt%. The optimization of this electrode exhibited Nernstian slope of -29.9 ± 0.9 mV decade⁻¹ in a working concentration range of 1.0×10^{-7} to 1.0×10^{-1} mol L⁻¹ of sulfate anion with lower detection limit of 7.0×10^{-8} mol L⁻¹. It was successfully applied for detection of zinc sulfate pharmaceutical capsule and indicator in Barium Chloride titration.

Badri *et al.*³⁷ synthesized Na-ZSM-5 zeolite via hydrothermal method and modified Na-ZSM-5 with 50 mmol L⁻¹ of HDTMA solution to become SMZ and used as ionophore for . Then they prepared the PVC membrane-based ISE by mixing thoroughly 10.0 mg of ionophore with 25.5 mg of PVC powder, plasticized by 64.5 mg of DOP and dissolved with THF. The resulting clear mixture was slowly evaporated until oily concentrated cocktail solution was occurred. A Pyrex tube was dipped into the oily mixture for about 10 s so that a nontransparent membrane was formed. The proposed electrode revealed very good selectivity to thiocyanate ion over wide linear concentration range of 1.00×10^{-6} to 1.01×10^{-1} mol L⁻¹ with limit of detection of 8.33×10^{-7} mol L⁻¹. This proposed sensor displayed a near Nernstian response slope of -58.9 ± 0.9 mV decade⁻¹. The optimized thiocyanate electrode was successfully used for potentiometric determination of SCN⁻ via Ag⁺ titration and determination of thiocyanate in drinking and river water.

The membrane composition of anion selective electrode mentioned earlier can be summarized in Table 2.1

Table 2.1 Summary of Anion Selective Electrode compositions

Author, reference	Compositions of Ion Selective Electrodes				Determination of anion
	Ionophores	Media	Plasticizer	The best Nernstian behavior (mV decade ⁻¹)	
Hasheminejad ²⁰	HDTMA- Clinoptilolite	PVC	DOP	-29.9 ± 0.2	Citrate
Esmailian ¹⁹	HDTMA-13X zeolite	Graphite powder	Nujol oil	-29.8 ± 0.8	SO ₄ ²⁻
Masoudipour ²	HDTMA-NaY zeolite	Graphite powder	Nujol oil	-29.9 ± 0.9	HPO ₄ ²⁻
Mirzaeyan ²¹	HDP-NaA zeolite	PVC	DOP	-29.5 ± 0.8	SO ₃ ²⁻
Badri ³⁵	HDTMA-NaY	PVC	DOP	-59.7 ± 0.9	ClO ₄ ⁻
Danesh- Khorasgani ³⁶	TDTMA- Clinoptilolite	PVC	DOP	-29.9 ± 1.2	SO ₄ ²⁻
Badri ³⁷	HDTMA-ZSM-5	PVC	DOP	-58.9 ± 0.9	SCN ⁻

According to literature reviews, our hypothesis is that NaY zeolite can be used as ionophores by modifying with cetyltrimethylammonium bromide (CTAB) concentration higher than critical micelle concentration (CMC) value to become anion carrier via bilayer formation. The selectivity of ISE can be modulated by varying CTAB concentration in zeolite modification process (100, 150 and 200 mmol L⁻¹), adjusting the content of ionophores in ion selective membrane fabrication process (10–20 %wt) with varied amount of PVC and *o*-nitrophenyl octyl ether (NPOE) relative to ionophore amount.

Objective of this research

1. To modify commercial NaY zeolite with various concentration of surfactant solutions
2. To fabricate anion selective membrane using surfactant modified NaY zeolite as ionophores and study responsibility, stability, reproducibility, ion selectivity coefficient of proposed ion selective polymeric membrane
3. To use ion selective membrane for real water sample analyses



CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

Chemicals and reagents for modification of NaY zeolite were purchased in molecular biology grade for cetyltrimethylammonium bromide (CTAB) from Merck, commercial grade for NaY zeolite from Alfa Aesar. The corresponding chemicals for preparation of anion selective membrane were obtained in Selectophore[®] grade from Sigma-Aldrich for high molecular weight polyvinyl chloride (PVC) as a polymeric backbone, *o*-nitrophenyl octyl ether (*o*-NPOE) as a plasticizer and tetrahydrofuran (THF) as a solvent. All chemicals and solvents were used as received without further treatment. Hydrochloric acid (37%) was employed to fabricate Ag/AgCl wire for ion selective membrane electrode. Aqueous solutions were prepared with ultrapure water from Milli-Q (Bedford, MA, USA) water purification system (Millipore). The surfactant modified NaY zeolite (SMZ) using cetyltrimethylammonium bromide (CTAB) as a cationic surfactant was adapted and modified according to the reported procedures^{16, 17}. The ion selective membranes were adapted and fabricated following literature procedures^{18, 20, 21, 35}.

3.2 Analytical Instrument

The crystalline and phase purity of the unmodified or modified NaY zeolites were identified by powder X-ray diffraction analysis on an X-ray Diffractometer using Rigaku SmartLab X-Ray Diffractometer which filtered by Cu-K α radiation (40 kV, 30 mA) with a wavelength of 1.544 Å. The Fourier Transform Infrared spectra were recorded with a Nicolet 6700 spectrophotometer via Attenuated Total Reflectance (ATR) mode in the range of 550–4000 cm⁻¹. The surface morphology and elemental mapping analysis of these samples were observed by Scanning Electron Microscopy-Energy Dispersive Spectrometry (SEM-EDS) using JSM-IT100 InTouchScope™ Scanning Electron Microscope. Thermogravimetric Analysis/Derivative Thermogravimetry (TGA/DTG) was analyzed by NETZSCH TG 209 F3 Tarsus from Scientific and

Technological Research Equipment Center (STREC, Chulalongkorn University) in the temperature range of 30.0–550°C with a heating rate of 10.0 K/min in an inert atmosphere of N₂ gas.

3.3 Modification of Commercial NaY Zeolite

3.3.1 Preparation of various concentrations of surfactant solutions

According to several literature reviews about modification of zeolites with various types of surfactant solution^{16-22, 35, 36}, surfactant namely cetyltrimethylammonium bromide (CTAB) which had molecular weight of 364.45 g mol⁻¹ has been chosen in this process. Next, preparation of surfactant solutions has been taken place by mixing solvent 80:20 %v/v between DI water and ethanol for approximately 200 mL for dissolving CTAB solid following literatures^{16, 17} briefly, we poured DI water 160 mL using 100 mL cylinder into 250 mL beaker and measured ethanol for 40 mL and then poured it into beaker, stirred with glass rod to mix solvent well. The desired CTAB concentrations are prepared in 50 mL volumetric flasks for 100, 150 and 200 mM, respectively.

Table 3.1 Calculation of CTAB mass in various concentrations

Desired CTAB concentrations (mM)	Calculated mass of CTAB (g)	Actual weight (g)
100	1.8223	1.8273
150	2.7334	2.7352
200	3.6446	3.6451

3.3.2 Modification of Commercial NaY Zeolite with various concentrations of surfactant solutions

After finished preparing surfactant solutions, a commercial NaY zeolite was weighed for approximately 2.0000 g in separate Erlenmeyer flasks. Then each concentration of surfactant solutions was poured into each Erlenmeyer flasks and stirred with magnetic stirred bars with speed of 400 rpm at room temperature for 24

hr. After 24 hr. later, the colloidal mixtures were obtained and were centrifuged with 3,000 rpm for 20 min, drained supernatant, washed with DI water, repeat few times until supernatant remained neutral and slowly drained supernatant until slurry leftover, dried them in hot air oven at 80 °C overnight. All products were collected and denoted as 100–200 SMZ (80:20) where SMZ came from Surfactant Modified Zeolite and (80:20) in parenthesis was from mixed solvent 80:20 %v/v DI water: ethanol. They have been kept in vials for further studies.

Table 3.2 Nomenclature of products

CTAB solution concentrations (mM)	Nomenclature
100	100 SMZ (80:20)
150	150 SMZ (80:20)
200	200 SMZ (80:20)

3.4 Preparation of Ion Selective Membrane

The PVC membrane cocktail solutions were prepared in 5 mL-glass vials using 15% w/w of ionophores (100 SMZ, 150 SMZ and 200 SMZ (80:20)), without any cationic additives according to charge reversal from bilayer formation on zeolite surface from CTAB loading, 28.33 %wt. of PVC and 56.67 %wt. *o*-NPOE (plasticizer), in the total mass of 100.00 mg for plastic syringe membrane (Figure 3.1). Compositions of membranes containing surfactant modified NaY zeolite (100–200 SMZ (80:20)) used in this experiment are listed in Table 3.3. All components were dissolved in 1.500 mL for syringe membrane preparation and the mixtures were ultrasonicated for half an hour and shaken with Scientific Industries Vortex-Genie 2. The resulting cocktail solution was dipped by 2-sided cut 1 mL plastic syringes (like cylindrical tubes) for about 30 s and waited for 30 s for mixture settled and let solvent slowly evaporated for 15-20 min so that non-transparent membrane was formed onto syringe tip and let syringe membranes dried for 1-2 hr. The syringe membranes were conditioned with 0.01 M of desired anion solutions overnight.

