DIRECT AND ALTERNATING CURRENT POLAROGRAPHY OF NITROBENZENE

IN AQUEOUS SOLUTIONS AND IN ACETONITRILE

by

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ABSTRACT

The polarographic reduction of nitrobenzene in aqueous buffered solutions, and that of nitrobenzene and o-nitrophenol in anhydrous acetonitrile was investigated. Alternating current polarography was used in addition to "conventional" polarography for the work done with aqueous solutions. Non-reducible surface-active agents, e. g. Triton X-100, split the d. c. waves of nitrobenzene in basic and neutral solutions, in two parts, the total current remaining nearly the same as in absence of the surface-active agent. The a. c. wave corresponding to the first step of the split d. c. wave becomes larger as the d. c. wave becomes smaller with increasing concentration of the surface-active agent. A limiting ratio of 1:3 is obtained for the heights of the two resulting d. c. waves in basic solution in presence of sufficient amount of the surface-active agent, and the height of the a. c. wave corresponding to the first d. c. step reaches its maximum value. In acid solution no splitting occurs, but the d. c. wave is shifted to more negative potentials. The a. c. wave does not become larger.

The results are interpreted by postulating a mechanism for the reduction of nitrobenzene involving the initial formation of the semi-quinone PhNO , whose stability toward further reduction increases with the pH of the solution and with the concentration of the surface-active agent. The latter hinders the reduction of the semi-quinone by forming a film at the mercury/solution interface by adsorption.

Application of Delahay's theory of irreversible polarographic waves is made, and some of its shortcomings are discussed.

In anhydrous acetonitrile nitrobenzene and o-nitrophenol are reduced stepwise, and their behaviour resembles that of nitrobenzene and several other aromatic nitro-compounds in aqueous basic solution in presence of surface-active substances.

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LIST OF SYMBOLS

A	–	area
a. c.	–	alternating current
b	–	as subscript, means backward
C_o	–	concentration of substance O at the electrode surface
D	–	diffusion coefficient
d. c.	–	direct current
E	–	potential
$E_{1/2}$	–	half-wave potential
e	–	electron
F	–	the Faraday
f	–	as subscript, means forward
$G^{\neq}$	–	free energy of activation
$H^{\neq}$	–	enthalpy of activation
h	–	Planck constant: if used as a subscript it means heterogeneous
I_d	–	diffusion current constant
i	–	current
i_d	–	diffusion current
K	–	Boltzmann constant
k_h^o	–	rate constant for a heterogeneous process at a potential of 0.0 volts vs. the normal hydrogen electrode
$k_{s,h}$	–	heterogeneous rate constant at the equilibrium potential of the redox system

m	–	rate of flow of mercury through the capillary in mg sec
mv	–	milivolts
N_o	–	number of moles of substance O
O	–	oxidized form of a substance
P	–	factor to convert homogeneous into heterogeneous rate constants
R	–	gas constant
R	–	reduced form of a substance
$S^{\ddagger}$	–	entropy of activation
T	–	absolute temperature
t	–	time; drop time
x	–	distance from the electrode surface
z	–	number of charges involved in an electrode process
z_a	–	number of charges involved in the rate-determining step of the overall process
α	–	transfer coefficient
λ	–	$\dfrac{k_h t^{1/2}}{D_o^{1/2}}$
μa	–	microamperes

ACKNOWLEDGMENT

INTRODUCTION

There is no universally accepted definition of polarography. Its inventor, Heyrovsky, defines it (1) as "the science of studying the processes occurring around the dropping mercury electrode. It includes not only the study of current-voltage curves, but also of other relationships, such as the current-time curves for single drops, potential-time curves, electrocapillary phenomena and the streaming of electrolytes, and its tools include, besides the polarograph, the microscope, the string galvanometer and even the cathode-ray oscillograph ...".

Other authors restrict the definition to the study of current-potential curves produced at the dropping mercury electrode (henceforth referred to as d. m. e.) in the presence of depolarizers, while many others extend it to include studies with solid electrodes, and even related techniques, like micro-coulometry.

In this work the only microelectrode used was the d. m. e. Since not only current-potential curves will be dealt with, Heyrovsky's definition can be used for all the aspects of this work.

It is outside the province of this thesis to present the theory of polarography. The most comprehensive treatment published to date is that of Kolthoff and Lingane (2). An excellent introduction can be found in the little monograph by Muller (3), and a brief condensation

of the fundamentals in the M. Sc. thesis of Jayadevappa (4). Recent developments, however, make it important to present at least a short treatment of the advances made during the last decade.

A. Irreversible processes

For a thermodynamically reversible electrode process the equation relating the current and the potential of the d. m. e. at any point in the polarographic wave is the following:

$$E \approx E_{1/2} + \frac{RT}{zF} \ln\left(\frac{i_d - i}{i}\right) \tag{A.1}$$

Polarographic waves which do not obey equation (1) are said to be irreversible. For many years all that was done about this type of wave was to notice their irreversibility, but since 1949 the problem has been dealt with by the application of the theory of absolute reaction rates (5 - 7). The treatment that follows is that of Delahay (7).

Consider the cathodic process

$$O + ze \longrightarrow R$$

It will be assumed that the process involves only one single rate-determining step, and that the effect of the backward process is negligible. The rate of the process is expressed by

$$-\left(\frac{dN_0}{dt}\right) = C_0 k_h^{\circ} \exp\left[\frac{-\alpha z_a FE}{RT}\right] \tag{A.2}$$

where $\frac{dN_0}{dt}$ is the no. of moles of depolarizer reduced per unit time

C_o' is the concentration of substance O at the electrode surface

E   is the potential of the d. m. e. with respect to the normal hydrogen electrode (NHE)

z_a is the number of electrons involved in the rate-determining step

k_h^o is the rate constant of the process at 0.0 V with respect to the NHE

α is the transfer coefficient, that is, the fraction of the applied potential that causes the reaction to proceed in the direction of reduction.

The depolarizer reaches the electrode surface by diffusion; therefore $\dfrac{dN_o}{dt}$ can be equated to the flux of substance O:

$$D_o \left[\frac{\partial C_o}{\partial x} \, (x, \, t) \right]_{x=o} = C_o k_h^o \exp \left[\frac{-\alpha z_a FE}{RT} \right] \qquad (A.3)$$

where D is the diffusion coefficient of O. The current caused by the process obeys the following relation:

$$i = zFA \times (\text{flux of O})$$

The other boundary condition is that the sum of the fluxes of substances O and R at the electrode surface is equal to zero:

$$D_o \left[\frac{\partial C_o}{\partial x} \, (x, \, t) \right]_{x=o} + D_R \left[\frac{\partial C_R}{\partial x} \, (x, \, t) \right]_{x=o} = 0$$

The initial conditions are

$$C_o \ (x, \ o) \ = \ C_o^o \ , \qquad C_R \ (x \ , \ o \ ) \ = \ 0$$

where C_o^o is the bulk concentration of substance O.

Also, $C_o \ (x, t)$ approaches C^o

and $C_R \ (x, t)$ approaches 0

as $x \longrightarrow \infty$

The solution of equation II that satisfies the initial and boundary conditions stated above was found to be

$$\frac{i}{i_d} \ = \ \pi^{\frac{1}{2}} \ \lambda \ \exp (\lambda^2) \ \mathrm{erfc} \ (\lambda)$$

where

$$\lambda \ = \ \frac{k_h \ t^{\frac{1}{2}}}{D_o^{\frac{1}{2}}}$$

and

$$k_h \ = \ k_h^o \ \exp \left[- \frac{\alpha \ z_a \ FE}{RT} \right]$$

A plot of i/i_d vs λ is shown in figure 1.

It can be seen that plots of $\frac{i}{i_d}$ vs λ give k_h at any potential in the polarographic wave ($D_o^{\frac{1}{2}}$ is obtained from Ilkovic's equation). By plotting $\log k_h$ vs E one obtaineğ, in absence of kinetic complications, a straight line whose slope gives the value of $\alpha \ z_a$.

The free energy of activation of the process can be calculated by applying the following equation:

$$k_h^o \ = \ \frac{kT}{h} \ \rho \ \exp \left[- \frac{\Delta G^{\ddagger}}{RT} \right] \ \exp \left[- \frac{\alpha \ z_a FE_a}{RT} \right]$$
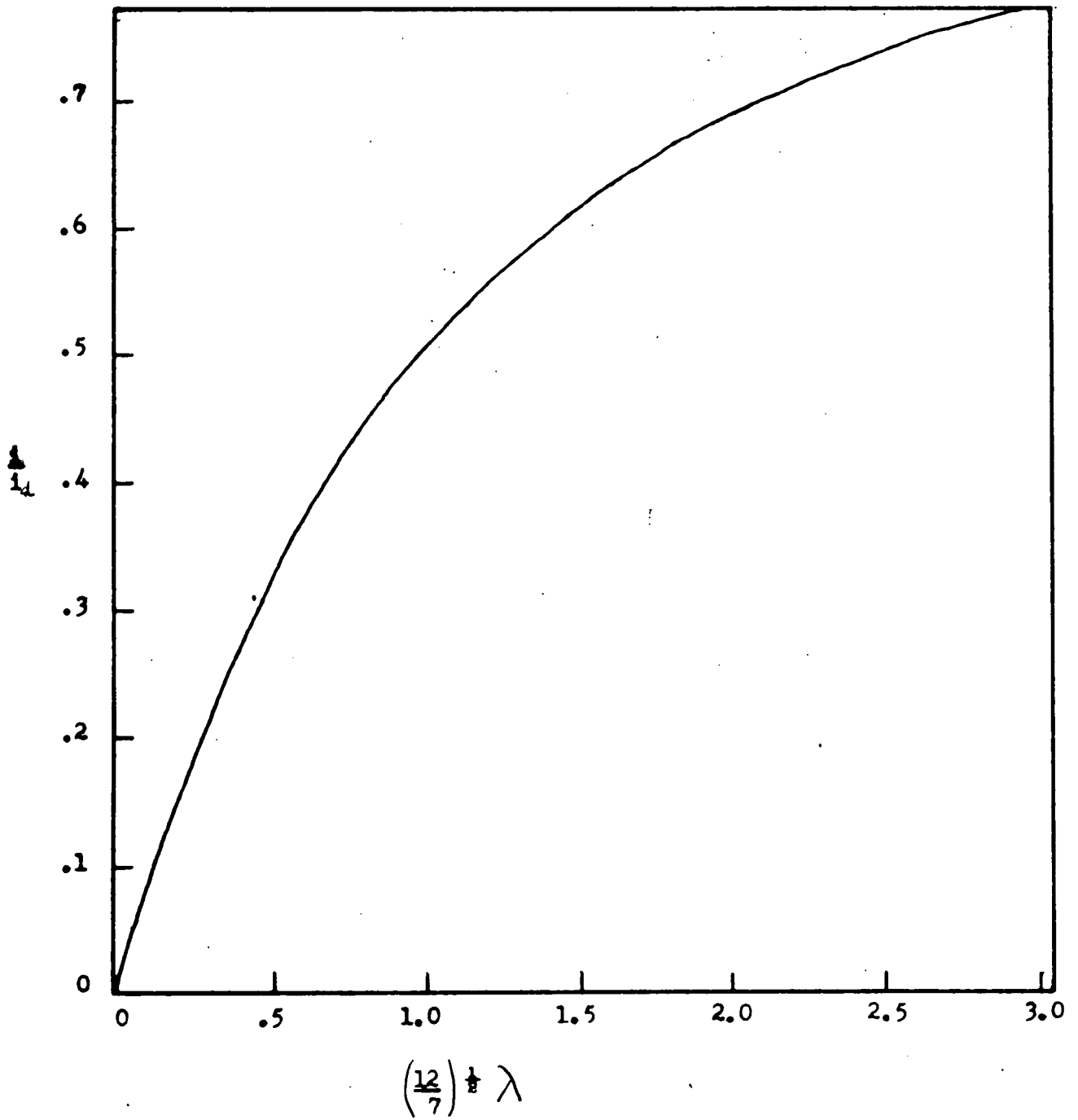
Figure 1

Plot of λ vs$\left(\dfrac{i}{i_{\alpha}}\right)$

where $\hat{k}$ is the Boltzmann constant

h is the Planck constant

$\Delta G^{\ddagger}$ is the free energy of activation

The factor ρ results from the use of the rate constant k_h for heterogeneous process, whereas the factor $\dfrac{\hat{k}\,T}{h}$ corresponds to a homogeneous reaction. The value of ρ is about 10^{-8} cm. E_α is the value of the potential at which the difference of potential at the interface is equal to zero.

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can be determined by the usual way.

B. Kinetic criterion of polarographic reversibility

It was assumed so far that the backward process occurs at a negligible extent. If this condition can not be fulfilled, equations II and III become respectively

$$- \frac{dN_\bullet}{dt} = C_o k^\circ_{f,h} \; \exp \left[- \frac{\alpha\, z_a FE}{RT} \right] - C_R k^\circ_{b,h} \; \exp \left[\frac{(1 - \alpha)z_a FE}{RT} \right] \qquad (B.1)$$

and

$$D_o \left[\frac{\partial C_o}{\partial t}\, (x,t) \right]_{x=o} = k_{f,h} \; C_o(o,t) - k_{b,h}\, C_R(o,t) \qquad (B.2)$$

where the subscripts f and b refer to the forward and backward processes respectively.

The solution for these equations, taking into consideration the former initial and boundary conditions, was found by Delahay (8) and compared with the equation for the reversible polarographic wave A 1. He found that both equations are equivalent when the rate constant $k_{s,h}$ at

the equilibrium potential of the system

$$O \; + \; ze \; \rightleftharpoons \; R$$

is larger than 2×10^{-2} cm sec^{-1}.

The wave is said to be totally irreversible when $k_{s,h}$ is smaller than about 3×10^{-5} cm sec^{-1} .

C. Alternating current polarography

(i) Electrolytic processes

The a. c. polarographic method has been described in detail by Breyer et al (9 - 11).

Briefly, the method can be described as follows. Let us suppose that we are obtaining a d. c. polarogram of a reversible system (say $Tl^{+} + e \rightleftharpoons Tl(Hg)$) in the conventional way. Now, let us superimpose an alternating voltage of small amplitude ($\Delta E = 5 - 50$ mv) over the direct applied voltage to the cell. When the latter corresponds to $E_{1/2}$ the total potential of the d. m. e. will vary from $(E - \Delta E)$ to $(E + \Delta E)$ and the system $Tl^{+} + e \rightleftharpoons Tl(Hg)$ will tend to adjust itself to the value corresponding to the instantaneous potential of the d. m. e. This will cause periodic changes in the concentration of the components of the system, and a resulting alternating current will flow whose magnitude depends on the nature of the system, the magnitude of the a. c. voltage, the concentration of the electrolyzed substance, the frequency of the a. c. voltage, and the non-faradaic properties of the Hg-solution interface.

