CHAPTER 4

DISCUSSION AND CONCLUSION

4.1 Construction of iodide CWISE

The construction iodide CWISE was investigated. The cleaned Cu-wire was dipped into the coating solution which composed of AgI and polymer matrix. In this experiment, the preparation of the coating solution; with solvent and without solvent, was studied. The coating solution with solvent was used in this experiment because the polymer matrix in the coating solution could be dissolved in the solvent to facilitate the coating. In the case of coating liquid without solvent, the coating solution was very thick, viscous and difficult to homogenize so it was unsuitable for coating electrode.

Epoxy resin, hardener of epoxy resin, epoxy resin mixed with its hardener and poly (vinyl chloride) were studied as the polymer matrix in this experiment. The epoxy resin as well as poly (vinyl chloride) was used to prepare the coating solution because the electrode, which was prepared with these, gave responsive by measurement of iodide ion. The epoxy resin mixed with its hardener suddenly hardened in 5 minutes and hardly dissolved in solvent so that it could not be used for coating the electrode. In the case of the electrode which was prepared with hardener of epoxy resin, it did not give responsive by measurement of iodide ion. Hence, the hardener of epoxy resin was unsuitable for coating electrode.

4.2 The investigation of the effect of optimum ratio of AgI and epoxy resin

To optimize the ratio of AgI and epoxy resin; 2:1, 3:1, 4:1, 5:1 and 6:1, were used to prepared iodide CWISE. Considering the slope of electrode in the ratio of 3:1, 4:1 and 5:1, they were close to Nernstian response. The results showed that AgI were well disperse in epoxy resin then they were laid to be even membrane with

proper length. However, the ratio of 3:1 was more economical than 4:1 and 5:1. So that in this experiment the ratio of 3:1 was chosen. Examining the slope of electrode in the ratio of 2:1, the lower Nernstian response was observed. The cause of this low sensitivity probably due to the fact that concentration of AgI was low so it must naturally be so far apart. On the other hand, in the rstio of 6:1 AgI might be clot because of its high concentration therefore experimental slope of electrode was upper Nernstian response.

4.3 Effect of the membrane thickness on the electrode slope of iodide CWISE

To study the effect of membrane thickness on the electrode slope of iodide CWISE, the electrodes were coated untill the difference and satisfier membrane thickness were observed. In this experiment, it could not measure the real thickness of membrane so that it was considered in the weight of membrane. Considering the electrode slopes in the three ranges of membrane thickness; 0.0080-0.0100, 0.0150-0.0250 and 0.0200-0.0270 g of weight of membrane, they were 55.3, 35.6 and 57.3 mV/decade, respectively. In fact, the membrane thickness was effective to electrode slope but from these results it was seemed to be of no effect to the electrode slope because of the lower slope of electrode in the medium membrane thickness. During the coating procedure, Cu-wire might not be in a vertical position so that a uniformed and symmetrical membrane was not obtained. Therefore, the medium weight of membrane might not be the medium membrane thickness. And the equal weight of membrane did not demonstrate the equivalent thickness of membrane.

4.4 Effect of particle size of silver iodide precipitate on electrode slope

Silver iodide precipitate was seperated into two portions; the first was controlled size of particle (200 mesh size) and the other was uncontrolled particle size. Electrode slopes of two sets of electrode, which were controlled particle size,

were 61.1 and 35.6 mV/decade whereas those of uncontrolled particle size were 57.1 and 60.6 mV/decade. In general, the membrane of electrode, which was prepared with controlled particle size, was expected to be smooth with perfect order AgI deposition. Then the researcher predicted that the electrode slope of controlled particle size might be better than uncontrolled particle size. The results of this experiment did not follow to this prediction then it could not be concluded that the slope of electrode of controlled particle size was better than uncontrolled or not. The great obstacle, which cause these results did not follow to the prediction, was dip; the coating procedure of electrode that might be the cause of variation of trait of membrane.

4.5 Comparison of response time of conditioned and unconditioned iodide CWISE

The comparison of response time of conditioned and unconditioned iodide CWISE was studied. The electrode was conditioned by soaking in 10^{-5} M iodide solution in approximately one night. The unconditioned iodide CWISE had values of response time in the range of 17.50-22.50 minutes whereas those of conditioned iodide CWISE were in the range of 2.00-7.50 minutes. These results showed that the response of conditioned iodide CWISE was faster than unconditioned CWISE. During the conditioned step, the ion diffusion across membrane has been occured then equilibrium prevails at the electrode. Consequently, when this electrode was immersed in analyse solution fast equilibrium was established. Therefore, short response time was obtained. In general, the new electrode often needs conditioning before use and thereafter it should be stored under suitable conditions when not in use[29]. From the results, it is necessary to condition the electrode to give fast response electrode before use.

