

CHAPTER 4

CONCLUSION

The electrochemical behavior of three substituted thioureas and nine complexes of copper(I) were performed by cyclic voltammetry in acetonitrile solution at glassy carbon electrode vs Ag/AgCl.

The cyclic voltammograms of three substituted thioureas exhibit the different behaviors. In the case of ethylenethiourea ligand which exhibits a redox couple in acetonitrile solution and this redox couple is purely diffusion controlled. The redox potentials of ethylenethiourea are observed to be near that of thiourea but the oxidation potential shift to more positive values and the reduction potential shift to more negative values. Because ethylenethiourea has $\text{CH}_2\text{-CH}_2$ group as a substituent, therefore this compound has steric effect compare with thiourea. This can make the delocalization of electron more difficult. The electrochemical behavior of ethylenethiourea is the same as that of thiourea, i.e., the redox reaction occurs at sulfur group. But in the case of substituted thioureas which have the phenyl group as a substituent, the oxidation reaction and the reduction reaction occurs at amine group due to the resonance effect in structure.

The cyclic voltammogram of diphenylthiourea complexes exhibits a redox peak of copper(I)/copper(0) process, which supports that the copper in the complexes is copper(I). The reduction potential of copper in the complexes shift to more negative value in the order of iodide > bromide > chloride, therefore the copper can be receiving electron difficult when the halide have a smaller molecule. The $[\text{Cu}(\text{dptu})_2\text{Cl}]\text{H}_2\text{O}$ and $[\text{Cu}(\text{dptu})_2\text{Br}]\text{H}_2\text{O}$ complexes exhibit to different behavior from $[\text{Cu}(\text{dptu})_2\text{I}]\text{H}_2\text{O}$ complex. The $\text{Cu}(\text{dptu})_2\text{I}$ complex exhibits the redox peak of halide ion but in the case of the $\text{Cu}(\text{dptu})_2\text{Br}$ and $\text{Cu}(\text{dptu})_2\text{Cl}$ complexes, the redox peak of halide ion disappears due to the fact that the bond strength of chloride and bromide with copper is more than iodide and due to intramolecular hydrogen bond of the type NH-X ($\text{X} = \text{Cl}$, Br and I) type which can contribute to the stabilization of copper(I) complexes. But the stabilization of complexes is decreased when the halide is larger. Therefore the stabilization of complexes is decreased in the order of chloride < bromide < iodide.

The electrochemical behavior of $[\text{Cu}(\text{ptu})_4]\text{Cl}$ complex is different from those of other phenylthiourea complexes. In the case of $[\text{Cu}(\text{ptu})_4]\text{Cl}$ complex, the behavior of chloride in the complex is similar to free chloride due to the fact that the chloride does not have any bonds with copper. This result is in good agreement with the X-ray results which show that the complex consists of a $[\text{Cu}(\text{ptu})_4]^+$ cation and a Cl^- anion in molecule (Tanchatchawal, 2004). In the case of $[\text{Cu}_4(\text{ptu})_6\text{Br}_4]_2$ complex and $[\text{Cu}_4(\text{ptu})_6\text{I}_4]_2$ complex, the redox couples of halide ion are exhibited but the reactions are uncompleted. Therefore, the halides still have the interaction with copper but weak. The interaction is decreased in the order of bromide > iodide.

The electrochemical behaviors of all ethylenethiourea complexes are all similar. The cyclic voltammogram shows the redox reaction of copper(I)/(0). The reduction reaction of copper(I)/copper(0) process in the complexes appears to be more difficult than that of copper ion because the reduction potential shift to more negative value in the order chloride > bromide > iodide. The behaviors of halide in the complexes are similar to those of free halides, suggesting the weak bond with copper. The electrochemical behaviors of ethylenethiourea ligand in complexes disappear, suggesting that sulfur has a strong bond with copper.

The complexes of copper(I) halides and substituted thiourea exhibit distinctive electrochemical behaviors. This behavior is in good agreement with the x-ray results. This research can be the important basics to describe the reaction and mechanism of the complexes and can be the typical example of interpreting electrochemical results for similar complexes in their applications. The preliminary electrochemical results provide good prospects for substituted thiourea complexes to be a lead compound in the discovery of new modifier the compound for the determination of copper ion because they have the functional groups to form complex with metal, such as amine ($-\text{NH}_2$) and sulfur ($-\text{S}$), especially ethylenethiourea complexes which exhibit the distinct redox peaks of copper. With similar consideration, the knowledge from this research can also be applied fruitfully to corrosion and catalysis researches.