Breyer's equations for the quantitative relations between the variables mentioned above have not been sufficiently tested and will not be used in this work. However, by keeping all variables except one constant, it is possible to get valuable information about the behaviour of the system under study, as it will be apparent below.

Interpretation of a. c. waves due to irreversible polarographic processes is a difficult problem. Breyer et al claim that irreversible systems do not produce an alternating current. This statement is somewhat misleading: the d. c. polarographic reduction of Ni^{++} in 0.1 M KCl solution is known to proceed irreversibly, but the present author obtained a. c. waves in the same solution (table 1). The magnitude of the current, however, was much less than the value corresponding to a reversible electron transfer process for the same concentration of depolarizer. Addition of small amounts of a non-reducible surface-active agent, Triton X-100 (a water soluble iso-octylphenoxypolyethoxyethanol) lowers the value of the alternating current. Further addition of Triton causes the a. c. wave to vanish.

Another substance whose polarographic reduction is known to proceed irreversibly is O_2 in acid solution. In this case no a. c. wave is observed.

Since an electrolytic alternating current results from periodic concentration changes at the mercury/solution interface, it must be concluded that in the case of the electroreduction of Ni^{++} there is some

Table I

Alternating current polarographic behaviour of Ni^{++} in

in a solution 4×10^{-3} M $Ni(NO_3)_2$ in 0.1 M KCl

Amplitude of the alternating voltage : 50 mv.

Concentration of Triton X-100	Current
0.0000%	18.6 μa ✦
0.0004%	13.0
0.0008%	11.0
0.0020%	4.8
0.0040%	0.0

✦ $Pb(NO_3)_2$ in an approximately equal concentration
in the same supporting electrolyte produces a cur-
rent of about $60 \mu a$. Pb^{++} gives a reversible d. c.
wave.

degree of reversibility. Therefore a non-theoretical log plot (equation A 1) does not rule out the possibility of the occurrence of a reversible step in an irreversible d. c. polarographic reduction. This criterion of reversibility does not coincide with Delahay's definition of a d. c. reversible polarographic wave.

It can be inferred from this discussion that, if two similar systems, under similar conditions of electrolysis, are reduced with different degrees of reversibility, the higher alternating current will be observed for the more reversible one.

(ii) Adsorption-desorption processes

If a solution contains an electro-inactive surface-active substance, and the potential of the d. m. e. corresponds to the adsorption-desorption potential of this substance, an a. c. wave is observed. Breyer et al (10) call this a "tensammetric wave". This type of process does not give a d. c. wave.

The mathematical treatment of the a. c. polarographic wave has been omitted here. The equations derived by Breyer et al have been severely criticized by several workers (12 - 14). It has been pointed out (14) that the measurement of the a. c. characteristics of the cell by means of a bridge gives more accurate information about the electrode process. A mathematical treatment has been developed by Grahame (15). (see also ref. 7, p. 146 - 78)

D. The polarographic reduction of aromatic nitro-compounds

(i) Historical

No systematic studies of the polarographic reduction of aromatic nitro-compounds that have been published so far have made use of the developments outlined above. The first investigations were reported by Shikata and co-workers (16 - 18). Their work was concerned mainly with the relative stability towards reduction of a number of substituted nitro-compounds, and the correlation of the observed "reduction potentials" with the nature and position of the substituents. The reduction potentials were obtained from the zero current intercept of a tangent to the polarographic wave, and did not correspond to the half-wave potentials, usually determined in modern work.

Several other investigations have been subsequently published by several workers (19 - 26). In almost all cases the nitro-compounds were first dissolved in ethanol to prepare the stock solution: then they were diluted with aqueous buffers. The final solutions contained appreciable amounts of ethanol. It is known that the presence of ethanol shifts the half-wave potentials to more negative values, and at the same time introduces some uncertainty in the pH measurements. The studies were mainly concerned with the evaluation of $E_{1/2}$, I_d and z for each compound studied and the effect of substituents on these quantities, although some attempts were made to determine the mechanism of the electrode process. However, no agreement is found among the different authors.
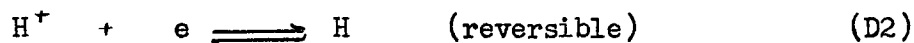
There are conflicting reports from Pearson (19) and Page et al (21) about the dependence of $E_{1/2}$ on the concentration of the depolarizer.

The former worker finds $E_{1/2}$ independent of concentration, while Page et al report a shift of $E_{1/2}$ to more negative values with increasing concentration of the nitro-compound.
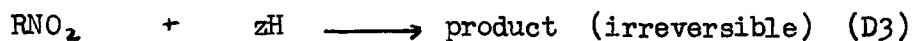
Page et al found that a plot of $E_{1/2}$ vs pH gives a straight line with a slope approaching 0.059 volts per pH unit over a limited range of pH. They interpret this behaviour as caused by a reversible potential-determining step involving one electron:
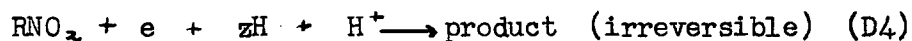
$$RNO_2 + e + H^+ \rightleftharpoons RNO_2H \tag{D1}$$

Pearson (19) finds the same slope in the range of pH from about 7.0 to 10.0, but finds a slope about twice the former value in the acid region. In order to explain these facts he postulates the following sequence of reactions:

$$H^+ + e \rightleftharpoons H \quad \text{(reversible)} \tag{D2}$$

followed by

$$RNO_2 + zH \longrightarrow product \quad \text{(irreversible)} \tag{D3}$$

in neutral or basic solution, or by

$$RNO_2 + e + zH + H^+ \longrightarrow product \quad \text{(irreversible)} \tag{D4}$$

in acid solution. He further claims that this sequence is general for organic electroreductions involving hydrogen. It will be shown in this thesis that this mechanism should be discarded.

The most up-to-date systematic study of the polarography of aromatic nitro-compounds was undertaken by Holleck and Exner (24 - 26). They found that in presence of surface-active substances the polarograms

of some nitro-compounds in neutral and alkaline solutions are split in two distinct waves, the sum of their individual currents being equal to the limiting current of the only wave obtained in absence of the surface-active substance. The effect is more pronounced in alkaline solution, where the height of the first wave tends to a limiting value corresponding to a mono-electronic reduction. No splitting occurs in acid solution, but the half-wave potential is shifted to more negative values.

In order to explain these phenomena Holleck and Exner (25) assume that two initial processes expressed by equation D1 and D5 compete during the reduction of aromatic nitro-compounds at the d. m. e.:

$$RNO_2 \;+\; e \;+\; H^+ \;\rightleftharpoons\; RNO_2H \qquad\qquad (D1)$$

$$RNO_2 \;+\; e \;\rightleftharpoons\; RNO_2^- \qquad\qquad (D5)$$
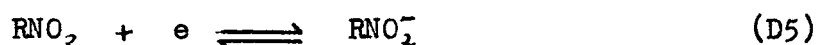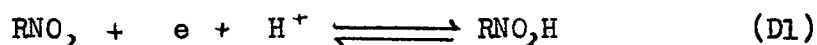
The surface-active substance would hinder the reaction involving H, but it would not interfere with a pure electron transfer. Thus, in acid solution, reaction D1 predominates and the whole wave is shifted to more negative potentials. In basic solution reaction D5 predominates, and the first wave occurs at a potential not much different from the $E_{1/2}$ obtained in absence of surface-active substances. The subsequent reaction, however, involves either H^+, $H^\bullet$, or H_2O; it is hindered, according to Holleck and Exner, until the desorption potential of the adsorbed film is reached. It has to be mentioned that no similar studies on nitrobenzene were reported by Holleck and Exner. However, Heyrovsky and Matyas (27) reported a similar phenomenon with nitrobenzene in basic solution using oscillographic polarography and a streaming mercury electrode.

The polarography of aromatic nitro-compounds in non-aqueous solvents has also been studied to some extent. The solvents used included glacial acetic acid (28, 29), methanesulphonic acid (30), glycerol (31), acetonitrile (4). These studies were limited to the measurement of diffusion-current-constants and half-wave potentials, and the correlation of $E_{1/2}$ with the structure of the depolarizer. An interesting feature in the behaviour of nitro-compounds in acetonitrile was that the reduction was stepwise, suggesting a mechanism similar to that of the nitro-compounds in neutral and basic aqueous buffers in presence of surface-active agents.

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Since nitrobenzene is the simplest aromatic nitro-compound, it was decided to study its polarographic behaviour by means of both d. c. and a. c. polarography, in aqueous solutions and in anhydrous acetonitrile. The main purpose of this study was to obtain information to establish the mechanism of the electroreduction of nitrobenzene. Some tests are also made on other aromatic mono-nitro-compounds in order to determine similarity of behaviour. These tests, however, are to be regarded only as preliminary, and more work should be done before the conclusions obtained for nitrobenzene are extended to other aromatic mono-nitro-compounds.

EXPERIMENTAL

A. Materials

(i) Buffer

Britton and Robinson universal buffer was used for all work in aqueous solution. The concentration of sodium ion in the buffer was kept constant in the whole pH range and equal to that of the alkaline buffer of pH 12 by the addition of the necessary amount of NaCl to the other solutions. This was done because of the observation (32) that irreversible waves are shifted to more negative potentials by the presence of cations. All the chemicals used in the preparation of the buffer were of reagent grade. pH values were measured with a Beckmann pH meter, model G.

(ii) Nitrobenzene

Fischer's reagent grade nitrobenzene was distilled, and less than one-third of the distillate (the middle fraction) was used to prepare the stock solution. No ethanol was used since the solubility of nitrobenzene in water is about 10^{-2} M, and the range of concentrations studied was from less than 10^{-4} M to about 10^{-3} M.

(iii) <u>Nitrosobenzene</u>

It was prepared according to directions in the literature (33), and it was recrystallized twice from ethanol.

(iv) <u>o-Nitrophenol and p-nitroaniline</u>

These chemicals were of reagent grade and were used without further purification.

(v) <u>Acetonitrile</u>

It was purified according to directions in the literature (33). Usually several distillations were required before a "polarographically pure" product was obtained.

(vi) <u>Tetra-n-butylammonium iodide</u>

It was prepared according to directions in the literature (34). It was recrystallized several times from anhydrous ethyl acetate. It was noticed that the residual-current-polarogram of a 0.1 M solution of the salt in acetonitrile exhibited a small wave at about -1.8 vs the mercury pool anode which could not be suppressed by further purification.

(vii) <u>Surface-active substances</u>

They included gelatin, basic fuchsin, camphor and Triton X-100. Their solutions in the supporting electrolyte were checked to be "polarographically pure". (fuchsin was used only at very small concentrations)

B. Apparatus and procedure

(i) Precautions regarding the use of acetonitrile as supporting

electrolyte

Since very small amounts of water affect the polarographic behaviour
of organic compounds in acetonitrile, the solvent was handled under a dry nitro-
gen atmosphere from its final distillation through the preparation of the
supporting electrolyte and stock solutions to the final recording of the polaro-
gram. The preparation of the supporting electrolyte and stock solutions is
illustrated by figure 2. A portion of the solvent is pumped with dry nitrogen
from its container A to flask B, where it dissolves the C_4H_9NI, and from there
to the volumetric flask C until the latter was filled up to the 500 (or 250)
ml. mark.

Various concentrations of the depolarizer could be prepared directly
in the polarographic cell by means of the apparatus described in figure 3. Dry
nitrogen could be used either to deaereate the solutions contained in flasks
A and/or B, or, by proper use of the stopcocks, to pump the solutions to the
burettes, from which a known volume of either solution could be delivered to
the cell. About 100 ml (measured to 0.1 ml) of the previously deaereated sol-
ution of the supporting electrolyte, contained, say, in flask A, were trans-
ferred to the dry polarographic cell via the burette A', and triple-distilled
mercury was added to make the mercury pool anode. A residual current polaro-
gram was then obtained. Then an accurately measured amount of the stock solu-
tion containing the same concentration of supporting electrolyte was introduced
into the cell from flask B, via the burette B', and the mixture was made homo-
geneous by bubbling nitrogen through it. Thus it was possible to work with
increasing concentrations of depolarizer by the addition of several successive
amounts of stock solution. The burettes were provided with Teflon plugs in
order to avoid contact of acetonitrile with stopcock grease.
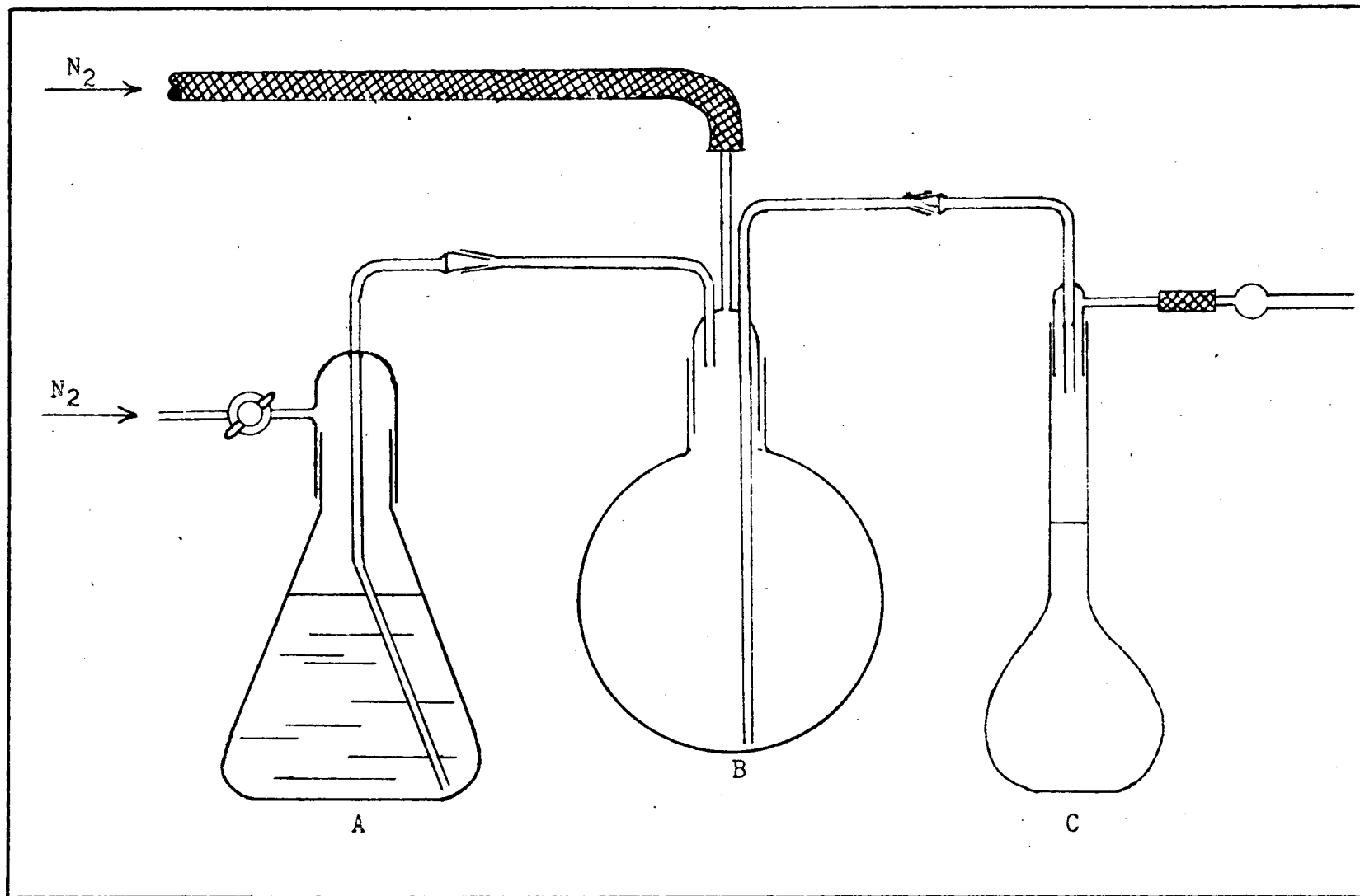
The polarographic cell is shown in figure 4.

