RESEARCH ARTICLES

J. Sci. Soc. Thailand 1 (1975), 114–119

POLAROGRAPHIC BEHAVIOR OF 1,10-PHENANTHROLINE IN AQUEOUS METHANOL SYSTEM

PROESPUN KANATHARANA and SITTICHAI LEEPIPATPIBOON

Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok.

(*Received 23 April 1975*)

Summary

The polarographic behavior of 1,10-*phenanthroline was studied in ca.* 67% *methanol in the pH range of* 3.20 *to* 6.80. *A well-defined wave is resulted in the pH range of* 6.00 to 6.50. *However, the electrode process of* 1,10-*phenanthroline in this pH range is irreversible. In addition, the electrode process of* 1,10-*phenanthroline in the concentration range of* 2.0 *to* 5.0 *mM is proved to be diffusion controlled at pH* 6.50. *The dependence of the half wave potential and the wave height on the pH range of* 3.20 to 6.80 *for* 1,10-*phenanthroline are reported. The proton transported and electron transferred mechanism of* 1,10-*phenanthroline in ca.* 67% *methanol are also discussed.*

Introduction

1,10-Phenanthroline or *o*-phenanthroline, one of diazaphenanthrenes with one nitrogen atom in each of the outer rings, has a well-marked tendency to combine with various metallic ions, especially with divalent ions of the transition groups. The relative inertness of 1,10-phenanthroline toward chemical reactions other than salt-formation or chelation is a significant asset in the analytical application. The polarographic reduction of 1,10-phenanthroline in aqueous and aprotic media have been recently investigated. Millefiori[1] reported the polarographic reduction potentials and the reduction mechanism of 1,10-phenanthroline in acetonitrile. Polarograms of 1, 10-phenanthroline in aqueous and aprotic solvents were also studied[2]. Little can be said about the literature concerning electrochemical studies of 1, 10-phenanthroline. This was a contributing reason for the present study.

Experimental

Chemicals and Reagents

Chemicals and solvents used are of reagent grade. No further attempt was made to purify these compounds unless otherwise stated. Thrice deionized water used throughout this study was prepared 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).

Amberlite IR–45 (OH), anionic resins were packed in the first column, Amberlite 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 potential range of 0 to –2.3 volts.

Owing to the limitation of solubility and the complicated reduction mechanism[2] of 1, 10-phenanthroline in aqueous solution, the mixed solvent of methanol (Mallinckrodt Chemical Works, St. Louis, Mo.) and thrice deionized water (2:1) was used for this study.

The buffer solutions used were McIlvaine buffer (0.2 M disodium hydrogen phosphate and 0.1 M citric acid). The composition of disodium hydrogen phosphate and citric acid was varied to give the pH desired. The supporting electrolyte, 0.1 M $NaClO_4$, in the mixed solvent at various pH of the buffer solution showed no polarographic wave in the potential range of 0 to –2.3 volts.

The test solutions were freshly prepared by mixing the appropriate amount of 0.1 M 1, 10–phenanthroline and buffer in 0.1 M $NaClO_4$ in ca. 67% methanol.

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 V519). The reference electrode was a saturated calomel electrode, SCE (Radiometer Electrode Model K501) and a dropping mercury electrode, DME (Radiometer Electrode Model B400) served as the indicator electrode. The pH measurements were obtained with a pH meter (Radiometer Copenhagen Type PHM28). 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, the second contained 10% alkaline solution, and the last one was a trapped tower.

All measurements in this work, except where noted, were made at 30.0 ± 0.1°C by means of a circulating constant temperature bath (Laudathermostat Type K2) with a designed cooling system by this laboratory; tap water was run through a 3-meter-copper coil being in an ice bath before running through the cooling coil of the circulating constant temperature bath.

Results and Discussion

Polarograms of 1,10-phenanthroline systems at pH 4.90, 6.40, and 6.80 are shown in Fig 1. The electrochemical data obtained from polarograms of 1,10-phenanthroline systems in the pH range of 3.20 to 6.80 are listed in Table I. A well-defined wave

