POLAROGRAPHIC STUDY OF SOME ORGANIC COMPOUNDS

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By
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TO MY PARENTS

who lacked University degrees

but not the will and vision to guarantee mine

BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE
PILANI (RAJASTHAN), INDIA

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SUPERVISOR'S CERTIFICATE

Certified that the research work described in the thesis entitled "Polarographic Study of Some Organic Compounds" was carried out by Shri P.S. Raghavan, M.Sc., under my guidance and supervision during the period August 1967, to November 1970, in the Department of Chemistry.

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CHAPTER I

GENERAL INTRODUCTION AND THEORY OF ELECTRODE PROCESSES

GENERAL INTRODUCTION

The polarographic method, first described by Heyrovsky in 1922, consists in recording current vs voltage curves using a dropping mercury electrode (d.m.e.). The theory of electrode reaction has been a matter of concern to chemists, since the time of Faraday. Not only is the study of the subject a worthy endeavour in its own sight but the information obtained is of vital interest to chemistry in other fields.

The scope of polarography has been continually widened in the last three decades or so, during which increasing number of variations on the classical polarographic method have been developed. In some procedures which include "conventional" or "d.c. polarography", the measurements are carried out while the polarizing potential remains essentially constant. In another variation of the method the measurements are carried out while the polarizing potential varies continuously over the wide range under investigation, and the name given to this procedure is voltage sweep method. The measurements carried out by superimposing small alternating voltages onto the direct polarizing potential and the resulting a.c. current being measured is another suggested procedure. This method is called "a.c. polarography" which is used in connection with the studies of electron transfer reactions. An offshoot of a.c. polarography is called 'tensammetry' which is used to study the behaviour of surface active substances and produces capacitance changes at the interface even in the absence of electron transfer.

In polarographic studies d.m.e. occupies a unique position, due to its reproducible character and ease of operation. The theoretical basis of the current-voltage curves in d.c. polarography[136,152] and a.c. polarography[8] has been thoroughly worked out.

D.C. Polarography

When a well-stirred solution containing a reducible (or oxidizable) substance, is electrolyzed between two large electrodes the current voltage curve has the form given in Fig. 1(a). Only a very small current flows when the potential applied to the cell is less than the decomposition potential of the solution 'E_d'. At higher potentials the current limited only by the electrolytic resistance of the solution is given by Ohm's law

$$i = \frac{E - E_d}{R}$$

The concentration of the reducible substance is the same at the surface of the cathode and the bulk of the solution and no concentration polarization is encountered.

However, in an unstirred solution with a small cathode, the curve takes the form as shown in Fig. 1(b). The concentration of the reducible substance at the electrode decreases as the potential is raised until a stage is reached when the concentration at the surface is practically zero and there is

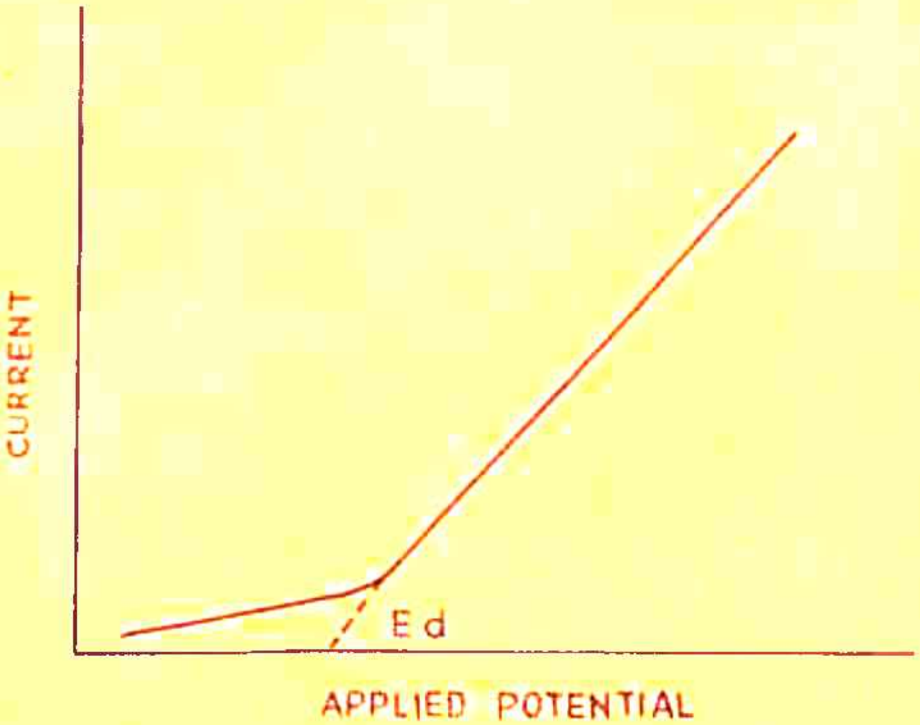
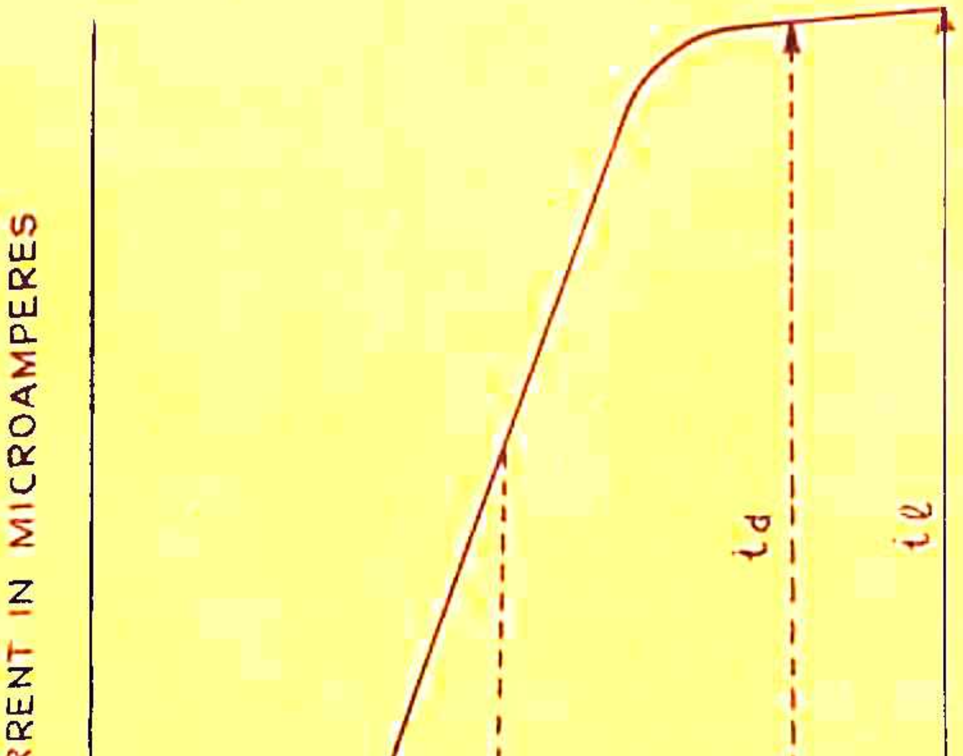

CURRENT
Ed
APPLIED POTENTIAL

FIG. 1a


CURRENT IN MICROAMPERES
i_d
i_l
i_r
$E_{1/2}$
APPLIED POTENTIAL

no longer any increase in the current value which is now controlled by the diffusion of the reducible substance towards the electrode. The cathode is then said to be concentration polarized and the resulting curve 1(b) is S-shaped and is called 'polarogram'.

The limiting current is composed of residual current, migration current, adsorption current, diffusion current, catalytic current and kinetic current. Methods are available by which each of these currents can either be measured or may be eliminated if not of significance in a particular situation. Residual current can be measured from blank run and migration current is eliminated in the practical work by the addition of a relatively high concentration of supporting electrolyte. The other remaining currents can be recognized by observing the dependence of the current upon the variation of the experimental factors as given in the Table by Zuman[283].

The potential at which the current is half of the diffusion current is known as the half-wave potential ($E_{0.5}$). While the $E_{0.5}$ is characteristic of the reducible or oxidizable substance, the magnitude of diffusion current (i_d) is proportional to its concentration. In thermodynamically reversible systems $E_{0.5}$ is almost identical with E^o in the familiar Nernst equation

$$E = E^o - \frac{RT}{nF} \ln \frac{(Red)_o}{(Ox)_o}$$

where $(Red)_o$ and $(Ox)_o$ are the concentration of Reduced and oxidized form respectively at the electrode.

The Heyrovsky-Ilkovic equation[130,131,237], the modified form of Nernst equation, applicable to polarographic technique is

$$E = E_{0.5} - \frac{RT}{nF} \ln \frac{i}{i_d - i}$$

From the simple theoretical considerations based on the linear diffusion of depolarizer towards the electrode an equation has been derived by Ilkovic[136]

$$i_{d_{max.}} = 706\ nc\ m^{2/3}\ t^{1/6}\ D^{1/2} \quad \text{(for instantaneous currents)}$$

$$i_{d_{ave.}} = 607\ nc\ m^{2/3}\ t^{1/6}\ D^{1/2} \quad \text{(for average currents)}$$

In deriving the Ilkovic equation, the curvature of the electrode was neglected and only linear diffusion was considered. This led a few workers[162,163,174,182,186,255,273,274] to take into account the spherical diffusion towards a growing spherical electrode (mercury drop) and the following equation was suggested

$$i_{d_{ave.}} = 607\ n\ D^{1/2}\ c\ m^{2/3}\ t^{1/6}\ (1 + \frac{AD^{1/2}\ t^{1/6}}{m^{1/3}})$$

where the numerical constant A is 39 according to Lingane-Loveridge[174] and 19 according to M. von Stackelberg[255]. The most sophisticated treatment by Koutecky[162,163] gives A = 34.7 and also provides the following equation.

$$i_{d_{ave.}} = 607\ n\ D^{1/2}\ c\ m^{2/3}\ t^{1/6} \left[1 + 34.7\ \frac{D^{1/2}\ t^{1/6}}{m^{1/3}} + 100 \left(\frac{D^{1/2}\ t^{1/6}}{m^{1/3}}\right)^2\right]$$

where c is the concentration of the depolarizer in millimole/litre in the body of the solution

D is diffusion coefficient (cm^2 sec^{-1})

m is mass of mercury in mg flowing per second

t is drop time in seconds

n is the number of electrons involved in the electrode process.

A.C. Polarography

Alternating current polarography began in 1938 with Müller, Garman, Droz and Petras[212] who were the first to apply a small sinusoidal alternating voltage under polarographic conditions with the aim to develop a more rapid method of polarographic analysis. Kivalo[149] gave a new theoretical analysis of the method of Müller et al. whose theoretical considerations were shown to be in error. Boeke and van Suchtelen[7] modified the method of Müller et al. by using phase shift measurements but the method was found to be laborious and not suitable for routine analysis.

The work of Müller et al. and of Boeke and van Suchtelen was aimed solely at improving the polarographic method for analytical purposes. A real insight into the actual processes occurring at the d.m.e. in the presence of an alternating field was first shown by Grahame[79,80]. He measured the resistance and capacity of the cell with an impedance bridge using an alternating voltage of 1 mV or less at a frequency of 1000 Hz. However, the difficulties in balancing the bridge made the method impracticable for routine work.

The first practicable instrument suitable for a.c. polarographic analysis was described by MacAleavy[180,181] in Belgian and French patents of 1941 and 1942. Breyer and Gutmann[9] in 1944, independently developed a similar instrument[239] and started a systematic investigation of the new field which they termed a.c. polarography. They substantiated Grahame's findings that only reversible reactions gave rise to pseudo-capacity. However, an important development has been the application, particularly since 1953 by Breyer and his coworkers[10] of a.c. polarography to the study of organic depolarizers. Almost invariably adsorption processes were found to play a decisive role in the electro-chemical reactions, and their influence could be detected in the base current changes, in the shape of a.c. wave, and in the dependence on concentration and temperature of the faradaic alternating current as well as in phase shift associated with the process.

A.C. polarography can also be used with advantage in the study of surface active but non-reducible substances, a field of investigation known as "tensammetry". The first detailed study of the effect of surface active substances on the capacity of mercury aqueous interface was made by Frumkin and coworkers[73,206,207,232]. They mostly worked with stationary mercury surface and used a sensitive impedance bridge for measurement of the capacity. Their experiments showed the existence of two maxima with a capacity-potential curve of aqueous solution of sodium sulphate saturated with octyl alcohol. Grahame and coworkers[81,82,210,211] studied the phenomenon using a d.m.e. and an impedance bridge with a special arrangement for measuring the capacity and resistance at a particular moment in the life of mercury drop. Heyrovsky[132] investigated the phenomenon by using an oscillograph and observing the current-voltage curves, which showed halts at certain stages indicating large changes in capacity. Breyer and coworkers[11-17] carried out extensive investigations making use of a simple technique of imposing a constant a.c. ripple of low amplitude and d.c. voltage and measuring the a.c. part of the current produced. Breyer and Hacobian termed it "Tensammetry". Doss and coworkers[48-56,86-92], however, at the same time independently applied a slightly modified procedure of a.c. polarography for tensammetric measurements. Gupta and coworkers[93-108] have successfully utilized this technique with advantage in the study of surface active substances at the d.m.e. in pulsating field. Loveland and Elving[175-179] carried out studies by employing an ingenious circuit for getting a straight picture on the oscillograph of differential capacities at the various imposed d.c. potentials.

The general results obtained indicate that at the electrocapillary maximum (e.c.m.) the surface active substances (s.a.s.) get strongly adsorbed and depress the differential capacity. The potential-differential capacity curve, therefore exhibits a minimum in the neighbourhood of e.c.m. At potential sufficiently cathodic or anodic to the e.c.m., desorption of the s.a.s. takes place due to the preferential adsorption of the solvent molecules caused by the highly charged mercury surface. This desorption appears to take place mostly in an abrupt manner at a fairly well defined potential leading to the exhibition of a dynamic capacitance and peak in the a.c. current - d.c. voltage curves which are referred to as the "desorption peak" or "tensammetric peak".

Characterization of Polarograms

In a current-voltage curve as we go from the foot to the plateau of the wave the rate of electron transfer process increases and the reduction or oxidation process becomes more and more complete. On the plateau of the wave the electron transfer is so fast that electroactive substances are reduced or oxidised as rapidly as they arrive or formed at the electrode surface. It is convenient to classify electrode reactions into two extreme categories.

(i) Polarographically reversible processes: These are so rapid that thermodynamic equilibrium is very nearly attained at every instant during the life of a drop at any potential. For such reactions Nernst equation aptly describes the variations of the current with potential which reflects the changing position of the equilibrium.

(ii) Polarographically irreversible processes: These are so slow that they proceed only a fraction of the way towards equilibrium during the life of each drop. For these reactions it is the rate of the electron transfer process and the manner in which this is influenced by the electrode potential that governs the relationship between current and potential. In addition to the irreversibility caused by slow electron transfer one encounters irreversibility consequent to some other rate-determining steps which can be either ordinary chemical reactions preceding the electrode reaction or catalytic reaction.