Fig. 2
Preparation of moisture-free solutions for acetonitrile
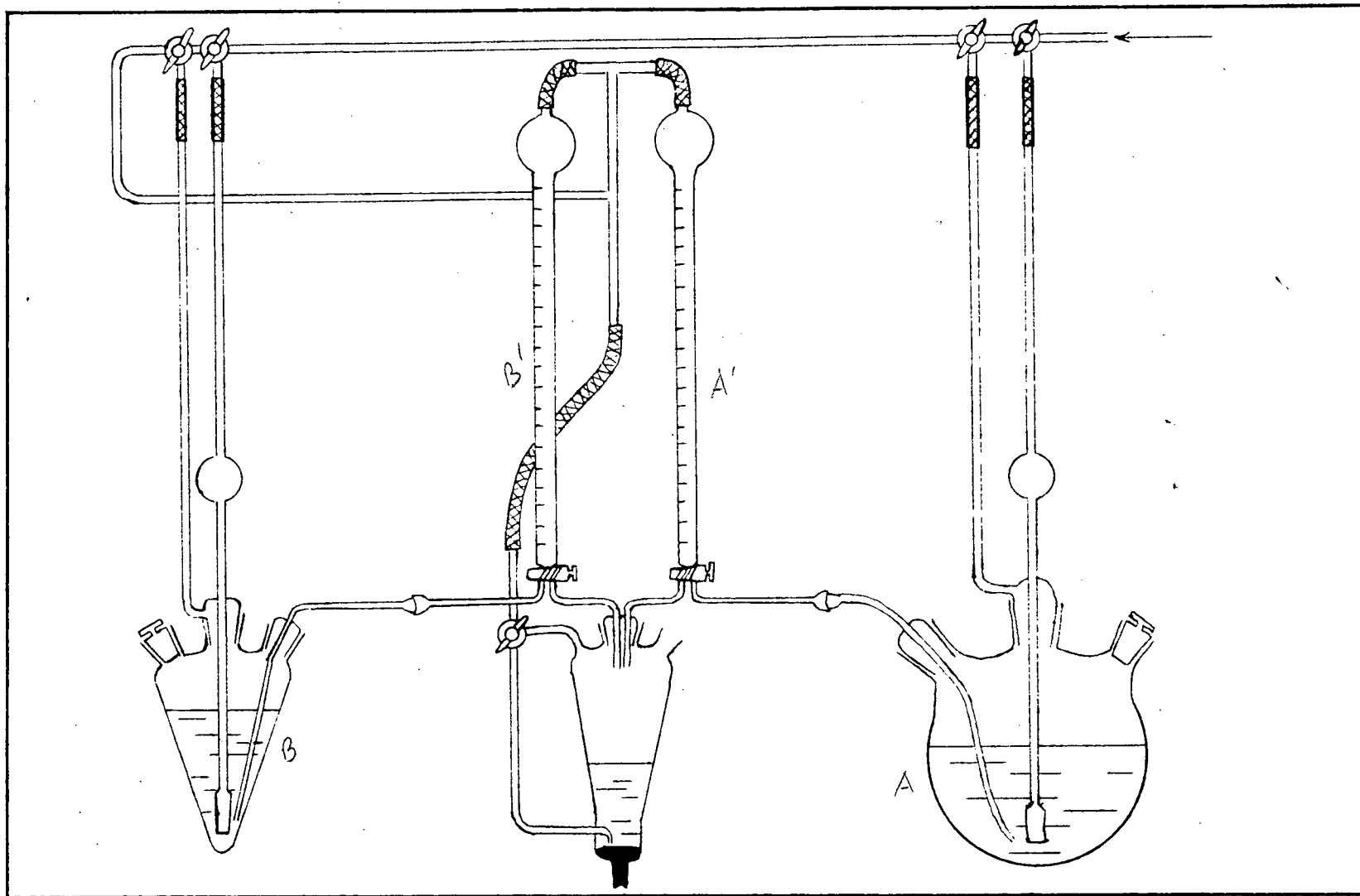polarography

18.

Fig. 3

Apparatus for polarography in acetonitrile.
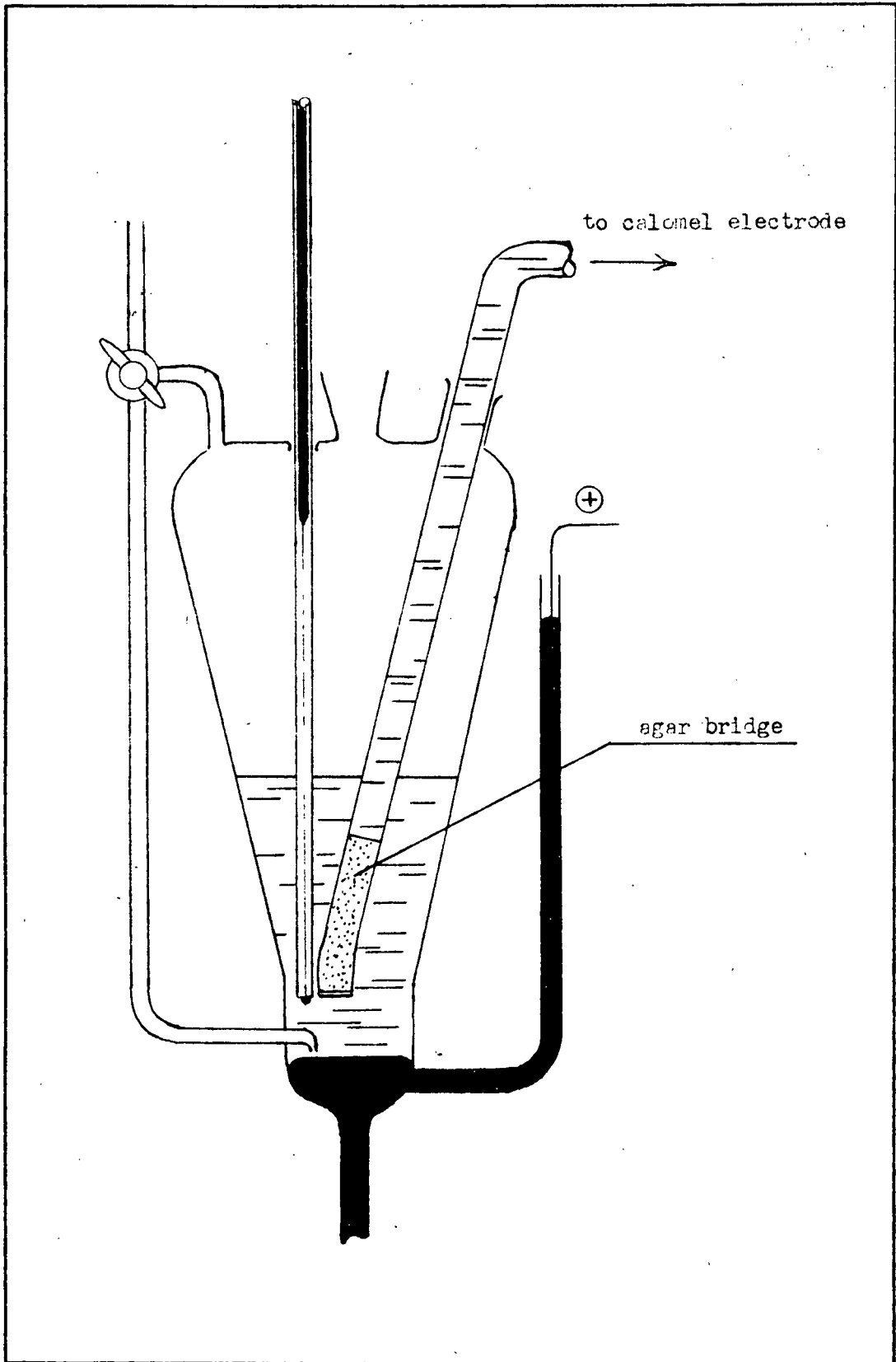
to calomel electrode

agar bridge

Figure 4

Polarographic cell

The reference electrode used for polarography in acetonitrile was the mercury pool in presence of 0.1 M C_4H_9NI. Its potential has been calculated by Wawzonek (35) to be about -0.78v vs SCE. An external refer-ence electrode has the disadvantage of introducing an unknown liquid-junction potential with the acetonitrile solution if it is aqueous, or with the normal hydrogen electrode if it is non-aqueous.

A saturated calomel electrode was used for aqueous polarography. It was kept out of the electrolytic circuit in order to minimize the ohmic potential drop in the cell. A mercury pool was the "active" anode.

Two capillaries, I and II were used at different stages of this work. Capillary I was used with a head of mercury of 50.56 cm. It had a drop time of 4.43 seconds and a rate of flow m = 1.463 mg/sec when dropping in 0.1 M KCl with the circuit open. It was used for all the work in ace-tonitrile. Capillary II was used with a head of mercury of 33.4 cm. When dropping in 0.1 M KCl (open circuit) it had a drop time of 4.3 seconds and a rate of flow m = 1.911 mg/sec.

The resistance of the cell was kept low by maintaining a distance between the mercury pool and the d. m. e. of less than 1 cm.

All the results obtained in this work were obtained with the polarographic cell in a constant-temperature bath, maintained at 25.0 ± 0.1 C.

(ii) Instrumentation

A Sargent Polarograph model XXI was used for all the runs. It was modified according to Miller (36) in order to make possible the

recording of a. c. polarograms, in addition to the d. c. ones. The voltage scale of the polarograph was calibrated by means of a Leeds & Northrup Student's Potentiometer. For accurate measurement of half-wave potentials a slow voltage scanning *rate* (0.0375 v/min) was used in order to minimize the recorder lag. The runs were stopped at two or three points in the vicinity of the $E_{1/2}$, and the corresponding potentials were measured with the potentiometer. $E_{1/2}$ was then found by interpolation.

The amplitude of the alternating voltage used for the obtention of a. c. polarograms was 50 mv. The frequency of the alternating voltage was 60 cycles per second.

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Unless otherwise specified, current values i will be expressed in microamperes (μa), and potential values E will be expressed in volts vs. the saturated calomel electrode (SCE).

RESULTS AND DISCUSSION

A. Nitrobenzene in aqueous solution

Previous work in nitrobenzene has been carried out in aqueous buffers in presence of ethanol. In ethanol-free solutions nitrobenzene behaves similarly; the overall electrode reaction is irreversible and proceeds in one wave to phenylhydroxylamine at a pH > 3.0. A small second wave, showing reduction to aniline, but ill-defined and coupled with at least one chemical reaction appears in solutions of pH lower than 3.0 (figure 5). There is no agreement as to the nature of the chemical reaction (23, 37). Plots of $E_{\frac{1}{2}}$ vs the pH of the solution give straight lines up to a pH of about 9.0 with a slope approaching 0.059 volts per pH unit at 25°C (figure 6). The steepness of the waves corresponds approximately to that of a monoelectronic reduction. The value of the diffusion current is proportional to the concentration of nitrobenzene below 10^{-3}M.