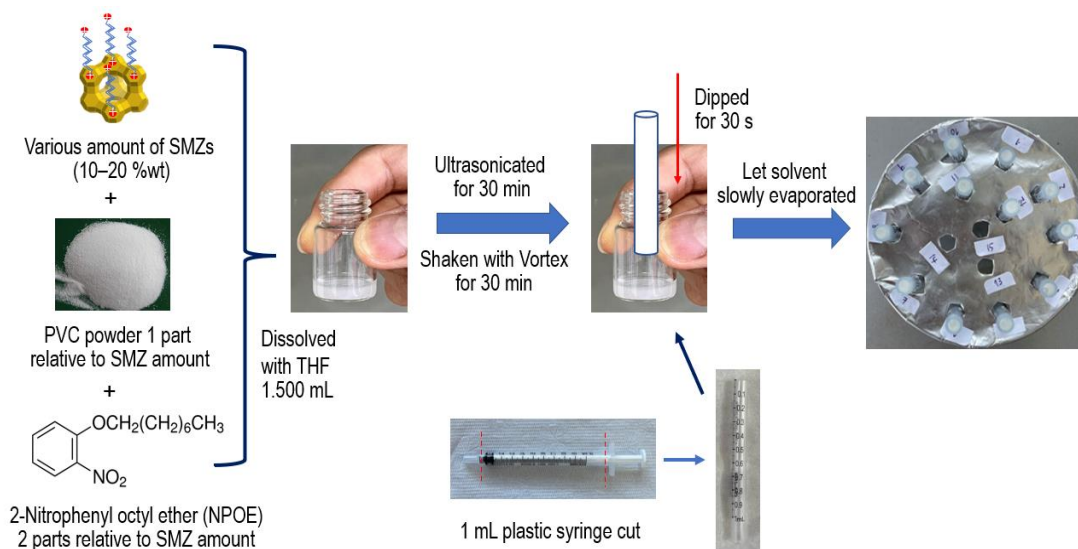


Figure 3.13 Fabrication procedure of ion selective syringe membranes

Table 3.3 Membrane composition (% w/w) of the constructed anion electrodes

Types	A	B	C	D	E	F	G	H
100 SMZ (80:20)	15	-	-	-	-	-	-	-
150 SMZ (80:20)	-	15	-	-	-	-	-	-
200 SMZ (80:20)	-	-	15	10	12.5	15.0	17.5	20.0
PVC	28.33	28.33	28.33	30.00	29.17	28.33	27.50	26.67
<i>o</i> -NPOE	56.67	56.67	56.67	60.00	58.33	56.67	55.00	53.33

3.5 Preparation of Ag/AgCl Wire

Ag/AgCl wire was made by cutting silver wire for 7 cm and prepared 4 mol L⁻¹ hydrochloric acid solution from 37% concentrate hydrochloric acid in the ratio of 1:2 %v/v by measuring for approximately 17 mL and mixed with Milli-Q water for 33 mL in 50 mL volumetric flask, shaken to mixed it well and poured solution into beaker, put silver wire and let it formed thin layer of AgCl coated on the silver wire surface, rinsed with Milli-Q water to drained excess AgCl particles out of surface. Finally, the Ag/AgCl wire was rinsed with Milli-Q before use.

3.6 Potentiometric Studies of Ion Selective Membranes

After conditioning syringe membranes overnight, we filled the syringes with inner filling solution (IFS) which made from the combination of 0.01 M anion with 0.001 M NaCl or KCl depended on cations for about 5 cm above membranes on tip of syringes and then immersed Ag/AgCl working electrode. For conditioned conventional membranes, they were connected with electrode body with IFS of desired anion.

All potential measurements were carried out with the following Voltaic cell:



The reference electrode, Ag/AgCl with double junction was used (type 6.0729.100, Metrohm AG, Ionenstrasse, 9100 Herisau, Switzerland) with 1 M LiOAc as salt bridge electrolyte. Continuous potential measurements were carried out with a 16-channel electrode monitor (Lawson Labs Inc., Malvern, PA 19355, USA).

The potential analysis of any solution was recorded when it became stable after spiking standard concentration of each ion. The plots between logarithmic function of ClO_4^- anion concentration and average potential may be used to calculate a Nernstian response slope and limit of detection (LOD). The activities of anions were based on the activity coefficient (γ) which calculated from Debye-Hückel equation³⁸

$$I_m = \frac{1}{2} \sum_i m_i z_i^2 \quad \text{---- (1)}$$

$$\log \gamma_A = \frac{-0.51 \times z_A^2 \times \sqrt{I_m}}{1 + (3.3 \times \alpha_A \times \sqrt{I_m})} \quad \text{---- (2)}$$

Where I_m is ionic strength, m_i and z_i are concentration and charge of i^{th} ion. γ_A is solution-dependent activity coefficient, α_A is effective diameter in nanometer.

3.7 Determination of Selectivity Coefficient

The selectivity factor ($K_{ClO_4^-,j}^{pot}$) was a measurement of the ion selective membrane preference of an interfering ion towards primary ion ClO_4^- . A selectivity coefficient lower than 1 meant that the membrane preference was of primary ion²⁶. Hereby, the selectivity coefficient was determined by Separate Solution Method (SSM). As mentioned previously, our primary anion is ClO_4^- ion, while interfering anions were SCN^- , I^- , NO_3^- , Br^- , Cl^- , CO_3^{2-} , SO_4^{2-} , NO_2^- , F^- , CN^- and CH_3COO^- . The dynamic response of the electrode was first measured against the same interfering anions (1×10^{-7} to 1×10^{-2} M). The electrode was then used to measure the response of perchlorate solution for 15%wt 200 SMZ (80:20).

The calculation method of selectivity coefficients was shown below following equation^{18-22, 35}.

$$\log K_{i,j}^{pot} = \frac{nF(E_j - E_i)}{2.303RT} + \log \left(\frac{a_i}{a_j^{n/m}} \right)$$

Where $\log K_{i,j}^{pot}$ is the potentiometric selectivity coefficient, n and m are charges of primary and interfering ions, respectively. E_i and E_j are the measured cell potential of primary and interfering ion activities, respectively whereas R, T and F have their common constant.

3.8 Real Samples Measurement

For the determination of real sample, all collected water were filtered with filter papers. After being filtered, each water sample was stored in a 1.5 L bottles. A precisely weight portion of each water sample was weighed with ca. 20.00 g in 50 mL beakers and used for determination of perchlorate content by spiking known concentrations of perchlorate anion compared to the potentiometric response of ultrapure water.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Modification of Commercial NaY Zeolite with various concentrations of CTAB solution

According to modification of surfactant solution process, the reasons that we decided to prepare CTAB solutions started from 100 mM are that there are several reports^{16, 22, 39} said about suitable bilayer formation on the zeolite surface at concentration higher than twice of critical micelle concentration value (CMC) or external cation exchange capacity (ECEC) that is 50 mM of CTAB solution. At higher concentration, the second layer of surfactant could be bound to the first layer by hydrophobic interaction between alkyl chains. The interaction of SMZ with anions can be illustrated in Figure 4.1. The positively charged head group of the second layer is oriented towards the aqueous solution due to the electrostatic repulsion of head groups between the inner and the outer layer and results in the electrostatic interaction with anions.

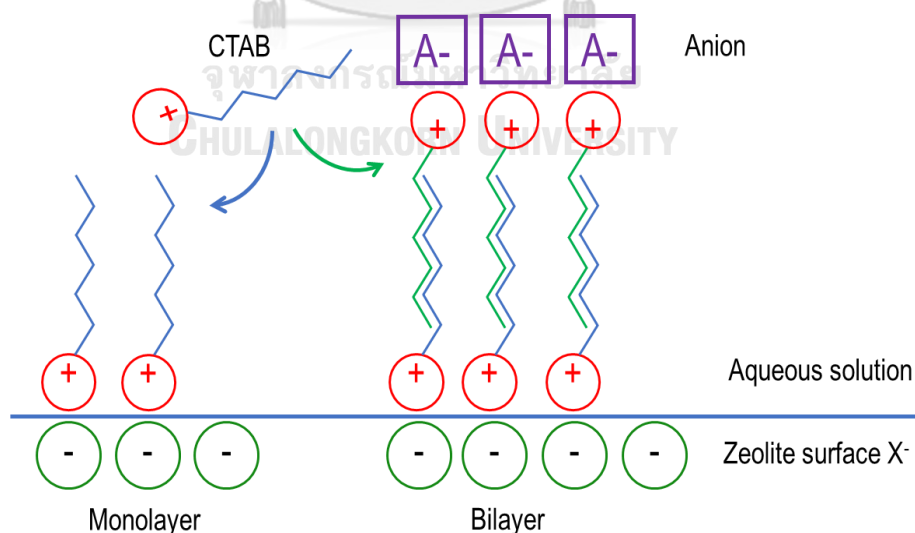


Figure 4.14 Interaction of CTAB on zeolite surface (SMZ) with anions adapted from literature²²

CTAB modified in various types of zeolites has shown different properties to anions owing to they have different cation exchange capacity (CEC) and external cation exchange capacity (ECEC) depending on their structures and Si/Al ratio, which later case worked on the more influence of anion exchange property of the obtained SMZ¹⁹. We can generate sorption mechanism by the following reaction:



Where R_4N^+ represented anion exchange sites of CTAB onto SMZ and n - represented charge of anion which adsorbed with SMZ. As previously discussed, the time of proposed ion selective electrode was immersed in perchlorate solution, anion exchange reaction occurred between anions on polymer-based electrode surface (Br^- ion from CTAB) and ClO_4^- solution.

Therefore, we decided to prepare CTAB solutions by varying concentrations of 100, 150 and 200 mmol L⁻¹ because we thought that when the CTAB concentrations exceed the maximum external cation exchange capacity, the more bilayer was densely formed onto zeolite surface and resulted in the nonpolar effect that enhanced solubility in mixing with PVC and *o*-NPOE.

4.2 Characterization techniques for SMZs

4.2.1 X-Ray Powder Diffractometry

The first technique was X-Ray Powder Diffractometry (XRD). The X-Ray Diffraction (XRD) patterns of reference NaY zeolite and surfactant modified zeolite (SMZ) were shown in Figure 4.2. The characteristic lines at 2θ of 6.24° [111], 10.18° [220], 11.92° [311], 15.70° [222], 20.40° [440], 23.70° [553], 27.10° [642], 30.76° [822], 31.40° [555] and 32.46° [840] are similar to those of commercial NaY zeolite. Therefore, the modification with various concentrations of CTAB did not change the original structure of NaY zeolite.