4.6 Effect of concentration on response time of iodide CWISE

The effect of concentration on response time of iodide CWISE was investigated. According to IUPAC recommendation [32], the response time is the length of time that elapses between the instant at which a potentiometric cell is formed by the immersion of its constituent electrode in a solution. The response time also depends upon the concentration of the solution previously analysed, temperature and stirring solution. In this experiment, temperature and stirring of solution were controlled and the concentration of iodide solution was varied from 10^{-5} to 10^{-3} M iodide concentration. The response time of 10^{-3}, 10^{-4}, 10^{-5} M iodide concentration were 1.50, 2.50, and 13.30 minutes, respectively. These results followed to the fact that when the concentration changes from high to low, the response time of electrode is increased[29].

4.7 Characteristics of iodide CWISE

The characteristics of iodide CWISE was investigated and compared to the commercial electrode;Orion iodide electrode. The results were shown in Table 4.1.

Under the same experimental conditions, the characteristics of iodide CWISE was found to be closed to that of Orion iodide electrode except the response time and selectivity coefficient.

The response time of iodide CWISE was longer than Orion iodide electrode. This may be due to the fact that, the nature of the charge-transfer reaction at the metal/polymer interfece of CWISE remains largely unknown and at the bare metal/polymer interface poor charge conduction is expected from the absence of significant redox couples. This may cause longer response times for CWISE[33].

In the study of selectivity of electrode in term of potentiometric selectivity coefficient; $K^{pot}_{A,B}$, bromide ion, fluoride ion and chloride ion were used as the interfering ions. The potentiometric selectivity coefficient of iodide CWISE and Orion iodide electrode were compared and result was shown in Table 4.2.

Table 4.1 Comparison of characteristics of iodide CWISE and Orion iodide electrode

Characteristics of electrode	Electrode	
	Iodide electrode *	Orion iodide electrode
Response time (min)	1.30	0.50
Detection limit (M)	0.8×10^{-5}	0.5×10^{-5}
Electrode slope (mV/decade)	55.1	55.2
Calibration curve		
-linear range	2 decade	2 decade
-correlation coefficient	0.996	0.999
-slope	58.1	55.4

* = mean value from 5 electrode samples

Table 4.2 Comparison of selectivity coefficient of iodide CWISE and Orion iodide electrode

Interferent ions	$K^{pot}_{A,B}$	
	Iodide CWISE *($\times10^{-4}$)	Orion iodide electrode ($\times10^{-4}$)
Br^-	2.08	1.26
Cl^-	1.34	2.34
F^-	3.72	1.41

*= mean value from 5 electrode samples

The selectivity coefficient is not a constant but depends on the concentration of the interfering species. The prefered method for its determination is to make a serie of measurements at various concentrations of the primary ion A with interferent B at a constant level[34]. In this experiment, the constant level of interfering ions was 10^{-2} M, and the used method was fixed interference method (mixed solution method)[28].

The value of the selectivity coefficient; $K_{A,B}^{pot}$ reflects the degree of selectivity of the electrode for the determinand ion A with respect to the interfering ion B. When $K_{A,B} < 1$, then the electrode is very much more selective toward the determinand than it is toward the interferent ; when $K_{A,B} = 1$, the electrode is equally responsive to the ion A and B; when $K_{A,B} > 1$, the electrode responds to preferentially to B rather than to A[29]. In this experiment, determinand ion A was iodide ion and interfering ions were bromide ion, fluoride ion and chloride ion. Potentiometric selectivity coefficient of iodide CWISE and Orion iodide electrode were < 1, it means that these two electrodes were very much more selective toward the iodide ion than fluoride ion, chloride ion and bromide ion. Both electrodes had difference in the effect of interfering ion. $K_{I,Br}^{pot}$ and $K_{I,F}^{pot}$ of iodide CWISE had higher than of Orion iodide electrode, then bromide ion and fluoride ion had more interferent to iodide CWISE than to Orion iodide electrode. On the other hand, $K_{I,Cl}^{pot}$ of iodide CWISE had lower than Orion iodide electrode, then chloride ion had more interferent to Orion iodide electrode than iodide CWISE.

The detection limit of both iodide CWISE and Orion iodide electrode was close to each other. The detection limit of both electrodes was about 10^{-5} M iodide concentration. Harsanyl et al.[35] reported that the anomalous behavior of silver iodide based on ion-selective electrode in the lower concentration region ($\leq 10^{-5}$ silver or iodide concentration), showing positive or negative deviations from the ideal Nernstian response. Similarly to Morf et al. [36], they observed ideal Nernstian response only above 10^{-5} M iodide concentration. Hulanicki et al. [37] explained this behavior that deviation was attributed to the adsorption of iodide ions on the electrode surface.

The electrode slope of both electrodes was near-Nernstian response and very near to each other.

4.8 Comparison of characteristics of electrode sets

The three sets of iodide CWISE (which each set had 5 electrode samples that were prepared in the same time) were compared their characteristics. Considering detection limit of them, it was close to each other and characteristics of calibration curve likewise. However, in other characteristics such as response time and electrode slope had different value. Examination of response time and electrode slope in each electrode set, they were close to each other but when comparing these characters between electrode sets, the different values were obtained. In case of electrode slope, upper, lower and near Nernstian response were observed. And considering response time of electrodes, they were very scattered value. Cause of these results might be concerned to physical of membrane of electrode. It was very difficult to make the membrane of electrode to even and to be the same typical membrane because coating procedure of electrode was dip that depend on technical skills of researcher. So the preparation of electrode was quite low stability.

