

CHAPTER 2

EXPERIMENTAL

2.1 Chemicals

Chemicals and solvents used are of reagent grade. No further attempt was made to purify these compounds unless otherwise stated. Hygroscopic compounds were kept in a desiccator over anhydrous silica gel. Thrice deionized water used throughout this study was prepared as described in the procedure part of this chapter. Derivatives of 1,10-phenanthroline, such as 1,10-phenanthroline-1-oxide, 2-cyano-1,10-phenanthroline, 2-carboxy-1,10-phenanthroline, and 4-nitro-1,10-phenanthroline-1-oxide, were synthesized by the modified methods of E.J. Corey, A.L. Borrer, and T. Foglia (18).

2.2 Apparatus

Polarograms were obtained with a Radiometer Copenhagen Type PO4g. Since the test solutions had very low resistance (ca. 40 ohms, measured with a Conductivity Bridge Model RC 216 B2) an IR corrector was not employed.

The cell employed in all measurements was a jacketed compartment (Radiometer Copenhagen Model V 519). The reference electrode was a saturated calomel electrode, SCE (Radiometer Electrode Model K 501) and a dropping mercury electrode, DME (Radiometer Electrode

Model B 400) served as the indicator electrode. The pH measurements were obtained with a pH meter (Radiometer Copenhagen Type PHM 28). All potentials in this work were measured against SCE.

In order to purify nitrogen gas before being used to deaerate the test solution, three bubbling towers were placed in the gas line. The first tower contained amalgamated zinc metals in a chromic acid solution; for reduction of any contaminated oxygen gas. The second tower contained an alkaline solution for neutralization of the nitrogen gas. The last one was a trapped tower for prevention of any solution from the second tower to flow into the test solution.

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All measurements in this work, except where noted, were made at $30.0^{\circ} \pm 0.1^{\circ}$ by means of a circulating constant temperature bath (LAUDATHERMOSTAT Type K 2) with a designed cooling system by this laboratory. Tap water was run through a 3 meters copper coil being in an ice bath before running through the cooling coil of the circulating constant temperature bath.

The IR spectra of these derivatives were obtained with a PYE UNICAM SP 200 G. GRATING IR spectrophotometer.

2.3 Procedure

Thrice deionized water was obtained by passing the deionized water from a Permutit Portable Deminrolet Unit Mark 12 through a series of three columns (3.5 cm, I.D. and 55 cm, long). Amberite IR-45 (OH), anionic resins were packed in the first column, Amberite

IR-120 , cationic resins were in the second column and the last column was one half filled with the anionic resins and another half with the cationic resins. The supporting electrolyte 0.1 M NaClO_4 in this thrice deionized water showed no polarographic wave in the range 0 - 2.3 volts.

1,10-Phenanthroline-1-oxide was prepared as the method in reference (18). A mixture of 10 g 1,10-phenanthroline monohydrate (Merck) in 60 cm^3 of glacial acetic acid and 6 cm^3 of 30% hydrogen peroxide was refluxed at $70^\circ - 75^\circ\text{C}$ for 3 hours. After reflux the mixture was concentrated by rotary evaporator, 15 cm^3 of water was added and the mixture was again evaporated to the volume of approximately 10 cm^3 . The mixture was neutralized with sodium carbonate paste. The solid mass was extracted several times with chloroform and the extracts were evaporated. The resulting residue was dried in an oven at 50°C , ground to the fine powder, and re-extracted with chloroform. The combined chloroform extracts were dried over sodium sulfate, boiled with decolorizing charcoal, and evaporated to give 1,10-phenanthroline-1-oxide. Crystallization from chlorobenzene gave fine pale yellow needles.

2-Cyano-1,10-phenanthroline was synthesized from 1,10-phenanthroline-1-oxide. A mixture of 2.98 g of 1,10-phenanthroline-1-oxide and 3.0 g of potassium cyanide in 50 cm^3 of water was stirred while 3 cm^3 of benzoyl chloride was added dropwise. The total addition required 15 minutes and the reaction was stirred for an additional 15 minutes. The precipitates were collected by suction filtration, washed with water, and dried at $60^\circ - 70^\circ\text{C}$. Crystallization from ethanol gave the light tan needles.

2-Carboxy-1,10-phenanthroline was prepared from 2-cyano-1,10-phenanthroline. A mixture of 1.0 g of 2-cyano-1,10-phenanthroline in 10 cm³ of 95% ethanol and 0.8 g of sodium hydroxide in 5 cm³ of water was refluxed until the evolution of ammonia ceased (about 2 hours). The solution was cooled to room temperature and made slightly acid with concentrated hydrochloric acid. The solvent was removed in vacuo. The residue was heated in 10 cm³ of water on the steam bath and filtered. The light tan product was crystallized from ethanol, giving the white solid.

4-Nitro-1,10-phenanthroline-1-oxide was synthesized by heating a mixture of 2.0 g of 1,10-phenanthroline-1-oxide in 10 cm³ concentrated sulfuric acid (Sp.gr. 1.84) and 1.1 g of potassium nitrate on the steam bath for one hour. An additional 1.1 g of potassium nitrate was added and the heating continued for a hour. The mixture was poured into 25 g of ice and neutralized with solid sodium carbonate. The solution was extracted with chloroform. The chloroform extracts were dried by evaporation. The residue was stirred with 20 cm³ of water, filtered and dissolved in dilute sulfuric acid. Neutralization with ammonia solution gave a yellow solid which was collected by suction filtration and dried. Crystallization from chloroform-ether mixture gave the yellow solid.

Corresponding to the solubilities of 1,10-phenanthroline and its derivatives in water (see Chapter 3), the mixed solvent of methanol (Mallinckrodt) and thrice deionized water (2:1) was used for this polarographic study. 0.1 M NaClO₄ in the mixed solvent



was used as supporting electrolyte. Sample solutions were freshly prepared by dissolving the appropriated substances in absolute methanol. Stock solutions of 1,10-phenanthroline and its derivatives were prepared as concentration of 0.100M and 0.010M, respectively; except 2-carboxy-1,10-phenanthroline and 4-nitro-1,10-phenanthroline-1-oxide the concentrations were 0.006M, 0.003M, respectively. The buffer solutions used for the polarographic investigations of 1,10-phenanthroline and its derivatives were McIlvaine Buffer (0.2M disodium hydrogen phosphate and 0.1M citric acid). The composition of disodium hydrogen phosphate and citric acid was varied to give the pH desired.

The test solution was prepared in a 50 cm³ volumetric flask by mixing the appropriated amount of the stock solution of the compound under investigated (giving final concentration of 5×10^{-4} M, except 1,10-phenanthroline concentration 4×10^{-3} M), 16.7 cm³ of the appropriated buffer solution, 10 cm³ of 0.5 M sodium perchlorate, and absolute methanol to give a final volume of 50 cm³. This solution gives approximately 67% methanol.

Before the test solution was placed in the polarographic cell, the test compartments were washed two or three times with thrice deionized water and finally washed with the absolute methanol. The test solution was poured into the test compartment, then deaerated with nitrogen for ten minutes by means of a disposable capillary. During measurements, a stream of nitrogen was maintained over the solution surface to prevent the redissolution of oxygen. The desired potential range, current sensitivity, mercury reservoir

height, scan rate and polarity were set on the instrument and the polarograms were recorded.