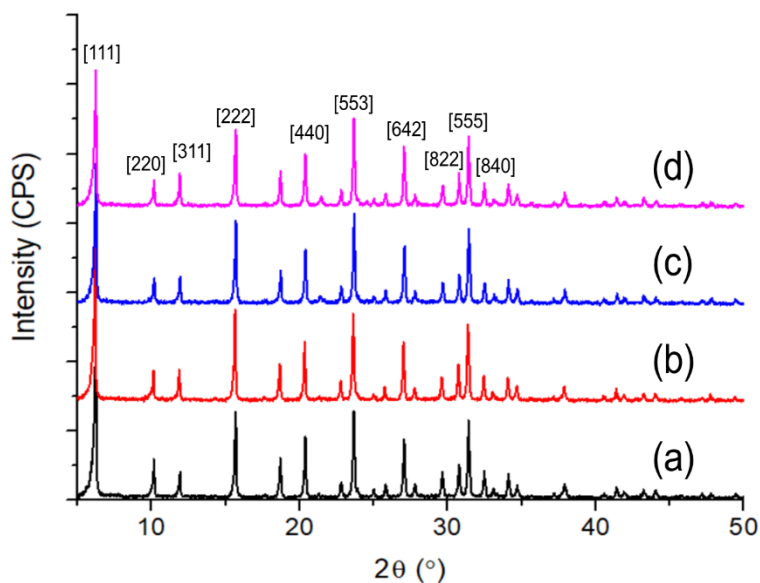


Figure 4.15 XRD patterns of (a) Commercial NaY zeolite, (b) 100 SMZ, (c) 150 SMZ, and (d) 200 SMZ

4.2.2 Fourier Transform Infrared Spectroscopy

Second characterization technique could be done by FT-IR spectroscopy by FT-IR (Nicolet 6700) via Attenuated Total Reflectance (ATR) mode. The FT-IR was used to characterize the commercial NaY and SMZ samples. Figure 4.3 showed the FT-IR spectra of all products, for 3 SMZs spectra compared to CTAB spectrum, showed characteristic peak at 2917, 2850, 1635, 1486 cm^{-1} , which related C-H, C-C, N-C vibrations in the surfactant, respectively³⁵. These indicated an incorporation of CTAB into zeolite structure. There are slightly shift in peaks for each wavenumber, however, all patterns are nearly the same. The presence of peaks at 3430 and 3407 cm^{-1} of commercial NaY and SMZs indicated stretching vibration of water molecules⁴⁰ and approximately 1000 cm^{-1} corresponded to symmetric stretching vibrations of T-O (T = Si and Al) that can be clearly seen in all zeolites²⁰. All information confirmed loading of CTAB onto zeolites.

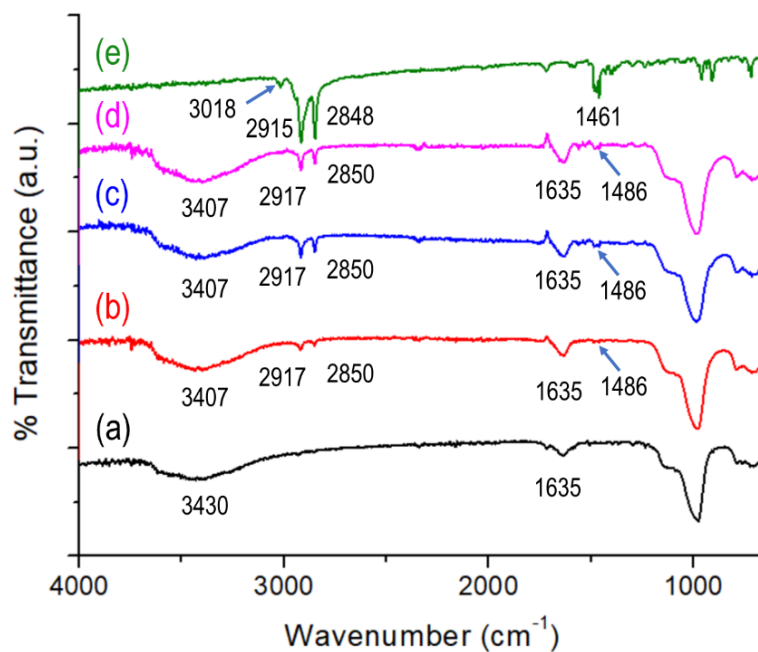


Figure 4.16 FT-IR spectra of (a) Commercial NaY zeolite, (b) 100 SMZ, (c) 150 SMZ, (d) 200 SMZ and (e) CTAB

4.2.3 Scanning Electron Microscopy-Energy Dispersive Spectrometry

SEM-EDS has been used to study morphology, particle sizes and elemental mappings of modified and unmodified zeolites. SEM images are shown in Figure 4.4, as can be seen, they suggested that morphologies of 3 modified samples were remain unchanged during cationic surfactant exchange process. On the other hand, cetyltrimethylammonium cation were formed bilayer on zeolite surface according to literature^{16, 17} and displaced Na^+ exchangeable cation in supercage of parent NaY zeolite and hence no significant changes were happened in morphology. The average particle sizes of raw and modified NaY zeolite were estimated to be around 500 nm from SEM images.

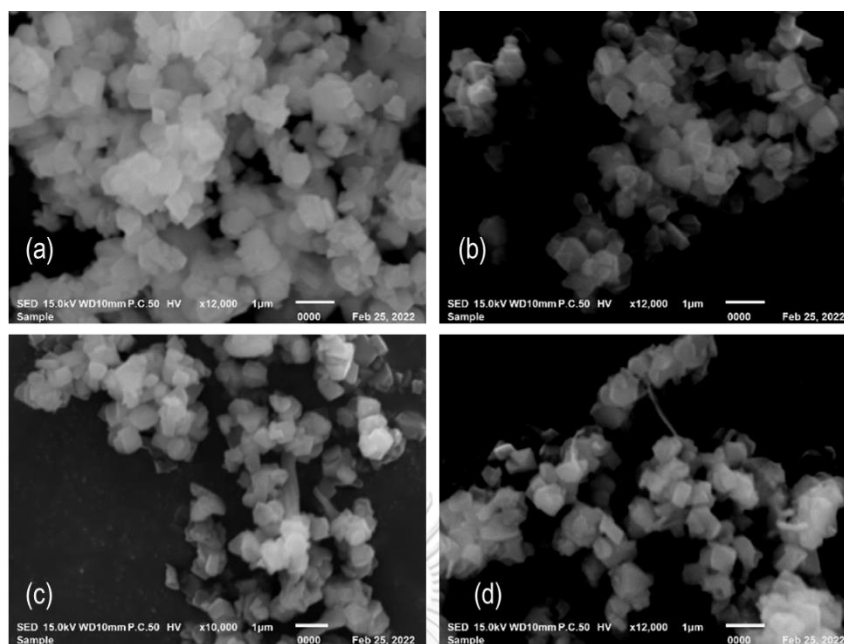


Figure 4.17 Morphology of (a) Commercial NaY zeolite, (b) 100 SMZ (c) 150 SMZ and (d) 200 SMZ

4.2.4 Thermogravimetric Analysis-Derivative Thermogravimetry

Thermogravimetric analysis (TGA) and Derivative Thermogravimetry (DTG) were the last technique to confirm successful loading of CTAB onto zeolite. TGA and DTG curves of CTAB, raw zeolite and SMZ were studied in the temperature range from 30 to 550 °C with a heating rate of 10 °C/min in nitrogen gas atmosphere and the acquired results are given in Figure 4.5. On the basis of TGA/DTG thermograms, it could be observed that the mass-loss curves were taken place continuously until completed at the temperature near 550 °C. The TGA/DTG curves (a) and (c) showed weight loss of commercial and SMZ between 75 and 250 °C, which related to physical water adsorbed on the zeolite surface and also water between particles⁴⁰. From our TGA/DTG results, commercial NaY had a mass loss of 23.43% according to loss of zeolitic water. CTAB reference curve (b) had completely degradation at temperature of approximately 250 °C. In TGA/DTG curve of 200 SMZ (80:20) (c), in addition of zeolitic water removal from the surface, there was also another weight loss at the temperature about 250–270 °C which suggested the loss of CTAB molecule from SMZ surface. The weak peak at the temperature about 375–425 °C

corresponded to the further decomposition of the surfactant at inner layer of CTAB. This analysis technique confirmed loading of CTAB and formation of double layer on the zeolite surface and is relevant to the FT-IR results.

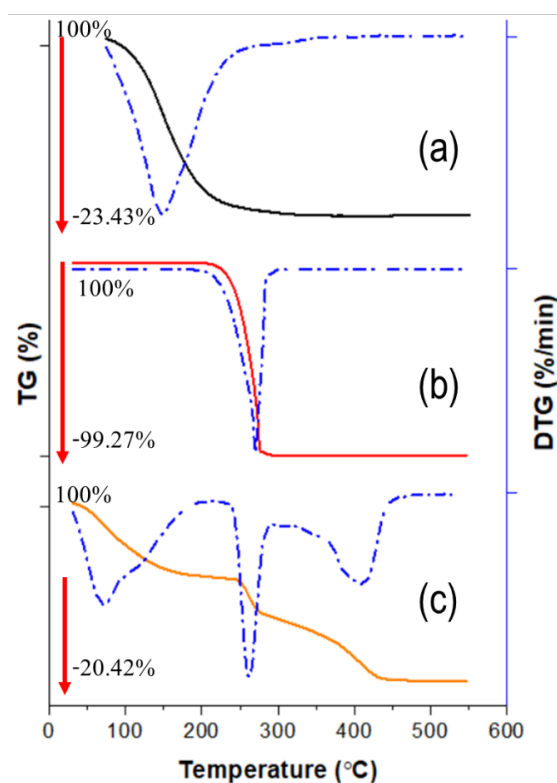


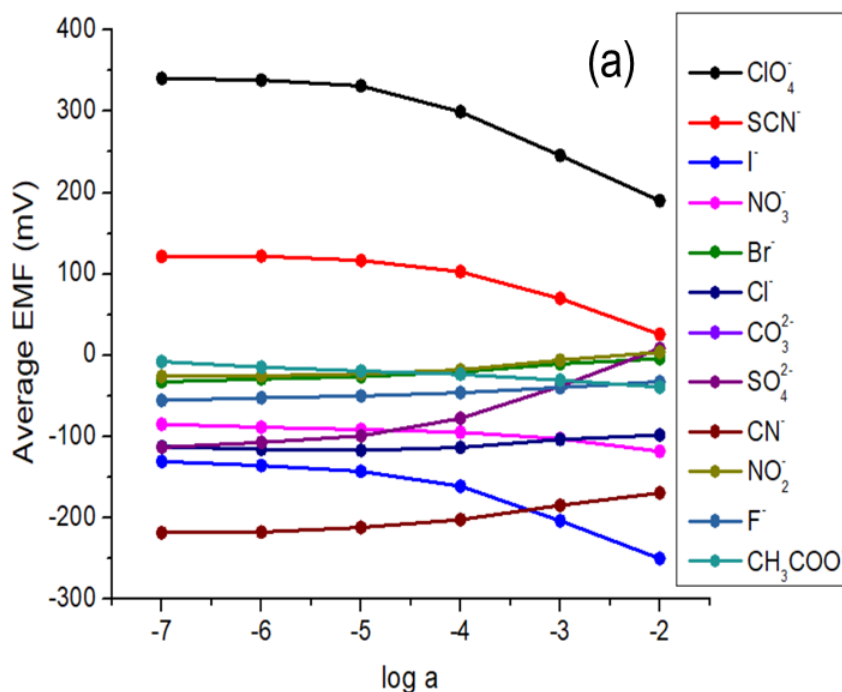
Figure 4.18 TGA and DTG images of (a) Commercial NaY zeolite, (b) CTAB reference and (c) 200 SMZ (80:20)

4.3 Potentiometric studies

We then used the prepared SMZs to fabricate anion selective electrodes and studied sensitivity, reproducibility, selectivity and real sample analysis. Basically anion selective electrodes required good characteristics that are (1) response slopes occurred near $-60 \text{ mV decade}^{-1}$ and (2) time trace line graph was stable in equilibrium concentration.

