POLAROGRAPHIC BEHAVIOR OF 1,10-PHENANTHROLINE

AND SUBSTITUTED 1,10-PHENANTHROLINE COMPOUNDS

Since the resistances of the test solutions for the range

of concentrations investigated are about 40 ohms and the maximum

limiting current obtained is about 8 microamperes, the product of

IR drop is negligible when compared to the working potential

studied. Thus all potentials in this thesis were recorded without

the IR drop correction.

4.1 1,10-Phenanthroline

Electrochemical data obtained from polarograms of 1,10-phenan-

throline systems are shown in Table 3.

4.1.1 Effect of pH on the half wave potential

The half wave potentials of most organic compounds are pH

dependence. Thus a variation of pH of the test solution was examined.

The concentration of 1,10-phenanthroline understudied

at various pH is 4×10^{-3}M. The pH of test solutions are controlled

by McIlvaine buffer as described in chapter 2. The pH recorded in

this study is the final pH of the test solution for polarographic

study.   The polarograms of 1,10-phenanthroline at pH 3.80 and pH

6.40 are shown in Figure 1 and at pH 4.90 is in Figure 2.

Table 3 Effect of pH on the half wave potential for

1,10-phenanthroline system

pH	$E_{1/2}$ (V)	$i_1 (\mu A)^b$	I_1	Remarks
3.20	a	-	-	-
3.80	a	-	-	-
4.50	a	-	-	-
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
 polarographic wave is hardly observed

b
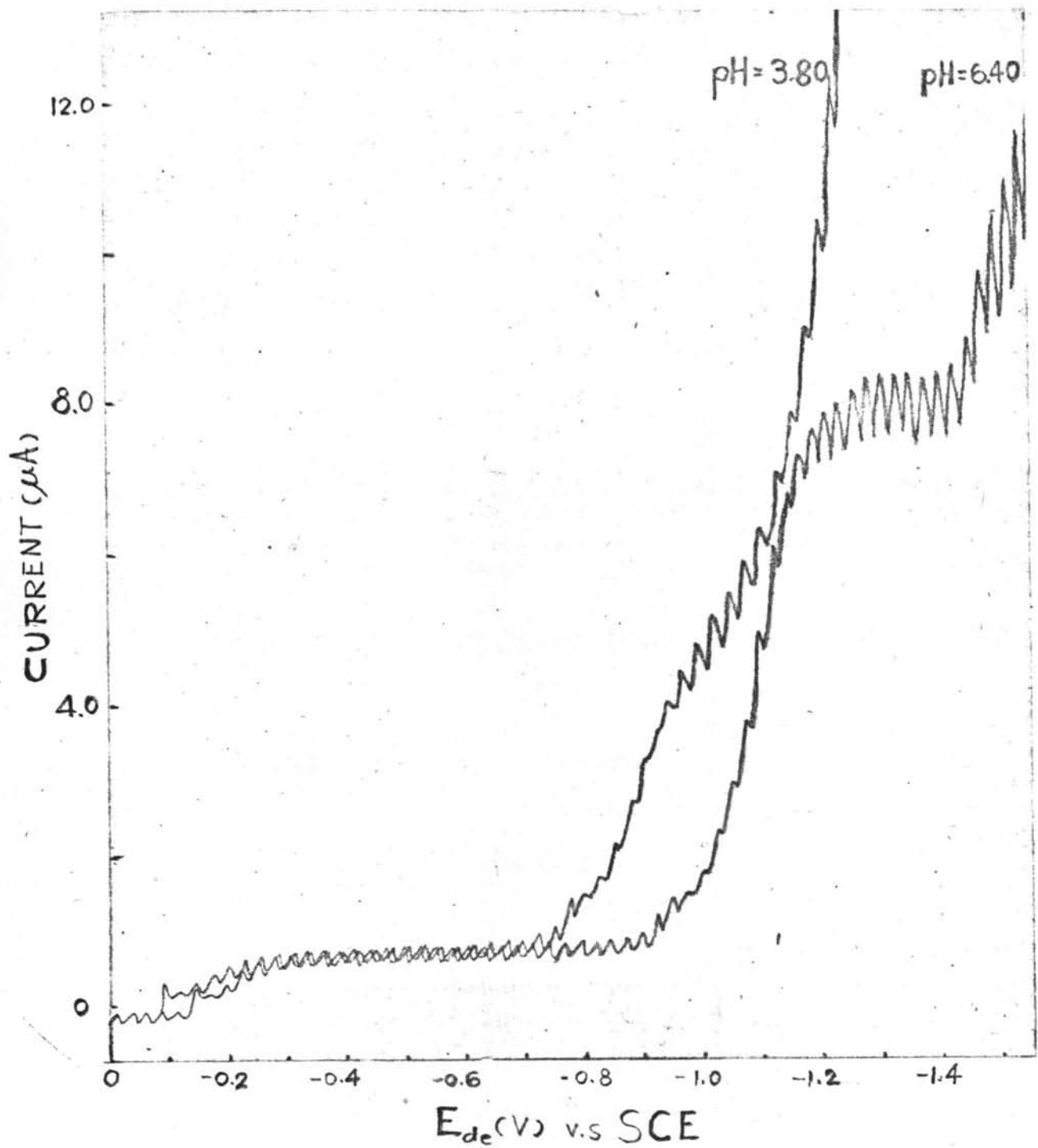 mercury height = 45 cm; $m^{\frac{2}{3}} t^{\frac{1}{6}}$ = 2.27

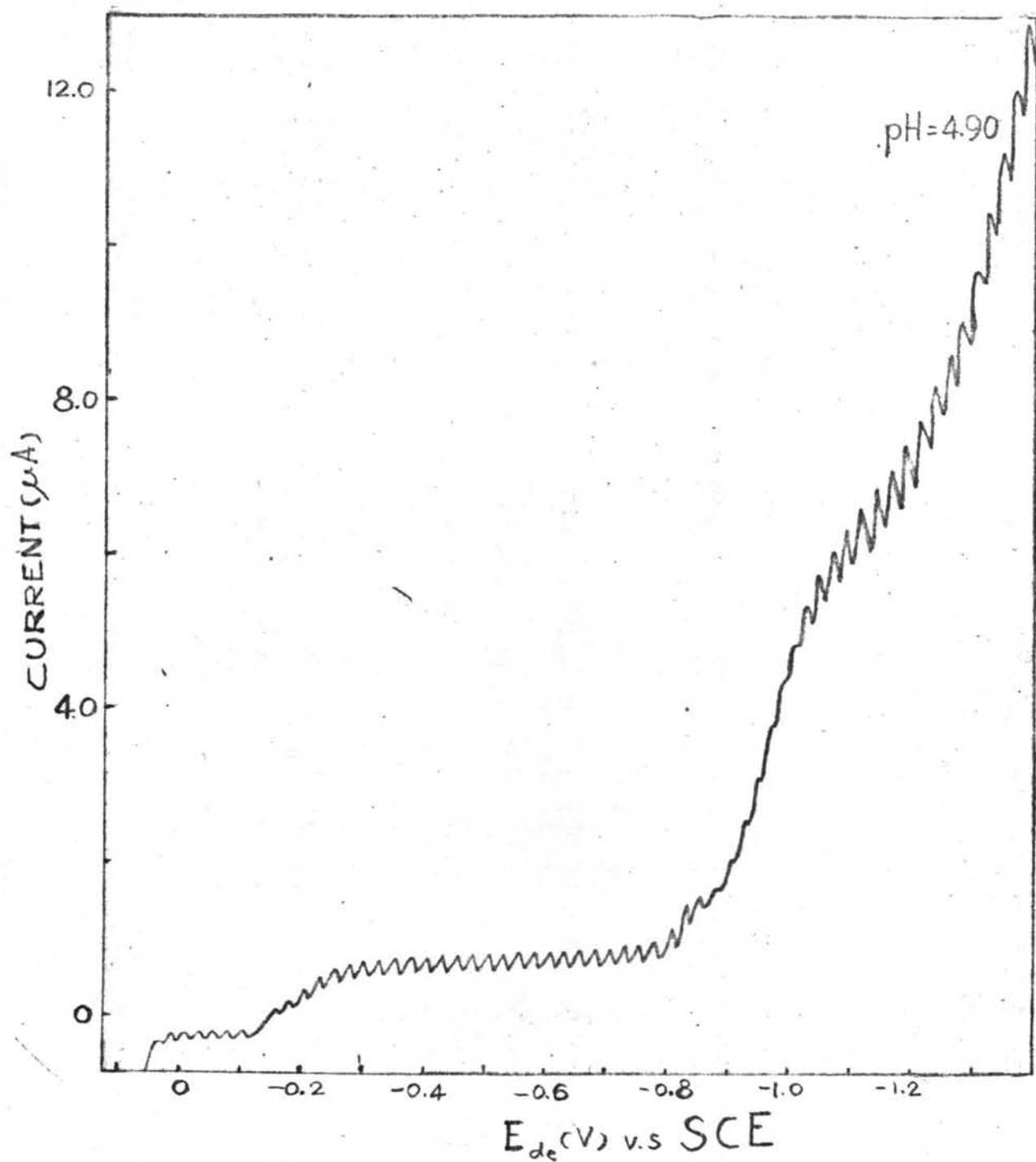Figure 1   The polarograms of 1,10-phenanthroline at pH 3.80 and 6.40

Figure 2   The polarogram of 1,10-phenanthroline at pH 4.90

The effect of pH on the half wave potential for 1,10-phenanthroline system is shown in Table 3 and Figure 3. 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 range of pH 4.90 to 6.80, giving a slope of -0.09. By equation (13) the $m/\alpha n$ for 1,10-phenanthroline is 1.50.

For pH 3.20 to 4.50 the polarographic wave is hardly observed (see Figure 1). It seems that the decomposition curve of the back ground electrolyte at the lower pH shifts to more positive potential (see Figure 1). This may come from the larger amount of protons in the lower pH solution.

4.1.2 Diffusion controlled process

Corresponding to Table 3 the 1,10-phenanthroline systems at pH 6.00 and pH 6.40 give well-defined waves for polarographic study. Therefore the electrode process of 1,10-phenanthroline at pH 6.50 is investigated. Two methods for testing of a diffusion controlled process were used here, by varying the concentration of 1,10-phenanthroline at a constant mercury height and by varying the mercury height at any fixed concentration in the range of study. The results of limiting currents at various concentrations of 1,10-phenanthroline are shown in Table 4. The dependence of limiting current on concentration of 1,10-phenanthroline system is illustrated in Figure 4. The line in Figure 4 indicates that the system is a diffusion controlled process.

Data of 1,10-phenanthroline systems at various mercury heights are shown in Table 5. The plot of the limiting current
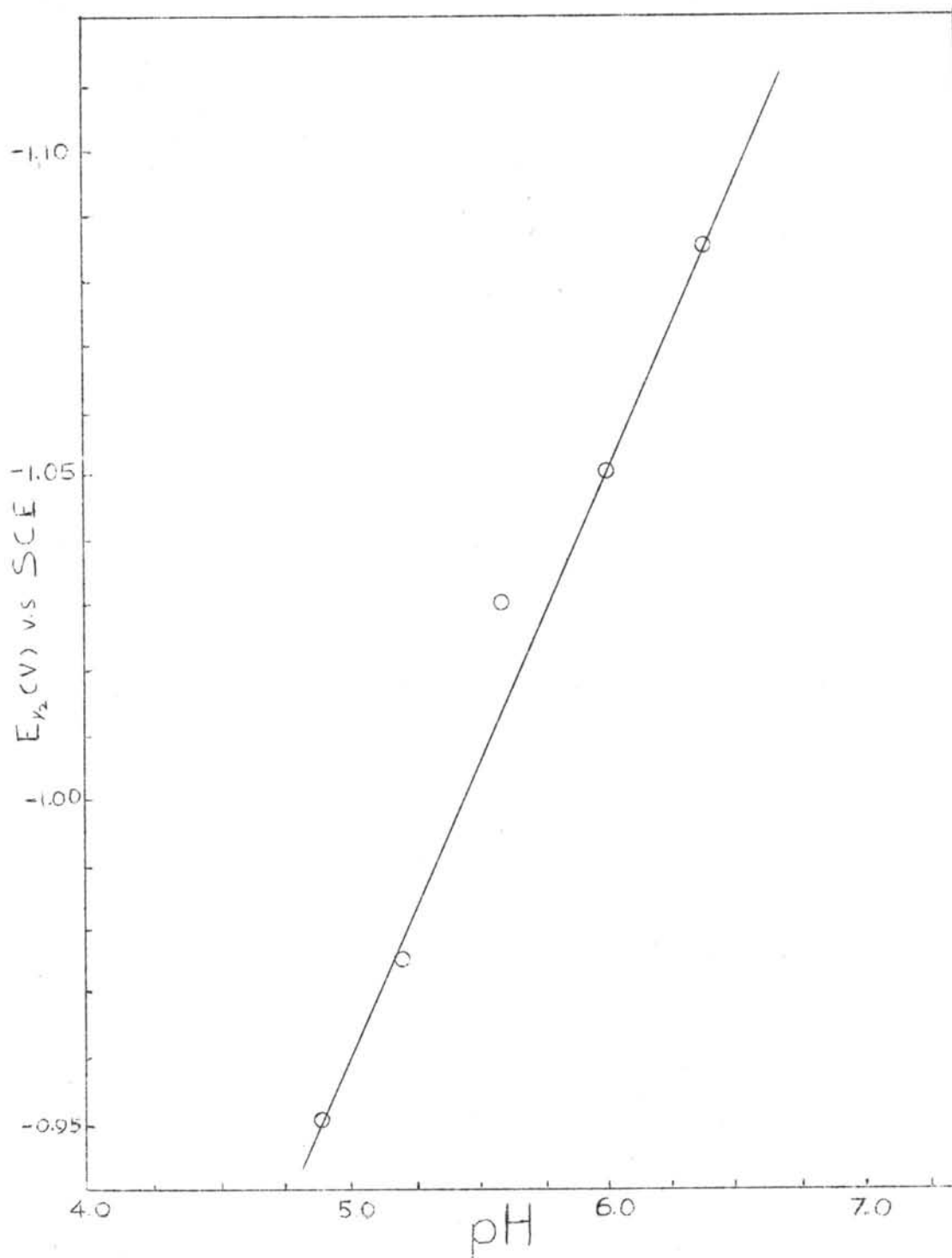
Figure 3   The effect of pH on the half wave potential for