Reversible waves follow the Heyrovsky-Ilkovic equation and give a straight line plot of E vs log $\frac{i}{i_d - i}$ with a slope equal to $-2.3 \frac{RT}{nF}$. If 't' (drop time) varies appreciably over the range of potentials covered by the rising part of the wave, a correction has to be applied as suggested by Meites[197] and E vs $\left[\log \frac{i}{i_d - i} - 0.546 \log t\right]$ plot is made to test the reversibility.

Another criterion, more rapid and convenient to apply, involving the measurements of $E_{3/4} - E_{1/4}$ from the polarograms (potentials corresponding to currents equal to $\frac{3}{4}\, i_d$ and $\frac{1}{4}\, i_d$, respectively) was originally suggested by Tomes[271]. For a reversible cathodic wave

$$E_{3/4} - E_{1/4} = -\frac{0.564}{n}$$

The $E_{0.5}$ of a reversible wave is nearly independent of drop time[269], while that of an irreversible cathodic wave becomes more positive, as the drop time is increased[36,150]. For a totally irreversible wave at 25°C,

$$\frac{\Delta E_{0.5}}{\Delta \log t} = \frac{0.02957}{\alpha\ n_a}$$

where the transfer coefficient (α) is defined as the coefficient of transformation of electrical energy into energy of activation or more usually described as the fraction of the applied potential effective in the forward reaction. "n_a" is the number of electrons involved in the slow step. $E_{0.5}$ and 't' have usual significance.

The theoretical considerations of Laitinen and coworkers[1] indicate that for irreversible processes the current at the foot of the wave is independent of the height of the mercury column (h) and that the diffusion current (i_d) varies linearly with changes in $\sqrt{h}_{\text{corrected}}$.

$E_{0.5}$ is independent of the concentration of the depolarizer or that of the supporting electrolyte in the case of reversible waves, unlike those of irreversible waves. Moreover $\frac{d\,E_{0.5}}{dT}$ is usually small for reversible systems, while, in case of irreversible systems $E_{0.5}$ usually has a positive temperature coefficient and exceeds several millivolts per degree.

Of the various criteria reviewed above E vs log $\frac{i}{i_d - i}$ plots and the values of $E_{3/4} - E_{1/4}$ have been the most popular tests for reversibility, whereas, for irreversibility the tests of E vs log $\frac{i}{i_d - i}$ and i vs $\sqrt{h}_{\text{corrected}}$ are often used.

A.C. polarography is useful for reversible reductions. Breyer and Bauer[8] have reviewed the kinetic treatment of the relationship between the current, the voltage, and the concentrations of the oxidized and reduced species at the electrode surface. They as well as Gupta and coworkers have also given methods to distinguish reduction and tensammetric waves.

Generally, irreversible reductions yield only very small or no a.c. polarographic waves[18]. Smith and McCord[254] have pointed out that theoretically an a.c. polarographic response is expected for totally irreversible electrode processes, regardless of the source of irreversibility (electron transfer, chemical reactions). Smith and coworkers[190-192] have extended the rigor of a.c. polarographic theory for coupled chemical reactions. Their calculations are now based on an expanding plane model for the d.m.e. McCord and Smith have tested experimentally[193] the theory[194] of second harmonic a.c. polarography for quasi-reversible systems. They have also published[195,196] second harmonic theory for coupled reactions and an expanding plane model. They found that second harmonic polarography possesses special advantages for studying chemical reactions following electron transfer.

Organic Polarography

The polarographic studies of various organic substances viz. aldehydes, halogenated compounds, ketones, nitro and nitroso compounds, quinones of various types and unsaturated acids, have been carried out from early stages. The nature of the reduction of organic compounds is made irreversible by the fact that in most cases the reduction occurs in more than one step, one of which is slow. Due to lack of suitable theoretical formulations it was not possible, until recently, to analyse and interpret the data on irreversible systems. However, in recent years satisfactory theoretical treatments have been developed which have given an impetus to the polarographic study of organic compounds. Further, sophisticated instruments have made the study interesting and informative.

In organic polarography the control of pH is of paramount importance because of the participation of hydrogen ions in the reduction process. Thus, it is desirable to work with buffered solutions as in unbuffered solutions the pH in the immediate vicinity of electrode surface changes considerably as a result of the consumption of hydrogen ions. This results in drawn-out wave or even the appearance of two waves. The type and concentration of the buffer system also affect the shape of the polarograms. Also, one has to guard against the possibility of interaction between the substances under examination and the components of the buffer systems[285].

Theory of Electrode Processes

A quantitative treatment of the current-potential curves was employed by Randles[234] and Sevcik[244] for reversible processes and by Delahay[37-39] for irreversible processes. Reactions which can be followed from polarographic curves fall into many categories.

The first and the foremost are the study of electrode reactions. Chemical reaction occurring close to the electrode surface and caused by perturbation of the chemical equilibrium of the system of the electrode reaction are another group of familiar studies. Further, homogeneous chemical reactions occurring in the bulk of the solution which are not influenced by the electrode reaction have formed basis of many investigations. The fourth process, which accompanies all polarographic processes is diffusion. For polarography it is characteristic that at least two of the mentioned processes proceed at the same time. From the kinetic point of view polarography is the oldest of the so-called competition methods[03] for following rapid reactions.

The electrode reaction is a fundamental polarographic process. During this process one form of the redox couple is consumed and the other one generated so that at the electrode the concentration distribution changes resulting in the disturbance of equilibria, which in turn induce further process.

It is assumed for the application of the Nernst equation to the oxidation-reduction reaction at the electrode that electrochemical equilibrium is achieved at the electrode. In some cases this is not true and the equilibrium is attained slowly. The interpretation of such electrode processes involves kinetic considerations. For a simple reaction represented by

$$\mathrm{Ox} + n\,\bar{e} \rightleftharpoons \mathrm{Red} \qquad (1)$$

if the electrode process is assumed to be of the first order, the rate of reaction expressed in moles of the substance transformed at the electrode surface per unit time and per unit area is

$$-\frac{d\,N_o}{dt} = \frac{d\,N_R}{dt} = k_{f,h}\,C_o - k_{b,h}\,C_R \qquad (2)$$

where the C's are the concentrations and the k's are the formal rate constants for the forward and the backward processes. The concept that a substance which undergoes a chemical transformation has to overcome an energy barrier is applicable to any type of reaction, but for an electrochemical reaction, the effect of the electrical field has to be taken into account. If E is the electrode potential referred to N.H.E., the fraction αE of the potential favours the cathodic process and $(1 - \alpha)\,E$ favours the anodic process. The parameter α is the transfer coefficient of the electrode process.

Taking these into consideration the rate constants can be expressed by

$$k_{f,h} = k^{o}_{f,h} \exp\left[- \frac{\alpha nF}{RT} E\right] \tag{3}$$

$$k_{b,h} = k^{o}_{b,h} \exp\left[\frac{(1 - \alpha)\ nF}{RT} E\right] \tag{3a}$$

where (k^{o}_{h})'s are the values of rates constants for E = zero (N.H.E.)

Knowing the rate of reaction, the current is obtained by multiplying the rate by the area of the electrode (A in cm^2) and by the charge involved in the reduction of one mole of the substance. Thus the current is expressed by

$$i = nFA \left[C_o\ k^{o}_{f,h} \exp\left\{\left(- \frac{\alpha nFE}{RT}\right)\right\} - C_R\ k^{o}_{b,h} \exp\left\{\frac{(1 - \alpha)\ nFE}{RT}\right\}\right] \tag{4}$$

or

$$i = nFA\ k_{s,h} \left[C_o \exp\left\{\frac{\alpha nF}{RT} (E - E^{o}_{c})\right\} - C_R \exp\left\{\frac{(1 - \alpha)\ nF}{RT} (E - E^{o}_{c})\right\}\right] \tag{5}$$

The value of E_c^o is generally not very different from the standard potential E^o, and E_c^o can often be identified with E^o comparing equations (4) and (5).

$$k_{s,h} = k_{f,h}^{o} \exp\left[- \frac{\alpha\ nF}{RT} E_c^o\right] \qquad (6)$$

$$k_{s,h} = k_{s,h}^{o} \exp\left[\frac{(1-\alpha)\ nF}{RT} E_c^o\right] \qquad (6a)$$

From eqn. (5), the current is now a function of the difference of potential $(E - E_c^o)$ whereas in eqn. (4), it depends on E. Therefore, $k_{s,h}$ is truly characteristic of the electrode process whereas the constants $k_{f,h}^o$ and $k_{b,h}^o$ depend on the difference between the potentials E_c^o and the zero of the scale of potentials. It is, therefore, more advantageous to use $k_{s,h}$ rather than $k_{f,h}^o$ and $k_{b,h}^o$, in comparing the kinetic characteristics of the electrode processes.

The nature of the irreversible processes can be explained quantitatively from the current-voltage curve. In the case of irreversible waves, a rather drawn-out wave is observed which is shifted to more cathodic potentials. This has been attributed to the increase in the rate of the electrochemical reaction as the potential is made more and more cathodic. The flow of current causes concentration polarization and at the plateau of the wave the current is virtually diffusion controlled. Ilkovic equation can, however, be applicable. The difference between the $E_{0.5}$ of the irreversible wave and the standard potential E^o (virtually equal to $E_{0.5}$ of a reversible wave) is the polarographic overpotential $\eta_{1/2}$[133]

$$\eta_{1/2} = (E_{0.5})_{irrev.} - E^{o}$$

Thus an electrochemical reaction occurring without any measurable over-potential is said to be reversible.

The slope of an irreversible wave differs from the thermodynamic value calculated from the equation for a reversible wave; the log $\frac{i}{i_d - i}$ vs E plot is often linear, but the number of electrons obtained from its slope is smaller than the actual number of electrons consumed in the electrode process (as found from the wave height provided that the limiting current is diffusion controlled). A slow electrode process i.e. the slow establishment of an equilibrium between the oxidized and reduced forms at the electrode surface, is regarded as the cause of irreversibility. The electrode process then refers only to the electron exchange between the depolarizer and the electrode and not to the mass transfer towards the electrode. If this is to be included, the term over-all electrode process or depolarization process is used. A slow exchange process results when the transition of the depolarizer into a form capable of exchange of electrons with the electrode is slow and requires a certain energy of activation[133].

The values of αn_a and k^{o}_{f} can be determined from the wave[39]. The significance of $E_{0.5}$, the dependence of this on the drop time[151] etc. have been derived from the theory. Delahay has deduced a general criterion for polarographic reversibility[36].

The general equation for the polarographic wave corresponding to the reduction of the oxidized form of the redox system is given by the expression

$$\frac{i_d - i}{i} = \exp\left[\frac{nF(E-E^o)}{RT}\right] + \frac{1.13}{k_{s,h}}\sqrt{\frac{D}{t}}\exp\left[\frac{\alpha nF(E-E^o)}{RT}\right] \qquad (7)$$

If $k_{s,h}$ is sufficiently high, so that $k_{s,h}\sqrt{\frac{t}{D}} \gg 1$, the second term on the right hand side in equation (7) can be neglected and the Heyrovsky-Ilkovic equation is obtained.

A number of methods are available for the theoretical analysis of irreversible polarographic waves. Among the first to develop the theory of irreversible waves were Eyring and coworkers[63] and Tanaka and Tamamushi[268]. Later several workers independently gave more rigorous treatments[36,144,164]. For totally irreversible systems the treatment of Meiman[208], Delahay[39,40], Koutecky[164] and Randles[235] are available. The mathematical treatments for quasi-reversible systems are given by Matsuda[187,188], Gelling[71], Koryta[161] and by Sathyanarayana[240] who modified the method of Randles and Stromberg[262].

It has so far been assumed that the overall electrode reaction occurs in a single step as represented by equation (1), but this is not necessarily true. One may have a rate-determining step involving n_a electrons, followed by one or more much faster steps in which additional electrons are consumed:

$$Ox + n_a\,\bar{e} \longrightarrow I \quad \text{(rate determining)}$$

$$I + (n - n_a)\bar{e} \longrightarrow Red \quad \text{(fast)}$$

The overall reaction is still $Ox + n\bar{e} \longrightarrow Red$, and its rate is still controlled by the rate at which Ox is reduced, but the total current obtained on reducing an ion or molecule of Ox depends on the number 'n' of electrons involved in the overall reaction rather than on the number n_a involved in the rate-determining step. The equation (3) takes the form

$$k_{f,h} = k^o_{f,h} \exp\left[- \frac{\alpha\, n_a\, F}{RT} \cdot E \right] \qquad (10)$$

The value of α in many cases is not far from 0.5. Both adsorption and double layer structure[198], however, may have appreciable effects and a few values of α below 0.1 or above 0.9 have been reported. The value of n_a must obviously be integral, and in most cases it is probably 1. Though it is generally believed that only a single electron can be transferred at a time during the course of an electrode reaction, a value of n_a exceeding 1 would not necessarily mean that two or more electrons are actually added simultaneously, but merely that the successive steps are too nearly simultaneous to be distinguished on the time scale implicit in a polarographic measurement[199].

Equation (10) can be written as

$$\log k_{f,h} = \log k^o_{f,h} - \frac{\alpha\, n_a\, F}{2.303\, RT} E \qquad (11)$$

A plot of $\log k_{f,h}$ vs E yields a straight line with a slope of $-0.4343 (\alpha\, n_a\, F/RT)$. $\alpha\, n_a$ can thus be determined for various values of E. This is done by taking the value of λ

corresponding to the ratio of i/i_d. The dimensionless parameter λ is defined by the equation

$$\lambda = k_{f,h} \, t^{1/2} \, D^{-1/2} \qquad (12)$$

λ is a complicated function of i/i_d.[42] By a measurement of the average currents during the drop-life and obtaining $k_{f,h}$ by a graphical integration method[39], Delahay and Strassner[36,41] utilized the above method to calculate the kinetic parameters. Koutecky[165] has tabulated the value of λ (reproduced by Heyrovsky and Kuta in their book[134]) for different values of i/i_d and thus calculated the value of $k_{f,h}$. From a knowledge of λ at various potentials, $k_{f,h}$ can be calculated from equation 12. $\alpha \, n_a$ can be calculated from the slope of the plot $\log k_{f,h}$ vs E. Finally, $\log k^{o}_{f,h}$ can be found out by utilizing equation (11), by direct simple calculation or as an intercept of the above mentioned plot.

By replacing λ by $\lambda_{1/2}$ at $E_{0.5}$ an equation has been derived[43] which is given below.

$$E_{0.5} = \frac{RT}{\alpha \, n_a \, F} \ln \frac{k^{o}_{f,h}}{\lambda_{1/2} \, D^{1/2}} + \frac{RT}{2\alpha \, n_a \, F} \ln t \qquad (16)$$

It can be observed from equation 16 that $E_{0.5}$ depends on the quantities t, D, $k^{o}_{f,h}$ and $\alpha \, n_a$.