4.3.1 EMF responses of the ISE prepared from 100, 150 and 200 SMZ (80:20) in the same content

Membrane types A, B and C (Table 3.3), which composed of 15%wt ionophores (100, 150, 200 SMZ (80:20), 28.33%wt of PVC and 56.67%wt *o*-NPOE were prepared and investigated their ISE characteristics. The properties of each membrane electrode were investigated from the calibration curves by plotting between the potential responses for all different of anion species and logarithm of activity. As it was seen from calibration curves (Figure 4.6) and summarized table (Table 4.1) that 15%wt 100–200 SMZ (80:20) could responded to any anions with much lower than the expected Nernstian slopes and plots suffered from limited linear concentration range. However, perchlorate, thiocyanate and iodide ions exhibited the Nernstian responses over a concentration range of 1.0×10^{-6} to 1.0×10^{-2} M. These results indicated that the SMZ ionophore may be used as potential anion sensors for perchlorate, thiocyanate and iodide.



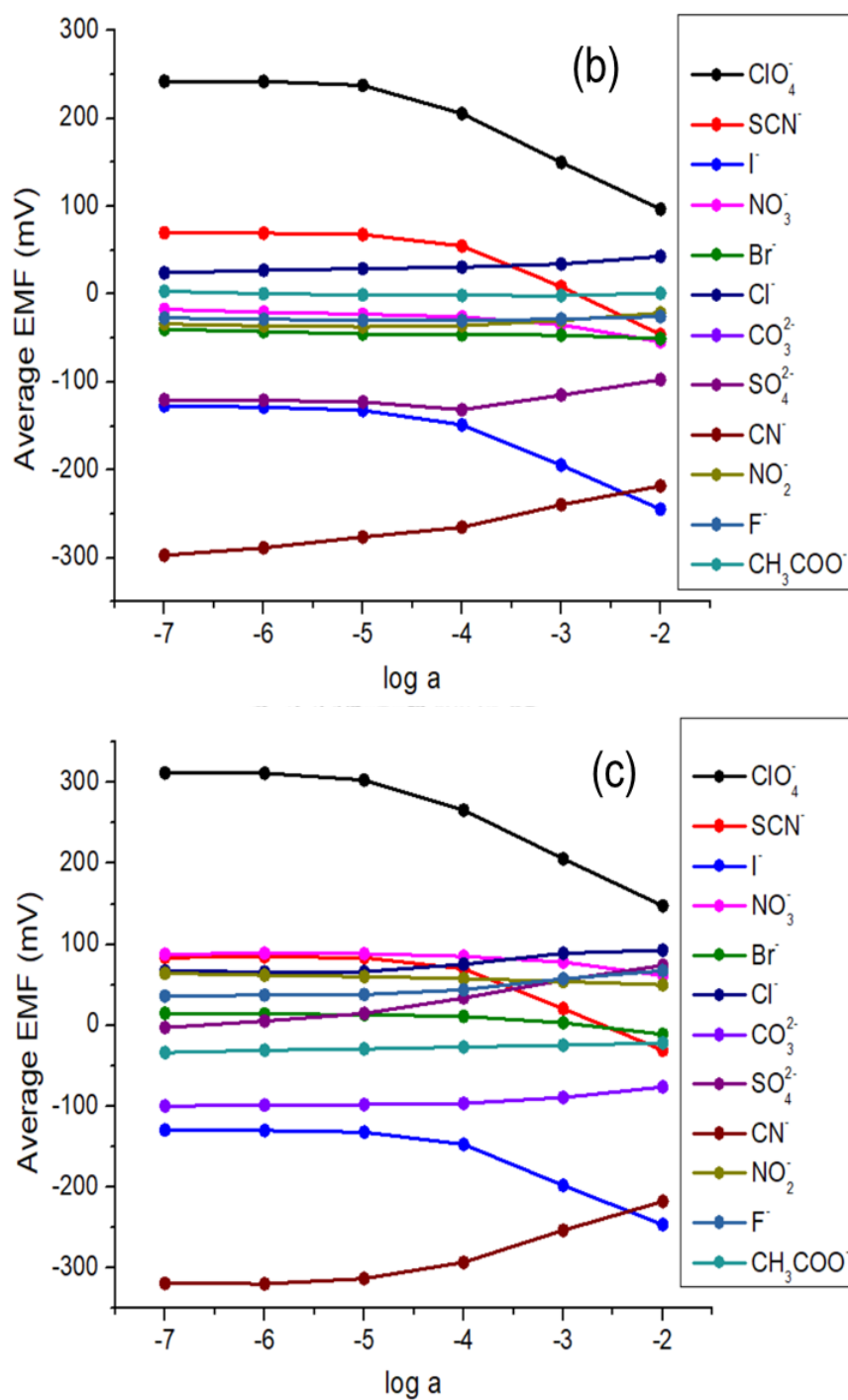


Figure 4.19 Calibration curves of anion responses for (a) 15%wt 100 SMZ (80:20), (b) 15%wt 150 SMZ (80:20) and (c) 15%wt 200 SMZ (80:20), respectively

Table 4.1 Summary of potentiometric responses of 15%wt 3 SMZs

Detection ions	Response slopes (mV decade ⁻¹)		
	15%wt 100 SMZ	15%wt 150 SMZ	15%wt 200 SMZ
ClO ₄ ⁻	-54.63 ± 0.58	-54.38 ± 0.68	-59.14 ± 0.62
SCN ⁻	-38.51 ± 3.22	-50.38 ± 2.36	-50.28 ± 0.61
I ⁻	-44.47 ± 1.19	-48.01 ± 1.17	-52.05 ± 0.82
NO ₃ ⁻	-11.75 ± 2.07	-14.15 ± 2.86	-11.95 ± 2.74
Br ⁻	+8.17 ± 1.13	-2.17 ± 1.02	-11.14 ± 1.88
Cl ⁻	+7.68 ± 1.20	+6.12 ± 1.52	+8.75 ± 2.79
CO ₃ ²⁻	N.D.	+17.04 ± 0.28	+10.16 ± 1.63
SO ₄ ²⁻	+39.29 ± 3.81	+24.56 ± 1.60	+20.03 ± 1.20
CN ⁻	+16.46 ± 0.65	+23.51 ± 1.51	37.53 ± 1.14
NO ₂ ⁻	+10.92 ± 0.65	+7.12 ± 0.82	-3.87 ± 0.11
F ⁻	+6.78 ± 0.25	+2.32 ± 0.22	+11.72 ± 1.09
CH ₃ COO ⁻	-7.76 ± 0.32	-0.40 ± 0.11	+2.55 ± 0.18

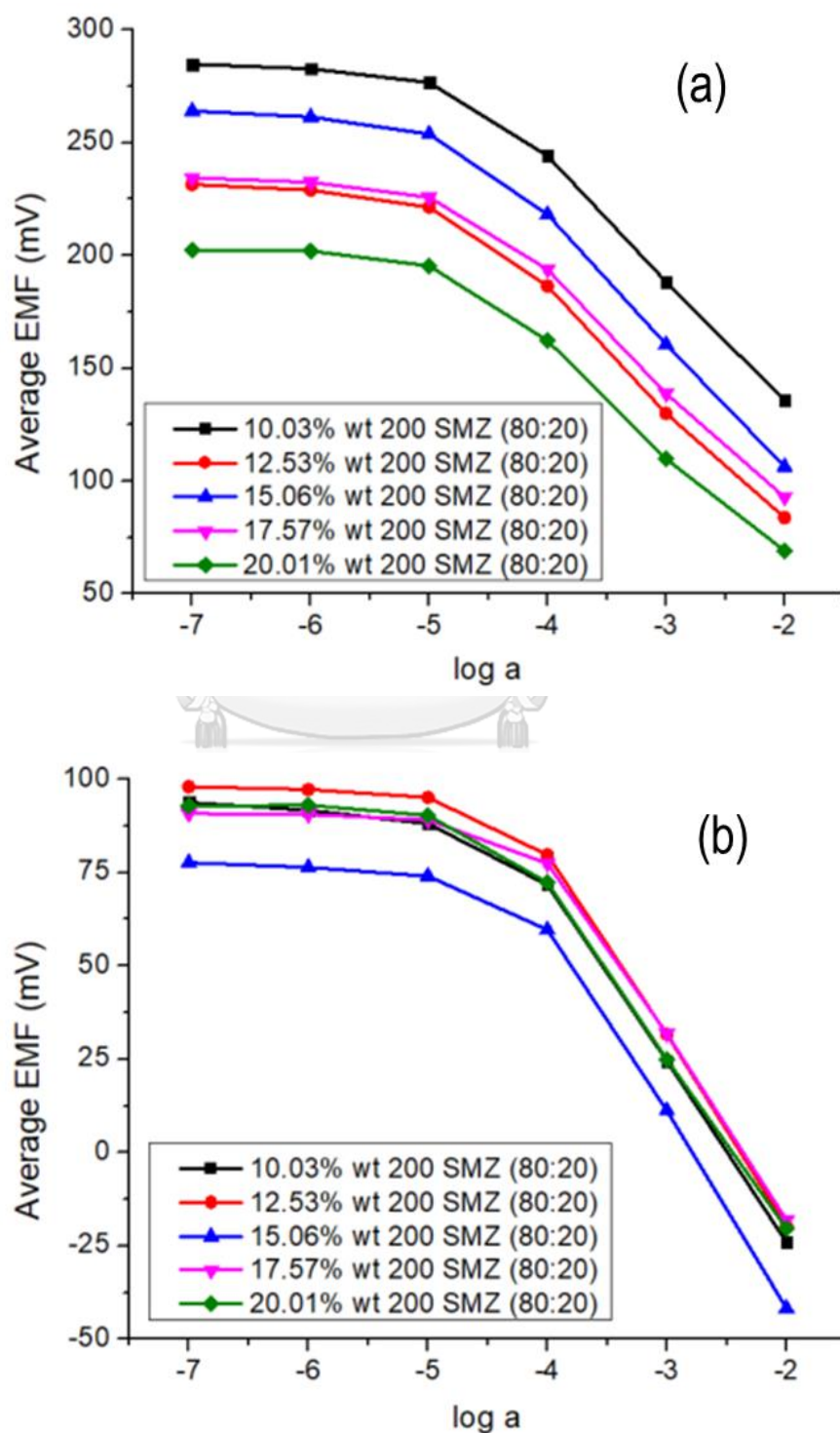
The minus sign implied the responses of anions towards ion selective electrode, whereas plus sign implied the responses of cation towards ion selective electrode or in the other words, the difficulties of anion diffused into polymeric membranes.