4.9 Lifetime of iodide CWISE

Lifetime of iodide CWISE was studied by measurement of electrode slope of 5 iodide CWISE every week for 10 weeks. At the initial weeks, the most electrode slopes showed near Nernstian response. In the last 5 weeks, the electrode deviated from Nernstian; showed lower Nernstian response. The lifetimes of iodide CWISE were 4-5 weeks. The lifetime of any CWISE is reliable to the typically active ion and to typically membrane of electrode. Some CWISE have a long lifetime such as 3 months (Ca^{2+} CWISE)[4], more than 7 months (dinonylnaphthalene sulfonate CWISE)[23], and some CWISE have a short lifetime such as 9 days (solid solvent membrane CWISE)[38], 7-10 days (Cd^{2+} CWISE)[17]. However, 6 weeks lifetime was observed in antimony CWISE[9] that was nearly to lifetime of iodide CWISE in this experiment.

4.10 Percent yield of iodide CWISE

To study the percent yield of iodide CWISE, 80 iodide CWISE were construced and measured the electrode slope. The 29 Nernstian-slope electrodes were obtained. The percent yield of iodide CWISE was 36.25, that was of low value. The causes influencing lower percent yield might be that ;

(1) The iodide CWISE was hand-made electrode that the preparation procedures depend on technical skills of researcher.

(2) It was very difficult to control the electrode surface to be smooth. Significant prefix was difficulty of deposition the AgI precipitate to even layer.

(3) The AgI precipitate was hardly to be homogenized with polymer matrix because of its solidity.

It can be concluded that tha stability of prepared of electrode was quite low.

4.11 Preparation of iodide CWISE with AgI in PVC

The potentials of iodide CWISE which was prepared with AgI in poly(vinyl chloride) was out of scale. The potentials were measured about 2 weeks in everyday. The poly (vinyl chloride) PVC is widely use in ion-selective electrode works because of its properties such relatively inert, stable, inexpensive, simple to use and therefore, recommended for student electrode[39]. The accomplishment ion-selective electrode which use PVC matrix is appeared in many works but it failed in this experiment, The cause might be that AgI, which has low conductivity and solubility product constant, disperse in the inert polymer. Hence, very low potential which was unable to measure.

4.12 Preparation of iodide CWISE with AgI/Ag_2S in PVC

In the use of AgI in preparation of iodide CWISE, the out of scale potentials were obtained. Consequently, AgI/Ag_2S was use instead of AgI. After 3 days of preconditioned step, the potential response was obtained. This results showed the success of AgI/Ag_2S use. Response time of electrode which prepared in various

percent of AgI/Ag_2S in PVC matrix, were studied. The results showed that every electrode had more than 60 minutes response time. The optimum ratio of AgI/Ag_2S in PVC was determined, that the results showed to be fluctuated. Therefore, improvement of PVC membrane was established to make shorter response time and stability potentials.

4.13 Preparation of iodide CWISE with AgI/Ag_2S in plasticized PVC

The significant object of this study was improvement of PVC membrane. Shorter response time and stable potentials were required. The plasticizer was added into PVC. According to definition, a plasticizer is a material incorporated in a plastic to increase its workability and flexibility or distensibility. The addition of the plasticizer may lower the melt viscosity, elastic modulus, and glass transition temperature (T_g) of a plastic. The effect of plasticizer may be explained by the lubricity, gel, and free volume theories. The first state that the plasticizer acts as an internal lubricant and permits the polymer chains to slip by each other. The gel theory, which is applicable to amorphous polymer, assumes that a polymer such as PVC has many intermolecular attractions which are weakened by the presence of a plasticizer such as DOP. It is assumed that the addition of the plasticizer increase the free volume of the polymer, and that the free volume is the space in a solid or liquid sample which is not occupied by polymer molecules, i.e. the "empty-space" between molecule[40,41]. The less toxic di-2-ethylhexyl phthalate (DOP) which is now the most widely used plasticizer was used in this experiment. A shorter response and stability potential were expected by a use of plasticizer PVC instead of PVC. However, a long response time and fluctuation potentials still appeared. The better charge-transfer at the metal/polymer interface of electrode was not occured although the addition of plasticizer increase the free volume of a polymer.

In conclusion, PVC and plasicized PVC were not suitable to use to prepare the iodide CWISE which AgI and AgI/Ag_2S were active materials.

Finally, the conclusion of this research work are as following :

1. The iodide CWISE were prepared by dipping Cu-wire into the coating solution which composed of AgI (active material) and epoxy resin (polymer matrix).

2. After characterization of iodide CWISE, the electrode showed the slope close to Nernstian response, and some characteristics were close to the commercial iodide electrode; Orion iodide electrode.

3. The lower stability of electrode preparation was demonstrated by the difference of characteristics of electrode sets, and the lower percent yield of electrode.

4. The iodide CWISE which prepared with active material and other polymer matrice; PVC and plasticized PVC, gave longer response time and fluctuation potentials. In summary, it was considered to be unsuitable for the purpose.