CHAPTER 5

CONCLUSIONS

The substituted 1,10-phenanthroline compounds, such as 1,10-phenanthroline-1-oxide, 2-carboxy-1,10-phenanthroline, 2-cyano-1,10-phenanthroline and 4-nitro-1,10-phenanthroline-1-oxide were synthesized. The purity and identification of 1,10-phenanthroline, 5-nitro-1,10-phenanthroline and the synthesized 1,10-phenanthroline derivatives are confirmed by their melting points and IR spectra. Owing to the limitation of solubilities of 1,10-phenanthroline and substituted 1,10-phenanthroline compounds in water, a mixed solvent of methanol and water (2:1) was used throughout this study. The pH of 1,10-phenanthroline solution and substituted 1,10-phenanthroline solution were controlled by McIlvaine buffer. Since the test solution gives some precipitates when the pH of the solution higher than 7.10, the pH of test solution studied is adjusted in the range of 3.20 to 7.10.

In the pH range of study the wave height of 2-carboxy-1,10-phenanthroline, 2-cyano-1,10-phenanthroline and 5-nitro-1,10-phenanthroline are pH-independence (see Table 9, 10 and 13). Moreover, the half wave potential of these three compounds are directly pH-dependence (see Figure 13, 15 and 20). This indicates the mechanisms of these three compounds in the pH range studied are the fast proton transfer preceding the electrode processes (10).

In the case of 1,10-phenanthroline both half wave potential and the wave height are pH dependence (see Table 3 and Figure 3).

This points to an acid-base reaction which either acidic or basic form is electroactive and the electroactive form can be generated from the electroinactive form at the rate that depends on pH (10). In addition one proton is consumed and 0.66 electron is used up in the electrode process for the pH range of 6.00 to 6.40. The process is diffusion controlled in the concentration of 2 to 5 mM 1,10-phenanthroline. For higher than 5 mM 1,10-phenanthroline the process seems to be adsorption controlled.

For 1,10-phenanthroline-1-oxide the wave height is independent on the pH range of study except at pH of 3.70 (see Table 7). The limiting current is obviously decreased. In addition, the dependence of half wave potential on pH for this system is unusual (see Figure 10); a jump of half wave potential at pH 4.10. The intersections of half wave potentials at pH of 4.10 and at pH of 5.70 may be the pK_1 and pK_2 of 1,10-phenanthroline-1-oxide.

In case of 4-nitro-1,10-phenanthroline-1-oxide. The half wave potential is directly dependent on the pH range studies (see Figure 17) and the wave height reaches a maximum at pH of 4.70 and then decreases as the pH increases further (see Table 11). This type of behavior must involve an acid-base equilibrium and it seems that the protonation reaction is the governing step (10).

It can be seen from this study that the well-defined waves of most compounds are shown in the pH range of 6.00 to 6.50. Most of these polarograms seem to be reversible processes, but the calculated values for testing reversibilities point to irreversible processes. The polarographic behavior of every compound studied

is summarized in Table 16. Since one proton transported is observed in 1,10-phenanthroline and its nitro derivatives, the protonation should occur at either nitrogen atom of 1,10-phenanthroline parent compound.

For substituent effects, it can be seen from Figure 22 that the decreasing order of the range of half wave potentials is 4-nitro-1,10-phenanthroline-1-oxide $>$ 5-nitro-1,10-phenanthroline $>$ 1,10-phenanthroline-1-oxide $>$ 2-carboxy-1,10-phenanthroline $\geqslant$ 2-cyano-1,10-phenanthroline $\geqslant$ 1,10-phenanthroline.

Further study should be made for the elucidation of the clear electrode process. Electrolysis at constant potential of the half wave potential of the compounds studied should be another project for identification of polarographic reduction products. Another interested project, by product of this study would be the relation of reaction constant or substituent constant to half wave potential.

Table 16 Summary   of polarographic behavior of 1,10-phenan-

throline and substituted 1,10-phenanthroline

Compound	pH	$E_{1/2}$ (V)	αn	m
1,10-Phenanthroline	6.00	-1.050	0.64	1.00
	6.40	-1.085	0.68	
1,10-Phenanthroline-1-oxide	6.10	-0.662	1.11	b
	6.50	-0.680	0.98	
4-Nitro-1,10-phenanthroline-1-oxide	6.05	-0.250	0.91	1.32
	6.50	-0.270	1.15	
5-Nitro-1,10-phenanthroline	6.00	-0.315	1.76	1.32
	6.40	-0.330	1.54	
2-Carboxy-1,10-phenanthroline	6.10	-1.045	a	a
	6.50	-1.082	a	
2-Cyano-1,10-phenanthroline	6.00	-1.118	a	a
	6.50	-1.140	a	

[a]
no calculation made due to its ill-defined wave

[b]
no calculation made because of the irregulated dependence of
the half wave potential on pH