As can be seen, when increased concentration of CTAB from 100 to 200 mM in modification of SMZ, the potentiometric responses increased for some anions in the same trends such as perchlorate, thiocyanate, iodide, bromide and nitrite.

4.3.2 EMF responses of the ISE prepared from 200 SMZ (80:20) in various percentages

As we knew that our 200 SMZ (80:20) played an important role for anion selective electrode, the next step was to fabricate anion selective membrane with various percentage of candidate ionophore. We decided to fabricate polymeric membrane for types D, E, F, G, H defined in Table 3.3 (briefly for 10, 12.5, 15, 17.5 and 20%wt of 200 SMZ (80:20), respectively) and focus studied only 3 anions (perchlorate,

thiocyanate and iodide) due to dominant Nernstian slope exhibition. The Calibration curves of ClO_4^- , SCN^- and I^- responses of those percentages were displayed in Figure 4.7 and Table 4.2. As can be seen, the optimized percentage of 200 SMZ (80:20) as ionophore was 15%wt similar to the previous study.



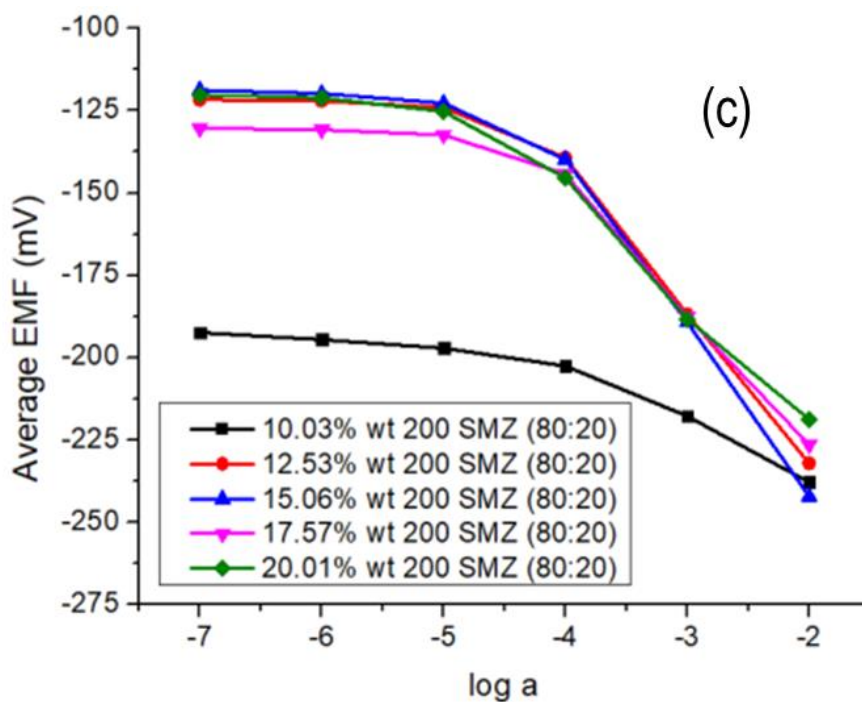


Figure 4.20 Calibration curves of (a) ClO_4^- , (b) SCN^- , and (c) I^- responses of 200 MZ (80:20) in various percentages of SMZ

Table 4.2 Summary of anion responses of 200 SMZ (80:20) in various percentages

Ionophore (200 SMZ (80:20))	Response slopes (mV decade^{-1})		
	ClO_4^-	SCN^-	I^-
10.03%wt	-54.23 ± 0.92	-47.85 ± 0.38	-17.65 ± 1.40
12.53%wt	-51.32 ± 3.00	-49.72 ± 0.94	-51 ± 3.00
15.06%wt	-55.87 ± 0.93	-50.71 ± 1.30	-51.11 ± 0.96
17.57%wt	-50.48 ± 2.61	-42.34 ± 0.72	-41.08 ± 1.29
20.01%wt	-46.55 ± 3.36	-46.35 ± 0.62	-46.55 ± 3.36

As can be seen from Table 4.2, perchlorate showed the highest Nernstian slope of $-55.87 \pm 0.93 \text{ mV decade}^{-1}$ compared to other anions in the percentage of 15.06 of 200 SMZ (80:20), so we selected this ratio for further studies.

4.4 Selectivity coefficient studies based on 15%wt 200 SMZ (80:20)

We then studied the potentiometric selectivity coefficients with 12 anions, ClO_4^- , SCN^- , I^- , NO_3^- , Br^- , Cl^- , SO_4^{2-} , CO_3^{2-} , CN^- , NO_2^- , F^- and CH_3COO^- . The potentiometric selectivity coefficients are one of the most crucial characteristics of ion selective electrode. It is determined from the relative response of primary ion over other ions presented in the solutions. Anion selectivity coefficients, $\log K_{i,j}^{\text{pot}}$ were determined by using separate solution methods (SSM). In logarithmic function of anion selectivity coefficients, i referred to primary anion (perchlorate) and j referred to interfering anions (other anions), an example of selectivity coefficient determination was shown in Figure 4.8.

All membrane electrodes gave value of $\log K_{i,j}^{\text{pot}}$ of ClO_4^- higher than that of any primary anions. This data can be concluded that our fabricated polymeric membrane based on 15%wt 200 SMZ (80:20) is selective to ClO_4^- over other anions despite changing primary anions to other anions, but they cannot compete ClO_4^- . The overall selectivity coefficient information shown in Figure 4.9.

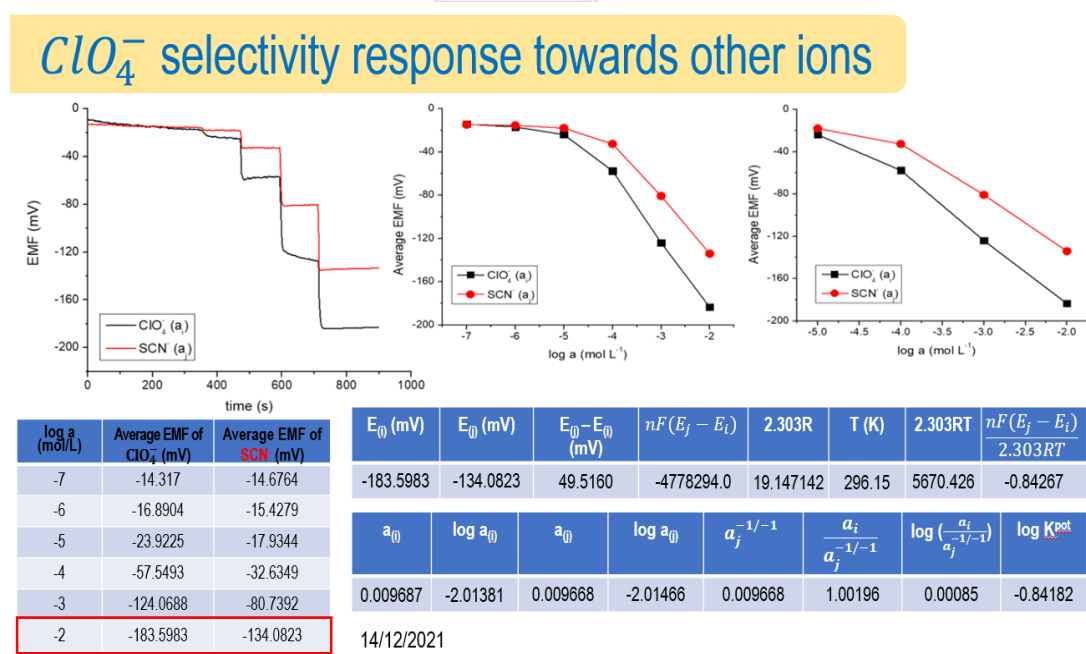


Figure 4.21 Example of selectivity coefficient determination between ClO_4^- (primary ion) substituted SCN^- (interfering ion)

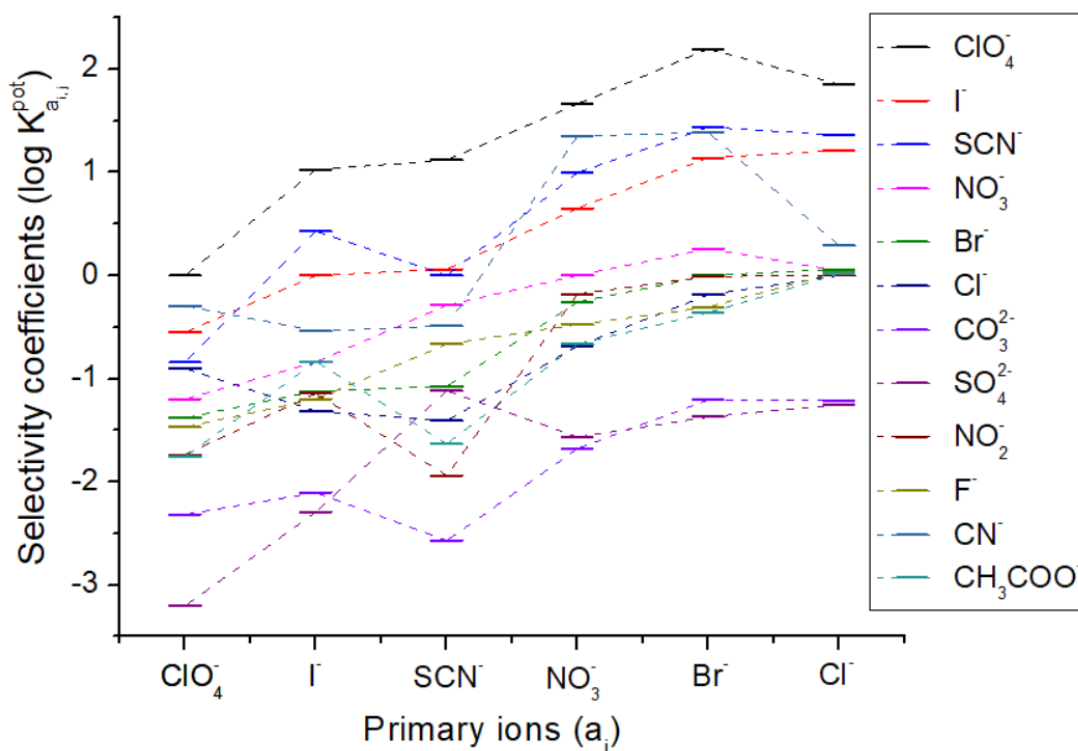


Figure 4.22 Selectivity coefficients of membrane based on 15%wt 200 SMZ (80:20) towards different primary ions