1,10-phenanthroline system

Table 4 Data of 1,10-phenanthroline systems at a

constant mercury height[a]

Concentration of 1,10-phenanthroline (mM)	i_1 (μA)
2.00	7.09
2.50	7.25
3.00	7.40
3.50	7.94
4.00	7.87

[a] mercury height = 45 cm; $m^{\frac{2}{3}}t^{\frac{1}{6}}$ = 2.27

Table 5 Data of 1,10-phenanthroline systems[a] at

various mercury heights

h (cm)	$h^{\frac{1}{2}}$	i_1 (μA)
25.0	5.0	4.98
30.0	5.5	5.66
35.0	5.9	6.16
40.0	6.3	6.46
45.0	6.7	7.69

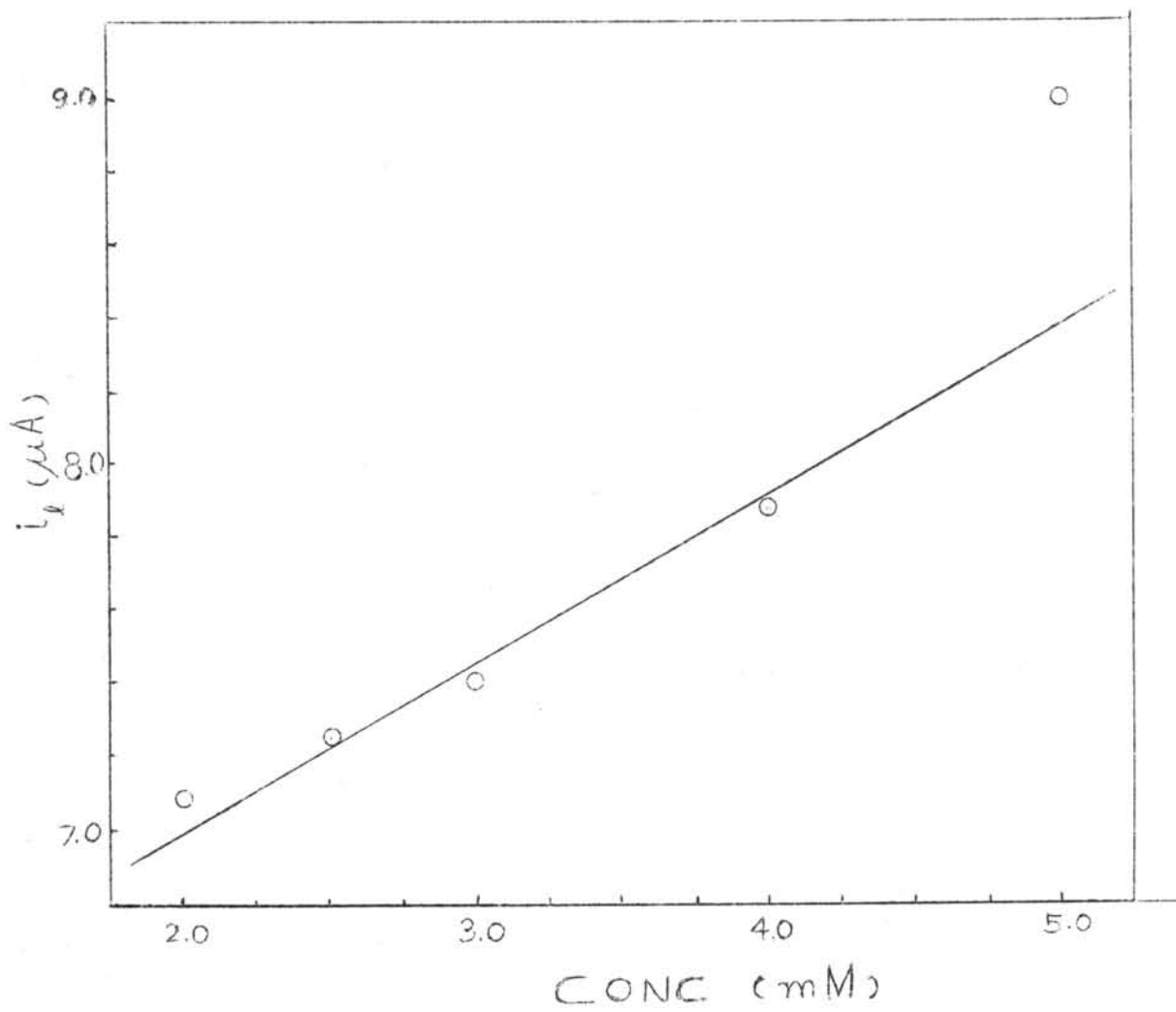[a] the concentration of 1,10-phenanthroline is 4 mM

Figure 4 The dependence of limiting current on the concentration of 1,10-phenanthroline

against the square root of the mercury height (see Figure 5)
points to a straight line. This dependence of limiting current on
the square root of the mercury height demonstrates the system is
of diffusion controlled process.

Therefore, 1,10-phenanthroline system at pH 6.50 which
shows a well defined wave has a diffusion controlled electrode
process. The same conclusion may be drawn out for 1,10-phenanthro-
line system at pH 6.00(well-defined wave) or any pH media which
give the well defined wave.

4.1.3 Reversibility

According to Table 3 polarograms of 1,10-phenanthroline
at pH 6.00 and 6.40are well-defined waves, the reversibilities of
both waves are tested. Data for testing reversibilities of the
1,10-phenanthroline systems are shown in Table 6. The plot of the
potential against its log $i/i_d - i$ (see Figure 6 and 7) gives a
slope of -0.094 for pH 6.00 and a slope of -0.087 for pH 6.40. The
slope of this plot is equal to $-2.303 \, RT/\alpha nF$. Thus, the number of
electrons transfer in 1,10-phenanthroline system at pH 6.00 and 6.40
are 0.64 and 0.68, respectively.

Since the calculated number of electrons transfer in
both systems are not integers, the mechanisms for 1,10-phenanthroline
systems at the pH range of 6.00 to 6.40should be an irreversible
electrode process and the average number of electrons transfer is
0.66.

As mentioned above the ratio of $m/\alpha n$ is 1.50 (see
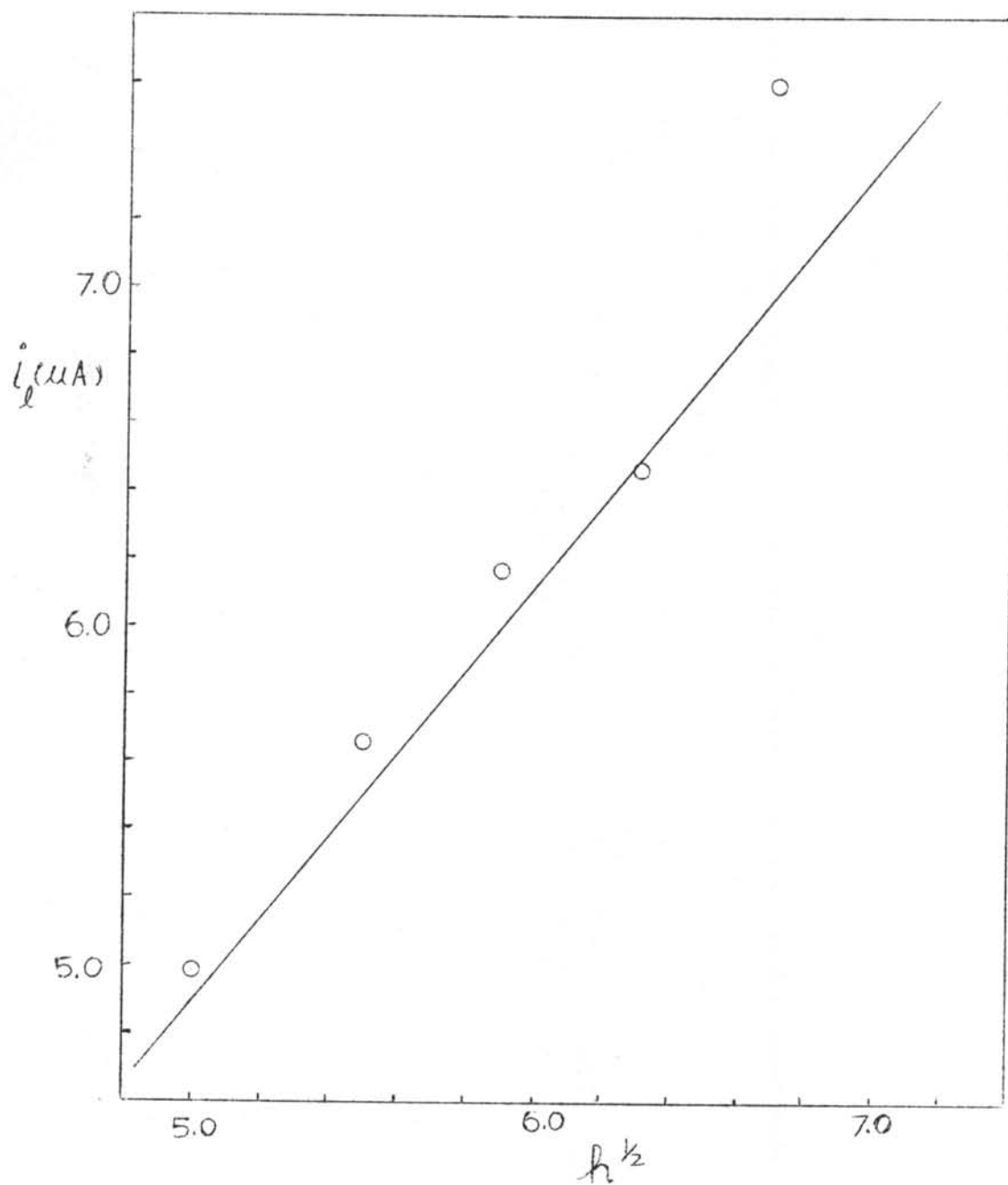and the average number of electrons transfer is 0.66,

Figure 5   The dependence of limiting current on the square
root of mercury height for 1,10-phenanthroline

Table 6 Data for testing reversibilities of 1,10-phenanthroline at pH 6.00 and at pH 6.40