The following information has not, to the author's knowledge, been previously reported. In ethanol-free solutions in presence of 0.01% gelatin, the half-wave potentials of nitrobenzene are consistently more positive by 0.03 or 0.04 volts than those obtained in presence of 8% ethanol, as can be seen by comparing figure 6 with Pearson's data (19). In absence of maximum suppresors the current potential curves are well defined only at concentrations lower than 10^{-4}M. At higher concentrations
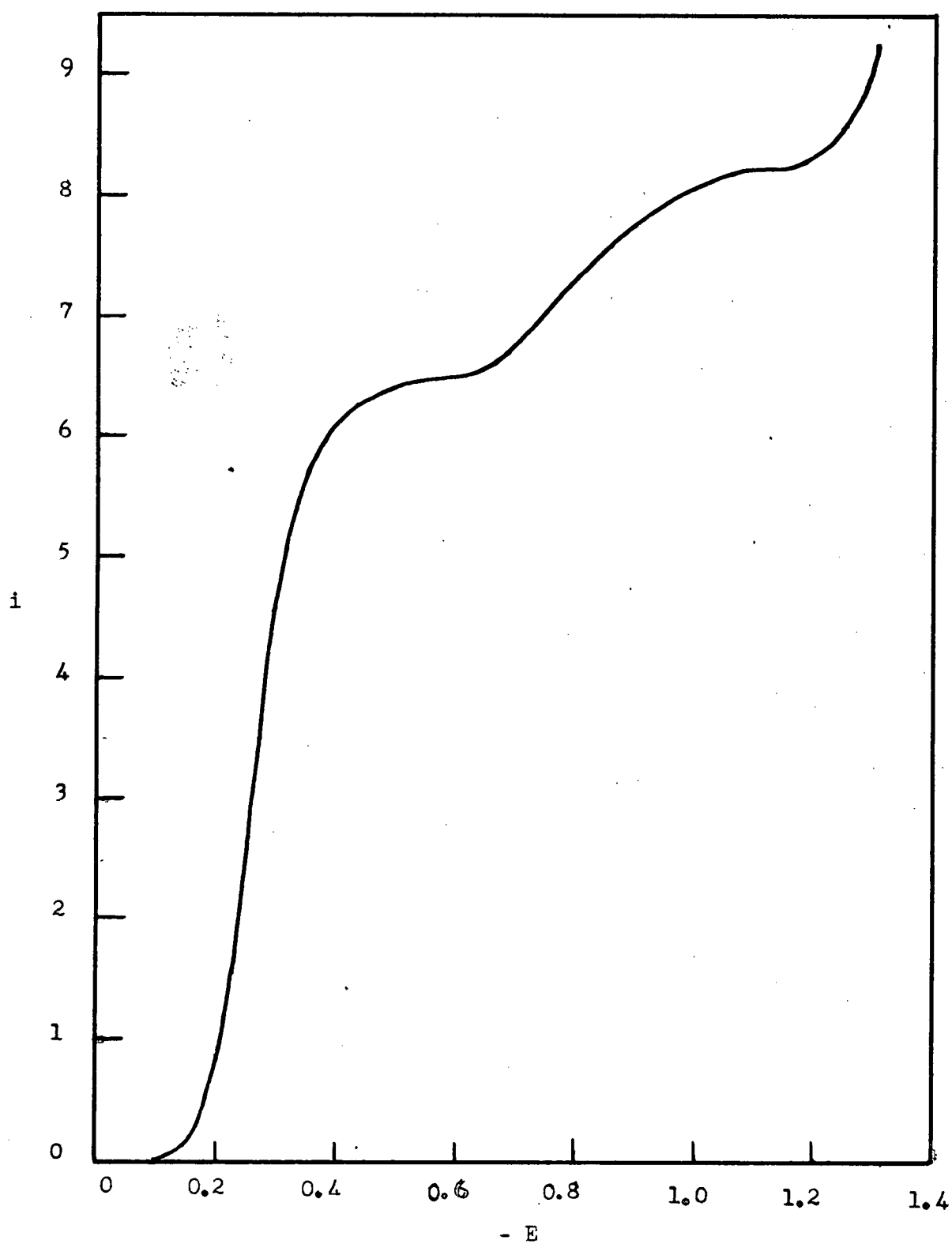
Figure 5

Polarogram of 3.92×10^{-4} PhNO$_2$

pH = 1.8
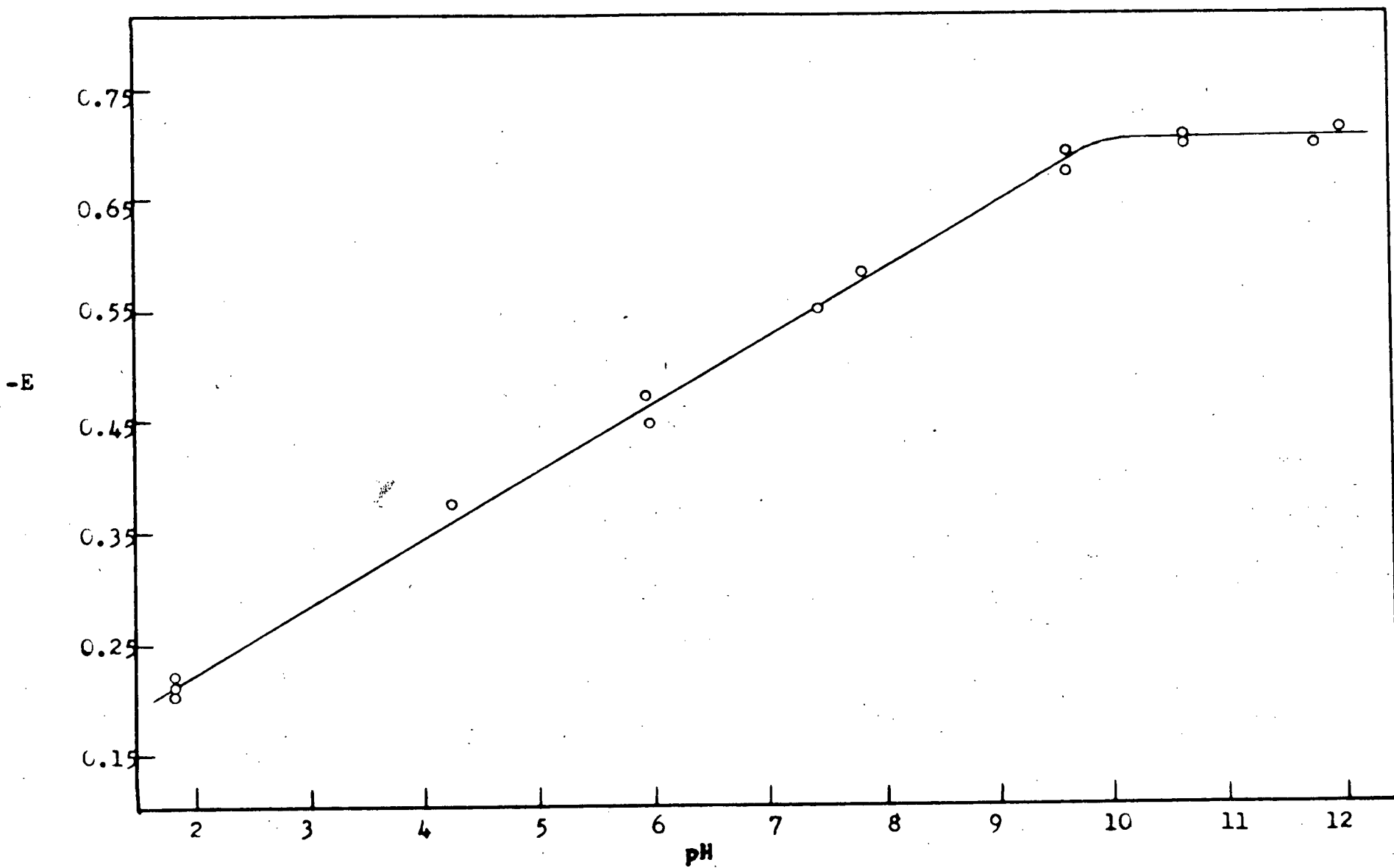
Fig. 6

pH - $E_{\frac{1}{2}}$ relationship.

maxima may occur. It was noticed that the tendency for maximum formation is greater at higher pH, but no quantitative relationship is apparent. Maxima may occur in basic solution even at concentrations lower than 5×10^{-5} M (figure 7). The heights of the maxima decrease on standing.

The origin of maxima in the current-potential curves of nitrobenzene at the mercury/solution interface. The evidence for adsorption is shown in the electro-capillary curves (figure 8) of mercury in a solution containing 8×10^{-3} M $PhNO_2$. In absence of nitrobenzene or other adsorbable substances curve "a" is obtained. The lowering of the surface tension of mercury in presence of nitrobenzene (curve b) is due to the adsorption of the latter at the mercury/solution interface. Non-reducible substances having a higher surface activity than nitrobenzene suppress the maxima by being adsorbed at the interface instead of nitrobenzene (curve c). The point of coincidence of curves "a" and "c" corresponds to the desorption potential of Triton X-100.

B. Alternating current polarographic behaviour

In absence of maximum suppresors, nitrobenzene gives small a. c. waves. A relatively high amplitude of the a. c. voltage had to be used (50 mv) in order to make the waves easily visible in acid solution. The same value of the a. c. voltage was used throughout this work for the other solutions. It was noticed that the height of the a. c. waves increased with increasing height of the mercury column (table II). This behaviour is different from that of a "well-behaved" system, where it is found that the a. c. does not vary with the mercury pressure. The height of the a. c. waves was found to increase with increasing pH of the solutions studied, although no quantitative relationship is apparent.
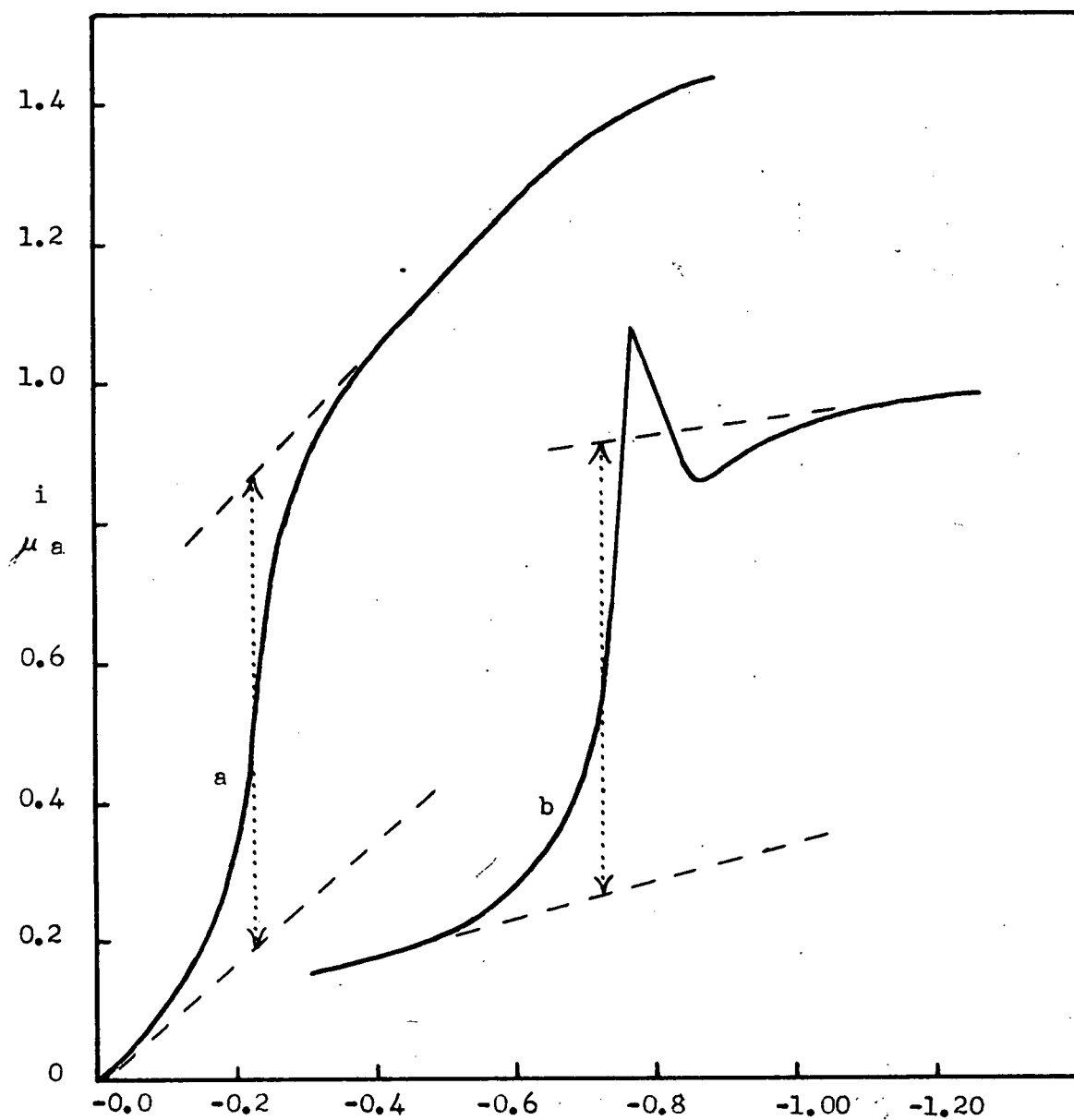
Figure 7

Influence of pH on tendency to maximum formation

a) 4.48×10^{-5} M PhNO$_2$, pH = 1.8
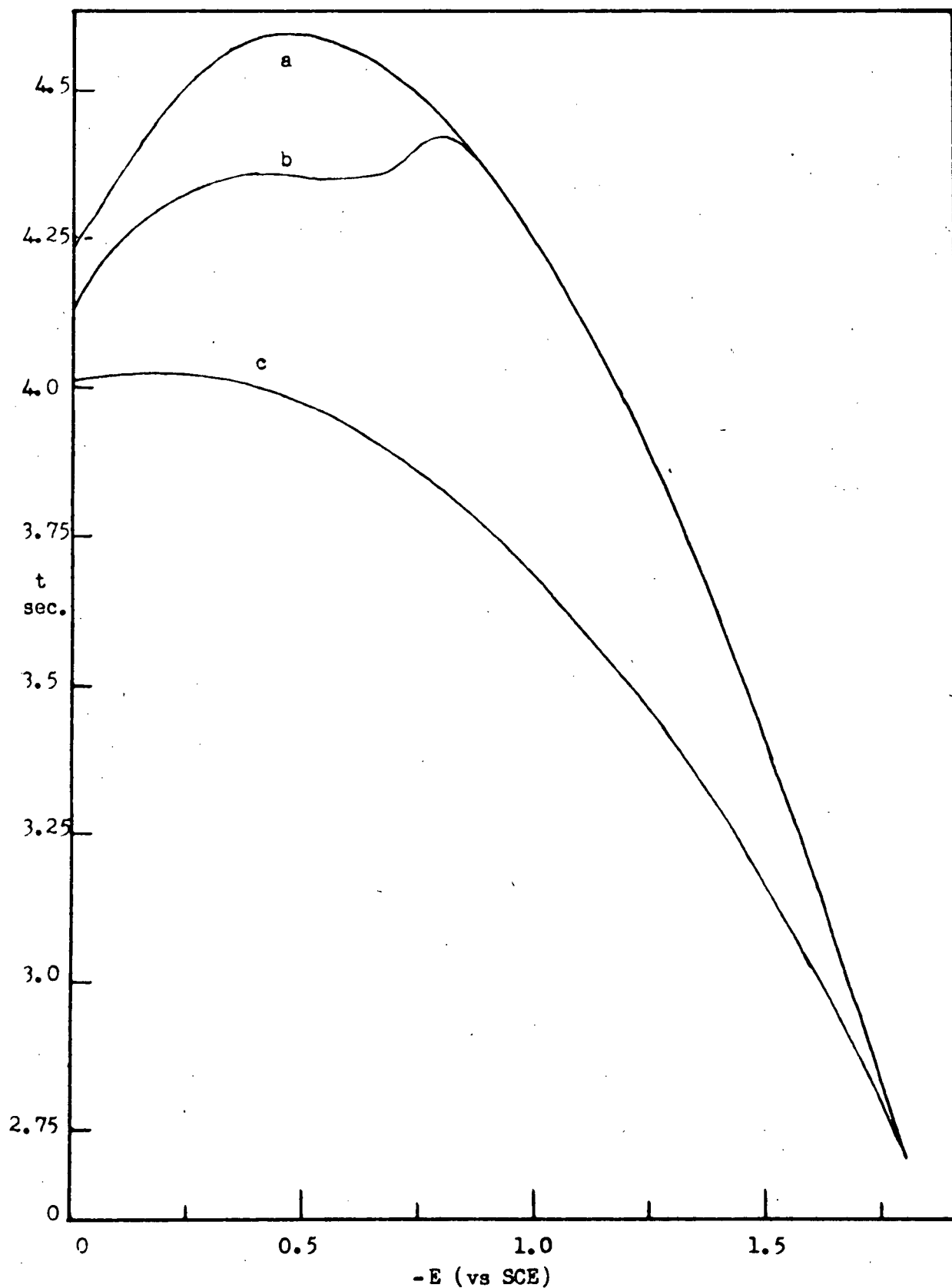
b) 4.48×10^{-5} M PhNO$_2$, pH = 9.0