Table 4.3 Selectivity coefficients of 15%wt 200 SMZ (80:20) membrane electrode

Interfering ions	$\log K_{ClO_4^-,j}^{pot}$	Interfering ions	$\log K_{ClO_4^-,j}^{pot}$
I ⁻	-0.55	NO ₂ ⁻	-1.74
SCN ⁻	-0.84	CH ₃ COO ⁻	-1.75
NO ₃ ⁻	-1.20	Cl ⁻	-1.90
CN ⁻	-1.29	CO ₃ ²⁻	-2.32
Br ⁻	-1.38	SO ₄ ²⁻	-3.20
F ⁻	-1.47		

Table 4.3 showed the selectivity coefficient of perchlorate selective electrode in order of $ClO_4^- > I^- > SCN^- > NO_3^- > CN^- > Br^- > F^- > NO_2^- \sim CH_3COO^- > Cl^- > CO_3^{2-} > SO_4^{2-}$.

4.5 Reproducibility of ion selective membrane electrodes

After we finished measuring selectivity of ion selective electrode, we knew that our sensor responded selectively to perchlorate anion. We have to re-measure the potentiometric response of perchlorate anion within 15%wt 200 SMZ (80:20) several times to ensure the reproducibility of potentiometric response. Table 4.4 showed reproducibility of perchlorate anion. As can be seen, the Nernstian response slopes of perchlorate are not that significantly different. So, we can conclude that our ion selective membrane shows good reproducibility.

Table 4.4 Reproducibility of perchlorate anion

Condition of membrane preparation	Response slope (mV decade ⁻¹)
15.06%wt 200 SMZ (80:20)	-55.87
15.00%wt 200 SMZ (80:20)	-55.20
15.00%wt 200 SMZ (80:20)	-55.58
15.00%wt 200 SMZ (80:20)	-55.68
15.00%wt 200 SMZ (80:20)	-55.06

4.6 Real sample analyses

The last part of experimental section is to apply the optimized ion selective electrode as a sensor to determine perchlorate ion in real water samples. In this case, we collected 2 types of water, tap water and drinking water. We started to study perchlorate anion in tap water by measuring calibration via Milli-Q water 2 times and change Milli-Q water to tap water. The tap water measurement cannot detect perchlorate anion because it does not contaminate perchlorate, we decided to spike known concentrations of perchlorate into tap water and calculate measured concentration from sensors and %recovery, the data of measurement shown in Table 4.5. For drinking water, we do the same method as tap water and the result shown in Table 4.5.

Figure 4.10 and 4.11 showed examples of tap water and drinking water analysis.

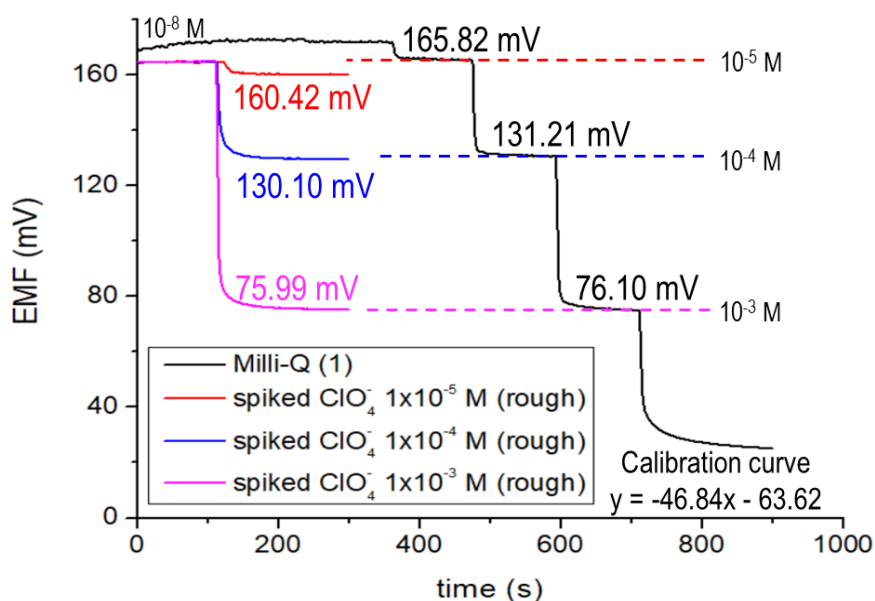


Figure 4.23 An example of tap water analysis

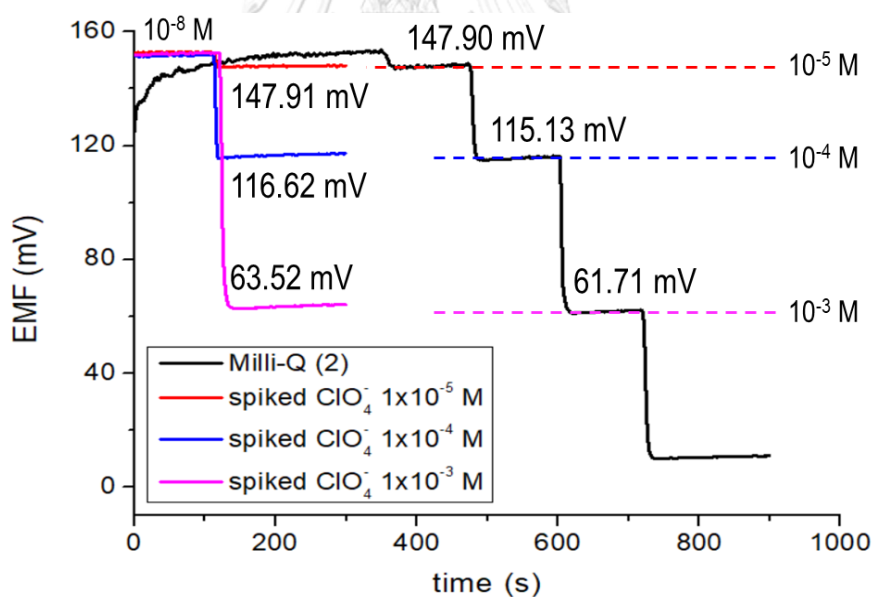


Figure 4.24 An example of drinking water analysis

After we measured perchlorate anion in both types of real water samples for several times, we selected the best performances of sensors for each concentration and found average concentration and %recovery. Table 4.5 showed the measuring data, %recovery, standard deviation (S.D.) and %R.S.D of real water samples.

According to Table 4.5, we can conclude that our sensors work well over 3 different concentrations in both types of real water samples.

Table 4.5 Calculation data of perchlorate selective electrode for real sample

Samples	Spiked (μM)	Found (μM)	Recovery (%)	S.D.	R.S.D.	%R.S.D.
Tap water	0.0000	N.D.	-	-	-	-
	0.0100	0.0104	103.6	2.3215	0.02240	2.24038
	0.1000	0.09857	98.57	0.4650	0.00472	0.47177
	1.0000	1.0283	102.80	1.5836	0.01543	1.54165
Drinking water	0.0000	N.D.	-	-	-	-
	0.0100	0.1042	115.83	0.1650	0.00142	0.14246
	0.1000	0.0936	94.36	0.2554	0.00271	0.27068
	1.0000	1.0100	100.99	0.7246	0.00725	0.72498

N.D. = not determined.

CHAPTER V

CONCLUSION

Ionophores based on Surfactant Modified NaY zeolites (100, 150, 200 SMZ (80:20)) have been modified. The modification pathway was beginning with commercial NaY zeolite mixed with various concentrations of surfactant solutions for 24 hr. and centrifuged at 3,000 rpm for 20 min. and dried at 80°C overnight. The surfactant modified zeolites were collected and characterized with various techniques. For XRD, the XRD patterns showed the same characteristic patterns of modified zeolite compared to commercial one. For FT-IR, the FT-IR spectra showed appearances of characteristic peaks at 2917, 2850, 1486 cm^{-1} in 3 SMZs which referred to C-H, C-C, and N-C vibrations of surfactant, respectively. These spectra confirmed the successful incorporation of CTAB onto zeolite surface. For TGA/DTG, the thermograms showed mass loss of CTAB from 200 SMZ (80:20) in accordance with literature.

The potentiometric response of polymeric membrane electrodes doped with surfactant modified NaY zeolite (100, 150, 200 SMZ (80:20)) as ionophores for anions were constructed. In this case, the mentioned ionophores in content of 15%wt of ionophores were found to detect perchlorate selectivity in comparison to other anions. The slopes of the obtained curves are near ideal Nernstian slope. However, perchlorate ion exhibited the Nernstian response over a wide concentration range of 1.0×10^{-5} to 1.0×10^{-2} mol L⁻¹.

According to study of real water samples, our perchlorate selective electrodes can be used to detect perchlorate ion in both tap water and drinking water with the satisfactory results.