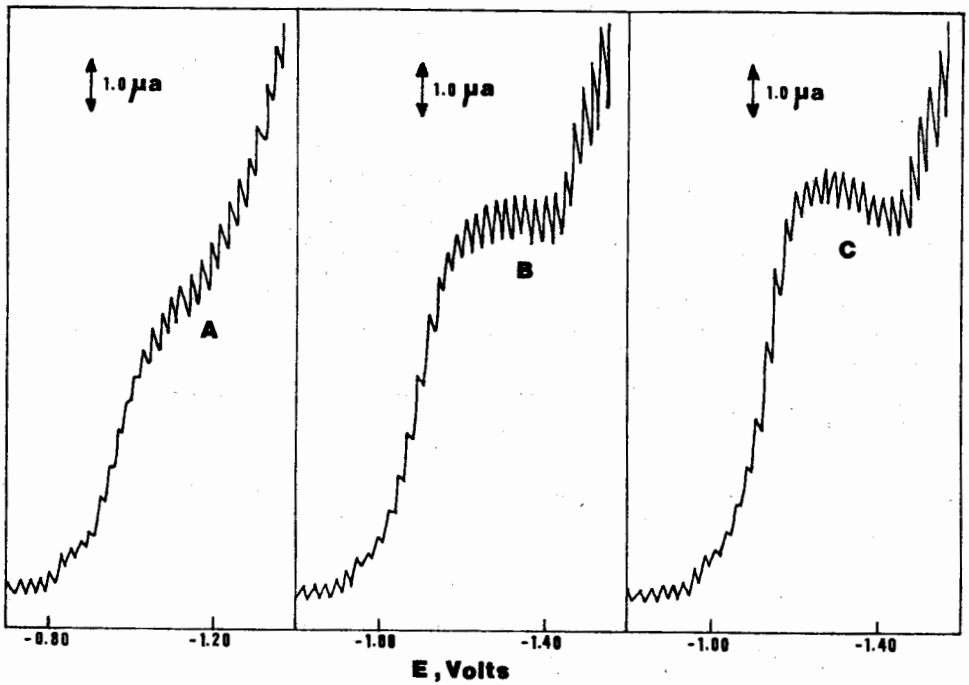

Fig. 1 Polarograms of 4.0 mM 1,10-phenanthroline in ca. 67% methanol, 0.1 M $NaClO_4$ at pH (A) 4.90, (B) 6.40, and (C) 6.80.

of 1,10-phenanthroline is obtained from the system in the pH range of 6.00 to 6.50. At pH 6.50, the limiting current of 1,10-phenanthroline is proportional both to 1,10-phenanthroline concentration (from 2.0 to 5.0 mM; least squares correlation factor > 0.99) and to the square root of mercury height (mercury height from 25.0 to 45.0 cm; least squares correlation factor > 0.96). Thus, the electrode process of the system is diffusion controlled[3].

Effect of pH

The effect of pH on the half wave potential for 1,10-phenanthroline systems is shown in Fig. 2A. As the pH of 1,10-phenanthroline system increases its half wave potential shifts to more negative potential. The plot of the half wave potential versus pH shows a linearity for the pH range of 4.90 to 6.80, giving a calculated least squares slope of 0.09 which is equal to $-0.060m/\alpha\ n$ at 30.0°C (where m = number of protons, α = the electron transfer coefficient, and n=number of electrons transferred)[3]. Thus, the $m/\alpha\ n$ is 1.50.

For the pH range of 3.20 to 4.50 the polarographic wave of 1,10-phenanthroline is hardly observed. It seems that the decomposition curve of the supporting electrolyte at lower pH shifts to more positive potential. This may come from the larger amount of protons in the lower pH solution. At pH 6.80, the polarographic maximum of 1, 10-phenanthroline begins to occur.

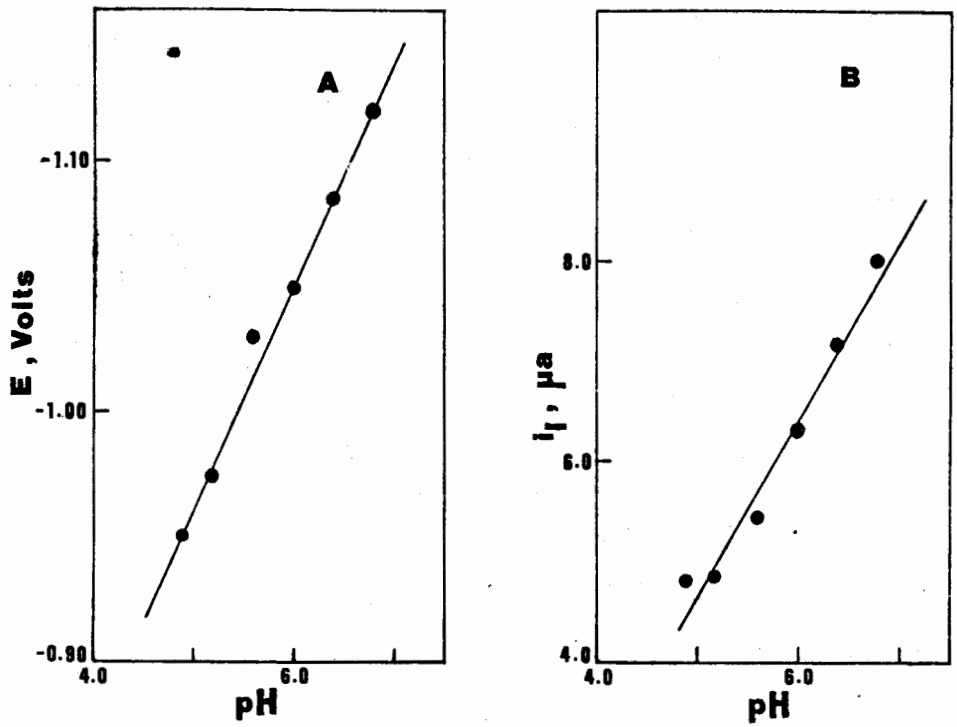

Fig. 2. Effect of pH on (A) half wave potential and (B) wave height of 4.0 mM 1,10-phenanthroline in ca. 67% methanol, 0.1 M $NaClO_4$. The lines are calculated least squares lines.