Figure 8 - Electrocapillary curves of Hg in
a) Buffer, pH 7   b) Same, plus 8 x 10⁻³ M PhNO₂
c) Same as a), plus 0.05% Triton x 100

Table II

Irregular dependence of the alternating current

on the height of the mercury column and the con-

centration of nitrobenzene in presence and absence

of Triton X-100

pH 11.9

Concentration	Pressure, cm. Mercury	Triton	Current
4.65 10^{-4} M	33.4	---	2.4 μa
4.65 10^{-4} M	84.0	---	6.17 "
9.3 10^{-4} M	33.4	0.002%	5.46 "
9.3 10^{-4} M	84.0	0.002%	5.62 "
1.39 10^{-3} M	33.4	0.002%	10.56 "
1.86 10^{-3} M	33.4	0.002%	14.00 "

In presence of 0.01% gelatin or 0.001% Triton X-100 the height
of the mercury column ceased to affect the a. c. wave heights, although
the other a. c. characteristics mentioned above persisted. In figure 9
the effect of pH is illustrated. The higher wave is still much smaller
than that corresponding to a reversible one-electron transfer. It can
also be noticed that the "summit potential" of the a. c. wave (referred
to below as E_s) does not correspond exactly to $E_{\frac{1}{2}}$ (figure 9). The con-
centration-dependence of the a. c. wave heights was not linear (table II).

C. Effects of surface-active agents

The effect of increasing concentrations of Triton X-100 on the
polarographic reduction of nitrobenzene in basic solution (pH 11.9) is
illustrated in figures 10 and 11. It can be seen that, as a limiting
property, two distinct waves are formed, the sum of their heights being
equal to the height of wave "a", while their ratio becomes 1:3. Since
the overall process involves 4 electrons, this ratio is evidence for a
monoelectronic reduction for the first wave. At lower concentrations of
Triton the effect is more pronounced the longer the drop time of the
d. m. e. (curves b and c).

In neutral solution the same splitting is found, and the $E_{\frac{1}{2}}$
of the first and second waves appear at about the same potentials as in
basic solution. However, the limiting ratio 1:3 is not reached, even
after increasing the concentration of Triton to more than 1% (figure 12).

In acid solution no splitting occurs, but the $E_{\frac{1}{2}}$ is shifted
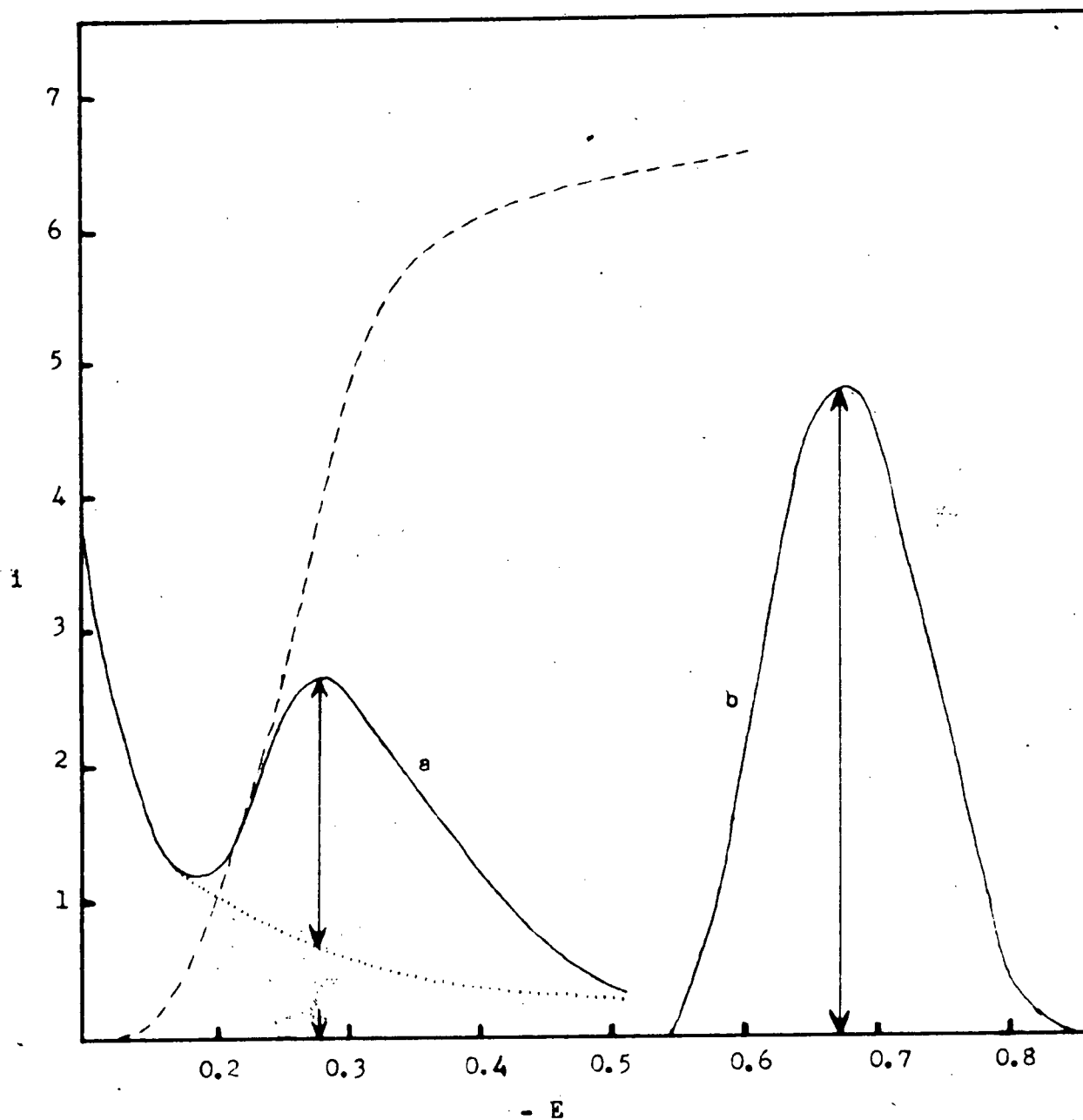to considerably more negative potentials.

Figure 9

pH and a. c. height

a) pH = 1.8, 3.92×10^{-4} M $PhNO_2$

b) pH = 9.6, 3.92×10^{-4} M $PhNO_2$

●—— d. c. polarogram of "a"

Figure 10

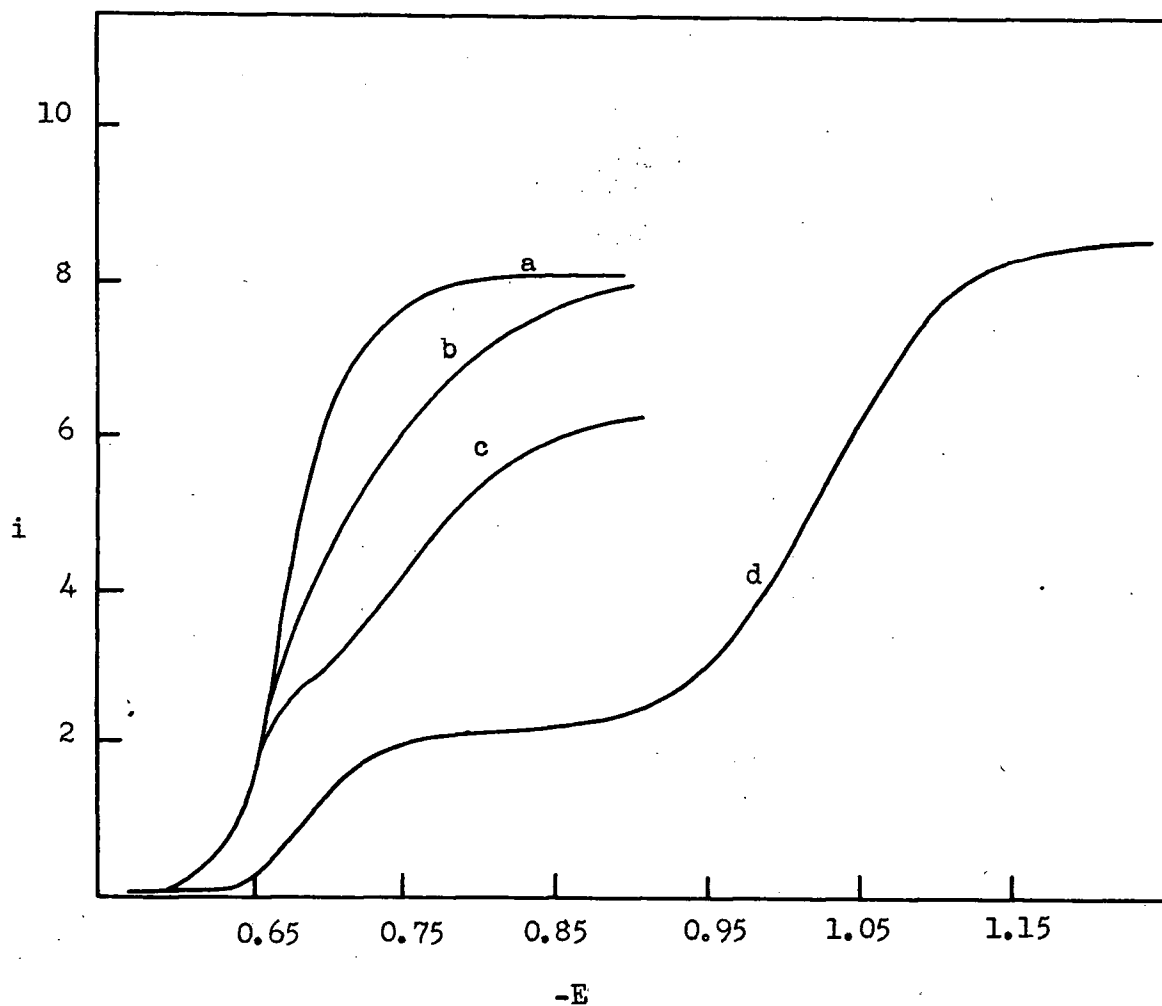Effect of Triton X-100 on the d. c.

polarograms of 5.6 x 10^{-4} M PhNO$_2$, pH 11.9

5.6 x 10^{-4} M PhNO$_2$ in a buffer of pH 11.9

a) 0.0006% Triton, t at E$_{1/2}$: 4.4 seconds

b) 0.0017% Triton, t at E$_{1/2}$: 4.4 seconds

c) 0.0017% Triton, t at E$_{1/2}$: 6.4 seconds

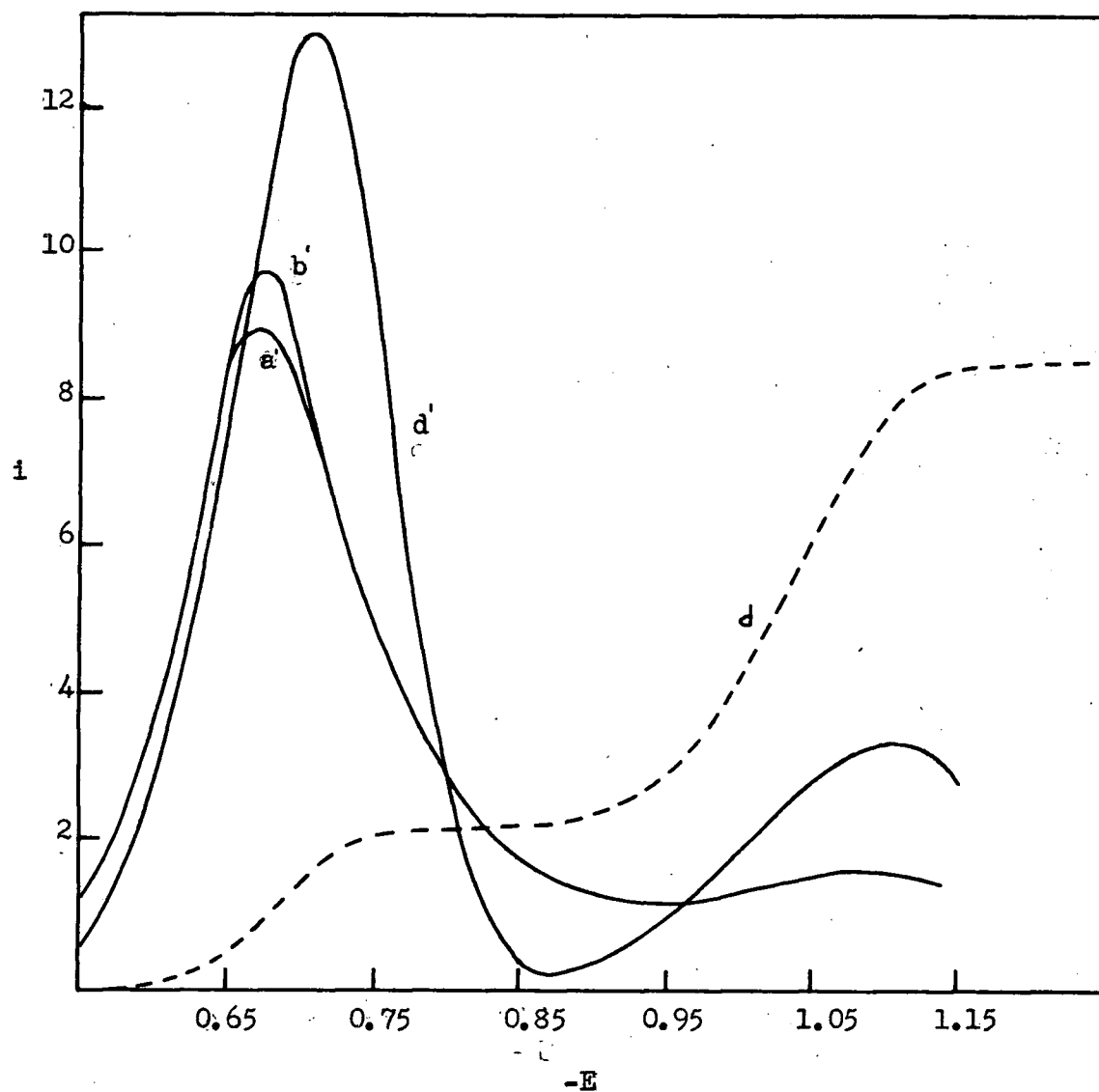d) 0.01% Triton, t at E$_{1/2}$: 4.2 seconds

