

## CHAPTER 3

### PHYSICAL PROPERTIES OF 1,10-PHENANTHROLINE AND SUBSTITUTED 1,10-PHENANTHROLINE COMPOUNDS

Since most substituted 1,10-phenanthroline compounds were synthesized as described in chapter 2, purity and identification of these compounds must be confirmed. Melting point and IR spectrophotometric method were chosen for the above purposes because of their simplicity and no solvent needed.

A solvent used for polarographic study of organic compound influences the electrode process. Adsorption effects are extraordinary pronounced with heterocyclic compounds, especially those containing nitrogen. However, an increase in the organic solvent content in the aqueous-organic mixture results in a decrease in the adsorptivity of organic substances on mercury and brings about a change in the shape of the adsorption isotherm (19).

To avoid the adsorption effect and the complexity of non-aqueous system, polarographic study of 1,10-phenanthroline and its derivatives were investigated in the aqueous-organic solvent. Solubilities of these compounds were qualitatively determined.

#### 3.1. Melting points and IR spectra

The purity and identification of 1,10-phenanthroline, 5-nitro-1,10-phenanthroline and the synthesized 1,10-phenanthroline

derivatives were confirmed by means of its melting point and IR spectrum as shown in Table 1.

Since every compound studied has illustrated aromatic characteristic peaks in IR spectrum, these peaks are not included in Table 1.



The melting points of 2-cyano- and 2-carboxy-1,10-phenanthroline obtained (see Table 1) are different from reference 18 (from reference 18 the melting points are  $237^{\circ}$ - $238^{\circ}$  C and  $209^{\circ}$ - $210^{\circ}$ C, respectively). However, the range of melting points obtained for both compounds are characterized as pure compounds and the IR spectra of both compounds show absorption peaks of cyano group for 2-cyano-1,10-phenanthroline and carboxylic group for 2-carboxy-1,10-phenanthroline. No impurity peak obtains in both spectra. Thus the compounds should be 2-cyano and 2-carboxy-1,10-phenanthroline which have purity enough for polarographic studies.

For other compounds, the melting points and IR spectra are corresponded to those obtained in the literature.

### 3.2 Solubilities

The solubilities of 1,10-phenanthroline and its derivatives in methanol and in water were tested. The results are given in Table 2. In all cases, about 0.02 g of the compound to be studied was added to approximately  $5 \text{ cm}^3$  of water or methanol. The data presented in Table 2 must be considered with the realization that it is the observation of only one person. Thus, what may be judged

Table 1 Melting points and IR spectra of 1,10-phenanthroline and its derivatives

Name of compound	m.p.(°C)	Characteristic absorption <sup>a</sup> peak, shown in IR spectrum (cm <sup>-1</sup> )
1,10-Phenanthroline	121° - 123°	1510, 1590 (C = N and C = C Stretch) 3460 (-NH)
1,10-Phenanthroline-1-oxide	177° - 179°	1580 (C = N and C = C Stretch) 1280 (-N-O Stretch)
2-Cyano-1,10-phenanthroline	230° - 232°	1500, 1580 (C = N and C = C Stretch) 2260 (-C ≡ N Stretch)
2-Carboxy-1,10-phenanthroline	205° - 208°	1600 (C = N and C = C Stretch) 1360 (-OH deformation, -C-O or  Stretch) 1730 (  Stretch) 3500 (-OH Stretch)
4-Nitro-1,10-phenanthroline-1-oxide	158°(d)	1490, 1610 (C = N and C = C Stretch) 1340 (C-NO <sub>2</sub> or N-O Stretch) 1530 (C-NO <sub>2</sub> Stretch)
5-Nitro-1,10-phenanthroline	205° - 206°	1600 (C = N and C = C Stretch) 1320, 1520 (C-NO <sub>2</sub> Stretch)

<sup>a</sup>

KBr pellet cells were used

Table 2 Solubilities of 1,10-phenanthroline and its derivatives in water and methanol

Name of compound	Solubility in water	Solubility in methanol
1,10-Phenanthroline	slightly soluble	very soluble
1,10-Phenanthroline-1-oxide	soluble	very soluble
2-Cyano-1,10-phenanthroline	insoluble	soluble
2-Carboxy-1,10-phenanthroline	insoluble	soluble
4-Nitro-1,10-phenanthroline-1-oxide	slightly soluble	soluble
5-Nitro-1,10-phenanthroline	insoluble	soluble

to be a soluble compound by one person may not be so judged by another.

1,10-Phenanthroline and most of its derivatives are slightly soluble or insoluble in water, and they are very soluble or soluble in methanol (see Table 2). A variety of the ratios of methanol and water were studied. It was found that the optimum ratio for these systems is 2:1 (methanol:water). This ratio of mixed solvent give about 67% methanol and were used as solvent for the polarographic study. The back ground electrolyte, 0.1 M  $\text{NaClO}_4$ , in this solvent at various pH of the buffer solution shows no polarographic wave in the range of potential of 0 to 2.3 volts.