Delahay and Berzins[42] considering the case of semi-infinite linear diffusion developed treatments in the case of an irreversible reaction involving more than one rate-determining step. Koutecky's procedures for analyzing irreversible reduction were applied by Suzuki and Elving[265] to evaluate the kinetic parameters of the first nitromethane wave assuming that the irreversible reaction involved contains only one rate-determining step. They examined certain limitations in the use of the Koutecky method. Based on Delahay's theoretical considerations, they have shown that, in general, when a rate determining step involves two consecutive irreversible reactions, αn_a and $k^o_{f,h}$ for each reaction cannot be calculated from the plot of $\log k_{f,n}$ against E which becomes a bent line.

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CHAPTER II

(i) EXPERIMENTAL TECHNIQUES

(ii) PROPOSED WORK AND RESULTS

EXPERIMENTAL TECHNIQUE

D.C. Polarographic Technique

A manual d.c. polarograph assembled in the laboratory consisted of the following parts.

1. Vernier potentiometer A, (Cambridge Instrument Co. Ltd., England) to measure the potentials developed across standard resistance (D).
2. Toshniwal polarograph (Type No. CLO2A, Sr. No. 083) for applying potentials to the dropping mercury electrode, d.m.e. (M).
3. Lead accumulator (C).
4. Weston standard cadmium cell (F).
5. Spot Galvanometer of long period (G) (Cambridge Instruments Co. Ltd., England).
6. Saturated colomel electrode, SCE. (H).
7. Polarographic cell (I).

The electrical circuit is given in Figure 1.1. The potentiometer B connected to a 4-volt lead accumulator 'C' gave potential 'V' of the desired magnitude. 'B' was initially calibrated with standard cell F. The potentials applied by B could be read with an accuracy of 0.01 mV with the help of the potentiometer A. Cathodic potentials were applied to d.m.e. (M)

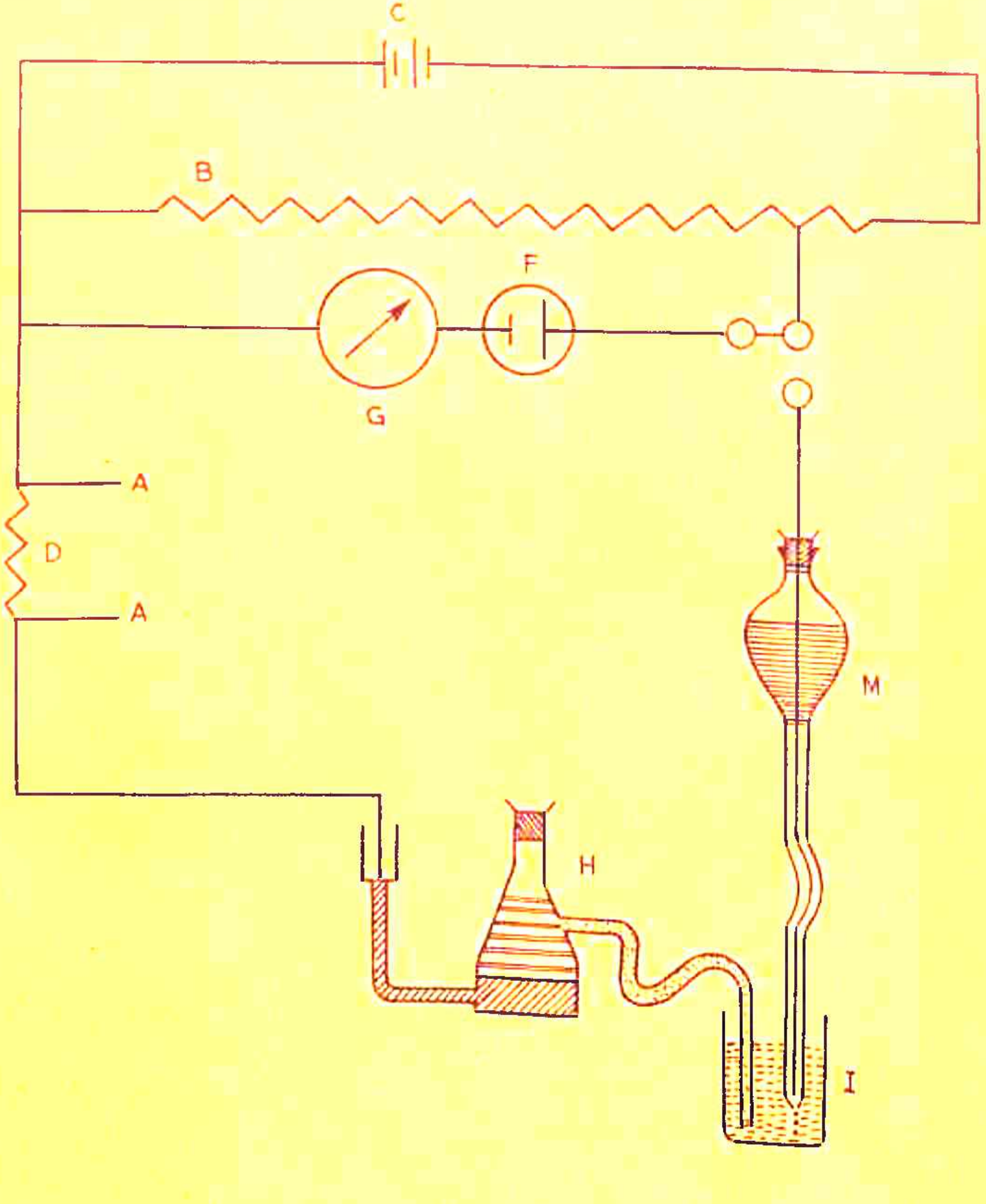

FIG. 2·1 POLAROGRAPHIC CIRCUIT (D.C.).

which consisted of a fine glass capillary (Sargent and Co., U.S.A.) connected through a polyethylene tubing to a reservoir of mercury which could be adjusted to any height.

The potentiometer A was also calibrated with the standard cell F and was employed for measuring potential (E) across the resistance 'D' in series with the d.m.e. The current i passing through the system at a particular applied potential V, is then calculated from the Ohm's law i.e. $i = E/R$. Thus the current is calculated for different applied potentials 'V' and the current-potential curve recorded. To ensure the correctness of the applied potential and current, the calibration of the potentiometers was checked with standard cell from time to time during the experiment.

The procedure employed for the determination of 'm' and 't' was the same as recommended by Meites and others[200].

The importance of the purity of mercury in polarographic work need hardly be emphasised. Slight contamination of the mercury leads to erratic behaviour or choking up of the capillary. Mercury was purified by treatment with 20% V/V nitric acid followed by repeated washings with distilled water, drying, passing through a pin-holed filter paper and finally distilling under reduced pressure.

The potentials applied to the d.m.e. were measured directly against saturated calomel electrode (SCE). SCE was prepared in the conventional manner and was connected to the polarographic test solution by means of an agar-KCl salt brige or agar-KNO_3 salt bridge.

The polarographic cell made of pyrex had a capacity of about 100 ml and was fitted with a lid having 3 holes for the insertion of the capillary, the salt bridge and a tube for passing N_2 gas. Nitrogen gas, less than 0.5% in oxygen content, was further purified by successively passing it through bottles containing alkaline pyrogallol and distilled water before passing it through the test solution. An atmosphere of N_2 was maintained in the cell during the recording of the current-voltage curves. Temperatures were maintained with an accuracy of ±0.1°C using a Townson and Mercer thermostatic unit. Beckman pH meter model H2 was used for pH measurements.

Determination of the diffusion coefficient and the number of electrons involved in the reduction process

The knowledge of the number of electrons involved in the reduction process is of great importance especially for gaining an insight into the mechanism of the electrode process. The conventional methods for the determination of the value of n from the slope of log i/i_d-i vs E plot or from $E_{3/4} - E_{1/4}$ values are applicable only to reversible systems. It is the limitation of Heyrovsky-Ilkovic equation that it cannot be applied to irreversible reduction processes.

To determine 'n' from Ilkovic equation it is necessary to find the value of diffusion coefficient of the species under investigation. For this the McBain Dawson cell[189], shown in Fig. 2.2, was used. This was a symmetrical double cell. Both the lower and upper compartments were fitted with pyrex stopcocks so that either compartment could be filled or emptied

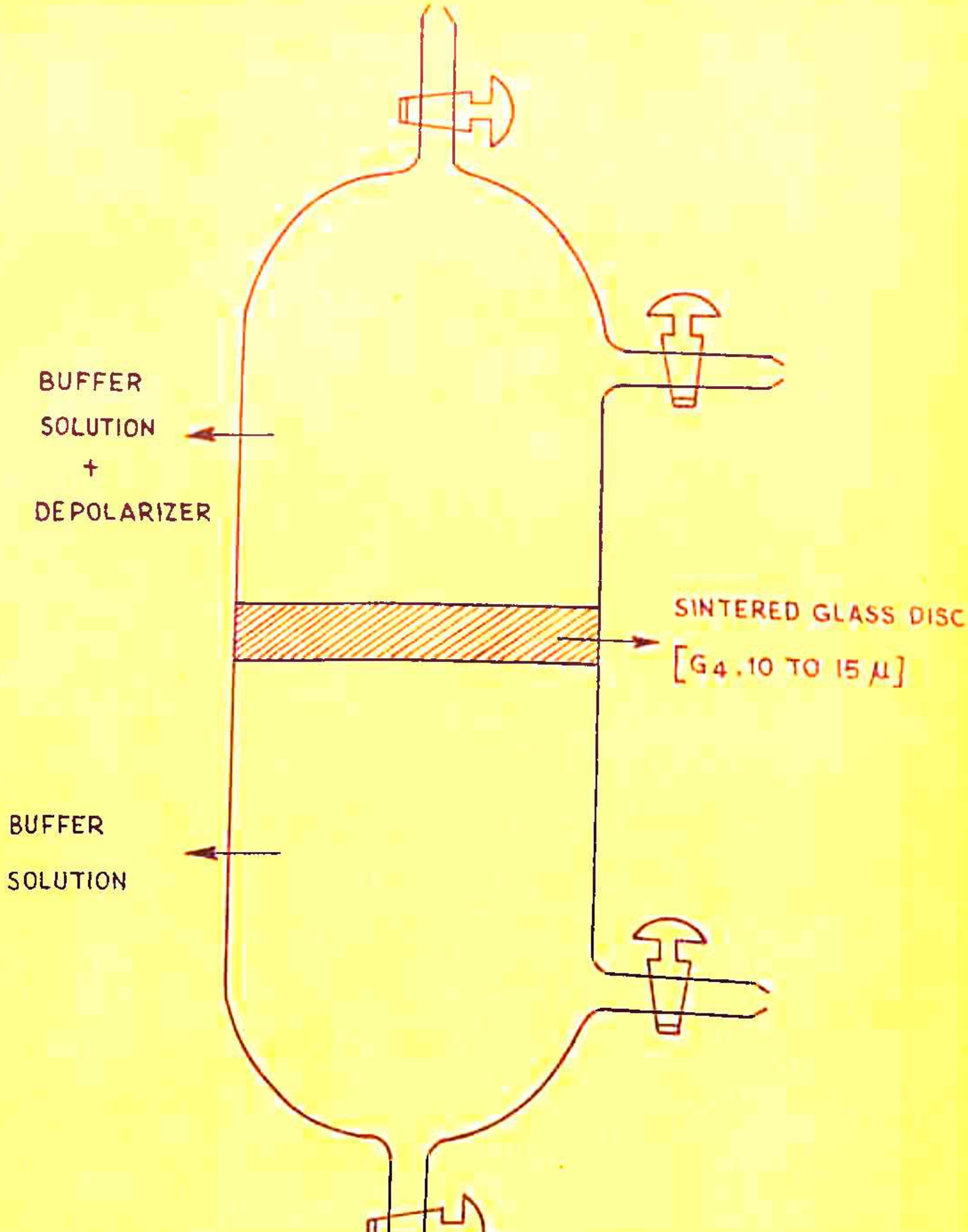

FIG. 2·2 McBAIN AND DAWSON CELL.

without disturbing the contents of other compartment. The diaphragm in between was made of pyrex sintered glass of medium porosity[233] (G4, 10 to 15 µ). The volumes of the upper and lower compartments were 168 ml each. To minimise any bulk flow through the diaphragm the supporting electrolyte concentration in compartments A and B was kept identical. The diffusion coefficient was calculated using the equation given by King and Cathcart[148].

$$\beta Dt = \frac{V_A\ V_B}{V_A + V_B} \ln \left[\frac{C_o}{C_o - (1 + \frac{V_A}{V_B})\ C} \right] \qquad (17)$$

where β is the cell constant, t is the time of diffusion in seconds, V_A and V_B are the volumes of the upper and lower compartments, C_o is the initial concentrations and C the concentration in the lower compartment after diffusion.

The cell constant of McBain Dawson cell 'β' was found as follows. The lower compartment of the cell was filled with the blank (buffer) solution and the upper compartment with the same buffer having C_o, millimole/litre, of nitrobenzene. The cell was kept in a vertical position in a constant temperature air thermostat. The amount of nitrobenzene (C, millimole/litre) diffused into the lower compartment in time 't' was determined by finding the value of diffusion current, i_d, from the polarographic current voltage curve recorded for the solution of the lower compartment. From this value of i_d the corresponding concentration of nitrobenzene was found from its calibration curve (i_d vs concentration). Also the value of D can be known from the Ilkovic equation as the number of electrons involved in the reduction process is known ($4\bar{e}$, 1st step). Thus the value of β obtained was 2.63.

By using the value of β, and from the amount of the depolarizer (read from its calibration curve) diffused in a certain time the value of D can be obtained and thereby 'n' can be calculated by incorporating the value of $\sqrt{D}$ in the Ilkovic equation.

A.C. Polarographic Technique

The technique of a.c. polarography aims at investigating electrode processes by the use of as small an alternating potential (usually sinusoidal) as is feasible superposed on the steady polarizing potential; the alternating current produced under these conditions is measured and recorded as a function of the applied steady potential, with the resulting graph termed "Alternating current polarograms". The main characteristic of an alternating current polarogram is the feature of observing, when a reversible redox process or adsorption - desorption process is being studied, a maximum alternating current at steady d.c. potentials. The potential at which the alternating current is maximum is termed 'peak potential', E_p or summit potential, E_s. The circuit, therefore, consists of a conventional circuit for d.c. polarographic work together with a source of alternating voltage and a device for measuring the alternating current in the circuit. Many methods are available to achieve this end. The bridge method of Grahame[81] is precise but is very cumbersome. The a.c. polarographic technique developed by Breyer and Gutmann[24] and modified by Doss and Kalyanasundaram[58] as well as Doss and Gupta[51] is shown to be very convenient for such investigations. The only further modification introduced was that the series resistance was made as small as possible. This was achieved by introducing suitable resistance in the a.c. ripple circuit and minimising the resistance across which the a.c. ripple is obtained.