Figure 11

a. c. polarograms of the same
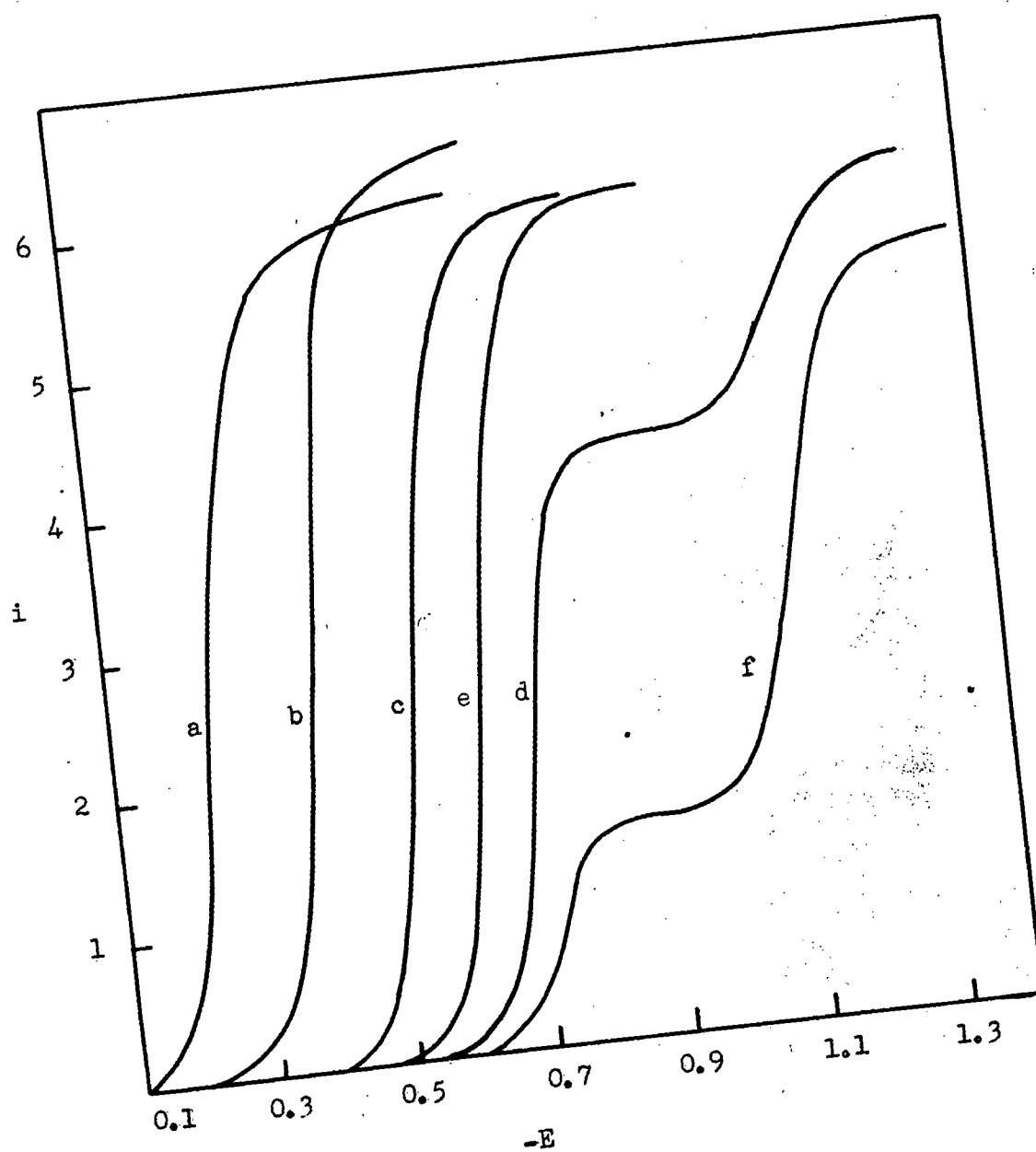
solutions as in figure 10

Figure 12

d. c. polarograms of 3.94×10^{-4} M $PhNO_2$

a) pH 1.8, no Triton

b) pH 1.8, 0.05% Triton

c) pH 7.4, no Triton

d) pH 7.4, 0.05% Triton

e) pH 9.6, no Triton

f) pH 9.6, 0.05% Triton

In neutral and basic solutions of $PhNO_2$ the a. c. polarograms show waves whose height increases with increasing concentration of Triton, until a limiting value is reached at the same concentration of the surface-active agent at which a limiting ratio is attained for the d. c. waves (figure 13). No substantial increase is found in acid solutions. The height of the a. c. wave is maximum in basic solution, when the ratio 1:3 for the two d. c. waves has been obtained.

Camphor and basic fucshin were found to cause the same effect as Triton. Gelatin was tried, too, but it caused only partial splitting at a concentration of 0.1% (figure 14).

The splitting of multi-electronic waves by non-reducible surface-active agents was first reported by Kolthoff and Barnum (39). Later Wiesner (40) found the same effect in the electroreduction of quinones caused by eosine dyes. He, too, found the effect more pronounced for longer drop-times. Wiesner interprets these effects as caused by film formation on the electrode surface, the rate of which depends on the concentration of the dye. At low concentrations of the surface-active substance the formation of a film is not immediate, and this would explain the more pronounced effect noticed with slowly dropping mercury. This interpretation seems to apply to the present case. Current-time curves obtained for single drops during the electroreduction of nitrobenzene (figure 15) show the process to be more hindered at the end of the drop-life. But then Wiesner interprets the splitting of the wave as due to a "sieve action" which prevents part of the electroreducible substance from reaching the cathode until more negative potentials are applied to the d. m. e. If this were true for the present work, the limiting ratio 1:3 for the two waves, and the increase in the a. c. current with increasing
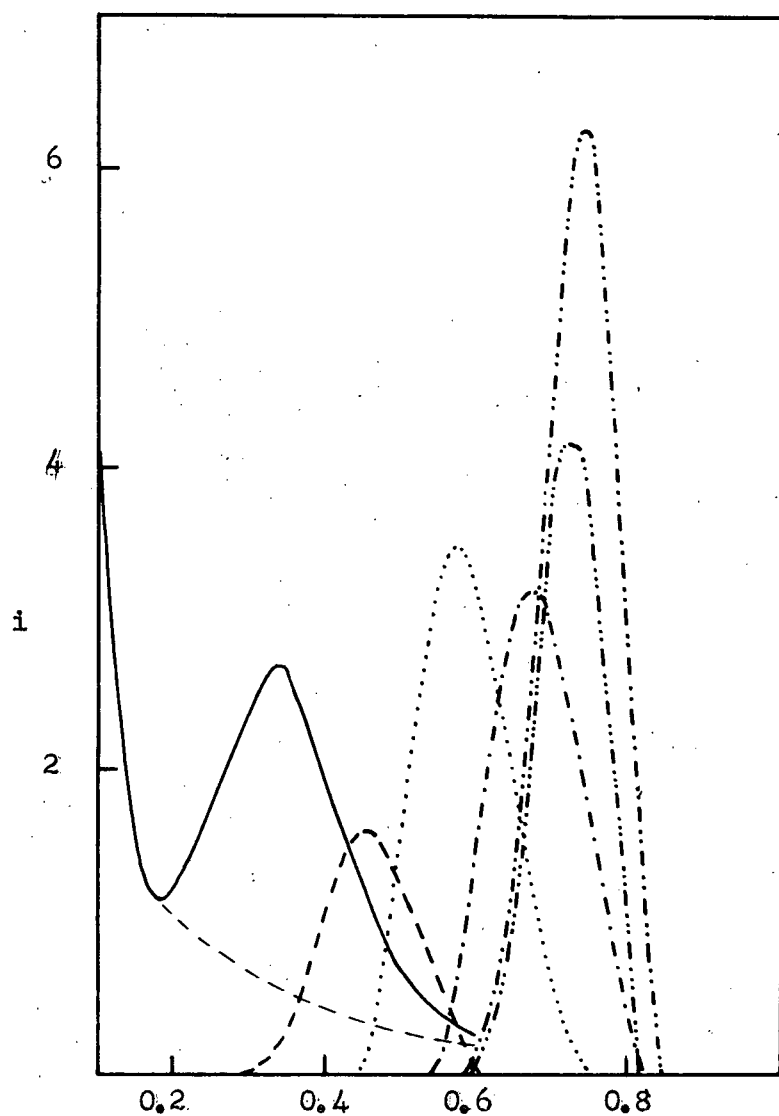
Figure 13

a. c. polarograms of the same

solutions as in figure 12

———— a	·····—·····d	
— — — b	—··—··—·· e	
······· c	—··—·· f	
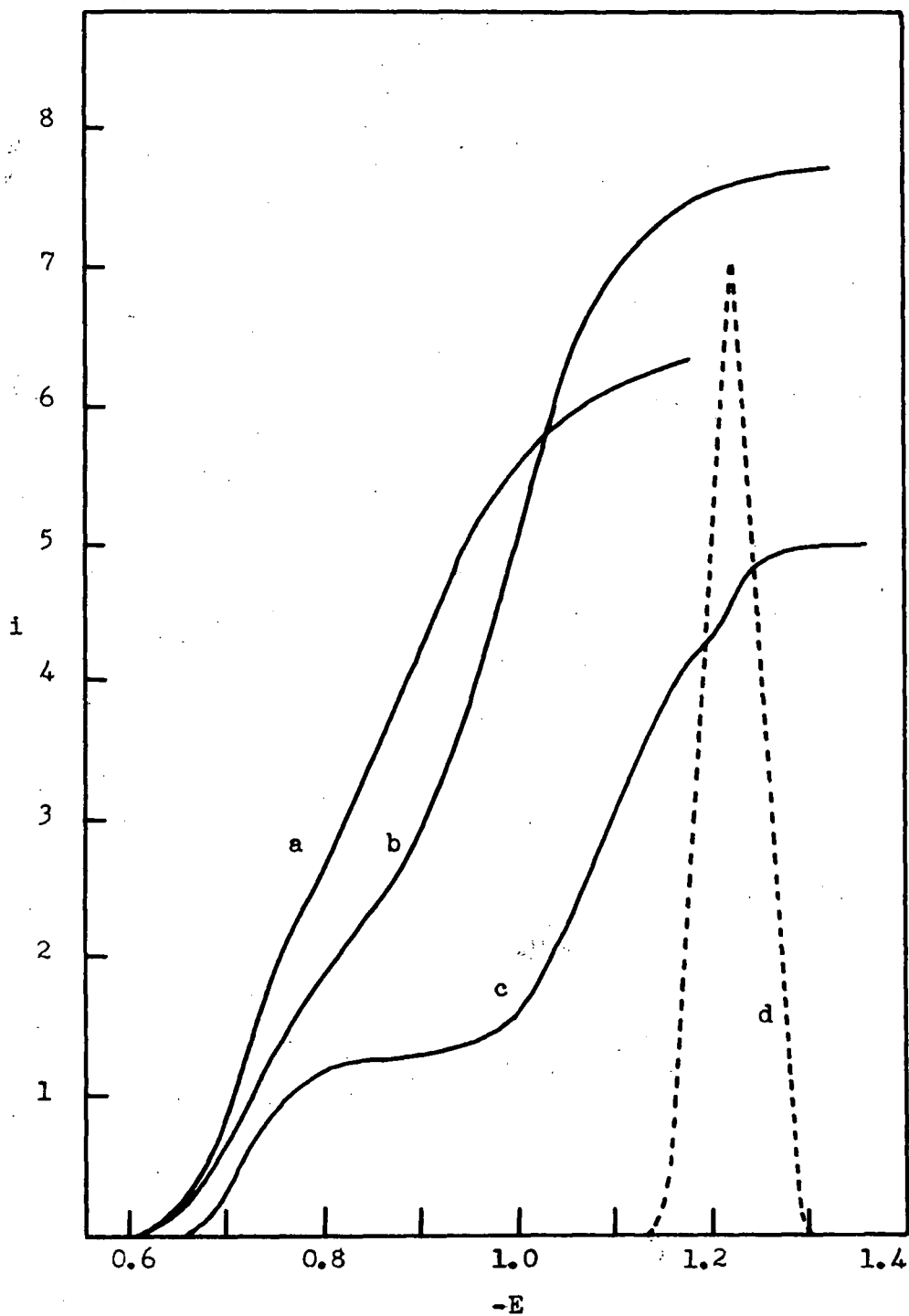
Figure I4

Polarograms of:

a) 4.5×10^{-4} M $PhNO_2$, 0.1% gelatin

b) 5.0×10^{-4} M $PhNO_2$, 0.006% fuchsin

c) 3.3×10^{-4} M $PhNO_2$, 0.1% camphor

d) Tensammetric wave of camphor

Fig. 15

i - t curves for individual Hg drops

t = 6.1 seconds

Triton concentration could not be explained. Probably the quinones studied by Wiesner were reduced in two one-electron stages, the first one corresponding to the reversible formation of a semi-quinone. A re-investigation of Wiesner's work seems to be desirable.