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APPENDIX

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

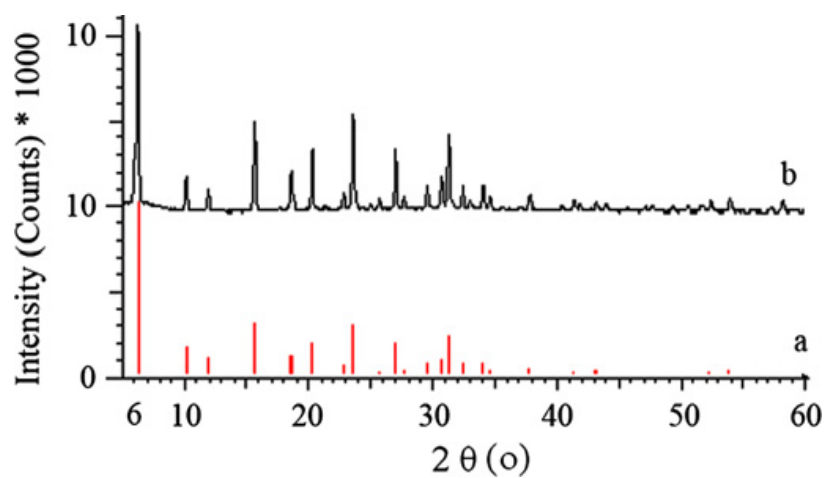


Figure S1 XRD patterns: (a) the pure phase zeolite Y, and (b) synthesized zeolite Y³⁵

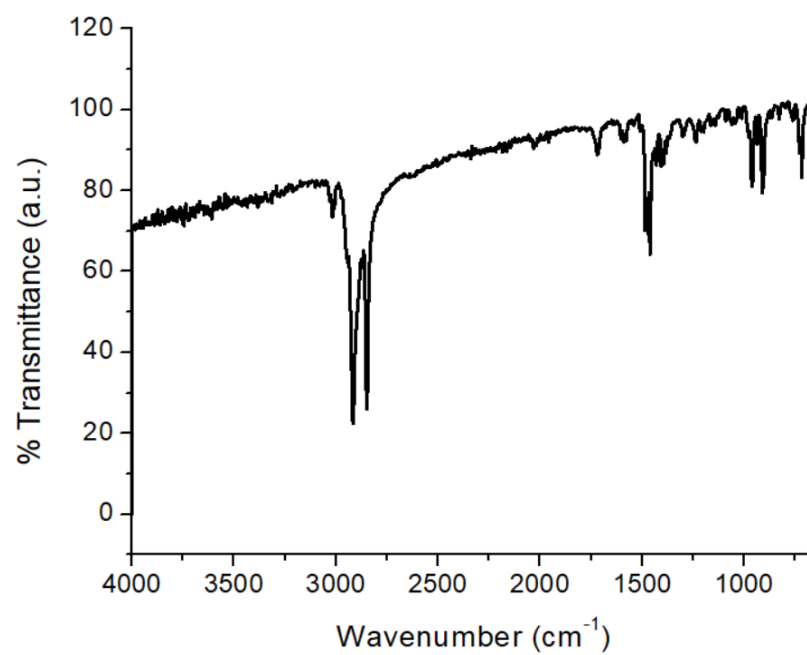


Figure S2 FT-IR spectrum of CTAB

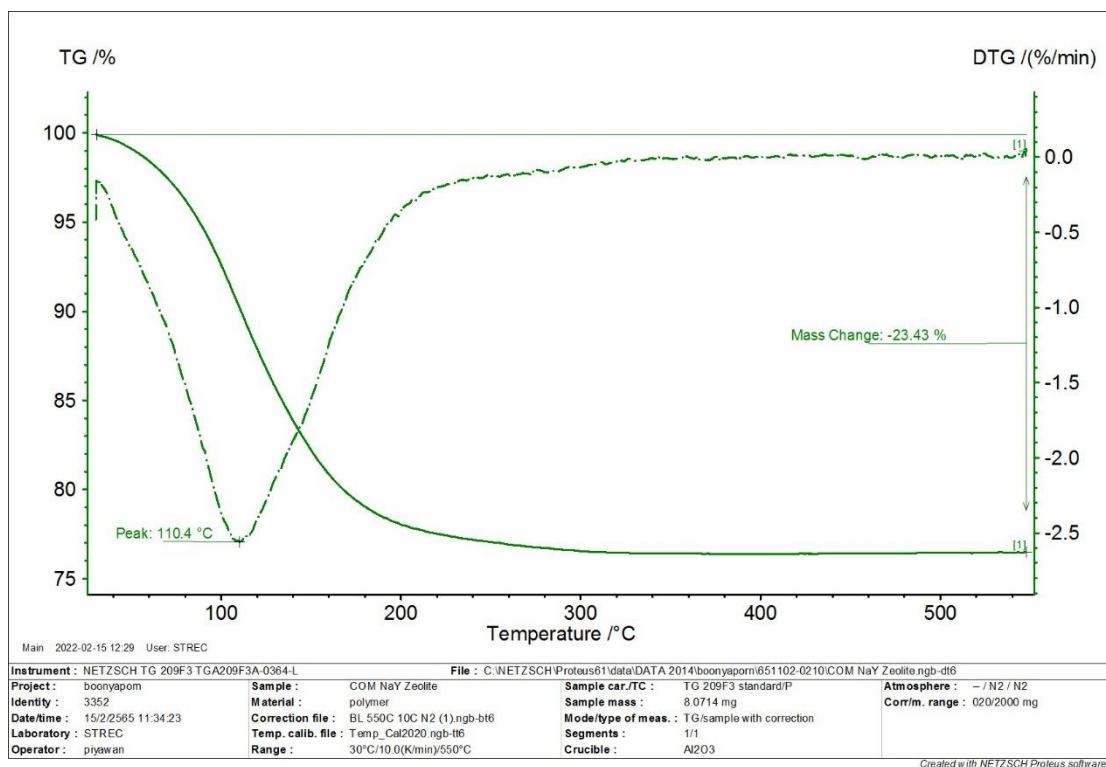


Figure S3 TGA/DTG curve of Commercial NaY zeolite

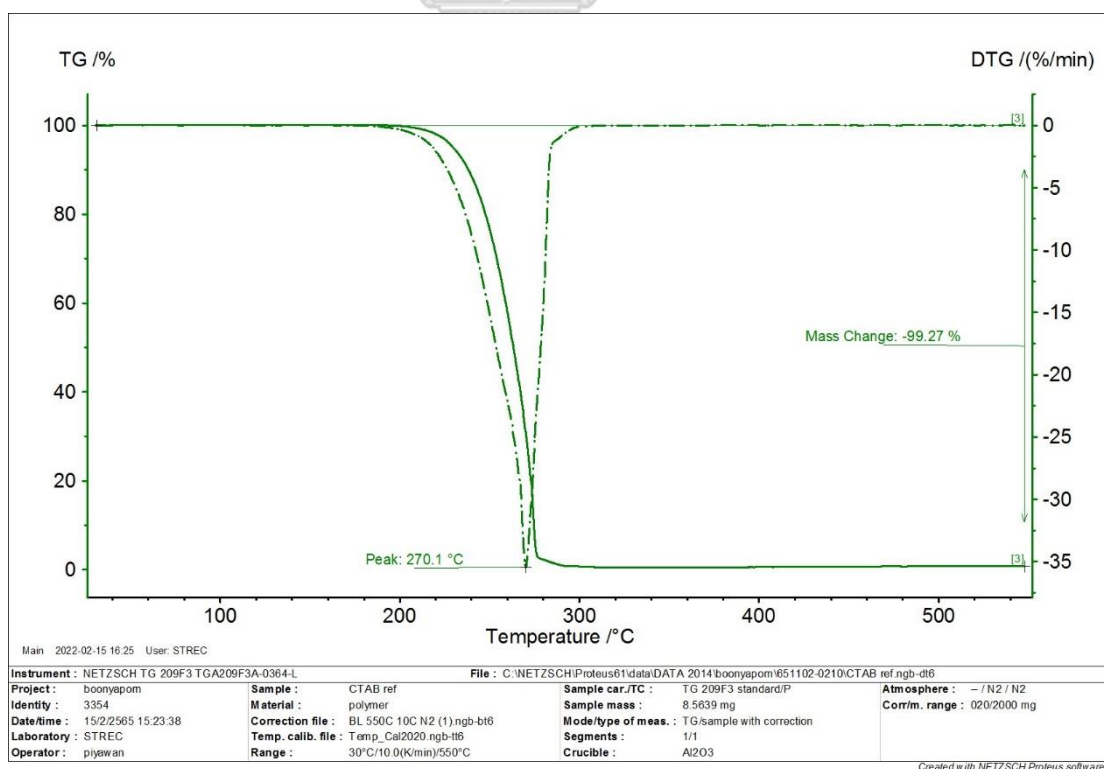


Figure S4 TGA/DTG curve of CTAB reference

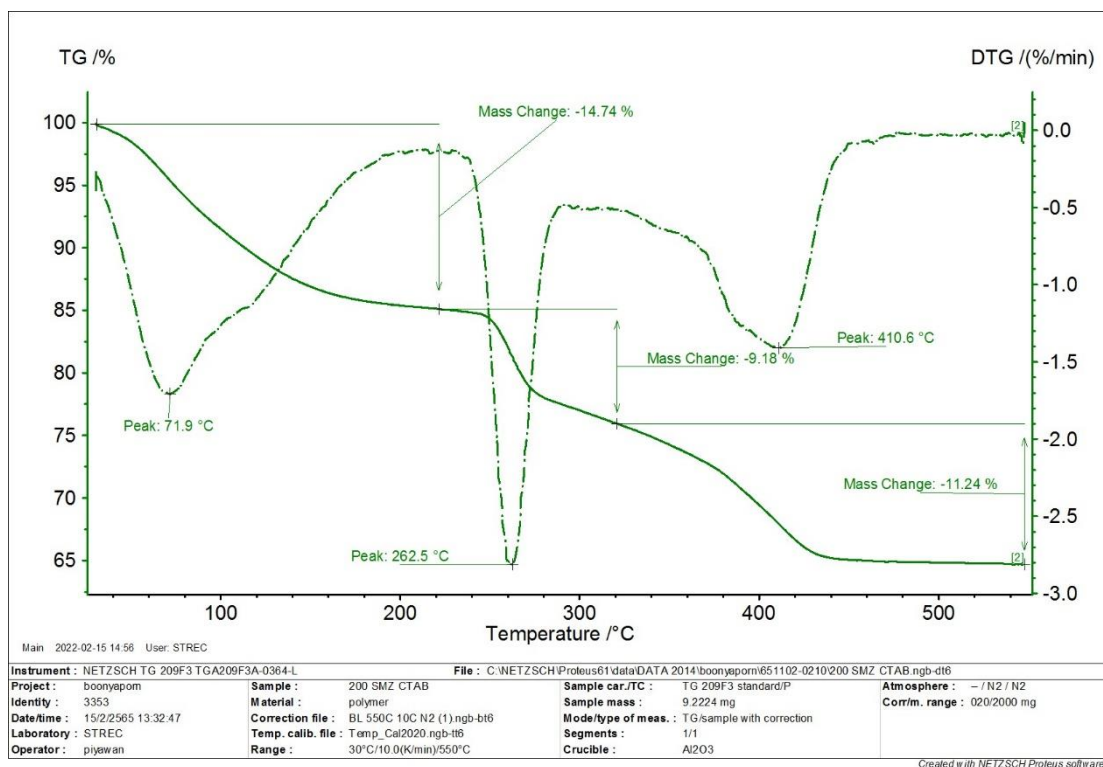


Figure S5 TGA/DTG thermogram of 200 SMZ (80:20)