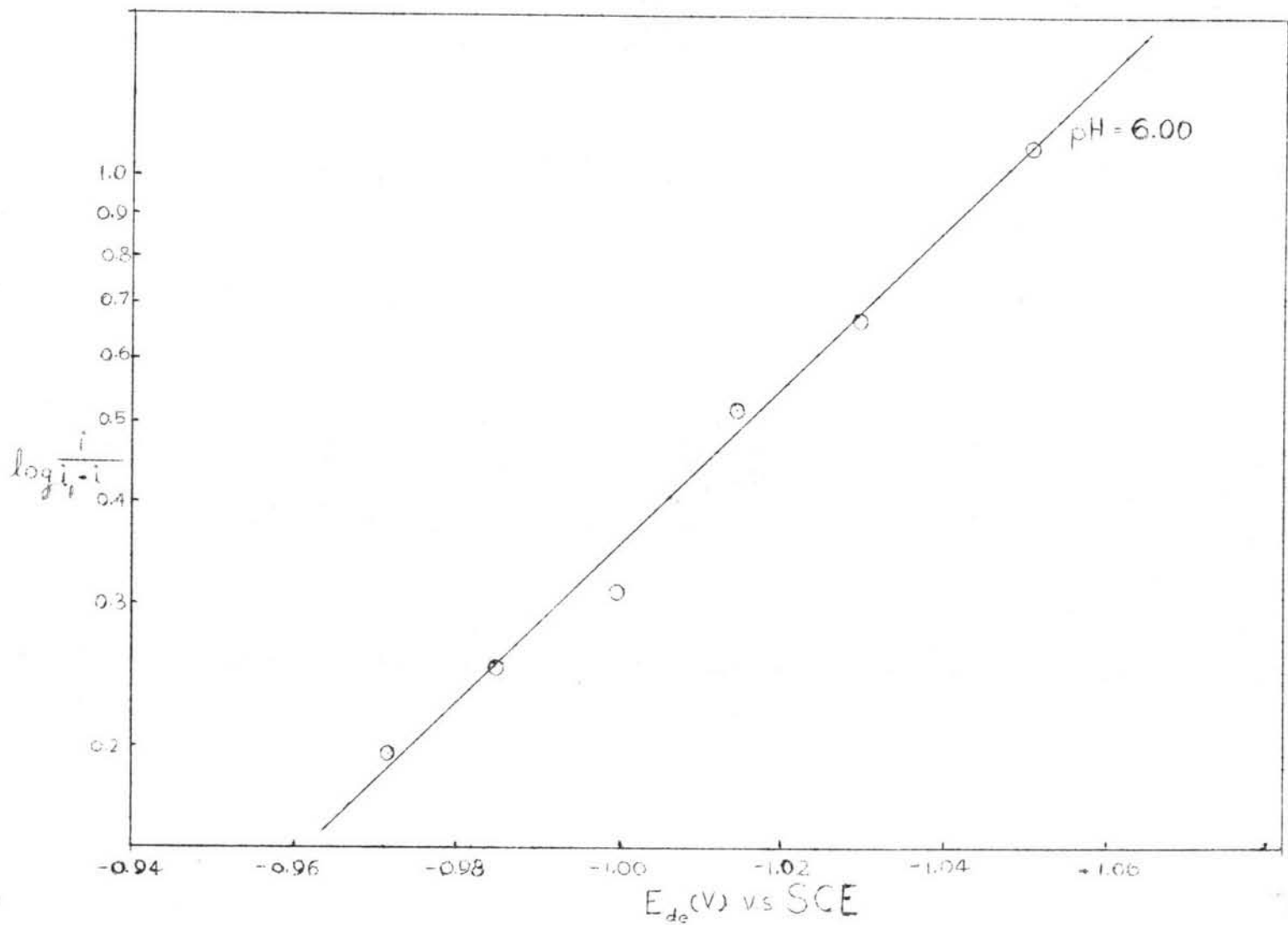| i (µA)	$\log \dfrac{i}{j_1 - i}$	$E_{de}(V)$
pH = 6.00		
1.09	0.19	-0.972
1.34	0.25	-0.985
1.58	0.31	-1.000
2.26	0.52	-1.015
2.64	0.67	-1.030
3.30	1.01	-1.050
4.02	1.65	-1.065
4.74	2.60	-1.080
pH = 6.40		
1.32	0.22	-1.010
1.42	0.24	-1.025
1.72	0.31	-1.038
2.17	0.42	-1.050
2.46	0.51	-1.063
3.02	0.71	-1.078
3.42	0.88	-1.090
4.45	1.57	-1.110

Figure 6   Graph of $\log \frac{i}{i_1 - i}$ versus E_{de} for 1,10-phenanthroline system at pH 6.00
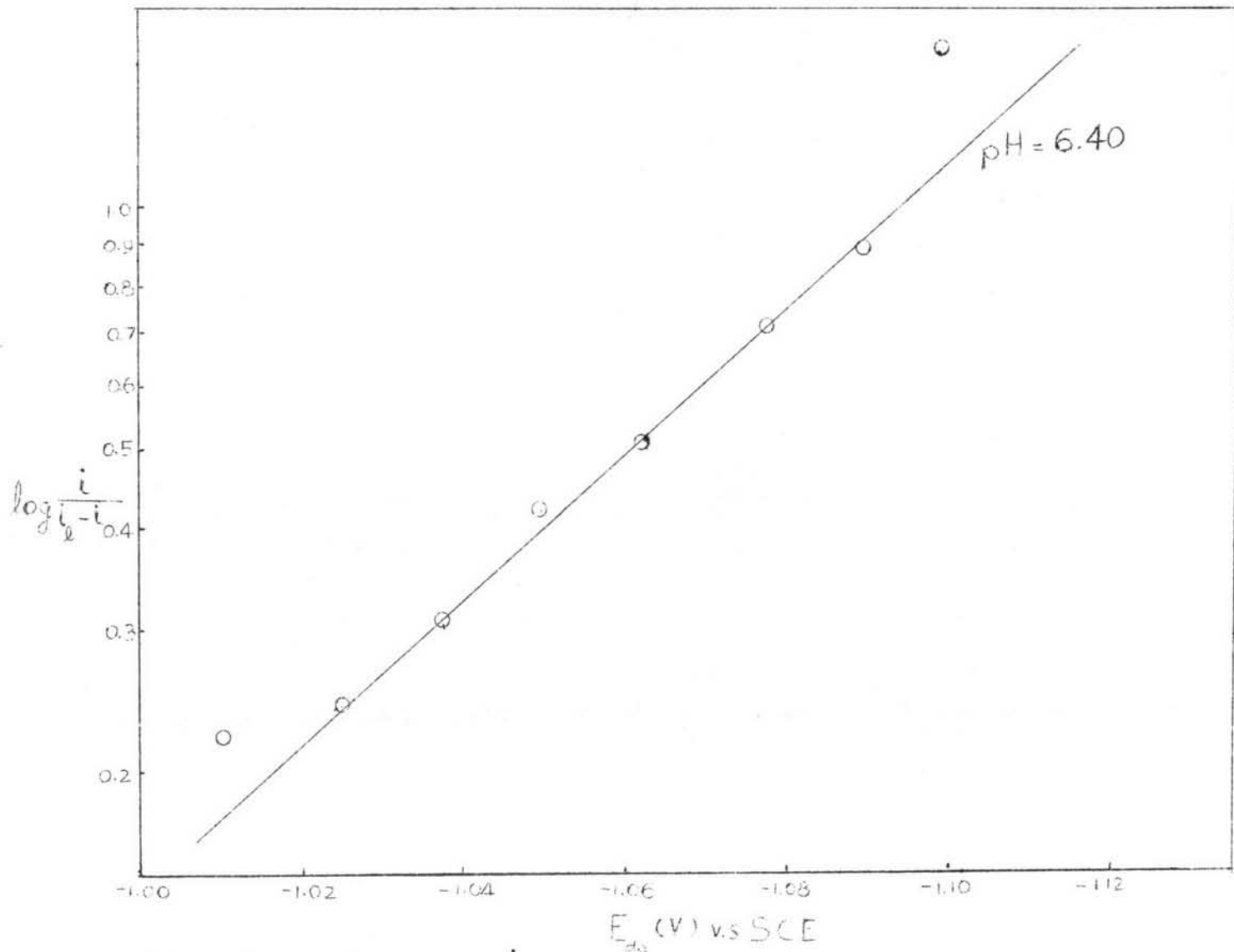
Figure 7 Graph of log $\frac{i}{i_1 - i}$ versus e_{de} for 1,10-phenanthroline system at pH 6.40

so m is 0.99. Therefore one proton is consumed in 1,10-phenanthroline system at the pH range of 6.00 to 6.40.

4.2 Substituted 1,10-phenanthroline

Substituted 1,10-phenanthroline compounds used for this study are 1,10-phenanthroline-1 -oxide, 2-carboxy-, 2-cyano-, 5-nitro-1,10-phenanthroline and 4-nitro-1,10-phenanthroline-1-oxide. The electrochemical behaviours of these compounds as effect by pH are discussed. In addition the reversibilities of substituted 1,10-phenanthroline systems at the pH resulting well-defined waves are examined.

4.2.1 1,10-Phenanthroline-1-oxide

Electrochemical data obtained from the polarograms of 5×10^{-4}M 1,10-phenanthroline-1-oxide at various pH are shown in Table 7. Polarograms of 1,10-phenanthroline-1-oxide at pH of 3.70 and pH of 6.50 are shown in Figure 8 and Figure 9, respectively. Well-defined waves are obtained in the pH range of 4.50 to 7.00.

The effect of pH on the half wave potential of these systems as shown in Figure 10 results the dependence of pH on the half wave potential at the pH higher than 5.40. In the pH range of 4.50 to 5.40 the half wave potential is independent of pH. At pH of 4.10 the half wave potential of 1,10-phenanthroline-1-oxide is extremely negative than other pH media. This probably results from the change of 1,10-phenanthroline-1-oxide to another form.

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Table 7   Polarographic data for 1,10-phenanthroline-1-oxide

system

pH	$E_{1/2}(V)$	$i_1(uA)^a$	I_1	Remarks
3.70	-0.730	2.28	4.56	ill-defined wave
4.10	-0.768	2.68	5.36	ill-defined wave
4.50	-0.656	2.94	5.88	well-defined wave
5.00	-0.655	2.72	5.44	well-defined wave
5.40	-0.655	2.81	5.62	well-defined wave
5.70	-0.658	2.68	5.36	well-defined wave
6.10	-0.662	2.66	5.32	well-defined wave
6.50	-0.680	2.72	5.44	well-defined wave
7.00	-0.690	2.58	5.16	well-defined wave