This technique essentially consists in applying to the d.m.e. an a.c. ripple of low amplitude over the d.c. potentials and measuring the a.c. component of the resulting pulsating current by measuring the a.c. voltage drop across a resistor put in series with the d.m.e. This is done by feeding the voltage to an amplifier (Brüel and Kjaer, vacuum tube voltmeter, type 2407, Copenhagen, least count 0.2 mV and maximum amplification 60 db), and applying the amplified and rectified current into a galvanometer. The voltage drop resistor consists of a resistance box, the magnitude of the resistance necessary for producing a particular voltage drop being measured for calculating the current passing. This has rendered the measuring system independent of the frequency of the ripple[58].

PROPOSED WORK AND RESULTS

Proposed work by the candidate

The importance of polarography among other electrochemical methods of analysis has been widely recognised. The possibilities that polarography offered for understanding the basic principles of both electrochemical processes and electro-analytical methods attracted the interest of numerous workers to the field, and resulted in what is sometimes called the renaissance of electrochemistry. During the last two decades or so, oxidation or reduction of a large number of organic compounds have been studied. The technique finds utility in detecting and estimating a large number of organic functional groups, in the study of the kinetics of the reaction taking place in the bulk of the solution, in the correlation between the structure and reactivity, in the study of complexes and in estimation of metal ions (amperometrically) by various reagents.

Although considerable work has been done on d.c. and a.c. polarographic studies on organic compounds and estimation of metal ions amperometrically by titrating with suitable reagents, there are many aspects which need systematic investigations. This thesis, therefore, embodies the results obtained in the following investigations on which very little or no data are available in the literature.

[A] Reduction mechanism of some organic nitro-compounds at the d.m.e. and the effect of various physical factors on their kinetic parameters.

The following nitro-compounds were taken up with a view to gain information on the mechanism of their reduction at the d.m.e. and to evaluate the kinetic parameters ($-\log k^{o}$ and αn_a), under the influence of various physical factors. The utility of computer in calculating the value of kinetic parameters has been examined.

1. 7-nitro-8-hydroxyquinoline-5-sulfonic acid, and
2. Substituted nitropyridines
    - (a) 2-hydroxy-5-nitropyridine
    - (b) 3-hydroxy-2-nitropyridine
    - (c) 2-Amino-5-nitropyridine
    - (d) 6-Methyl-2-nitro-3-pyridinol.

[B] Studies on the estimation of metal ions by amperometry and determination of composition and stability constants of complexes.

Many metal ions are known to form soluble or insoluble complexes with organic compounds or inorganic ions. It is sought to investigate their stoichiometry and to determine the stability constant in the case of soluble complexes. Further, the work on the estimation of some metal ions using organic precipitants is to be done using conventional and a.c. polarographic techniques from the point of view of their analytical applications. The following systems have been investigated.

(i) Indirect polarographic determination of Zr(IV) as 7-nitro-8-hydroxyquinoline-5-sulfonate.

(ii) Estimation of thorium (IV) and zirconium (IV) with m-nitrobenzoic acid by indirect polarographic method, a.c. and d.c. amperometric methods.

(iii) Estimation of Ba^{2+}, Ag^{+} and Tl^{+} as chromates by a.c. amperometry.

(iv) Determination of stability constant of the complexes between Fe^{3+} and 7-nitro-hydroxyquinoline-5-sulfonic acid by a.c. polarography and spectrophotometry.

(v) Determination of the stability constant of the complex formed between Cd^{++} and the following nitropyridines by a.c. polarography.

    (a) 2-hydroxy-5-nitropyridine
    (b) 3-hydroxy-2-nitropyridine
    (c) 2-amino-5-nitropyridine
    (d) 6-methyl-2-nitro-3-pyridinol.

[C] A.C. polarographic studies on reaction kinetics in solution.

The use of d.c. polarography in the study of reaction kinetics is well-known. The applicability of a.c. polarography in the investigation of the reaction kinetics is to be evaluated. To study the kinetics of the neutralization of some pseudo acids by a.c. polarography , the following compounds were selected.

(a) Nitromethane

(b) Nitroethane

(c) 1-nitropropane

(d) 2-nitropropane

(e) β-nitropropionic acid

/D/ Tensammetric studies on the interaction between surface active substances.

Surface active complexes are sometimes formed between organic compounds. It is proposed to study the complex formed between phenol and organic bases such as pyridine, o- and m-toluidines and aniline by tensammetry and to confirm the results by conductometric and spectrophotometric studies.

It is expected that these studies will throw more light on the elucidation of electrode processes at the d.m.e. and assess the applicability of a.c. polarographic technique in particular. The role of computer for the calculation of the kinetic parameters has also been emphasised.

RESULTS

/A/ Reduction mechanism of some organic nitro-compounds at the d.m.e. and the effect of various physical factors on their kinetic parameters.

The work deals with the studies on the reduction of

(1) 7-nitro-8-hydroxyquinoline-5-sulfonic acid and

(2) Substituted nitropyridines

(a) 2-hydroxy-5-nitropyridine
(b) 3-hydroxy-2-nitropyridine
(c) 2-amino-5-nitropyridine
(d) 6-methyl-2-nitro-3-pyridinol.

The following are the main results obtained as a result of such investigations:

(1) Polarography of 8-hydroxyquinoline, 8-hydroxyquinoline-5-sulfonic acid and 7-nitro-8-hydroxyquinoline-5-sulfonic acid has been carried out in aqueous buffers (pH 2.0 to 12.0) of constant ionic strength (0.54 M) at 25 ± 0.1°C. The observations with 8-hydroxyquinoline and 8-hydroxyquinoline-5-sulfonic acid were similar to those reported in the literature.[221,258] The behaviour of the parent molecule of the 7-nitro derivative resembled that of 8-hydroxyquinoline-5-sulfonic acid. The nitro group gave a single step upto pH 8.5, above which it split into two. The number of electrons involved in the reduction of the nitro group over the whole pH range, using McBain and Dawson cell and applying King-Cathcart equation, was found to be six. A pre-wave, of adsorption characteristics, preceded the nitro group wave over the whole pH range. The kinetic parameters (αn_a and $-\log k^o$) in the case of single step for the nitro group reduction have been calculated by Koutecky's method and the reduction mechanism has been proposed.

The effect of the nature of cations, anions and the ionic strength of the supporting electrolyte revealed that the height of the step due to the reduction of the nitro group did not alter much and -log k^o increased in the order $K^+ > Na^+ > Li^+$ in solutions of monovalent cations, $Ba^{2+} > Ca^{2+} > Mg^{2+}$ in solutions of bivalent cations and $La^{3+} > Ca^{2+} > Na^+$ in solutions of mono-, bi- and tri-valent cations respectively. The increase in -log k^o in solutions of mono-, di- and tri-valent cations were small compared to the values in solutions of indifferent electrolytes having cations of the same valence but increasing atomic weight. In the case of anions it was seen that -log k^o decreased in the order $Cl^- < Br^- < I^-$ and this has been attributed to the increased adsorbabilities as we go from Cl^- to I^-. -log k^o also decreased with increasing ionic strength of the supporting electrolyte.

The effect of the drop time, concentration of the depolarizer, pH, concentration of ethanol and temperature on the kinetic parameters have also been studied.

The values of αn_a and -log k^o were almost independent of drop time, whereas, $E_{0.5}$ shifted to more cathodic values with increase in height of the mercury column. The value of αn_a and -log k^o were not appreciably affected by the concentration of the depolarizer. With increase in temperature the reduction became less irreversible and $E_{0.5}$ shifted slightly to more positive values. The values of αn_a decreased and -log k^o increased as the concentration of ethanol was increased in solution. The effect of various alcohols (in 5% concentrations) on -log k^o were also studied. The values of -log k^o increased with increase in chain length of alcohol. The values of -log k^o decreased on going from normal butyl alcohol to tertiary butyl alcohol. In solutions containing saturated alcohols the values of $-\log k^o$ were found to be more than in solutions containing unsaturated alcohols. Further the values of $-\log k^o$ increased in the media (5% in various alcohols) in the order propyl alcohol > isopropyl alcohol > propylene glycol > glycerol. As the pH was increased from 1 to 8.5, the values of αn_a decreased. The $-\log k^o$ increased and $E_{0.5}$ showed a cathodic shift with increase in pH. These effects have been discussed.

(2) Substituted nitropyridines. The following compounds were selected for the study.

a. 2-hydroxy-5-nitropyridine (A)
b. 3-hydroxy-2-nitropyridine (HNP)
c. 2-amino-5-nitropyridine (ANP)
d. 6-methyl-2-nitro-3-pyridinol (MNP)

Polarographic studies were carried out in aqueous buffers (pH 1.6 to 12.0) at a constant ionic strength (0.54 M) and temperature (30 ± 0.1°C).

(A), (HNP) and (MNP) have hydroxyl group in o- or p-position to the nitro group and ANP has a p-amino group. A $6\bar{e}$ wave was expected due to their ability to form quinonoid structures. They exhibited two waves. However, the second one being ill-defined in most cases. The first wave was analyzed and was found to be diffusion controlled irreversible reduction. McBain and Dawson cell was used to find the diffusion coefficient. Using this value of diffusion coefficient the number of electrons involved was found to be 6.

To calculate the kinetic parameters αn_a and $-\log k^o$ by Koutecky's method, the slope of the plot of $-E$ and $-\log k$ was found (by least square fit) using IBM 1130 computer. The slopes of the plots of $\log \frac{i}{i_d - i}$ vs E were also calculated using the computer. For a set of data the slopes of the above mentioned plots could be calculated in eight seconds. Generally, the value of αn_a did not show any regularity and $-\log k^o$ showed an increase with increase in pH.

2-hydroxy-5-nitropyridine had the most cathodic $E_{0.5}$ amongst the four compounds studied. Further, the value of αn_a was found to be the least in the case of (A). It was seen that p-amino group in ANP influenced the reduction of the nitro group more than p-OH group in (A). In the cases of HNP and MNP the $E_{0.5}$ and i_d were almost same except in strongly alkaline media. The value of $-\log k^o$ showed that in the case of MNP the reduction became more irreversible compared to HNP, presumably due to the presence of methyl group. HNP and MNP did not exhibit any maximum whereas (A) (pH 5.0, 6.0 and 7.0) and ANP (pH 6.0, 7.0, 9.0) showed a maximum which was suppressed by Triton X-100.

A.C. polarographic studies for concentrations used in d.c. polarographic studies did not yield any peak corresponding to the reduction of the nitro group except in cases where a maximum in d.c. polarographic wave was present. A.C. peaks could be observed in those cases in which a hump was seen in d.c. polarographic wave which has been attributed to the desorption at the d.m.e. However, at higher concentrations of the compound a small peak appeared corresponding to the nitro group reduction.

[B] Studies on the estimation of metal ions by amperometry and determination of composition and stability constants of complexes.

This work deals with the study of soluble and insolube complexes formed between some metal ions and organic or inorganic ligands. The stoichiometry and stability constant of soluble complexes have been found. Further, certain metal ions have been estimated by the use of precipitants. In some cases the comparison of d.c. amperometric, a.c. amperometric and indirect d.c. polarographic methods have been made. The following are the main results.

(i) Indirect polarographic determination of Zr(IV) as 7-nitro-8-hydroxyquinoline-5-sulfonate.

7-nitro-8-hydroxyquinoline-5-sulfonic acid (NOSA) has been used both as a precipitant and polarographic active substance in an indirect d.c. polarographic method for the estimation of Zr(IV) at pH 1.5. Direct d.c. amperometric titration was not found suitable. As Zr(IV) and NOSA do not give good a.c. waves, a.c. amperometry could not be used. The composition of the precipitate was found to be Zr(NOSA)$_4$. The effect of various ions were studied. UO$_2^{+2}$, tri-valent Al, Pr, Sm, La, Lu, Yb, Er, Gd, Nd and tetravalent Th did not interfere when present in concentrations about 20 times that of Zr(IV). Interference was caused by di-valent ions such as Ba, Ca, Sr, Mn, Cd, Zn, Co, Ni and Cu when present in concentrations greater than about one-fifth that of Zr(IV). The error in most cases was $\leqslant$ 2%.

(ii) Estimation of thorium (IV) and zirconium (IV) with m-nitrobenzoic acid by indirect polarographic, a.c. and d.c. amperometric methods.

Th(IV) and Zr(IV) have been estimated using m-nitrobenzoic acid (NBA) both as a precipitant and as polarographic reducible substance by a.c. amperometry. D.C. amperometric and indirect polarographic methods have also been carried out for comparison of results. In a.c. amperometric method best results were obtained at pH 3.4 for Th(IV) and at pH 3.0 for Zr(IV). Reverse titrations were also performed by a.c. amperometry. Error in most cases was $\leqslant$ 2%. The composition of the precipitate was found to be $Th(m-NO_2C_6H_4COO)_4$ and $(m-NO_2C_6H_4COO)ZrO(OH)$.

(iii) Estimation of Ba^{2+}, Ag^+ and Tl^+ as chromates by a.c. amperometry.

A.C. amperometric method has been employed to estimate Ba^{++}, Ag^+ and Tl^+ by titrating with K_2CrO_4 at pH 6.8. In the case of Ba^{++} best results were obtained in 10% methanol, 20% ethanol or 5% acetone by the addition of excess chromate and back titrating with standard $BaCl_2$ solution. Tl^+ could be titrated in 10% methanol at -0.47 V vs S.C.E. or in 20%

ethanol at -1.32 V vs S.C.E. For Ag^+ 20% ethanolic medium was found most efficient. Error in most cases was within 1.5% in a.c. amperometry. D.C. amperometric methods have also been used for comparison of results. It was also seen that in a.c. amperometric titration of Ba^{++}, 0.1 M KCl or 0.2 M KCl as supporting electrolyte yielded best results. In supporting electrolytes containing KI, KCNS, $CaCl_2$, $MgCl_2$ $AlCl_3$ erroneous results were observed. KNO_3, NaCl, $NaNO_3$, $NaClO_4$ and LiCl as supporting electrolytes also gave fairly good results for Ba^{++}.

(iv) Determination of the stability constant of the complex between Fe^{3+} and 7-nitro-8-hydroxyquoline-5-sulfonic acid (NOSA) by a.c. polarography and spectrophotometry.

A.C. polarography has been advantageously used to study the complex formation. D.C. polarography could not be used because of the fact that nitro group of the ligand gave a reduction wave prior to the Fe^{+++} wave and this interfered in determining the shifts in half wave potential of Fe^{+++}. The fact that the peak potential of Fe^{+++} shifted to more cathodic values as the concentration of NOSA was increased showed complex formation. Using Kolthoff and Ligane method the coordination number was found to be 3 and the dissociation constant was determined to be 0.513×10^{-13} at pH 2.5 and ionic strength 1.0M. Further, the dissociation constant value found by a.c. polarography agreed with that found by spectrophotometric method (0.45×10^{-13}).

(v) Determination of the dissociation constant of the complex formed between Cd^{++} and some nitropyridines.

Kolthoff and Lingane's method was used to determine the dissociation constants of the complexes formed by the following compounds with Cd^{++} at pH 2.0, temperature 25°C and ionic strength 1.0 M.