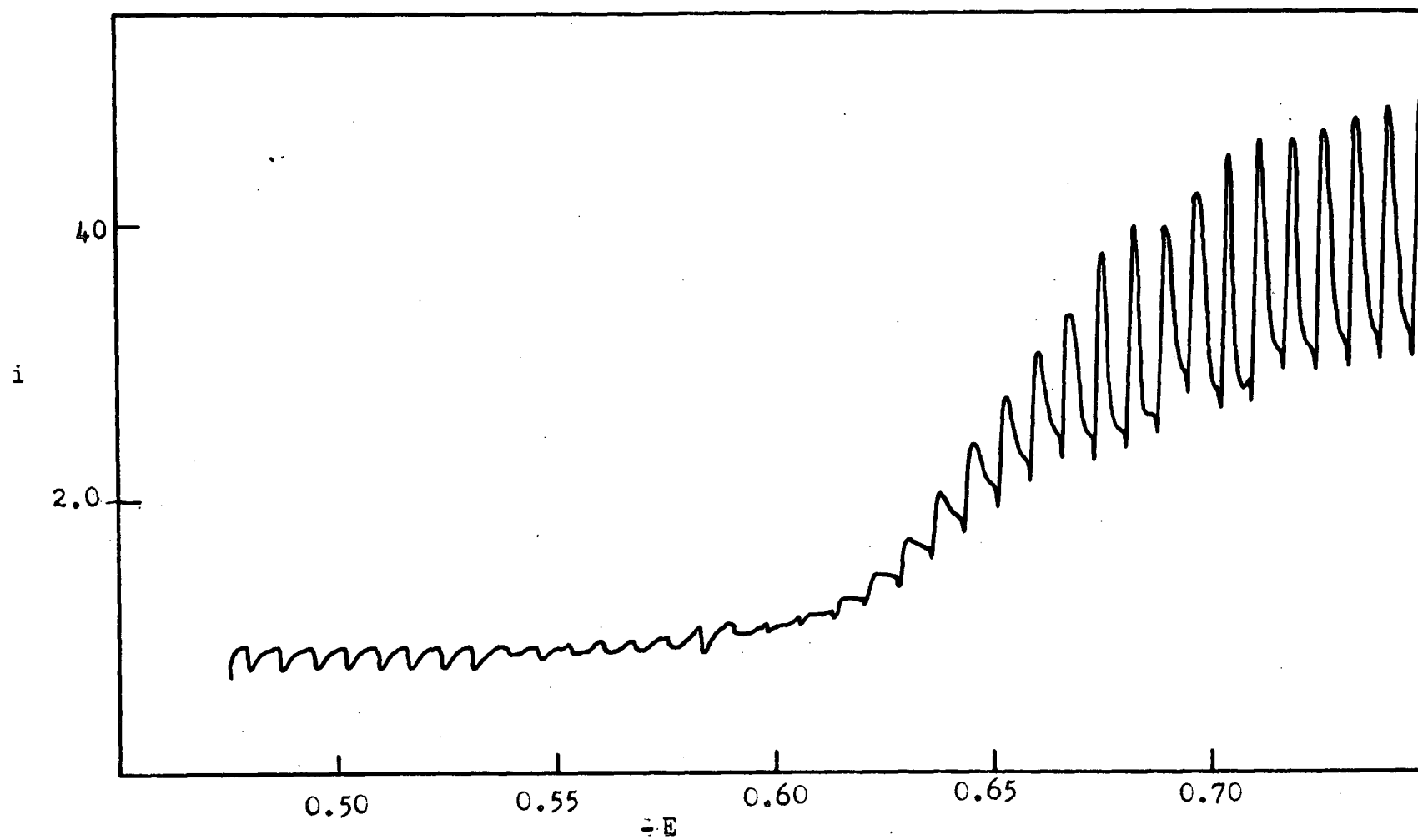The author's results obtained with d. c. polarograph are similar to those of Holleck and Exner (24 - 5) for other aromatic nitrocompounds already mentioned. Their interpretation is here re-examined in the light of the experimental evidence obtained with a. c. polarography.

In basic solution the primary reaction seems to be the one proposed by Holleck and Exner, that is

$$PhNO_2 + e \rightleftharpoons PhNO_2^- \qquad (A1)$$
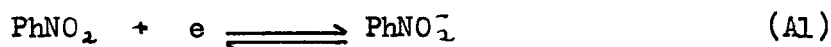
The fact that the $E_{1/2}$ of $PhNO_2$ is independent of pH in basic solution is in agreement with this step. The increase in the alternating current due to the addition of Triton indicates that the process is rendered more reversible by hindering the following irreversible reactions. This hindrance also shows that the second step is not a pure electron transfer (for a discussion of hindrance of electrode processes, see references 41,-43, 27).

A probable second step would be

$$PhNO_2^- + H_2O + e \longrightarrow PhNO + 2OH^- \qquad (A.2)$$
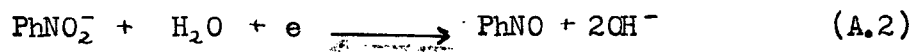
Since the reduction potential of PhNO is much more positive than the value at which the above reactions occur, the reduction to phenyl-hydroxylamine proceeds at once.

The Triton would tie-up the $PhNO_2^-$ and hinder its reaction with H_2O until an overpotential is applied to the d. m. e. high enough to

overcome the barrier introduced by the Triton.

Holleck and Exner (24 - 5) used tylose, camphor, gelatin and agar-agar as surface-active agents in an extensive study of the polarographic reduction of p-nitroaniline. They found the desorption potential of camphor to nearly coincide with the second wave of the reducible substance in basic solution. They concluded that, in general, the second wave in the reduction of nitrocompounds occurs only after the surface-active agent is desorbed. The author found this conclusion not true: Triton is desorbed at -1.80 vs SCE at a concentration of 0.05% as can be seen from the electrocapillary curves of mercury in solutions with and without Triton (figure 8). However, the second wave of nitrobenzene in a solution of pH 9.6 occurs at about -1.15 v. vs SCE. It seems then that the results of Holleck and Exner were just a coincidence. This was conclusively proven by obtaining a polarogram of p-nitroaniline in presence of 0.05% Triton. The $E_{1/2}$ of the second wave in a solution of pH 7.0 was found to be about -1.4 volts vs SCE (figure 16).

For acidic solutions the German authors postulate the following mechanism

$$RNO_2 \ + \ e \ + \ H^+ \rightleftharpoons RNO_2H \qquad (43)$$

which they consider to be essentially different from that in basic solution. They also claim that the two processes overlap in neutral solution. Recent work by V. Stackelberg and Weber (44) has shown, however, that the electroreduction of nitrobenzene and several other organic compounds proceeds through electron transfer as the initial step, even at low overvoltage cathodes, and that the dependence of the reduction potential on
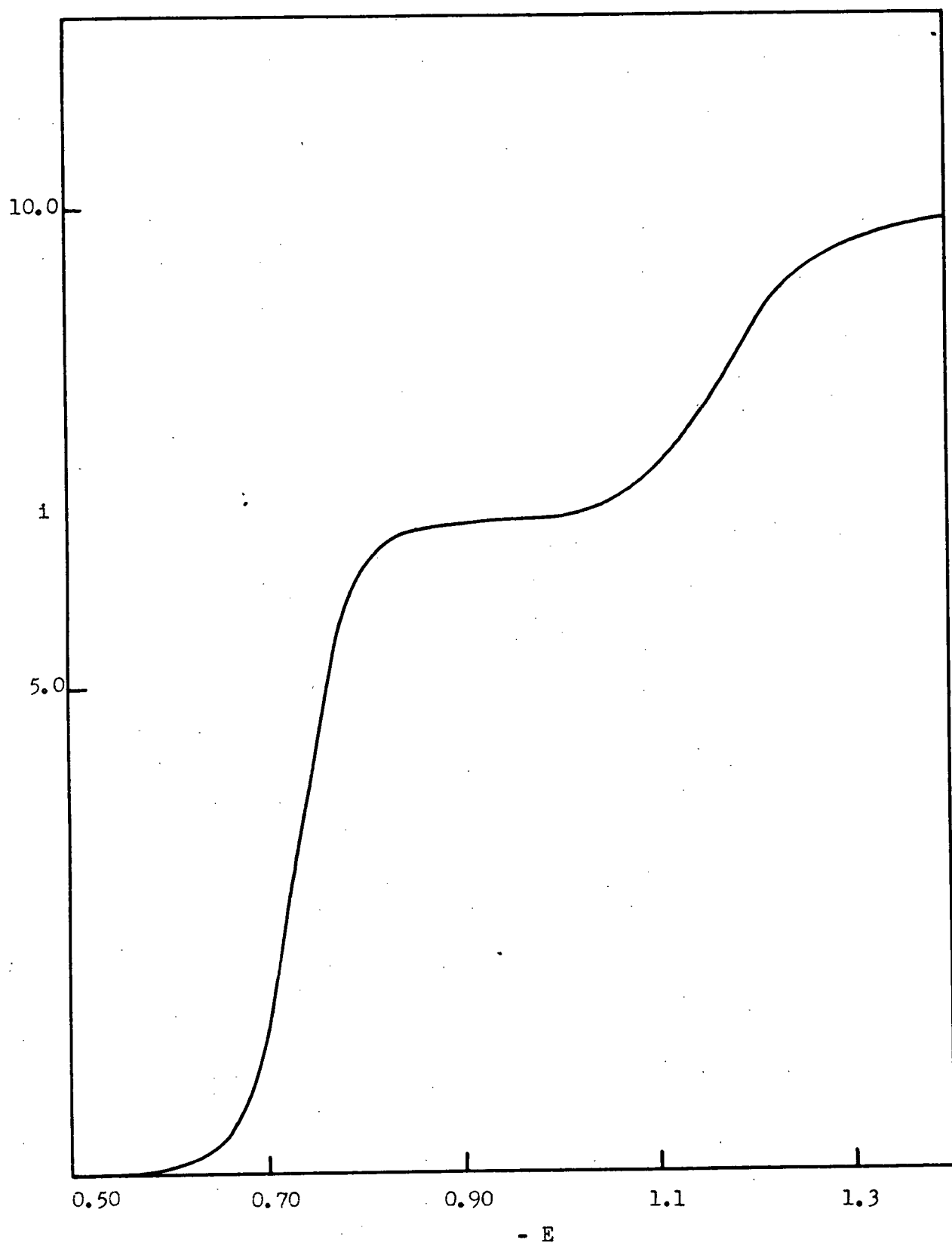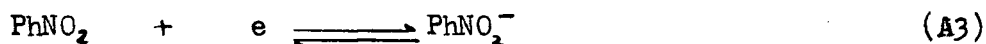
Figure 16

Polarogram of p-nitroaniline, pH 7.0, 0.05% Triton

concentration approximately 4.5 x 10^{-4} M

the pH in buffered solution is due to a fast reaction of the intermediate semi-quinone with hydrogen ions.

It appears, then, that the polarographic reduction of nitrobenzene obeys the following general mechanism:

$$PhNO_2 \quad + \quad e \quad \rightleftharpoons \quad PhNO_2^- \tag{A3}$$

followed by

$$PhNO_2^- \quad + \quad H^+ \quad \longrightarrow \quad PhNO_2H \tag{A4}$$

in acid or neutral solutions, or by

$$PhNO_2^- \quad + \quad H_2O \quad + \quad e \quad \longrightarrow \quad PhNO \quad + \quad 2OH^- \tag{A5}$$

(or other reaction involving H_2O) in basic solution.

The experimental results obtained in this work can thus be explained as follows: as the pH increases, the rate of reaction (A4) decreases, therefore on obtaining an a. c. polarogram there will be a higher concentration of unreacted $PhNO_2^-$ just before the positive half of the alternating voltage cycle at the E_5 of the wave. Thus, increasing a. c. wave heights should be expected with increasing pH. This is actually the case.

In the alkaline pH region the semi-quinone reacts with water. Therefore the half-wave potential should be independent of pH, again in agreement with experiment.

Surface-active agents hinder reactions involving water at a mercury/solution interface more effectively than reactions involving

hydrogen ions. This explains why the subsequent reaction of the semi-quinone with $PhNO_2$ is only partially hindered in neutral solution, where the H^+ concentration is several orders of magnitude higher than in solutions where the reaction is hindered completely. The possibility that nitrosobenzene is stabilized by hindrance (due to the presence of Triton X-100) of its further reduction to phenyl-hydroxylamine was ruled out by obtaining a polarogram of nitrosobenzene under the same conditions (figure 17).

Strassner and Delahay (45), too, studied the influence of surface-active agents on the polarographic reduction of nitro-compounds. They investigated the behaviour of p-nitroaniline in the presence of gelatin, and observed splitting of the wave in two not very distinct parts. They made use of the theory of irreversible waves for their interpretation of the phenomena. Unfortunately they applied the treatment to the whole distorted six-electron wave without first obtaining more information as to the nature of the process. Their conclusions can not, therefore, be accepted.