a
Mercury height = 45 cm; $m^{\frac{2}{3}}t^{\frac{1}{6}}$ = 2.27
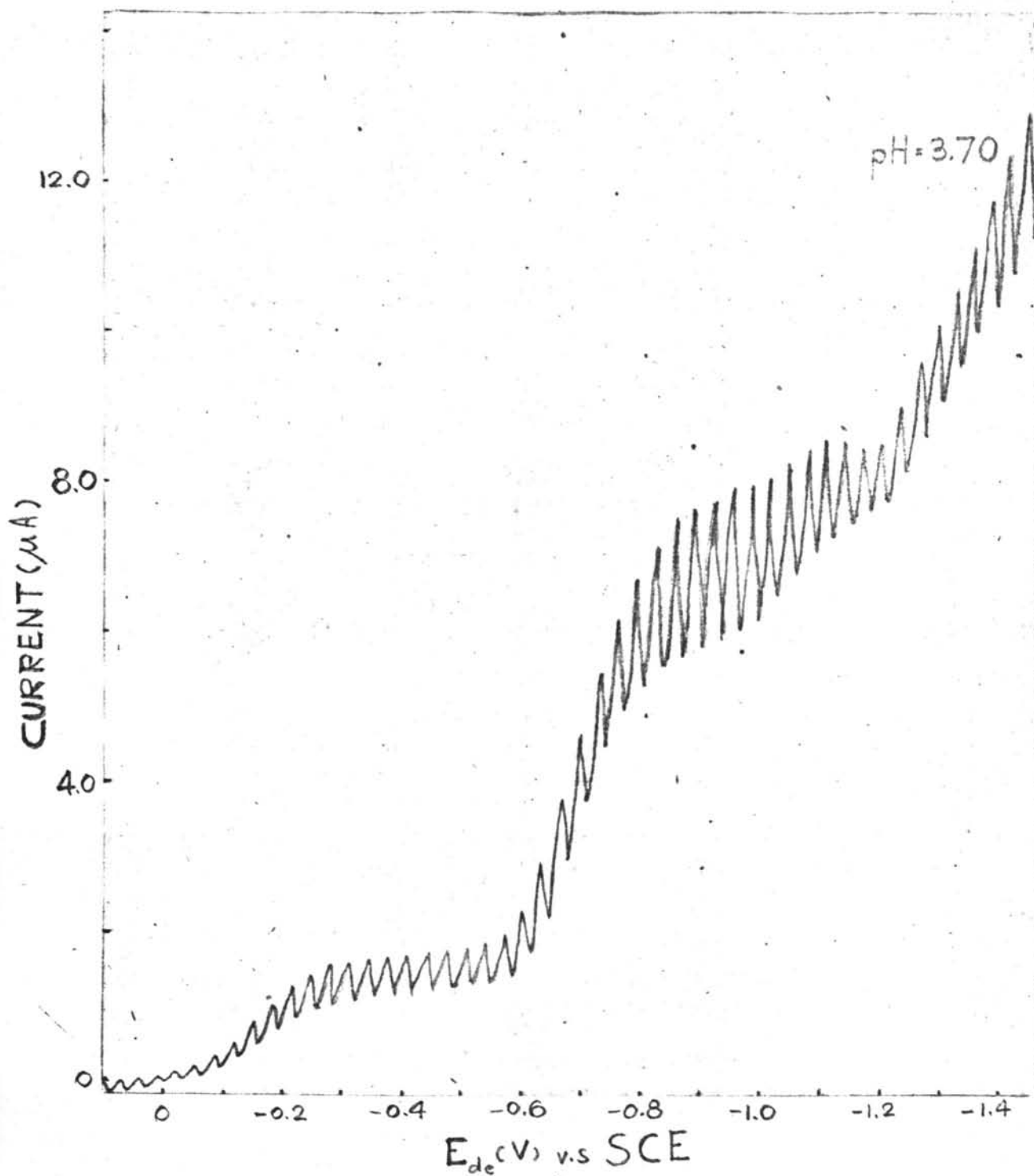
Figure 8   The polarogram of 1,10-phenanthroline-1-oxide at pH 3.70
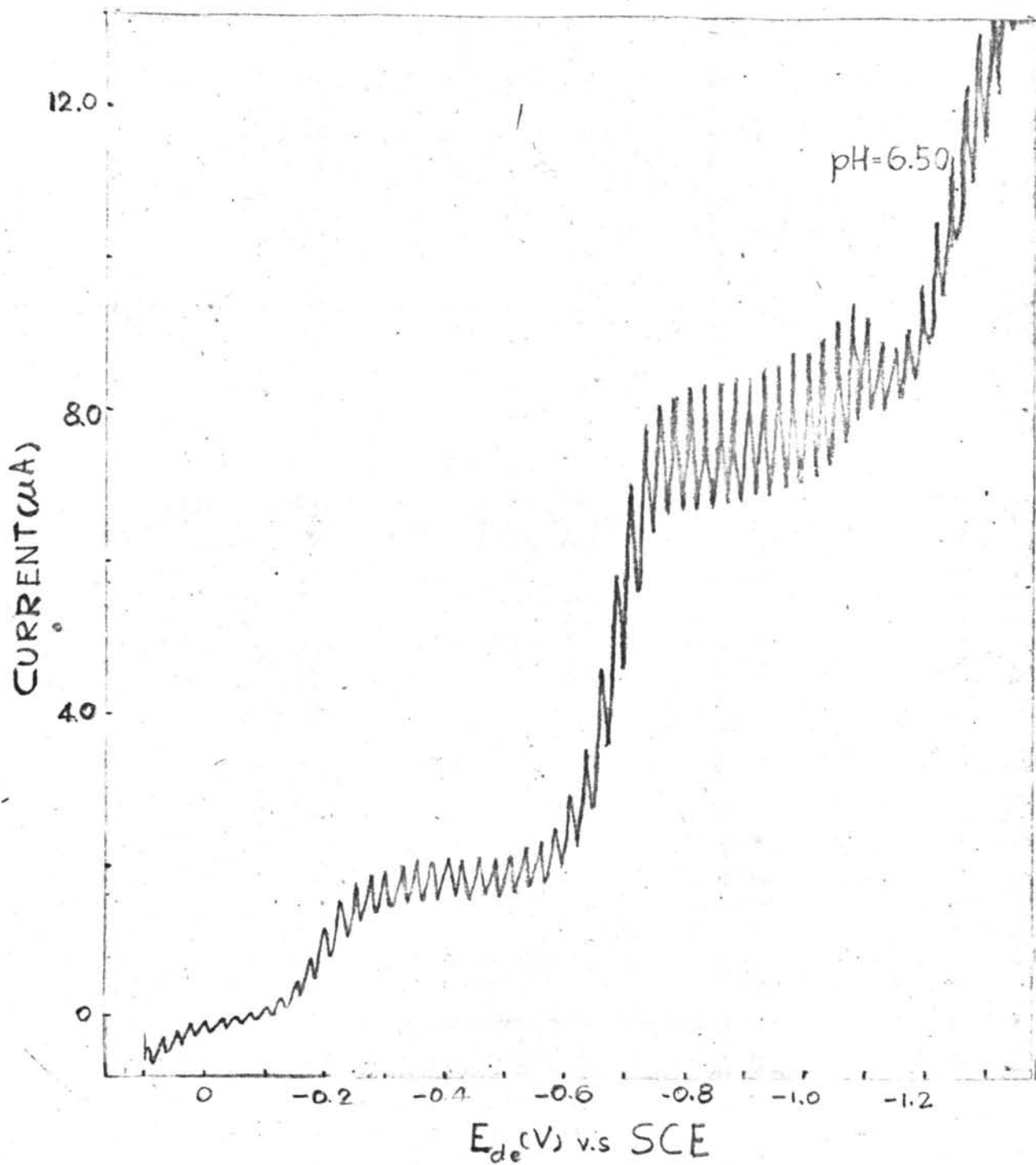
Figure 9   The polarogram of 1,10-phenanthroline-1-oxide at pH 6.50
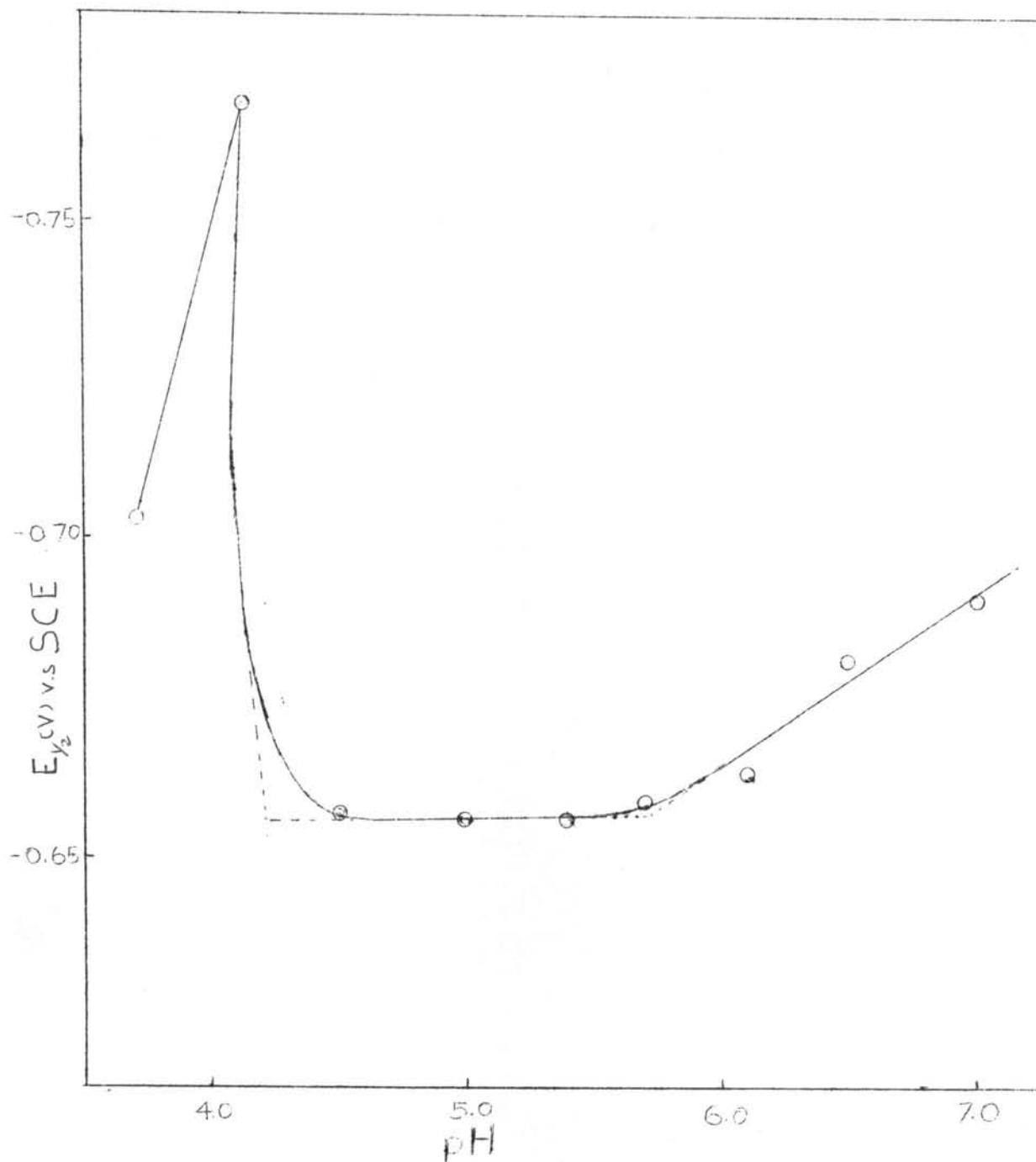
Figure 10   The effect of pH on the half wave potential for
1,10-phenanthroline-1-oxide system

The reversibilities of 1,10-phenanthroline-1-oxide systems at the pH giving well-defined waves are tested. Data for testing reversibilities of these systems at pH = 6.10 and at pH = 6.50 are listed in Table 8. The plot of the potential versus its $\log \frac{i}{i_l - i}$ of both systems (figure 11) gives the slope of -0.054 for pH = 6.10 and the slope of -0.061 for pH = 6.50. The calculated number of electrons for both systems are 1.11 for pH 6.10 and 0.98 for pH 6.50. Thus the electrons transfer mechanisms for 1,10-phenanthroline-1-oxide at pH 6.10 and at pH 6.50 seem to be reversible electrode processes.

4.2.2 2-Carboxy-1,10-phenanthroline

Polarographic data for 2-carboxy-1,10-phenanthroline at various pH are illustrated in Table 9. Polarograms of 2-carboxy-1,10-phenanthroline systems in the pH range studied are ill-defined waves (see Figure 12). The shape of the polarogram is more defined wave as the pH of the system increases. However, the dependence of the half wave potential on pH for these systems is linear (see Figure 13) and the ratio of $m/\alpha n$ is 1.25.

Owing to the ill-defined wave obtained, the reversibilities of 2-carboxy-1,10-phenanthroline systems at the pH range studied are not investigated.

4.2.3 2-Cyano-1,10-phenanthroline

Polarographic data for 2-cyano-1,10-phenanthroline at various pH are listed in Table 10. Polarograms of 2-cyano-1,10-phenanthroline at pH 3.20 and pH 6.50 are shown in Figure 14. All

Table 8 Data for testing reversibilities of 1,10-phenanthro-
line-1-oxide at pH = 6.10 and at pH = 6.50

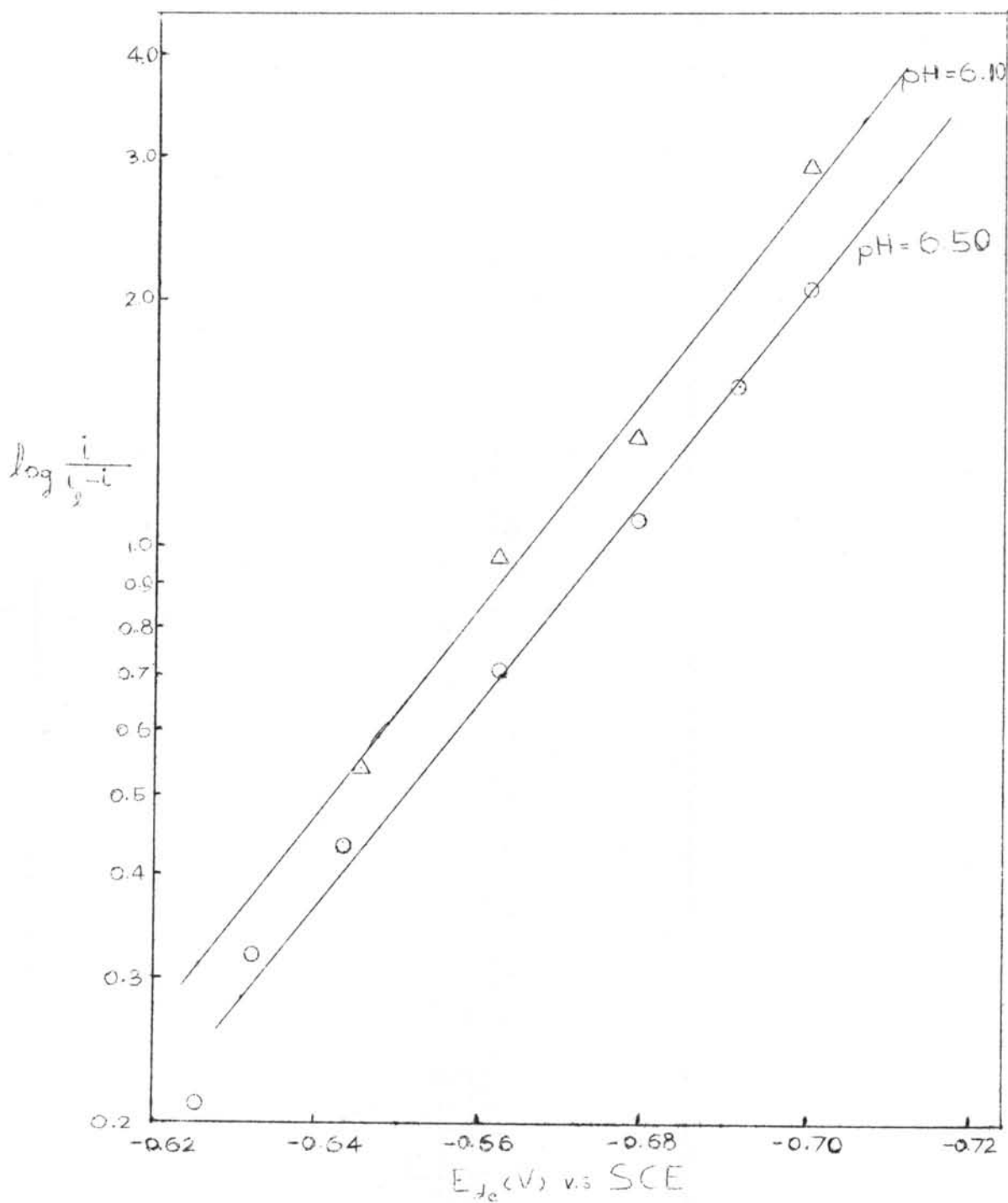| i (μA)	$\log \frac{i}{i_1 - i}$	E_{de} (V)
pH = 6.10		
0.26	0.10	-0.610
0.58	0.27	-0.630
0.94	0.54	-0.645
1.32	0.98	-0.662
1.54	1.37	-0.679
1.98	2.91	-0.700
pH = 6.50		
0.26	0.10	-0.610
0.48	0.21	-0.625
0.67	0.32	-0.632
0.84	0.44	-0.643
1.14	0.72	-0.662
1.42	1.09	-0.679
1.66	1.59	-0.691
1.84	2.09	-0.700
2.28	5.18	-0.720

Figure 11 Graph of log $\dfrac{i}{i_1 - i}$ versus E_{de} for 1,10-phenanthroline-1-oxide systems at pH 6.00 and pH 6.50