(a) 2-hydroxy-5-nitropyridine (A).
(b) 3-hydroxy-2-nitropyridine (HNP).
(c) 2-amino-5-nitropyridine (ANP).
(d) 6-methyl-2-nitro-3-pyridinol (MNP).

The general formula of the complex was found to be $[Cd\ (L)_2]^{++}$ where L denotes the ligand. The dissociation constants for the systems Cd-(A), Cd-HNP, Cd-ANP and Cd-MNP were found to be 0.4169×10^{-5}, 1.318×10^{-5}, 0.8185×10^{-5} and 1.146×10^{-5} respectively.

[C] A.C. polarographic studies on reaction kinetics in solution.

To study the tautomeric conversion of certain nitro compounds into their aci-forms, the following compounds were taken to investigate the applicability of a.c. polarography in the study of reaction kinetics.

(i) Nitromethane
(ii) Nitroethane
(iii) 1-nitropropane
(iv) 2-nitropropane
(v) β-nitropropionic acid

A.C. polarograms were taken for all compounds (in the entire pH range 1.0 to 12.0) after keeping them for 12 hours for the attainment of equilibrium between the normal nitro compound and its aci-form. The currents increased with increase in pH upto about neutral pH after which it started decreasing. The peak potential (E_p) also shifted to more cathodic potentials. In alkaline pH the E_p became almost constant and the magnitude of current decreased and finally in strongly alkaline media no peak was observed. The decrease in the magnitude of the peak is due to the formation of the aci-form which is not reducible at the d.m.e. This fact has been used to study the concentration of the nitro compound at various intervals of time and it was found that the kinetics was of first order. In the pH region (8.5 to 10.0) and at two different temperatures the kinetics of the transformation have been studied and the thermodynamic parameters are derived for the activated complex. The results agree fairly well with the literature values. However, 1-chloro-1-nitropropane did not give good peaks and hence a.c. polarographic technique could not be used in this case.

[D] Tensammetric studies on the interaction between surface active substances.

A.C. polarography has been successfully used to study the tensammetric complex formed between phenol and organic bases such as pyridine, o-toluidine, m-toluidine and aniline. Conductometric studies have also been used to confirm the composition of the complexes. Infrared spectroscopy has been used to establish, qualitatively, the existence of hydrogen bonded interaction between phenol and the organic bases. The composition of the complex was found to be 1:1 in the case of phenol with pyridine or aniline and 3:1 in the case of phenol with o-toluidine or m-toluidine.

LIST OF PAPERS PUBLISHED/COMMUNICATED

1. A.C. polarographic studies on the kinetics of the neutralization of some pseudo acids. Indian J. Chem. (in press).

2. Polarography of 7-nitro-8-hydroxyquinoline-5-sulfonic acid. Electrochim Acta (communicated).

3. Indirect polarographic determination of Zr(IV) as 7-nitro-8-hydroxyquinoline-5-sulfonate. Indian J. Chem. (in press).

4. Estimation of Thorium (IV) and Zirconium (IV) with m-nitrobenzoic acid by a.c. amperometry. J. Indian Chem. Soc. (communicated).

5. Polarography of 5-nitro orotic acid. Electrochim. Acta (communicated).

6. Thermodynamics of Fe(III)-7-nitro-8-hydroxyquinoline-5-sulfonate. Chem. Age of India (in press).

7. Estimation of Ba^{2+}, Ag^{+} and Tl^{+} as chromates by a.c. amperometry. Presented in the Eleventh Seminar on Electrochemistry, Karaikudi, India, 1970.

8. Tensammetric studies on the complexes of phenol with some organic bases. Presented in the Eleventh Seminar on Electrochemistry, Karaikudi, India, 1970.

9. Polarographic studies on some substituted nitropyridines. Anal. Chim. Acta (communicated).

10. A.C. polagraphic studies on the complexes of cadmium with some nitropyridines. Indian J. Chem. (communicated).

11. A.C. polagraphic studies on the complex of Fe(III) with 7-nitro-8-hydroxyquinoline-5-sulfonic acid. Chem. Age of India (communicated).

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CHAPTER III

REDUCTION MECHANISM OF SOME ORGANIC NITRO COMPOUNDS AT THE d.m.e. AND THE EFFECT OF VARIOUS PHYSICAL FACTORS ON THEIR KINETIC PARAMETERS

INTRODUCTION

The study of organic compounds has been made possible by satisfactory theoretical treatments of irreversible systems. Shikata studied nitrobenzene[247] at various pH values and subsequently with the help of his collaborators he studied the nitrophenols[248], dinitrobenzenes, dinitro-phenols[249] and nitroanilines[250]. Later, Winkel and Proske[251] also investigated nitrobenzene. Due to arbitrary reduction potentials, rather than $E_{0.5}$ quoted by earlier workers, Astle, Elving, Holleck, Pearson and Page individually investigated additional nitro-compounds in addition to repeating the earlier work. The substances investigated included mono-, di- and tri-nitrobenzenes[44,64,153,160,215,217,257], nitrotoluenes, nitrophenols[2,218], nitroresorcinols[4,219], p-nitroaniline, mononitro cresols[3], nitroanisoles, nitrobenzoic acids and the methyl nitrobenzoates.

The studies with nitrobenzene showed two steps below pH 4. The first one ($4\bar{e}$) corresponding to the hydroxylamine and the second ($2\bar{e}$) to the amine. The second step, however, disappeared beyond pH 4. The addition of alcohols resulted in the cathodic shift of the steps and a better defined second step. The nitrotoluenes, nitroanisoles and methyl nitrobenzoates differed from nitrobenzene in the pH value at which the second wave disappeared.

Di-nitrobenzenes and di-nitrotoluenes yielded a $12\bar{e}$ step in acidic media and a $10\bar{e}$ (or less) step in alkaline media. With tri-nitrobenzene and tri-nitrotoluene a step corresponding to greater than $12\bar{e}$ reduction in acidic and a $12\bar{e}$ reduction in basic media was observed. It was deduced that mono-, di- and tri-nitrobenzenes and nitrotoluenes were reduced to the corresponding hydroxylamine in neutral and alkaline media whereas in acidic media the reduction proceeded in a stepwise fashion through the corresponding hydroxylamine to the amine. Between pH 3 to 6 a mixture of the hydroxylamine and amine was formed. $E_{0.5}$ values varied linearly with pH but the slope changed at about pH 4 where the reduction process also changed.

The studies on p-dinitrobenzene were carried out by Holleck and Exner[125] and Holleck and Herman[126]. They observed multistage curves caused by two concurrent processes. In acid solution one of the nitro group underwent a $4\bar{e}$ reduction to hydroxylamine and the second nitro group underwent a $6\bar{e}$ reduction to form amine. However, in alkaline solution a stable tautomeric quinonoidal intermediate state was formed via a $2\bar{e}$ reduction process which was then reduced ($8\bar{e}$). The second reaction was inhibited over a wide pH range.

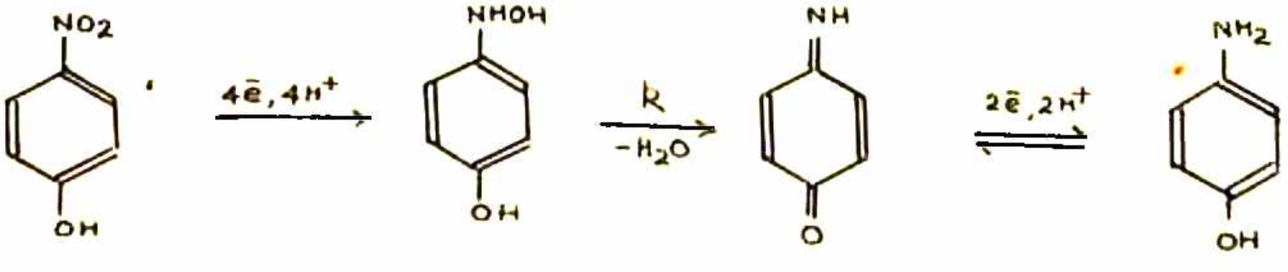
Holleck and Kastening[127] have suggested the following mechanism of the polarographic reduction of aromatic nitro-compounds in alkaline solution and weakly acidic solutions where the rate determining step is the second electron transfer process.

$$\begin{tikzcd} (R\text{-}NO_2)_{ads.} \arrow[r, shift left, "1\bar{e}"] & (R\text{-}N\bar{O}_2)_{ads.} \arrow[l, shift left, "Rev."] \arrow[r, shift left] \arrow[d, "1\bar{e}"] & (R\text{-}N\bar{O}_2)_{soln.} \arrow[l, shift left] \\ & (R\text{-}NO_2^{-2}) \arrow[r, "fast"] & Product. \end{tikzcd}$$

(R denotes - C_6H_5)

The rate of the electrode reaction is affected by the substituents in the benzene ring, the composition of the solution and the nature of the electrode surface especially in the presence of surface active substances.

The o-, m- and p-nitrophenols resembled nitrobenzene in acidic solutions in giving two steps. The o- and p-isomers, however, differed from nitrobenzene in that a $6\bar{e}$ step appeared with an increase in pH. o- and p-aniline also showed similar behaviour at higher pH values. In the case of 2-nitroresorcinol a $6\bar{e}$ wave appeared over a wide pH range (pH 2 to 12). With p-benzoquinone mono-oxime (p-nitrosophenol)[59], it was seen that in the first place the quinonimine was formed in a two-electron step. Because the oxidation-reduction potential of the $2\bar{e}$ reduction of the quinonimine is more positive than that of the reduction of the quinone mono-oxime, one single $4\bar{e}$ step, corresponding to the reduction of the quinone mono-oxime to p-aminophenol, was observed. An analoguous explanation has been proposed for the reduction of p-nitrophenol and p-nitroaniline[257]:



Because the potential for the reduction of quinonimine is more positive than that for the nitro group, one $6\bar{e}$ wave is observed, whereas, for other nitrobenzenes only a $4\bar{e}$ reduction occurs in the first step. The situation in this particular case is complicated because the dehydration of p-(hydroxyamino) phenol occurs at a finite rate, and hence, the increase of current above that required for the $4\bar{e}$ reduction possesses a kinetic character[257]. Finally, the $4\bar{e}$ reduction of the nitro group in the first step (the impossibility of detecting two separate $2\bar{e}$ waves and the absence of the corresponding nitroso compound as intermediate) is explained by the fact that the $E_{0.5}$ of nitroso compounds are more positive than those of the corresponding nitro derivatives. Every nitroso group formed is immediately transformed further into the hydroxylamine. Thus in the case of o- or p-nitrophenols and anilines such phenylhydroxylamines are formed which can be converted into the rapidly reduced quinonoid form. The quinonoid compounds undergo rapid electrode processes (described as reversible)[284]. An exceptional feature of quinonoid systems is that the net result of what is usually a $2\bar{e}$ oxidation-reduction process is a simultaneous change in two reactive groups in the molecule. This change is accompanied by a pronounced change in the aromaticity - from the oxidized form, resembling, an α, β-unsaturated ketone in its behaviour, to the aromatic reduced form[284].

Nitropyrimidines containing hydroxyl group at positions suitable for a single $6\bar{e}$ step through the formation of quinonoid form were 5-nitrobarbituric acid[137], 5-nitro uracil[138] and

and 5-nitro orotic acid[139] which were studied by Jain and Kapoor over a wide pH range.

The reduction of 4-nitrocatechol[4] showed an interesting behaviour in that the reduction of the intermediate nitroso-compound occurred at a more cathodic potential than the reduction of the nitro form. The wave for the hydroxylamine was well defined only upto pH 2.0 after which it became more drawn-out with decreased wave height and finally disappeared at pH 6.3. This behaviour indicated that the cation corresponding to the aryl hydroxylamine was the reducible form and that the unionized hydroxylamine was usually not polarographically active.

The behaviour of 2:4 and 2:6 dinitrophenols resembled the dinitrobenzenes but picric acid exhibited a 17$\bar{e}$ reduction wave probably corresponding to 3:5-diamino-4-hydroxyl phenylhydrazine which rearranges in acid to give a benzidine[173]. Styphnic acid also behaved like picric acid in giving a 17$\bar{e}$ step[4]. The respective amine is formed in the case of 2-nitro, 2:4 dinitro- and 2:6 dinitroresorcinol at all pH values. The nitrobenzoic acids yield two reduction waves both in acid and in alkaline solution. Their $E_{0.5}$ did not change with concentration but varied linearly with pH over a limited pH range[215]. Kemula and Chodowska[147] investigated nitrofurazone in aqueous-alcoholic mixture. Gorokhovski and Ponomarova[75] studied the reduction of o- and p-nitrobenzoic acid, p-nitrosalicylic acid, 5-nitroanthranilic acid and 5-nitroaniline over a pH range 2 to 10. They showed that at a low pH value the reduction of the nitro group was facilitated by the carboxyl group in the para position whereas at higher pH the reduction of the nitro group was retarded possibly owing to the negative charge of the ionized carboxyl group.

Runner et al.[238] found that the o-isomer of N-nitrophenyl-N'-phenylacetamide was reduced more readily than the m- or p-isomer, indicating the formation of intramolecular hydrogen bonding. The presence of intramolecular hydrogen bonding was established in the case of α-nitroso-β-naphthol by Ramaiah and Tewari[270].

Goward and coworkers[76] carried out the studies on 5-nitro-5-phenylcyclohexane and its derivatives.

The studies on 2-nitrofuran[159, 259, 260] showed a $4\bar{e}$ process which decreased to a $1\bar{e}$ process with the increase in the concentration of alcohol in the aqueous-alcohol mixtures. This was explained to be due to the retardation of the rate of protonation of the nitro-group and the formation of its anion radical. They suggested that the reduction of the nitro-group occurred via a protonized $R\text{-}NO_2H^+$ to 2-hydroxylamine furan and to 2-aminofuran via the 2-hydroxylammonium cation. Maurice and Pearson[220] investigated the polarographic reduction of nitro derivative of thiophene and pyrrole. Novikov and Pozdeva[214] carried out the polarographic behaviour of 4-nitro derivatives of N-oxides of pyridine, picolines, lutidines, quinolines and quinaldines.

Reduction data as a function of pH were reported for nitrobenzene[135], 4-nitroisooxazole[253], 4-nitroaniline[225], 1-phenyl-2-nitroethanol, 1-(p-bromophenyl)-2-nitroethanol, and 1-phenyl-2-nitroethanol methylate[170,171], different forms of the nitro group in solution[45,46] and for 2-methoxy-4-nitroaniline.[226] The polarographic behaviour of 2-ethyl-4-nitroaniline,[227] n-phenylnitramine and n-butylnitramine[168], N-nitramines derived from secondary amines[69], o- and p-nitrophenol[29] and for β-phenylnitroethane[124] was described.

Penttinen and Lindberg[222] reported polarographic data on nitro-derivatives of guaicol, o-vanillin and o-vanillic acid. Adams[1] described electrochemical and E.P.R. spectroscopic measurements of several p-nitro-triphenylamine compounds. Palyi[216] observed a $4\bar{e}$ step for the reduction of 3-nitro-4-chlorobenzene sulfonic acid.