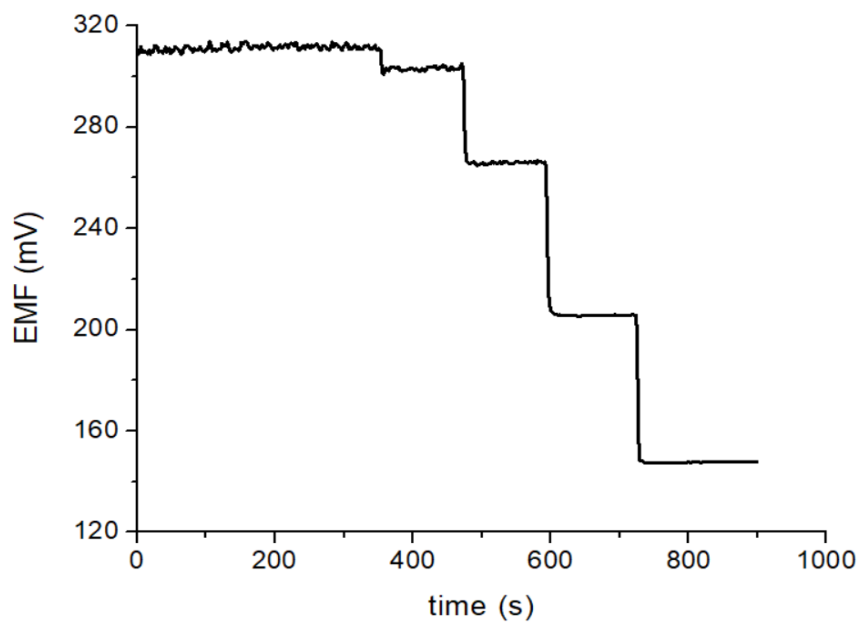


Figure S6 Time trace line curve of ClO_4^- ion with 15%wt 200 SMZ (80:20)

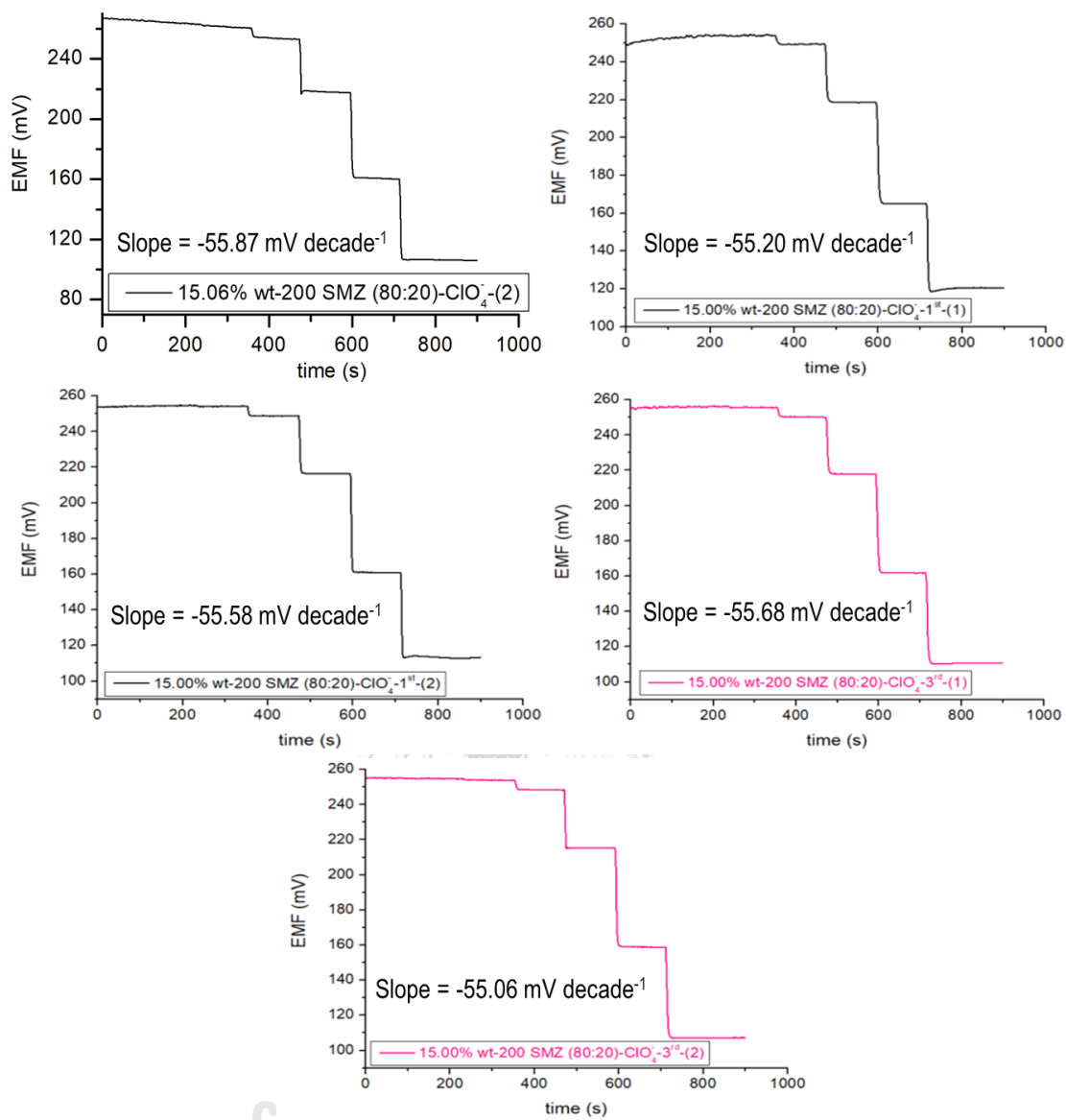


Figure S7 Reproducibility of ClO_4^- ion

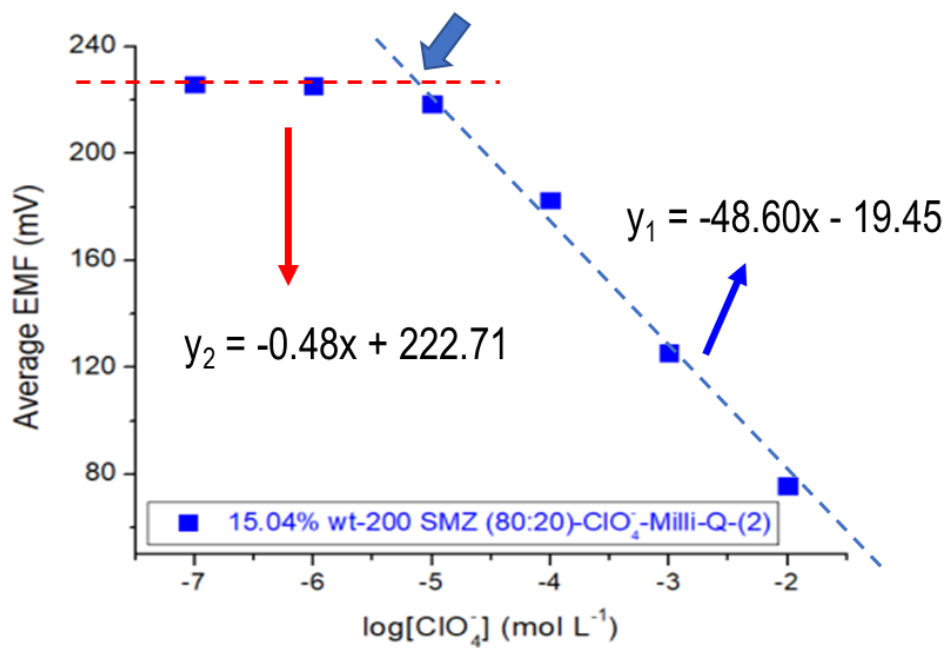
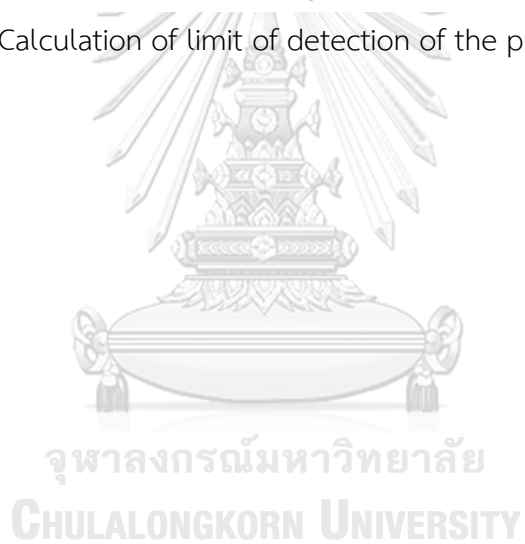


Figure S8 Calculation of limit of detection of the proposed electrode



VITA

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DATE OF BIRTH 26 พฤษภาคม 2539

PLACE OF BIRTH นครราชสีมา

INSTITUTIONS ATTENDED สาขาวิชาเคมี สำนักวิชาวิทยาศาสตร์ มหาวิทยาลัยเทคโนโลยีสุรนารี

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AWARD RECEIVED ได้คะแนนสูงสุดในวิชาเคมีอินทรีย์ ในการสอบเพื่อรับรองมาตรฐาน
ความรู้เคมี ครั้งที่ ๑๑ จากสมาคมเคมีแห่งประเทศไทย ในพระ
อุปถัมภ์ของ ศาสตราจารย์ ดร. สมเด็จพระเจ้าลูกเธอ เจ้าฟ้าจุฬา
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