Table 9   Polarographic data for 2-carboxy-1,10-phenanthroline
system

pH	$E_{1/2}$ (V)	i_1 (μA)[a]	I_1	Remarks
3.20	−0.830	4.26	8.52	ill-defined wave
3.90	−0.885	4.31	8.62	ill-defined wave
4.20	−0.920	4.24	8.48	ill-defined wave
4.60	−0.932	4.30	8.60	ill-defined wave
4.90	−0.974	4.27	8.54	ill-defined wave
5.20	−0.988	4.29	8.58	ill-defined wave
5.60	−1.010	4.28	8.56	ill-defined wave
6.10	−1.045	4.33	8.66	ill-defined wave
6.50	−1.082	4.20	8.40	ill-defined wave
6.90	−1.125	4.20	8.40	ill-defined wave

a
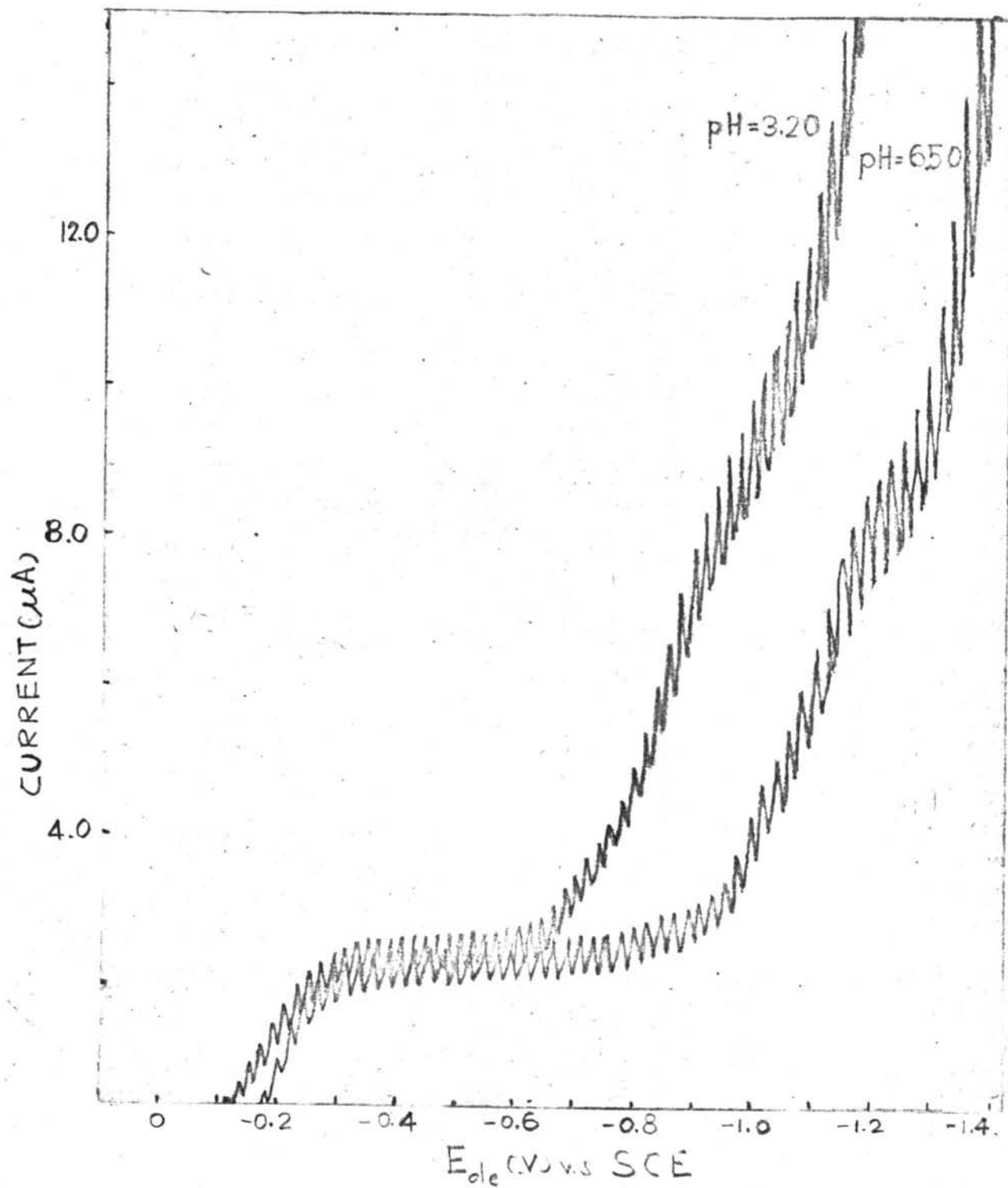Mercury height = 45 cm; $m^{\frac{2}{3}}t^{\frac{1}{6}}$ = 2.27

Figure 12   The polarograms of 2-carboxy-1,10-phenanthroline
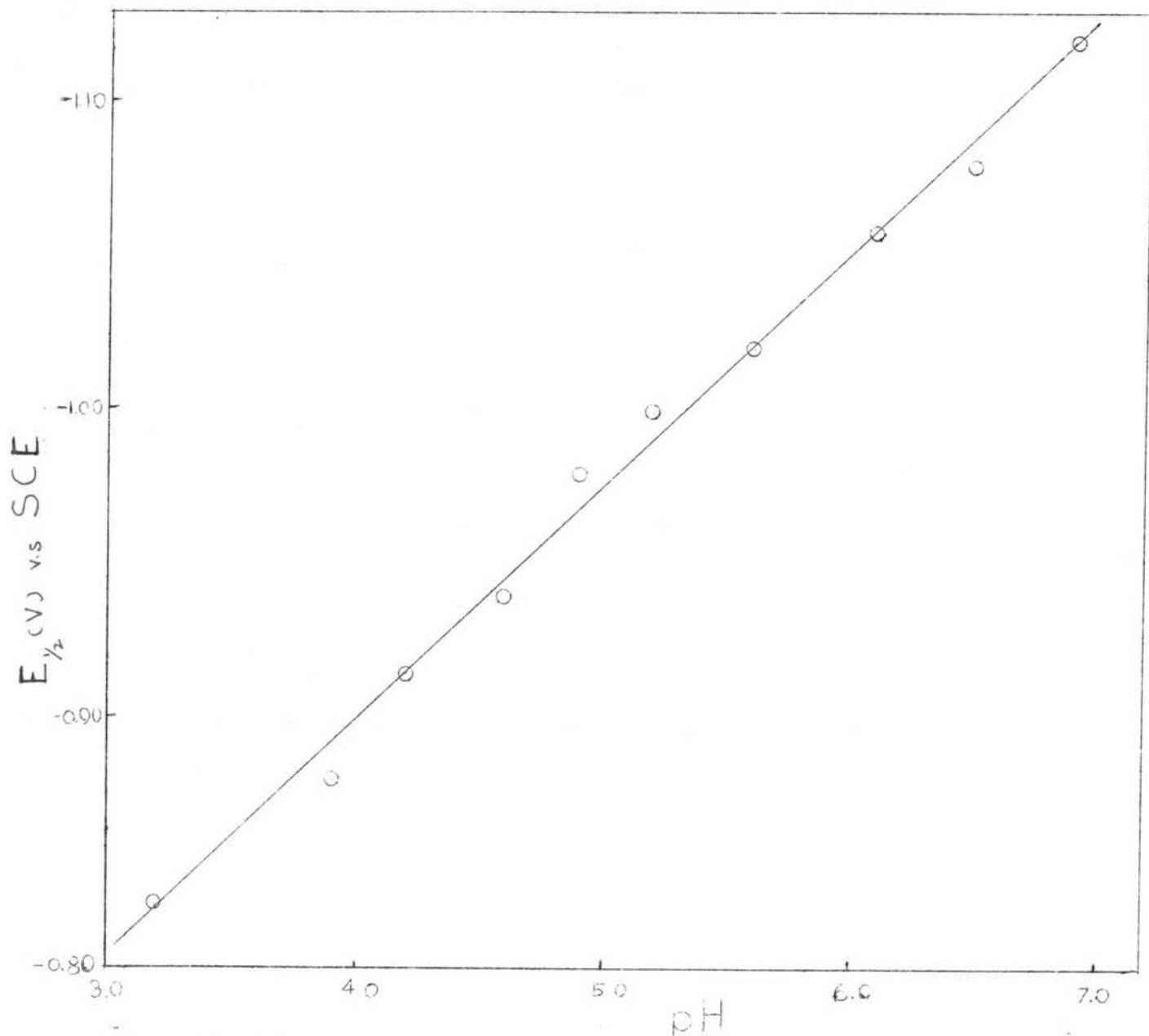at pH 3.20 and pH 6.50

Figure 13 The dependence of pH on the half wave potential for 2-carboxy-

1,10-phenanthroline system

Table 10 Polarographic data for 2-cyano-1,10-phenanthroline
system

pH	$E_{1/2}$ (V)	i_1 $(\mu A)^a$	I_1	Remarks
3.20	−0.865	5.33	10.66	ill-defined wave
3.70	−0.915	5.33	10.66	ill-defined wave
4.30	−0.945	5.35	10.70	ill-defined wave
4.60	−0.980	5.33	10.66	ill-defined wave
4.90	−1.010	5.35	10.70	ill-defined wave
5.30	−1.040	5.34	10.68	ill-defined wave
5.65	−1.074	5.36	10.72	ill-defined wave
6.00	−1.118	5.32	10.64	ill-defined wave
6.50	−1.140	5.31	10.62	ill-defined wave
6.90	−1.164	5.33	10.66	ill-defined wave

[a]
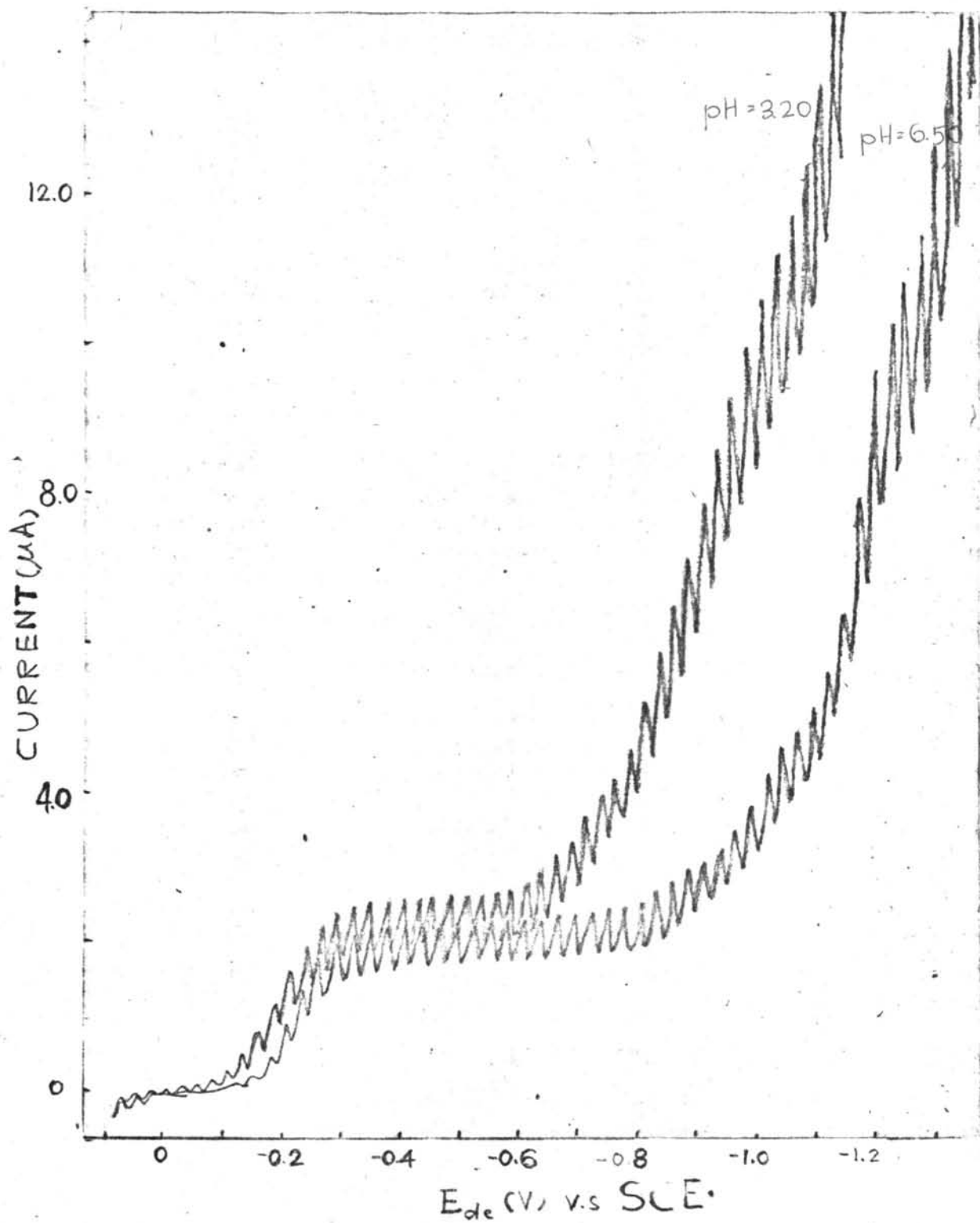Mercury height = 45 cm; $m^{\frac{2}{3}} t^{\frac{1}{6}}$ = 2.27

Figure 14   The polarograms of 2-cyano-1,10-phenanthroline

at pH 3.20 and pH 6.50

polarograms obtained in the pH range of study are ill-defined wave.
At pH 3.20 the polarographic wave is hardly observed. In the pH
range of 3.70 to 6.90 the shapes of polarograms of 2-cyano-1,10-
phenanthroline systems are similar and the half wave potentials
shift to more negative potentials as the pH increases. However,
the half wave potential is directly proportional to the pH of
2-cyano-1,10-phenanthroline system (see Figure 15). The ratio of
$m/\mathcal{U} n$ for these systems is 0.75.