Nitroparaffins yield a single step, in strongly acidic solutions, which has been attributed to the formation of the alkyl hydroxylamine. In weakly acidic media, a second step that has been attributed to the alkylamine appears[228].

$$CH_3NO_2 \xrightarrow[4H^+]{4\bar{e}} CH_3NHOH \xrightarrow[-H_2O]{2\bar{e},\,2H^+} CH_3NH_2$$

Stewart and Bonner[256] observed one $4\bar{e}$ step in well buffered solutions at all pH values. The reduction probably proceeded in acidic and basic solutions according to the following equations

$$R-NO_2 + 4H^+ + 4\bar{e} \longrightarrow RNHOH + H_2O \quad \text{(acidic solution)}$$

$$R-NO_2 + 3H_2O + 4\bar{e} \longrightarrow RNHOH + 4OH^- \quad \text{(basic solution)}$$

Miller et al.[209] studied the pseudo acid properties of nitroparaffins whereas those of phenyl-nitromethane and nitrocyclohexane were examined by Jannakoudakis[140,141]. Elving[60,61] has discussed the reduction of hydroxy nitrobutanes and their ethers and esters.

Polarographic data for m-nitrophenol[27], aliphatic nitroalcohol derivatives[184], nitrourea[229], several N'-substituted-2-methyl-4 (and -5)-nitroimidazoles[252], and 1-substituted 2,4-dinitrobenzenes in H_2SO_4-EtOH-H_2O solutions[267] were reported. Several aliphatic tertiary nitro compounds were studied in alkaline media[241].

The effect of proton donors on p-dinitrobenzene reduction[128] and the ability of pyridine and diethylamine to catalyze the proton transition between acids and nitro or carbonyl compounds were discussed[183]. 2-nitroacetaldehyde oxime was studied cathodically as well as anodically[47], while o-substituted p-nitroacetophenone oximes were examined in order to gain insight into ortho effects[6].

An anamolous dip was observed in the polarographic wave for nitro derivatives of imidazole at pH 6 to 10.[223] In another study the steepness of the reduction wave for 1-(p-bromophenyl)2-nitroethyl alcohol and other aromatic nitro alcohols was suggested to be measure of the extent of adsorption[172]. The various important experimental variables were emphasized in a study in which p-dinitrobenzene served as the model compound[129].

A detailed electrochemical study including a.c. and d.c. polarography of nitrobenzene reduction was also reported[264]. Effect of structure and pH on the reduction of 2-substituted-5-nitrofuran derivatives in water-ethanol was described[261]. Reduction and oxidation studies of several nitro paraffins and their sodium and potassium salts, respectively, were discussed in detail[263]. Polarographic data for 24 nitro compounds were determined in 63:27:10 ethanol-pyridine-water and used in studies on the pyrochlorophyll-sensitized photo-reduction of nitro compounds[242].

A.C. polarographic studies on organic compounds gained momentum after the work of Breyer and coworkers[19,20]. Suzuki[266] investigated nitro compounds with oscillographic polarography. Nitrophenols were found to be reduced reversibly in alkaline pH rather than acidic pH values. Nitromethane was irreversibly reduced as were o- and p-nitrophenols in acidic solutions. Suzuki[266] was able to show that, while the overall reduction of nitrobenzene were irreversible, the intermediate redox reaction involving nitrosobenzene and N-phenylhydroxylamines was a reversible step in the process. Breyer and Bauer[17] found that nitrobenzene either gave two different waves or a single wave with increased wave height where a maximum was present in d.c. polarographic studies. Kastening and Holleck[145,146] studied the effect of surfactants on the reduction of nitro compounds such as p-nitroaniline, p-nitrochlorobenzene and p-nitrobenzoic acid. The literature on a.c. polarography has been reviewed through 1955 by Breyer et al.[21]

Gupta and Sharma[245] extensively studied organic compounds by a.c. polarography. The effect of pH and buffer, supporting electrolyte, medium, temperature and frequency of a.c. ripple and series resistance, on the magnitude and peak potential of some organic compounds were investigated by them. Gupta and Chatterjee[30] carried out studies on mixture of reducible organic compounds. They estimated p-nitrophenol quantitatively from its mixture with nitrobenzene as well as with o-nitrophenol or m-nitrophenol and vice versa within specified concentration ranges. The studies on mixtures of organic reducible species and surface active substances (s.a.s.) were also carried out. They observed that the magnitude of the reduction peak was not influenced upto a certain concentration of s.a.s. after which the magnitude of the peak progressively decreased. Gupta and Chatterjee also studied the effect of concentration on the peak potentials of some organic nitro compounds. They found that nitrobenzene, o- and m-nitrobenzoic acids and p-nitrophenol peaks did not shift with concentration in alkaline pH values whereas the peak potentials of o- and m-nitrophenols, di- and tri-nitrophenols, o- and m-nitrotoluenes and m- and p-nitroaniline progressively shifted to more cathodic values with increase in their concentration. The studies on nitrobenzene was also carried out.

A.C. polarographic data were collected for o-, m- and p-halo-substituted nitrobenzenes[68]. The effect of pH and inhibitors were considered in d.c. and sine wave polarographic study of o-, m- and p-nitrophenols[31,32].

(i) POLAROGRAPHY OF 7-NITRO-8-HYDROXYQUINOLINE-5-SULFONIC ACID (NOSA)

As no polarographic studies have been reported on NOSA it was chosen to study its reduction at the d.m.e. at various pH and also to investigate the effect of various physical factors on the kinetic parameters (αn_a and $-\log k^o$) of the reduction of the nitro group.

EXPERIMENTAL

Recrystallized oxine (Ward Blenkinsop Co., London) was used for experiments and preparation of its derivatives. Oxine-5-sulfonic acid (OSA) and 7-nitro-oxine-5-sulfonic acid (NOSA) were prepared and purified as described by Welcher[280]. Stock solutions (0.01 M) of oxine, OSA and NOSA were prepared in 50% ethanol for preliminary studies (25°C). However, for subsequent studies with NOSA (35°C) the stock solution was prepared in double distilled water. All other chemicals were of analytical reagent grade. HCl/KCl, Na_2HPO_4/citric acid, Boric acid/NaOH and NaOH buffers were used. The ionic strength was maintained at 0.54 M by KCl. No maximum suppressor was needed except for oxine at neutral pH when gelatin (0.04%) was used. The capillary used for d.m.e. had m = 2.931 mg/s, t = 3.05 s in 0.54 M KCl (open circuit) at h = 40.0 cm (uncorrected for back pressure) in d.c. polarography and m = 4.564 mg/s and t = 1.8 s in 0.1 M KCl (open circuit) in a.c. polarography.

RESULTS AND DISCUSSION

In order to identify the wave due to the nitro group and due to the lack of data on oxine and OSA in the same buffer system and ionic strength, preliminary studies on oxine, OSA and NOSA were carried out under identical conditions at 25°C.

Current-voltage curves at various pH values

Oxine: The current-voltage curves are shown in Fig. 3.1. Oxine gave a single poorly defined wave A in strongly acidic solutions. Between pH 4 and 7 an ill-defined wave B, probably due to adsorption, preceded the wave A. Another wave C at pH greater than 7 showed signs of following the wave A but hydrogen discharge interfered with the observations. At pH 7 the wave A was surmounted by a pronounced maximum which disappeared at higher pH values (pH > 8.5). Gelatin (0.04%) suppressed the maximum at pH 7 and shifted the waves A and C to more cathodic potentials. The wave C persisted upto pH 10.0 and then merged into the decomposition curve of the supporting electrolyte at pH 12 whereby only one well-defined wave remained. These observations are similar to those reported by Stock[258] who attributed these waves to the formation of dihydro- and tetra-hydro oxine. The slight variations in the $E_{0.5}$ values observed by us may be due to the different nature of the buffer system used.

Oxine-5-sulfonic acid (OSA): In acidic side OSA gave a well-defined single step whose height decreased with increase

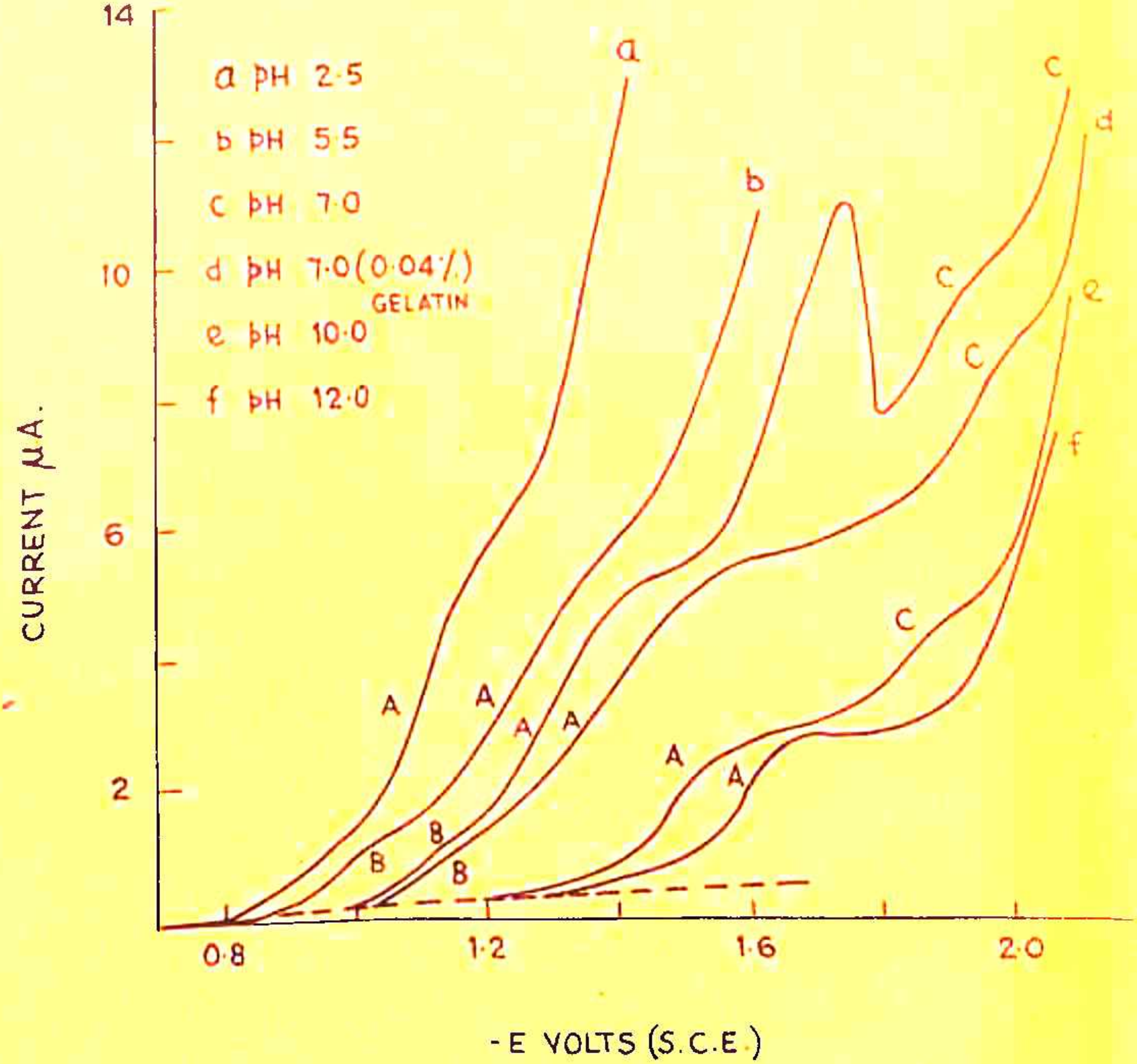


FIG. 3·1 POLAROGRAMS OF 0·5 mM OXINE AT VARIOUS pH VALUES.

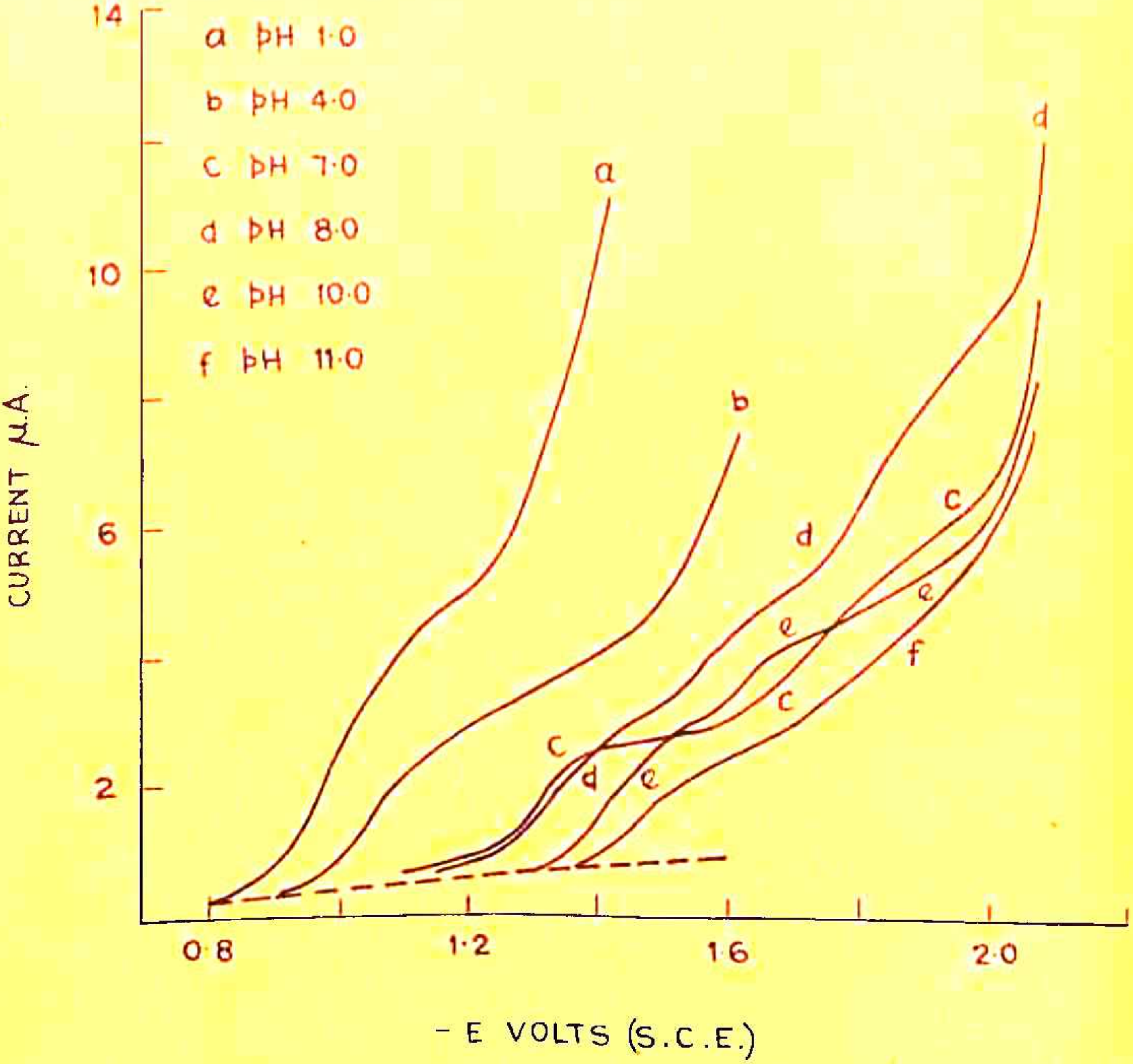


FIG. 3·2 POLAROGRAMS OF 0·5 mM OXINE-5-SULFONIC ACID AT VARIOUS pH VALUES.

in pH. At pH 7 it gave a two step reduction and was free from maximum whereas with oxine a sharp maximum was observed. At pH 8.5 a third step appeared which again disappeared at pH 10. However, at pH 11 only the first step remained. No wave appeared at pH 12. The current-voltage curves are shown in Fig. 3.2. These observations, except at pH 8.5, are similar to those reported on OSA by Philips and Fernando[2.1] who characterised the reduction wave(s) to be due to the formation of dihydro- and tetrahydro OSA. Probably Philips and Fernando missed the third wave at pH 8.9 as they did not record current-voltage curves beyond -1.8 volts whereas in our case the $E_{0.5}$ of the third wave was found to be -1.84 volts. The fact that the $E_{0.5}$ of the first wave ($E^{1}_{0.5}$) at pH 8.5 is very close to ($E^{1}_{0.5}$) at pH 7 and the $E_{0.5}$ of the second wave ($E^{2}_{0.5}$) at pH 8.5 is more positive than ($E^{2}_{0.5}$) at pH 7 shows that the reduction mechanism at pH 8.5 is different from that at pH 7. The disappearance of the third wave at pH > 8.5 may be due to further cathodic shift of its $E_{0.5}$ which appears very close to the discharge of the cations of the supporting electrolyte. The non-redicibility of OSA at pH 12 may be due to the double negative charge which prevents the acquisition of further electrons.