In the present case, however, enough information has already been obtained to make use of the theory. The first double step of the electroreduction in acid or neutral solution,

$$PhNO_2 \quad + \quad H^+ \quad + \quad e \quad \longrightarrow \quad PhNO_2H$$
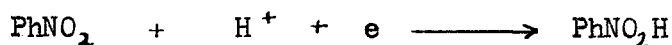
is rapid, otherwise no linear relationship would be obtained between $E_{1/2}$ and pH. Similarly, the first step in basic solution

$$PhNO_2 \quad + \quad e \quad \rightleftharpoons \quad PhNO_2^-$$

is fast, since it follows readily the changes in the potential of the
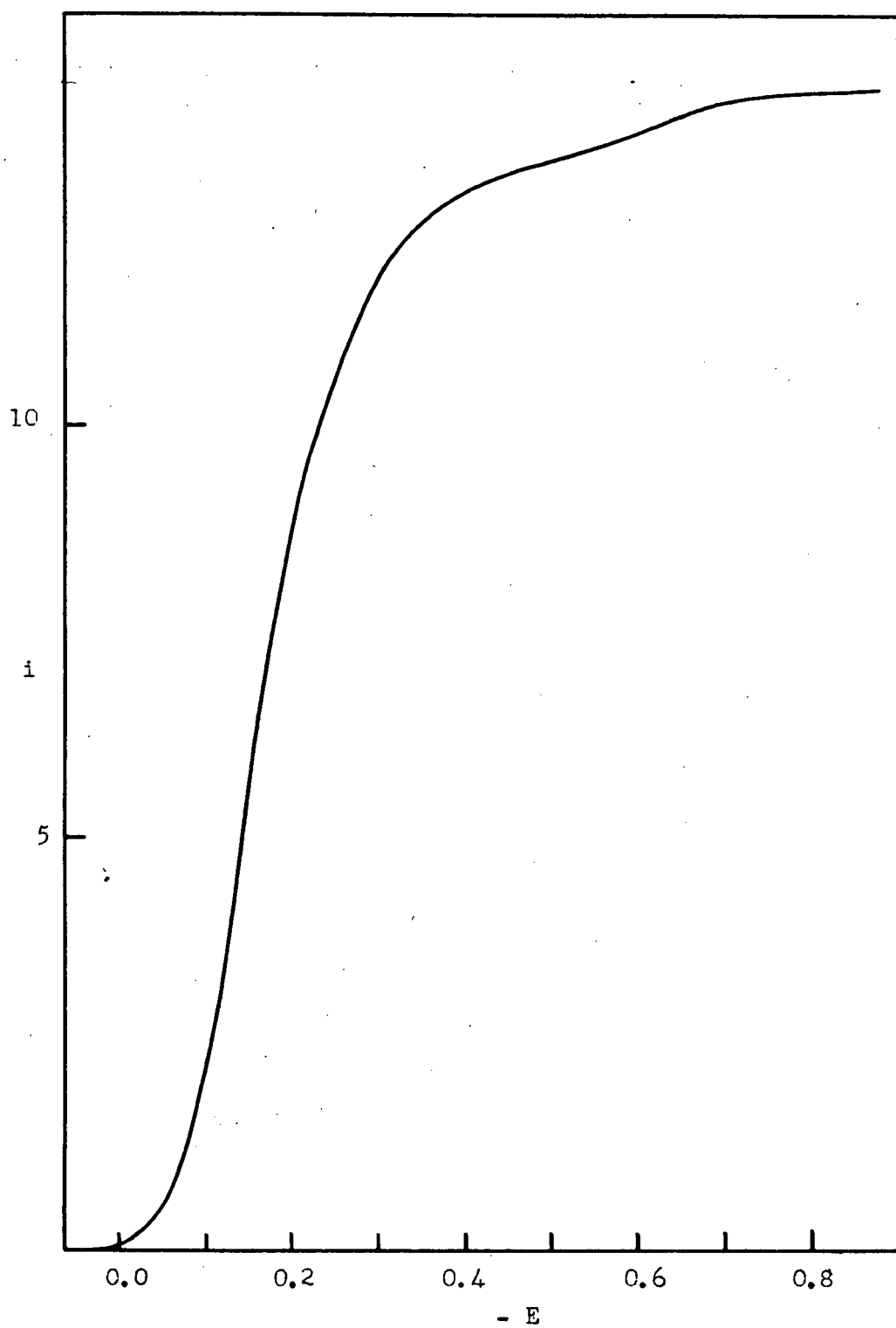
Figure 17

Polarogram of nitrosobenzene (about 1.5×10^{-3} M) pH 7.4,

0.05% Triton

d. m. e. caused by a superimposed alternating voltage of 60 cycles per second. Nitrosobenzene, which is known to be formed as an intermediate in the electroreduction of nitrobenzene, is reduced reversibly at potentials much more positive than the reduction potential of nitrobenzene, other things being equal (43). Therefore, its electroreduction, at the reduction potential of nitrobenzene, is fast. This step consumes two electrons, while the first consumes one. Since the overall reduction involves four electrons, the step corresponding to the formation of nitrosobenzene from $PhNO_2H$ or $PhNO_2^-$, which is probably the rate-determining step, consumes one electron. Therefore, αz_a should be equal to α. However, it is seen from table III that values of αz_a higher than unity can be obtained when Delahay's theory is applied. Since the transfer coefficient can not be higher than unity (according to Delahay, reference 7, it falls between 0.3 and 0.7) this seems to contradict the reasoning in this paragraph according to which $z_a = 1$. However, the following considerations must be taken into account before reaching a final conclusion. It is not certain that polarographic reductions can occur through the simultaneous transfer of two or more electrons (27). If only one electron can be transferred at a time, then, for any single step $\alpha z_a = \alpha$. Then, the fact that αz for several processes (7, 45) has been found to be higher than unity could mean that, either a "rate-determining step" includes actually more than one single step, or that Heyrovsky's theory of the multi-stage reduction is not true. Further work on this subject seems to be desirable. Another factor that should be taken into consideration is the probable dimerization of two $PhNO_2^-$ radicals before further reduction takes place, in which case no final conclusion as to the meaning of the value of αz_a can be arrived at.

Table III

Values of the parameter $\alpha\, z_a$ for the reduction

of nitrobenzene at three different pH values

Concentration : $5.24 \times 10^{-4}\, M$

Triton: 0.0008%

pH	$\alpha\, z_a$
4.2	1.18
7.8	0.82
9.6	1.39

D. Nitro-compounds in acetonitrile

Polarograms of nitrobenzene and o-nitrophenol in 0.1 M C_4H_9NI in anhydrous acetonitrile were obtained at different concentrations and different heights of the mercury column. The waves were found to be diffusion-controlled. The results are summarized in tables IV and V.

Previous results obtained on o-nitrophenol by Jayadevappa (3) do not seem to be acceptable. The present author could reproduce his results only after intentionally contaminating the solutions by bubbling moist air through them for several hours in presence of mercury.

The shape of the polarograms of both compounds is shown in figure 18. Analogy with the reduction of nitrobenzene in basic solutions in the presence of surface-active agents is apparent. Since in this latter case the hindered reaction is the combination of the intermediate semi-quinone with water (according to the mechanism proposed above), it is to be expected that the hindrance would be more pronounced in absence of water. That this actually happens in acetonitrile seems to support the above mechanism. Another interesting behaviour is the shift of the second wave of the nitro-compounds in acetonitrile to more positive values by the addition of water, while the $E_{1/2}$ of the first wave is not appreciably shifted. This is to be expected, since the final reaction must involve hydrogenation, easier in presence of water or acids, while the first wave involves only electron transfer. In the case of basic aqueous solution, surface-active agents produce only a small shift of the step corresponding to the formation of a semi-quinone, while the step corresponding to hydrogenation is shifted to much more negative potentials.

Table IV

Polarographic reduction of nitrobenzene. Supporting electrolyte: 0.1 M tetra-n-butylammonium iodide

Concentration 10^{-3} M	$H_2O\%$	Wave No.	$m^{2/3} t^{1/6}$ (mg$^{2/3}$ sec$^{1/6}$)	$-E_{\frac{1}{2}}$ volts vs Hg pool	i_d
0.363	0.00	1	1.53	0.57	2.00
0.363	0.00	2	1.42	1.55	4.46
0.882	0.00	1	1.53	0.58	4.71
0.882	0.00	2	1.42	1.57	9.50
1.200	0.92	1	1.53	0.58	6.22
1.200	0.92	2	1.42	1.45 ✭	13.9
1.190	1.83	1	1.53	0.58	6.20
1.190	1.83	2	1.42	1.35 ✭	13.6
1.68	0.00	1	1.53	0.60	8.6
1.68	0.00	1	2.02	0.60	10.9
1.68	0.00	2	1.42	1.6 ✭	18.3
1.68	0.00	2	1.87	(?)	22.8

Average value of diffusion current constant $I_d = 6.68$

✭ Value only approximate: wave distorted by maximum

(?) Wave too distorted to allow measurement of $E_{\frac{1}{2}}$

Table V

Polarographic reduction of o-nitrophenol in acetonitrile.

Supporting electrolyte   0.1 M tetra n-butylammonium iodide.

Concentration 10^{-3} M	$H_2O\%$	Wave No.	$m^{2/3} t^{1/6}$ $(mg^{2/3} sec^{-1/2})$	$-E_{1/2}$ volts vs Hg pool	i_d
0.386	0.00	1	1.53	0.33	2.46
0.386	0.00	2	1.42	i.d.	i.d.
0.920	0.00	1	1.53	0.35	5.20
0.920	0.00	2	1.42	1.44	16.40
2.005	0.00	1	1.53	0.34	10.52
2.005	0.00	2	1.42	1.43	35.30
2.005	0.00	1	1.85	0.35	12.24
2.005	0.00	2	1.72	1.44	41.90
3.330	0.00	1	1.53	0.35	16.60
3.330	0.00	2	1.42	1.44 [a]	58.10
3.240	3.24	1	1.53	0.33	16.40
3.240	3.24	2	1.42	1.08 [a]	62.20

Average value of diffusion current constant: 8.58

[a] Approximate value only: wave distorted by maximum

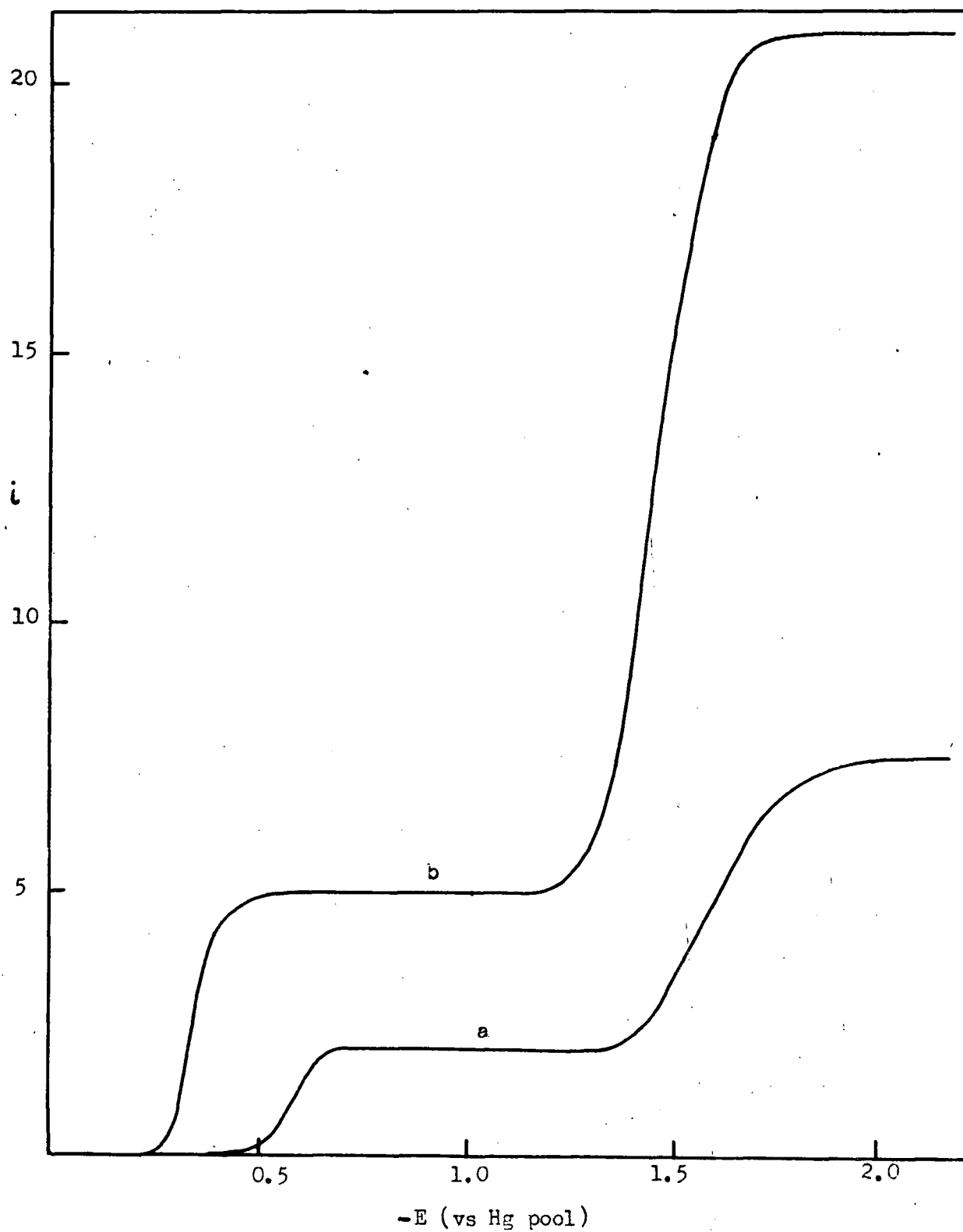Figure 18

d. c. polarographic behaviour of o-nitrophenal and nitrobenzene in a solution

of 0.1 M C$_4$H$_9$NI in acetonitrile

a) 3.63×10^{-4} M nitrobenzene   b) 9.2×10^{-4} M o-nitrophenol

CONCLUSIONS

From the results obtained in this work the following conclusions can be arrived at.

In aqueous solutions the reduction of nitrobenzene proceeds via a reversible formation of a semi-quinone intermediate:

$$PhNO_2 + e \longrightarrow PhNO_2^-$$

The steps in the overall electrode process involving reaction of the semi-quinone are irreversible, and as a result an irreversible d. c. wave is produced. By means of a. c. polarography it was shown that it is possible to hinder the irreversible steps in the electrode process in neutral and basic solution, by addition of non-reducible surface-active agents. The irreversible steps occur then, only after a high overpotential is applied to the d. m. e., but desorption of the surface-active substance does not necessarily precede them. In acid solution the whole electrode process is hindered, and the wave is shifted to more negative potentials. It was shown that a mechanism of reduction that postulates two different reactions depending on whether the solution is acid or basic (Holleck's theory) is not necessary to explain the experimental facts.

In anhydrous acetonitrile the reduction of nitrobenzene is step-wise. The semi-quinone formed in the first step is electrochemically stable over a wide range of potentials. Its stability decreases upon addition of water.

If the discussion of the last paragraph is correct, a prediction can be made: a. c. waves of nitro-compounds in acetonitrile corresponding to the first step should be considerably higher than those corresponding to the second d. c. wave. Upon addition of sufficient amounts of water or acids the height of the first a. c. wave should decrease, because the electron transfer would be accompanied by hydrogenation, which would make the step less reversible. These tests have not yet been made. If performed, their results could either confirm the mechanism proposed above for nitrobenzene in aqueous solutions, or, if giving results in disagreement with the prediction, demand a re-examination of the problem.

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