The reversibilities of 2-cyano-1,10-phenanthroline
systems in the pH range studied are not tested because of their
ill-defined waves obtained.

4.2.4 4-Nitro-1,10-phenanthroline-1-oxide

Data of 4-nitro-1,10-phenanthroline-1-oxide in the pH
range of polarographic study are listed in Table 11. All polaro-
grams obtained are well-defined waves. The polarogram of 4-nitro-
1,10-phenanthroline-1-oxide at pH 6.05 is shown in Figure 16. The
half wave potential of 4-nitro-1,10-phenanthroline-1-oxide shifts
to more negative potential as the pH increases. The dependence of
half wave potential on pH (Figure 17) demonstrates a linear section
for the pH range of 5.00 to 7.10. The calculated ratio of $m/\mathcal{U} n$
for this pH range is 1.28.

Data for testing reversibilities of 4-nitro-1,10-
phenanthroline-1-oxide at pH = 6.05 and pH = 6.50 are shown in
Table 12. The plot of the potential versus its $\log \frac{i}{i_1 - i}$ shows a
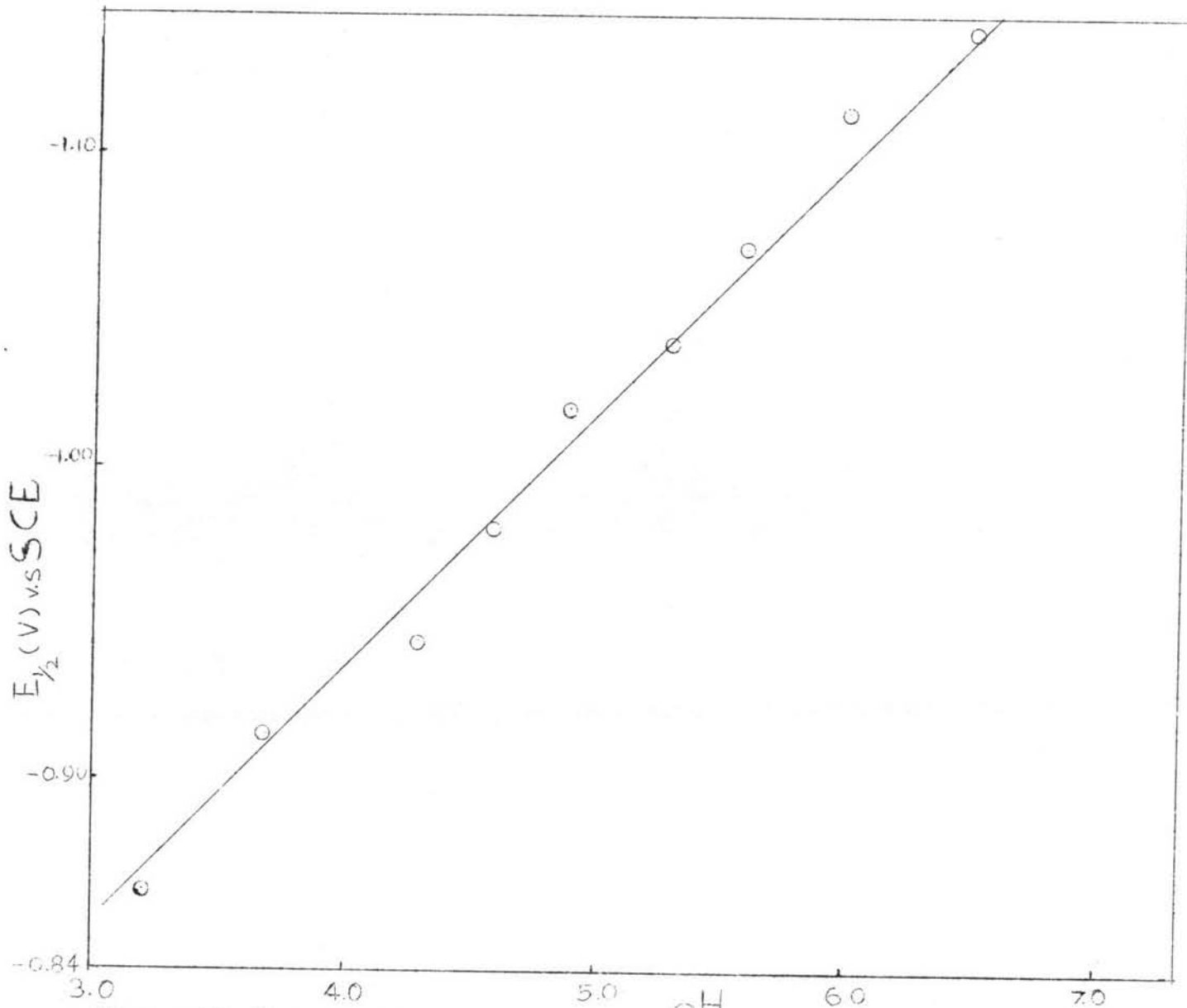linearity for both systems (see Figure 18). The calculated number

Figure 15 The effect of pH on the half wave potential for 2-cyano-1,10-
phenanthroline system

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Table 11 Polarographic data for 4-nitro-1,10-phenanthroline-
1-oxide system

pH	$E_{1/2}$ (V)	i_1 $(\mu A)^a$	I_1	Remarks
3.80	-0.120	5.12	10.24	well-defined wave
4.30	-0.140	5.28	10.56	well-defined wave
4.70	-0.180	6.00	12.00	well-defined wave
5.00	-0.200	5.92	11.84	well-defined wave
5.40	-0.221	5.84	11.68	well-defined wave
5.75	-0.240	5.88	11.76	well-defined wave
6.05	-0.250	5.68	11.36	well-defined wave
6.50	-0.270	5.40	10.80	well-defined wave
7.10	-0.300	4.88	9.76	well-defined wave

a
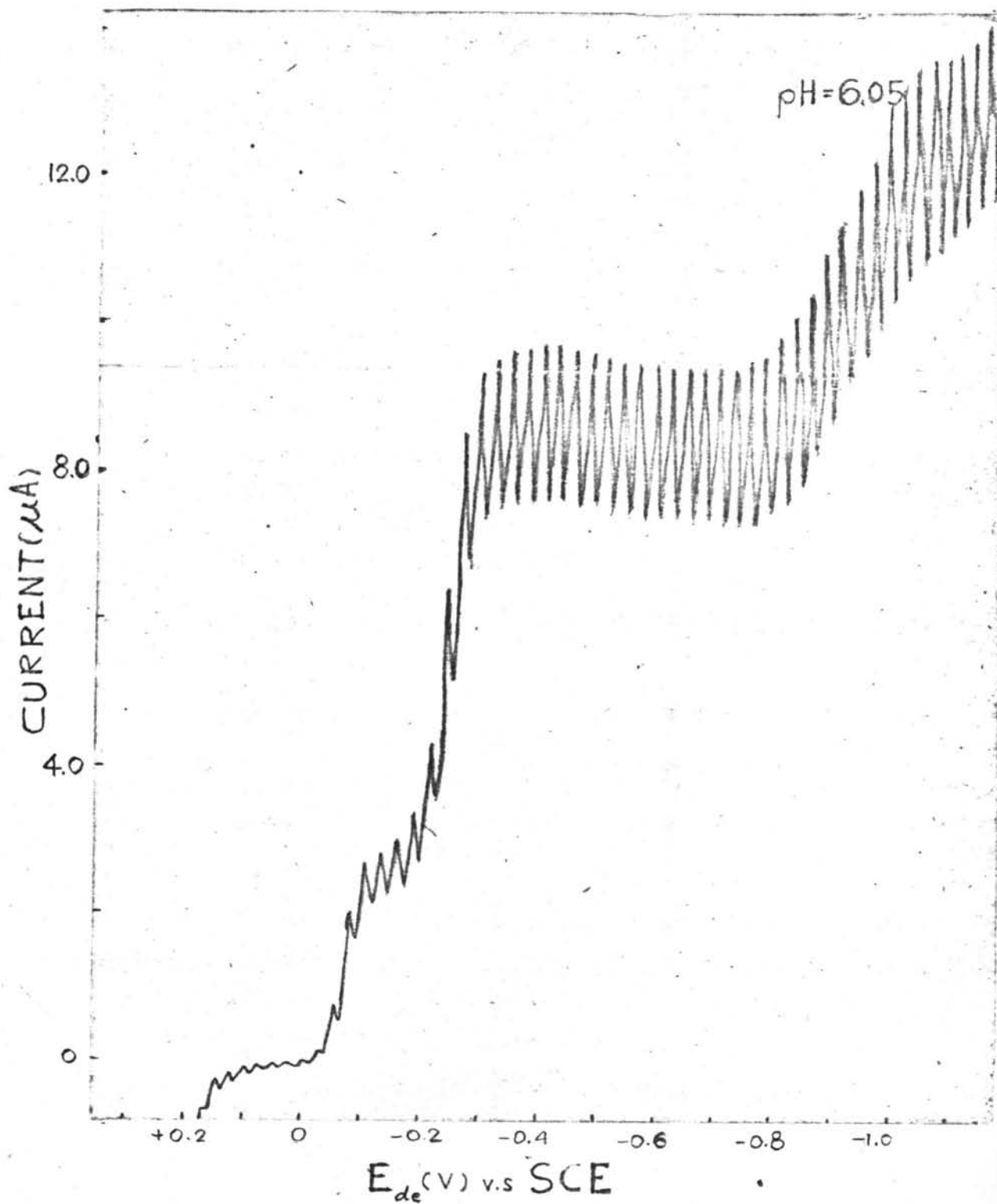Mercury height = 45 cm; $m^{\frac{2}{3}} t^{\frac{1}{6}}$ = 2.27

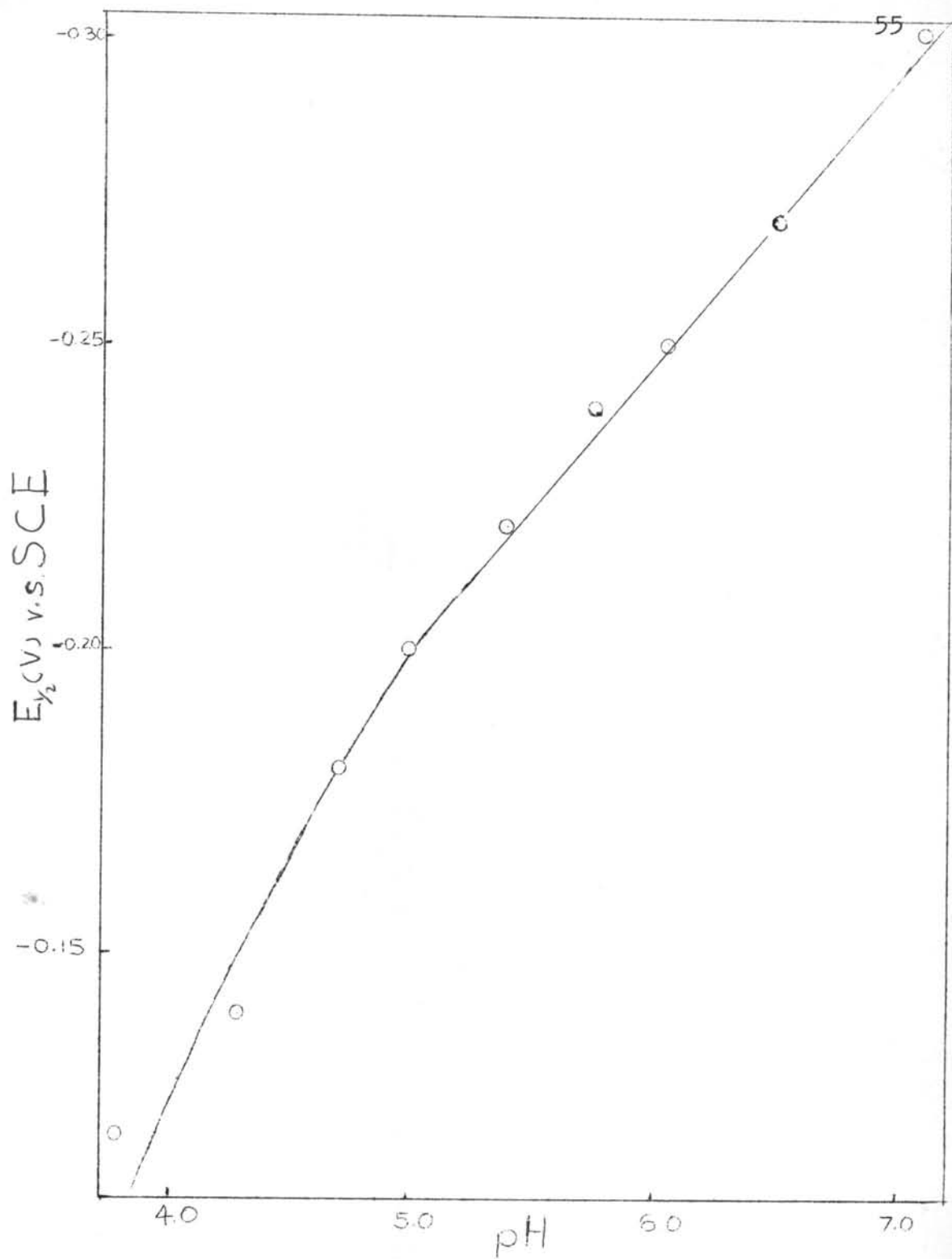Figure 16 The polarogram of 4-nitro-1,10-phenanthroline-