<u>7-nitro-oxine-5-sulfonic acid (NOSA)</u>: The current-voltage curves are shown in Fig. 3.3. With NOSA the current-voltage curves due to the oxine-5-sulfonic acid molecule were similar to those of OSA except that the waves appeared at more negative potentials. The nitro group gave a single step upto pH 8.5. At pH > 10 the nitro group split into two but the

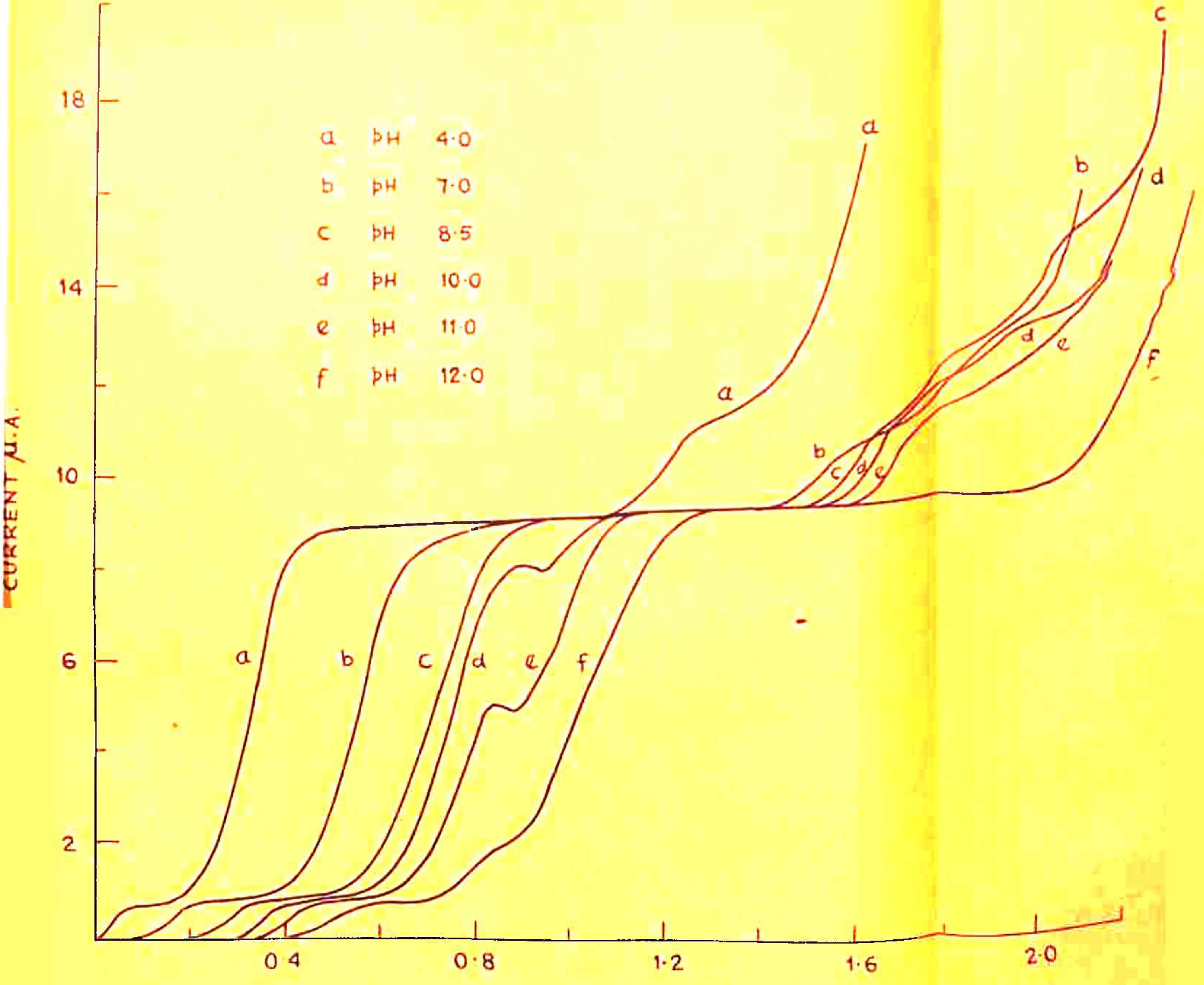


FIG. 3.3 POLAROGRAMS OF 0.5 mM 7-NITRO-OXINE-5-SULFONIC ACID AT VARIOUS pH VALUES.

total wave height remained the same. This split occurred at the upper part of the step at pH 10, at the middle part of the step at pH 11 and at the foot of the step at pH 12.

In order to analyse the nature of the reduction of the nitro group the tests of i_d/c , $i_d/\sqrt{h}$ and negative shifts of $E_{0.5}$ with concentration were performed at pH 4.0, 5.5, 7.0, 8.5, 10.0 and 11.0. Table 3.1 gives the effect of concentration and Table 3.2 gives the effect of height of the mercury column at pH 8.5. Similarly i_d/c (Table 3.3) and i_d/h and $i_d/\sqrt{h}$ (Table 3.4) at pH 10.0 have been recorded. Table 3.5 gives the i_d/c values and Table 3.6 gives the i_d/h and $i_d/\sqrt{h}$ at pH 11.0. These tests were also made for the second step resulting from the splitting up of the main reduction wave of the nitro group. Further log $\frac{i}{i_d-i}$ vs - E plots were made at pH 1.0 to 8.5 as shown in Fig. 3.11. All these tests showed that the nitro group underwent diffusion-controlled irreversible reduction upto pH 8.5. The effect of concentration on wave height is shown in Figs. 3.5 (pH 8.5), 3.6 (pH 10.0), 3.7 (pH 11.0) and 3.8 (pH 12.0). Fig. 3.9 shows the effect of height of the mercury column on the wave at pH 8.5. Over the whole range of pH a small wave preceded the nitro group wave. A.C. polarograms shown in Fig. 3.4 give two peaks, though small in magnitude, which correspond to the small d.c. pre-wave and the reduction wave. The first peak, corresponding to the d.c., pre-wave, decreased in height with temperature. This shows that it possesses adsorption characteristics[22]. The second peak though small in magnitude increased with temperature. This peak was broad and hence the peak potential could not be measured

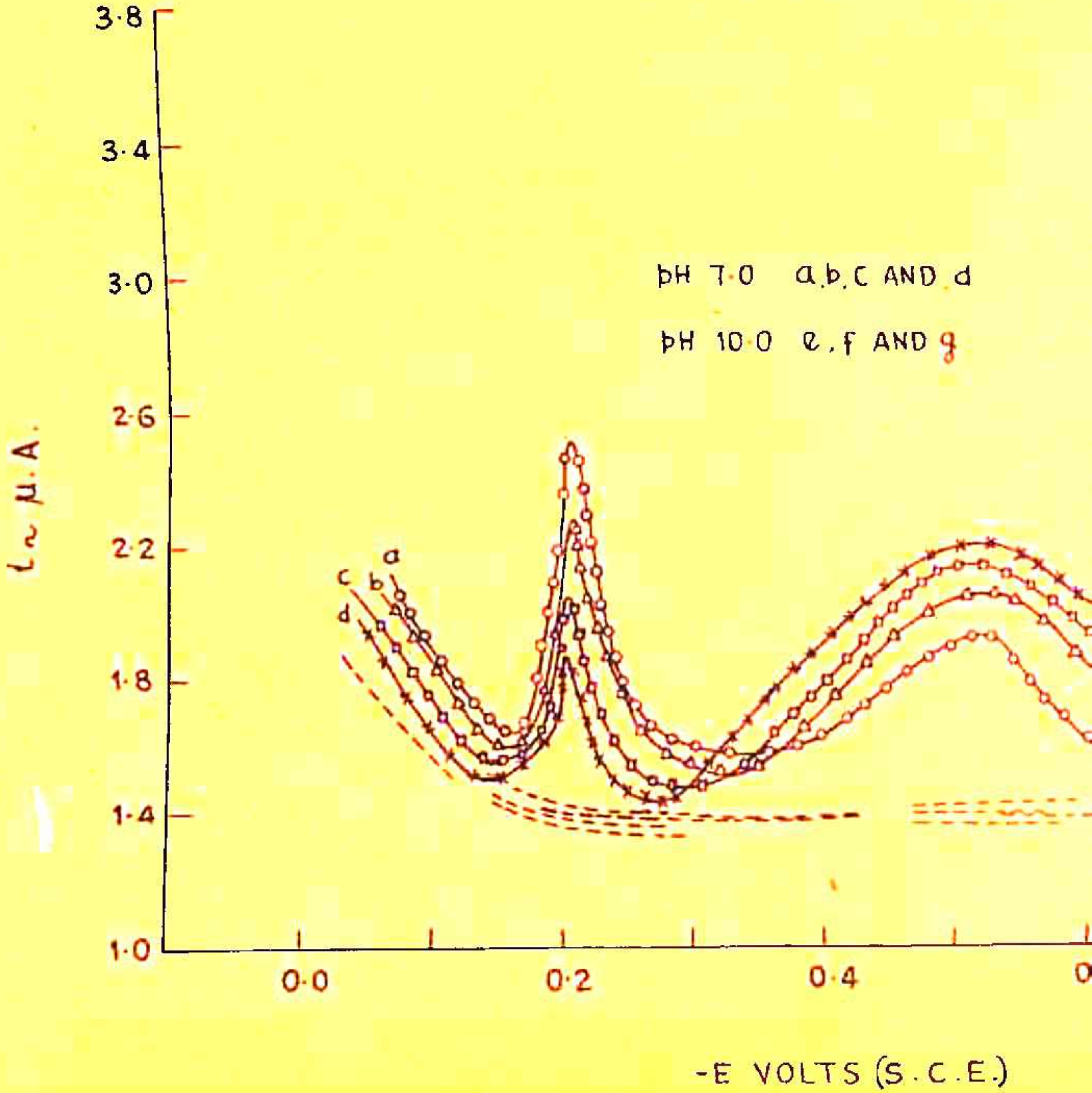
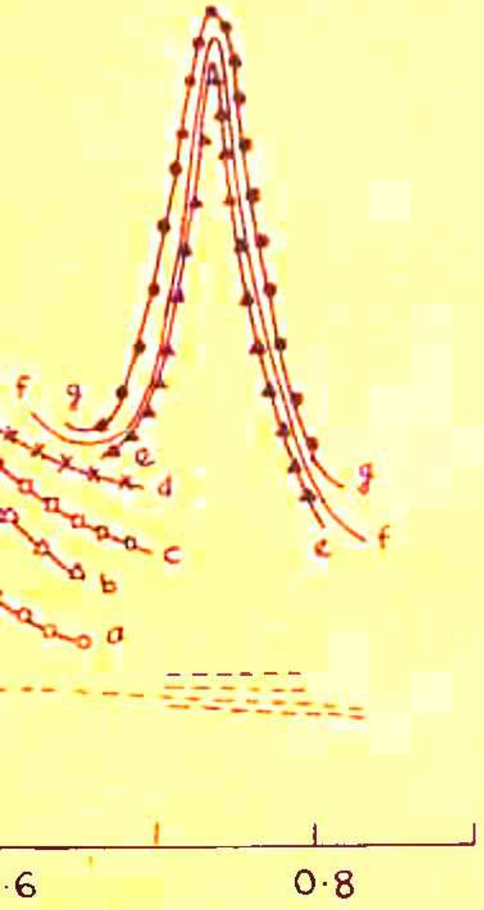

3·8
3·4
3·0
2·6
2·2
1·8
1·4
1·0
i ~ μ.A.
pH 7·0 a,b,c AND d
pH 10·0 e,f AND g
a
b
c
d
0·0
0·2
0·4
0
-E VOLTS (S.C.E.)