In addition, the polarographic wave height of 1,10-phenanthroline is pH dependent; the limiting current is directly proportional to the pH from 5.20 to 6.80 (see Fig 2B).

The dependence of both half wave potential and wave height of 1,10-phenanthroline on pH indicates an acid-base reaction in 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[4].

Reversibility

Since polarograms of 1,10-phenanthroline systems at pH 6.00 and 6.40 are well-defined waves (Table I), the reversibilities of both waves are tested. Data for testing reversibilities of 1,10-phenanthroline systems are shown in Table II. The plot of the potential against its log i/i_d-i, where i_d is the diffusion current, gives a calculated least squares slope of –0.10 for pH 6.00 and –0.11 for pH 6.40. This slope is equal to $-0.060/\alpha$ n at 30° C[3,4]. Thus, the total number of electron transfer (α n) in 1,10-phenanthroline system at pH 6.00 and at pH 6.40 are 0.60 and 0.54, respectively.

Table I

Polarographic data of 1,10-phenanthroline [a] in ca. 67% methanol

pH	$E_{\frac{1}{2}}$ (V)	i_1 (μa)	I_1 [b]	Remarks
3.20	—	—	—	c
3.80	—	—	—	c
4.50	—	—	—	c
4.90	–0.950	4.80	1.20	ill-defined wave
5.20	–0.975	4.84	1.21	ill-defined wave
5.60	–1.030	5.44	1.36	ill-defined wave
6.00	–1.050	6.32	1.58	well -defined wave
6.40	–1.085	7.16	1.79	well-defined wave
6.80	–1.120	8.00	2.00	ill-defined wave

[a] concentration of 1, 10-phenanthroline is 4.0 mM

[b] mercury height =45.0 cm; $m^{\frac{2}{3}} t^{\frac{1}{6}}$ =2.27

[c] polarographic wave is hardly observed.

Table II

Data for testing reversibilities of 1, 10-phenanthroline systems

E_{de} (V)	i (μa)	log $i/(i_d-i)$
pH 6.00 (i_d 6.32 μa)		
–0.985	1.34	–0.57
–1.000	1.58	–0.48
–1.015	2.26	–0.25
–1.030	2.64	–0.14
–1.050	3.30	+0.04
–1.065	4.02	+0.24
pH 6.40 (i_d 7.16 μa)		
–1.025	1.42	–0.60
–1.038	1.72	–0.50
–1.050	2.17	–0.37
–1.063	2.46	–0.28
–1.078	3.02	–0.14
–1.090	3.42	–0.04

Since the calculated total number of electron transfer in both systems are not integers, the mechanism for electron trnsfer of 1,10-phenanthroline in the pH range of 6.00 to 6.40 should be irreversible [3,4].

As mentioned above the $m/\alpha n$ is 1.50, so m is 0.90 for 1,10-phenanthroline system at pH 6.00 and 0.82 for the system at pH 6.40. Therefore, one proton is consumed in 1, 10-phenanthroline system at the pH range of 6.00 to 6.40.

References

1. Millefiori, S. (1970) *J. Heterocycl. Chem.* **7**, 145–148.
2. Shozo, K., Junichi, N. and Eiji, I. (1971) *Rev. Polarogr.* **17**, 1–15.
3. Zuman, P. and Perrin, C.L. (1969) *Organic Polarography*, pp. 177–195, John Wiley & Sons, Inc., New York.
4. Zuman, P. (1969) *The Elucidation of Organic Electrode Processes* (Meites, L., ed.), pp. 11 11–19, Academic Press, New York.

บทคัดย่อ

การศึกษาคุณสมบัติทาง polarography ของ 1,10—phenanthroline ในสารละลายที่ประกอบด้วย methanol ประมาณ 67 % ในช่วง pH 3.20 ถึง 6.80 ปรากฏว่าสารประกอบนี้ให้ well-defined wave ในช่วง pH 6.00 ถึง 6.50 และ electrode process ของ 1,10-phenanthroline ในช่วง pH นี้เป็น irreversible process นอกจากนี้ยังได้พิสูจน์ว่า electrode process ในช่วงความเข้มข้นของ 1,10 - phenanthroline 2.0—5.0 mM ที่ pH 6.50 เป็น diffusion controlled process ค่าของ half wave potential และ wave height ของ 1,10-phenanthroline ขึ้นอยู่กับ pH และยังได้วิจารณ์ mechanism ของการเปลี่ยนแปลงของ proton และ electron ของสารประกอบนี้