1-oxide at pH 6.05

Figure 17   The effect of pH on the half wave potential for
4-Nitro-1,10-phenanthroline-1-oxide system

Table 12 Data for testing reversibilities of 4-nitro-1,10-

phenanthroline-1-oxide at pH = 6.05 and at pH = 6.50

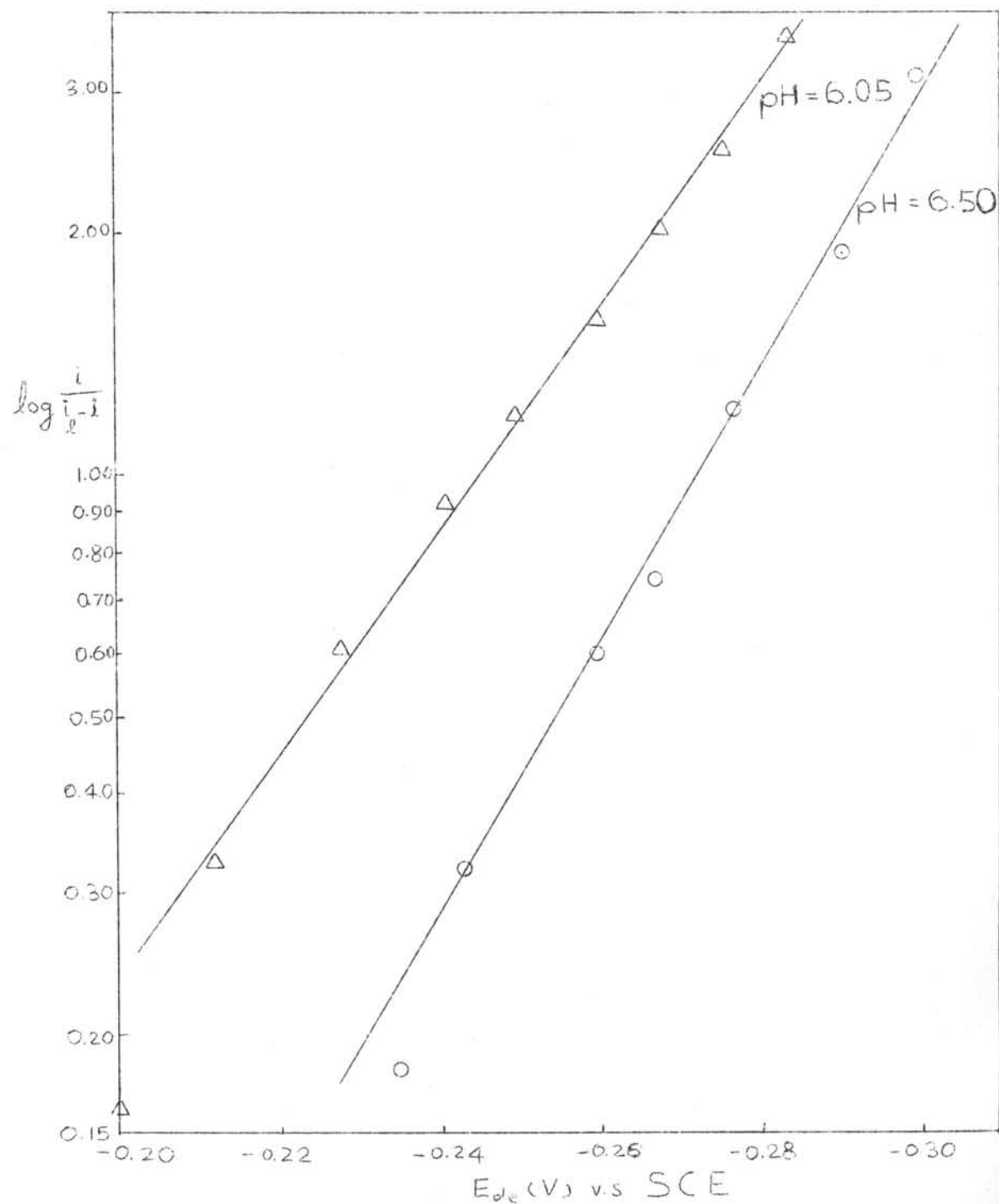| i (μA)	$\log \frac{i}{i_1 - i}$	$E_{\text{d.e}}$ (V)
pH = 6.05		
0.80	0.16	−0.200
1.40	0.33	−0.212
2.12	0.61	−0.228
2.64	0.91	−0.241
3.03	1.19	−0.250
3.36	1.54	−0.260
3.70	2.01	−0.268
3.98	2.55	−0.276
4.30	3.46	−0.284
pH = 6.50		
0.80	0.18	−0.235
1.30	0.32	−0.243
1.98	0.60	−0.260
2.24	0.74	−0.267
2.86	1.20	−0.275
3.42	1.87	−0.290
3.98	3.15	−0.300

Figure 18   Graph of $\log \frac{i}{i_l - i}$ versus E_{de} for 4-Nitro-1,10-phenanthroline-1-oxide at pH 6.05 and pH 6.50

of electrons transfer in both systems are 0.91 and 1.15, respectively. Therefore, the electron transfer mechanism for both pH seems to be a reversible process with an average number of electrons transfer of 1.03. In addition, one proton is involved in 4-nitro-1,10-phenanthroline-1-oxide reaction in the pH range 6.05 to 6.50 (calculated m = 1.32).

4.2.5 5-Nitro-1,10-phenanthroline

Polarographic data for 5-nitro-1,10-phenanthroline systems at various pH are listed in Table 13. All polarograms obtained are well-defined waves and the polarogram at pH of 6.40 is shown in Figure 19. The half wave potential of 5-nitro-1,10-phenanthroline shifts to more negative potential as the pH increases. This dependence of half wave potential on pH (Figure 20) shows a linearity. The calculated ratio of $m/\alpha n$ for the pH range of 3.80 to 6.80 is 0.08.

The reversibilities of 5-nitro-1,10-phenanthroline system at pH = 6.00 and pH = 6.40 were tested (see Table 14 and Figure 21). Straight line is obtained from the plot of the potential and its $\log \frac{i}{i_1 - i}$. The number of electrons transfer are 1.76 and 1.54 for pH of 6.00 and pH of 6.40, respectively. The average electrons transfer in the pH range of 6.00 to 6.40 is 1.65. Thus the electrons transfer mechanism in the pH range 6.00 to 6.40 is an irreversible process and one proton is involved (calculated m = 1.32).

Table 13 Polarographic data for 5-nitro-1,10-phenanthroline

pH	$E_{1/2}$ (V)	i_1 (μA)[a]	I_1	Remarks
3.80	-0.205	7.79	15.58	well-defined wave
4.30	-0.225	7.60	15.20	well-defined wave
4.60	-0.250	7.28	14.56	well-defined wave
4.90	-0.265	7.72	15.44	well-defined wave
5.30	-0.285	7.21	14.42	well-defined wave
5.65	-0.300	7.46	14.92	well-defined wave
6.00	-0.315	7.13	14.26	well-defined wave
6.40	-0.330	7.47	14.94	well-defined wave
6.80	-0.360	7.41	14.82	well-defined wave

[a]
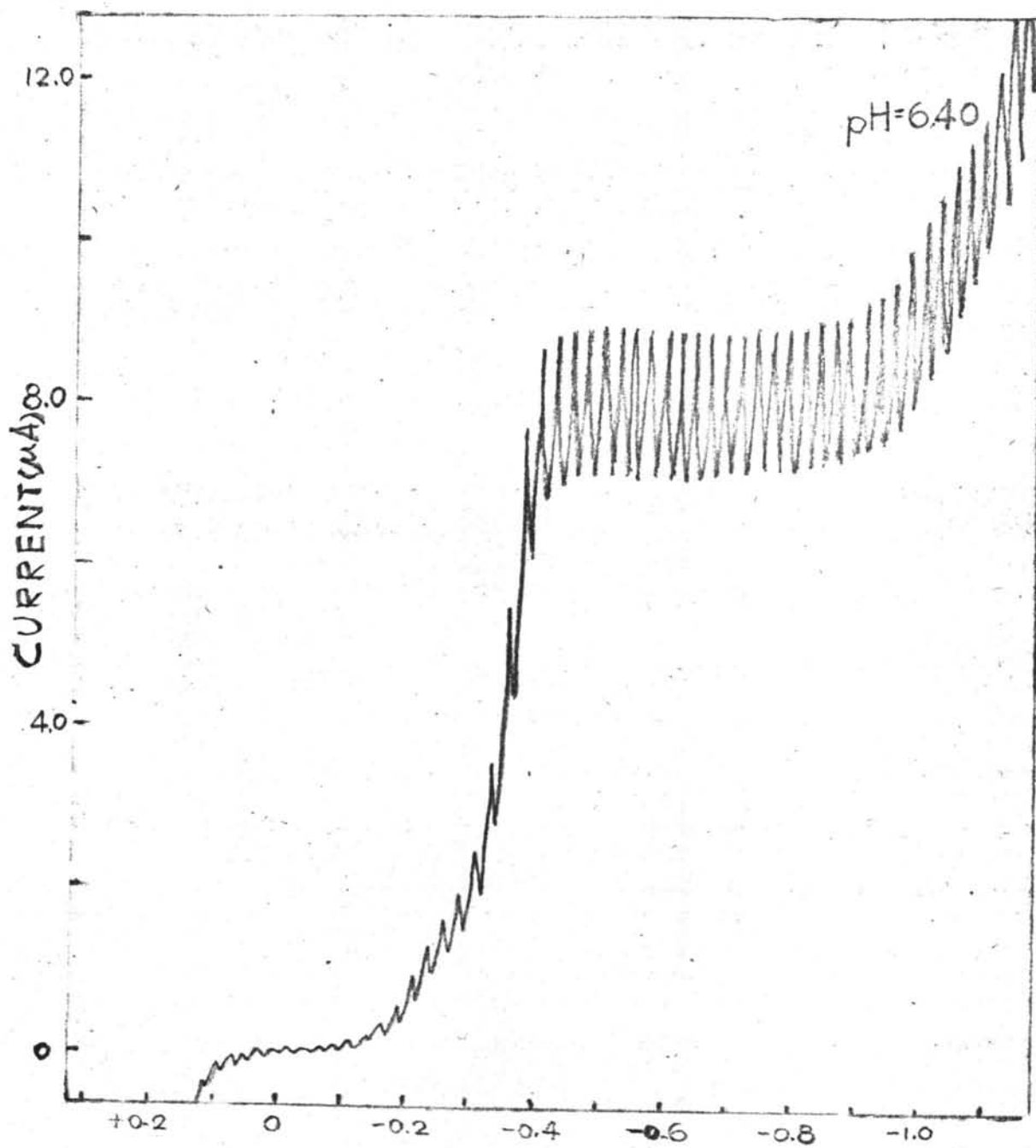Mercury height = 45 cm; $m^{\frac{2}{3}} t^{\frac{1}{6}}$ = 2.27

Figure 19   The polarogram of 5-nitro-1,10-phenanthroline at pH 6.40
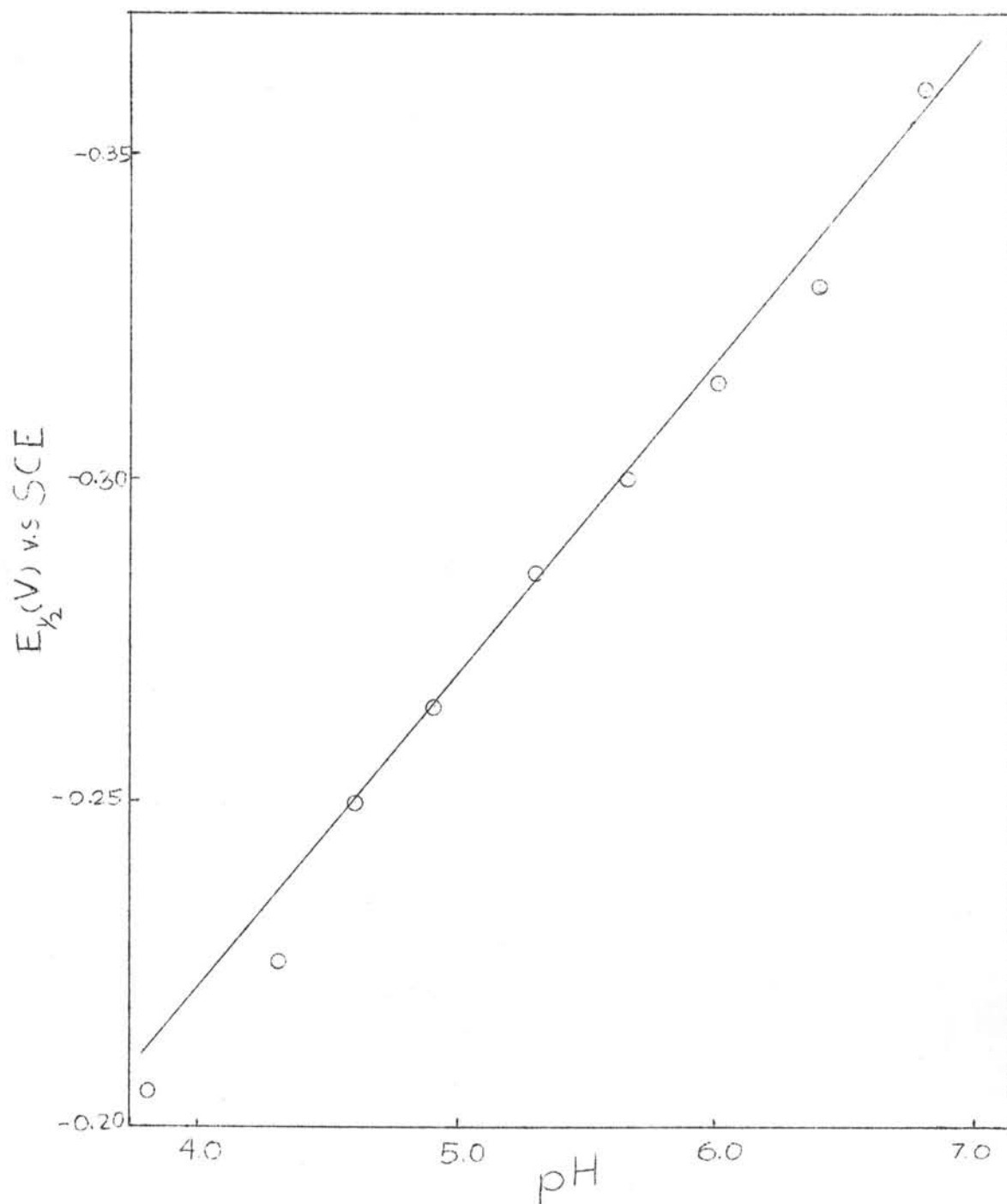
Figure 20   The effect of pH on the half wave potential

for 5-Nitro-1,10-phenanthroline system

Table 14 Data for testing reversibilities of 5-nitro-1,10-phenan-
throline at pH = 6.00 and at pH = 6.40

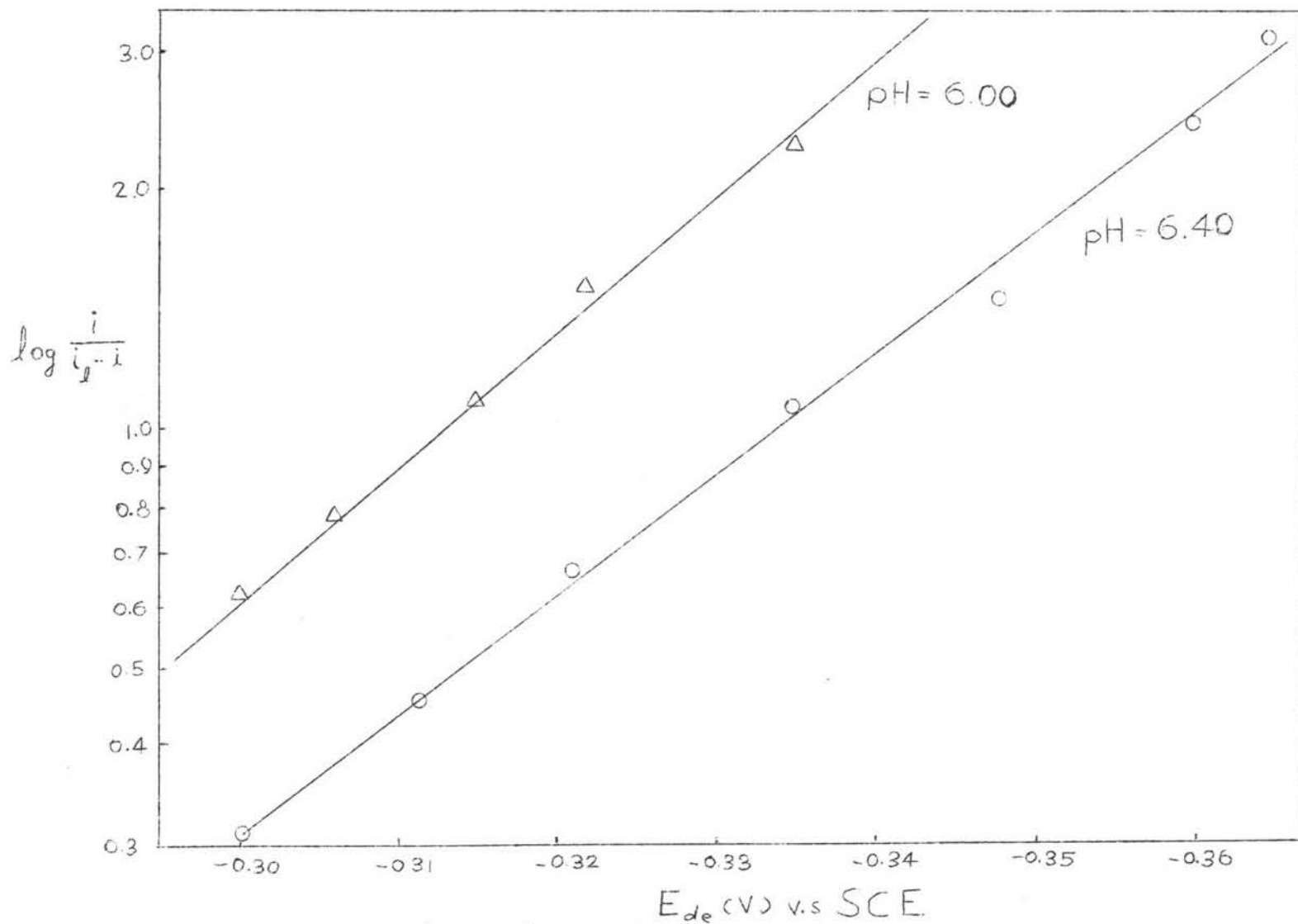| i (μA)	$\log \frac{i}{i_l - i}$	$E_{de}(V)$
pH = 6.00		
1.96	0.37	−0.287
2.29	0.46	−0.293
2.77	0.62	−0.300
3.14	0.77	−0.306
3.88	1.17	−0.315
4.32	1.51	−0.322
4.98	2.26	−0.335
pH = 6.40		
1.80	0.31	−0.300
2.36	0.45	−0.311
3.00	0.66	−0.321
3.86	1.06	−0.335
4.44	1.45	−0.348
5.31	2.42	−0.360
5.64	3.03	−0.365
6.01	4.03	−0.375

Figure21 Graph of log $\frac{i}{i_l - i}$ versus E_{de} for 5-Nitro-1,10-phenanthroline at pH 6.00 and pH 6.40

4.3 Substituent Effects

In this section the substituent effects of 1,10-phenanthroline on the half wave potential are examined in the pH range of 3.20 to 7.10 (see Table 15 and Figure 22). Compounds used for this study are those that have been investigated in the preceding sections. From Figure 22 it can be seen that the range of the half wave potentials of 1,10-phenanthroline-1-oxide, 4-nitro-1,10-phenanthroline-1-oxide and 5-nitro-1,10-phenanthroline shift to more positive potential than that of the parent compound. This effect is due to the mesomeric effect of nitro and oxy group (-T effect) (12). From Figure 22 the range of half wave potentials of nitro compounds are more positive than the oxy compounds; due to the stronger -T effect of the nitro group over the oxy group.

Since the carboxylic and cyano group also have -T effect the range of half wave potentials of 2-carboxy-1,10-phenanthroline and 2-cyano-1,10-phenanthroline should shift to more positive potentials than that of 1,10-phenanthroline. From the experiment the range of half wave potentials of both compounds shift slightly to more positive potentials. However, in the pH higher than 5.60 the half wave potential of 2-carboxy-1,10-phenanthroline is almost the same as the of 1,10-phenanthroline and in the pH higher than 5.30 the half wave potential of 2-cyano-1,10-phenanthroline shifts slightly to more negative potential. Owing to the ill-defined wave of 2-carboxy-1,10-phenanthroline and 2-cyano-1,10-phenanthroline in the pH range of study, the recorded half wave potential

Table 15 Substituent effects of 1,10-phenanthroline in the pH
range 3.20 to 7.10

Compound	$E_{1/2}$ in the pH range of 3.20 to 7.10 (V)
1,10-Phenanthroline	−0.950 to −1.120
1,10-Phenanthroline-1-oxide	−0.655 to −0.768
4-Nitro-1,10-phenanthroline-1-oxide	−0.120 to −0.300
5-Nitro-1,10-phenanthroline	−0.205 to −0.360
2-Carboxy-1,10-phenanthroline	−0.830 to −1.125
2-Cyano-1,10-phenanthroline	−0.865 to −1.164

2-Cyano-1,10-phenan-
throline

2-Carboxy-1,10-phenan
throline

5-Nitro-1,10-phenan-
throline

4-Nitro-1,10-phenan-
throline-1-oxide

1,10-Phenanthroline-
1-oxide

1,10-Phenanthroline

0   -0.2   -0.4   -0.6   -0.8   -1.0   -1.2   -1.4
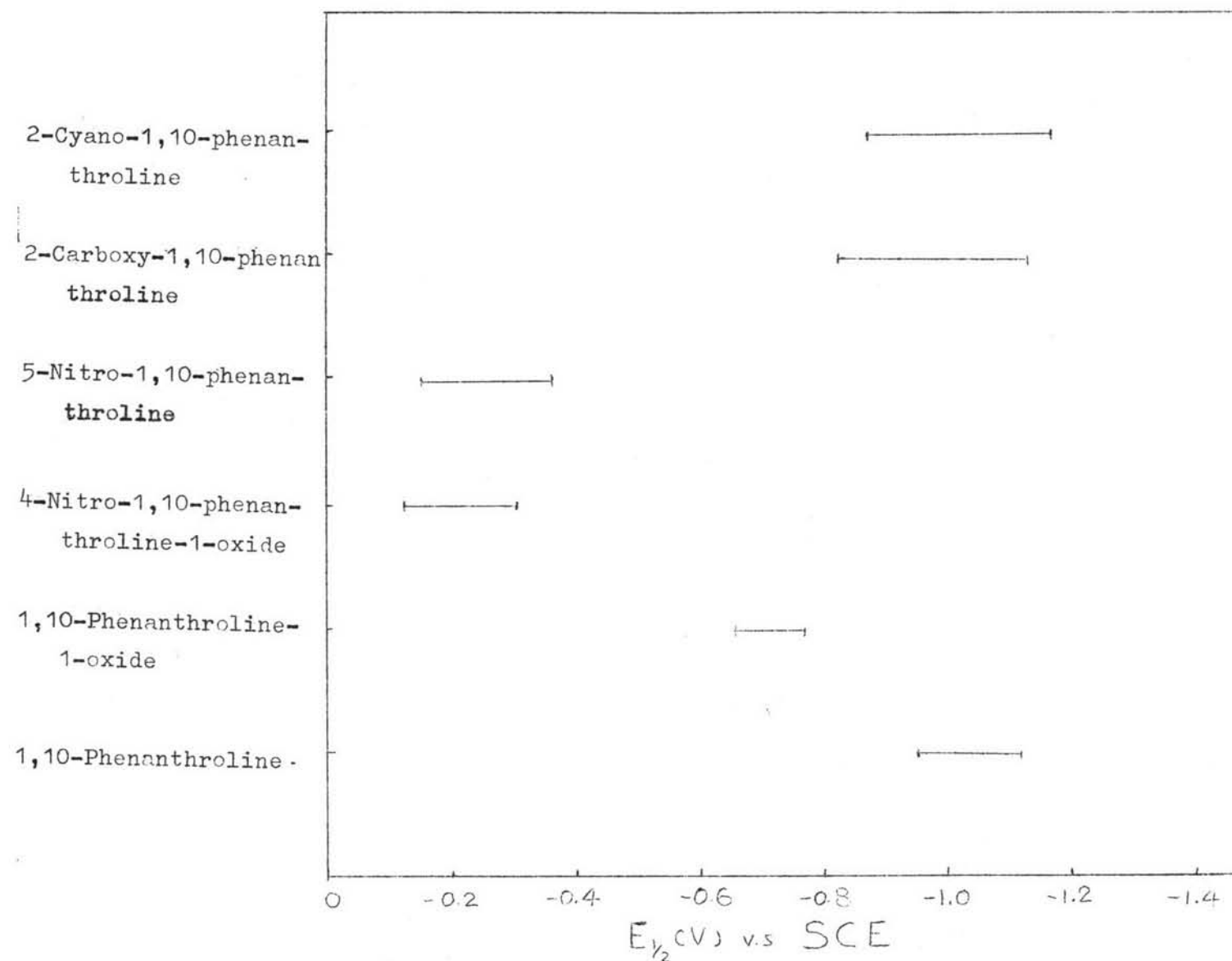
$E_{1/2}$ (V) v.s SCE

Figure 22   Substituent effects of 1,10-phenanthroline on the half
wave potential

might not be accurate. The substituted position of the carboxylic and cyano group on 1,10-phenanthroline is also influenced the mesomeric effect. Thus the carboxylic and cyano group attached position 2 of 1,10-phenanthroline would not affect the half wave potential of 1,10-phenanthroline in the pH range of study.