FIG. 3·4


f
g
e
d
c
b
a
g
f
e
·6
0·8

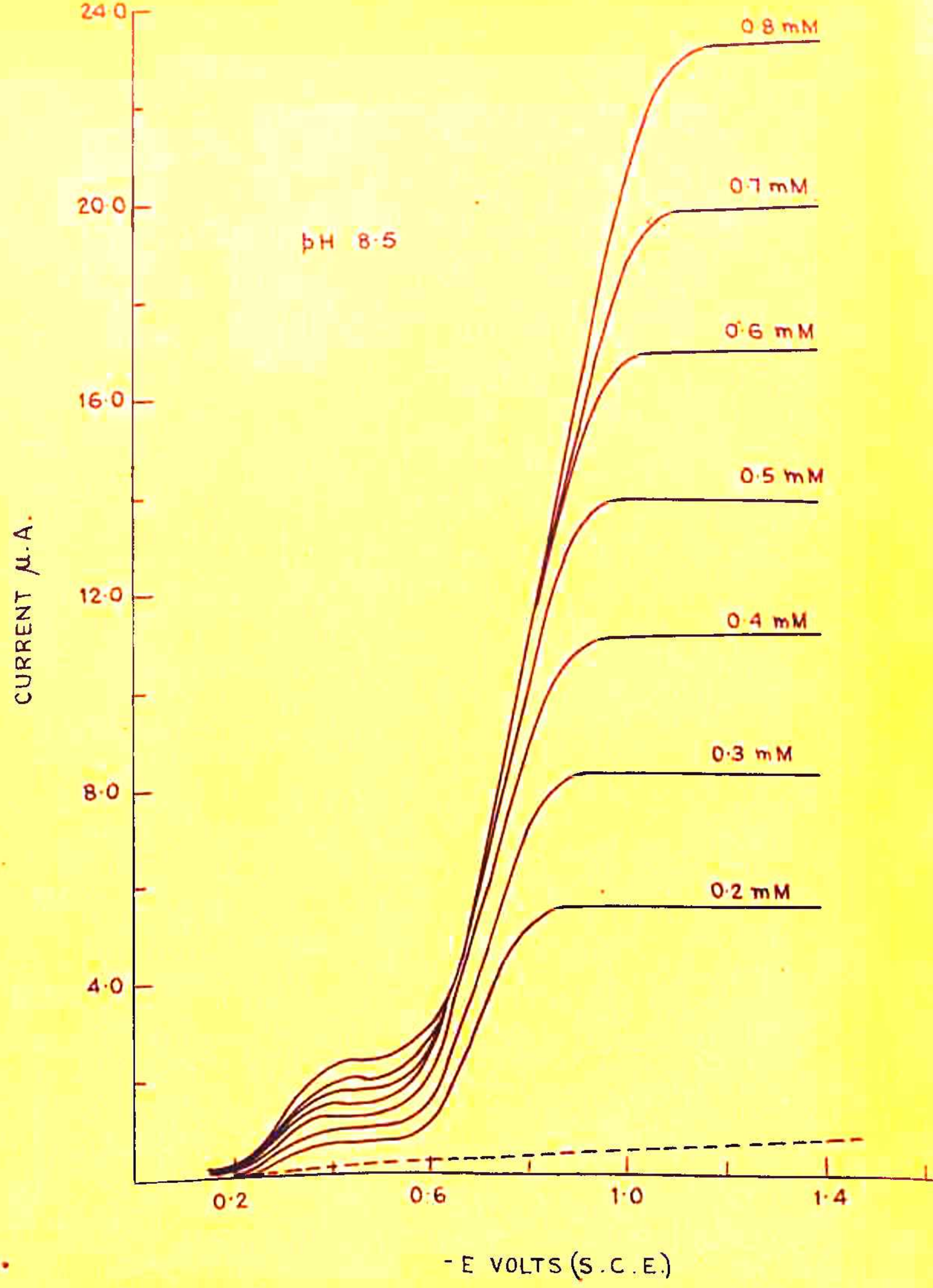
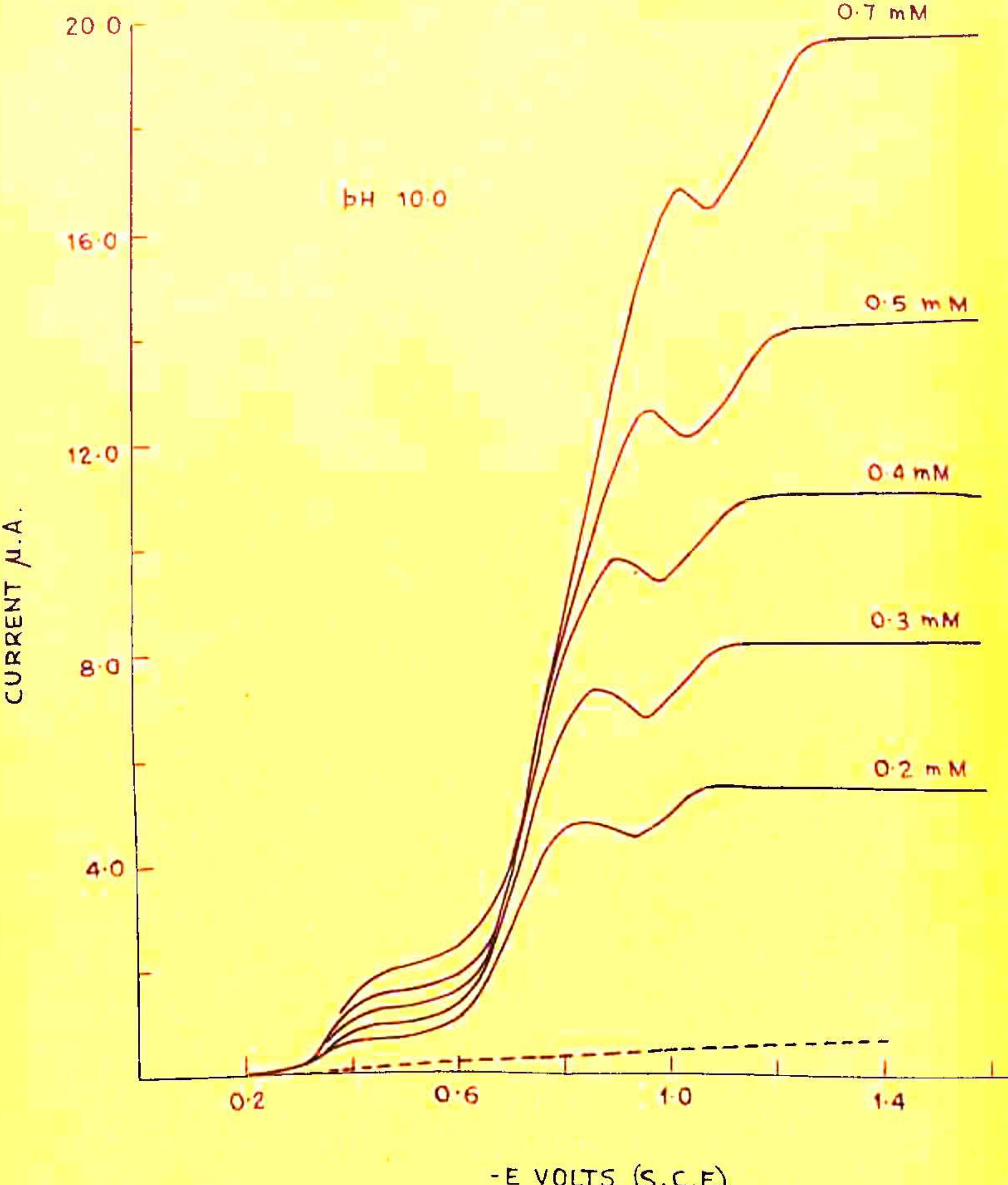

24·0
20·0
16·0
12·0
8·0
4·0
CURRENT μ.A.
pH 8·5
0·8 mM
0·7 mM
0·6 mM
0·5 mM
0·4 mM
0·3 mM
0·2 mM
0·2
0·6
1·0
1·4
- E VOLTS (S.C.E.)

FIG. 3·5



20·0
16·0
12·0
8·0
4·0
CURRENT μA.
pH 10·0
0·7 mM
0·5 mM
0·4 mM
0·3 mM
0·2 mM
0·2
0·6
1·0
1·4
-E VOLTS (S.C.E)

FIG. 3·6

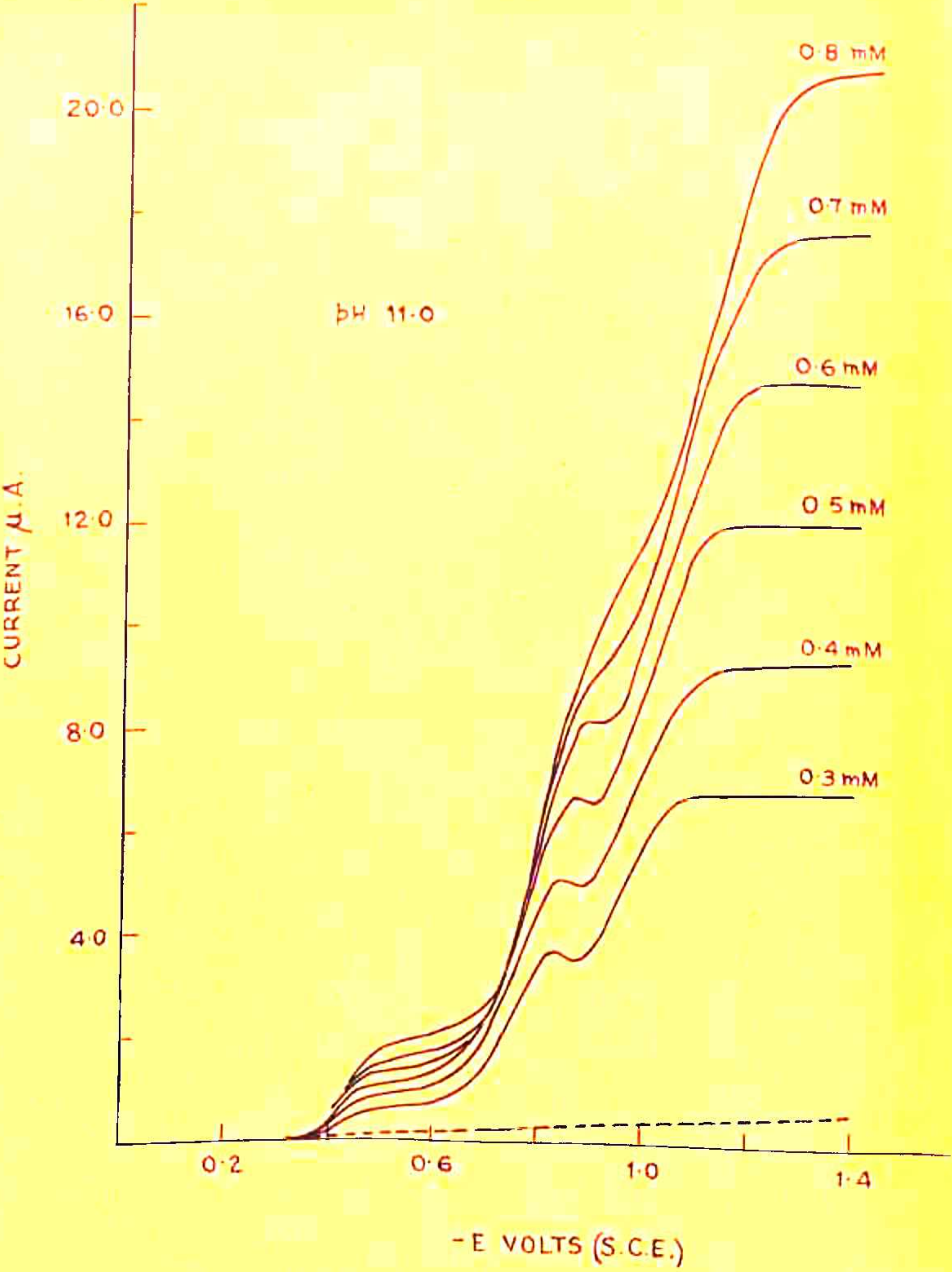

0·8 mM
0·7 mM
0·6 mM
0·5 mM
0·4 mM
0·3 mM
pH 11·0
20·0
16·0
12·0
8·0
4·0
CURRENT μ.A.
0·2
0·6
1·0
1·4
-E VOLTS (S.C.E.)

FIG. 3·7

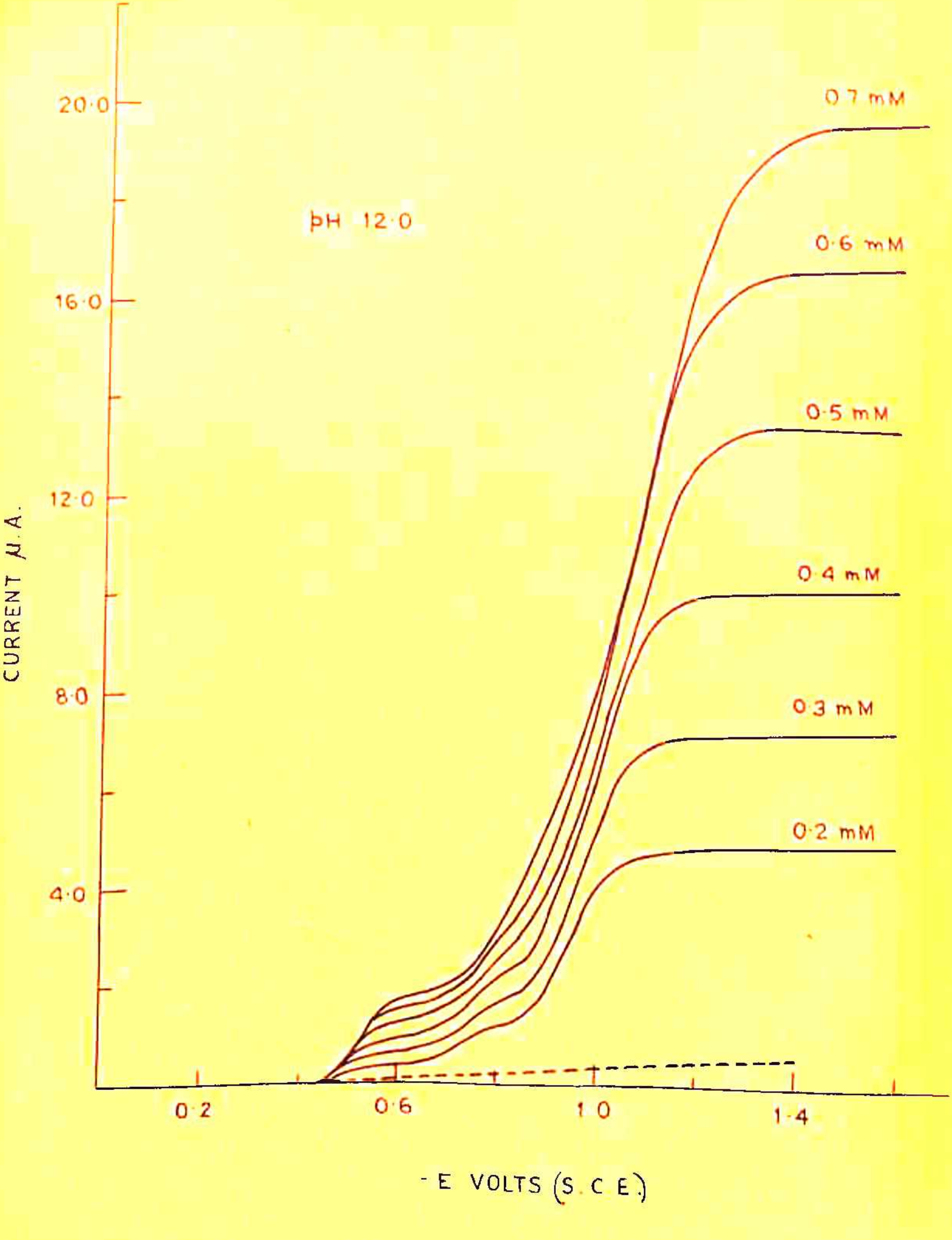

pH 12·0
0·7 mM
0·6 mM
0·5 mM
0·4 mM
0·3 mM
0·2 mM
20·0
16·0
12·0
8·0
4·0
CURRENT μA.
0·2
0·6
1·0
1·4
- E VOLTS (S.C.E.)

FIG. 3·8

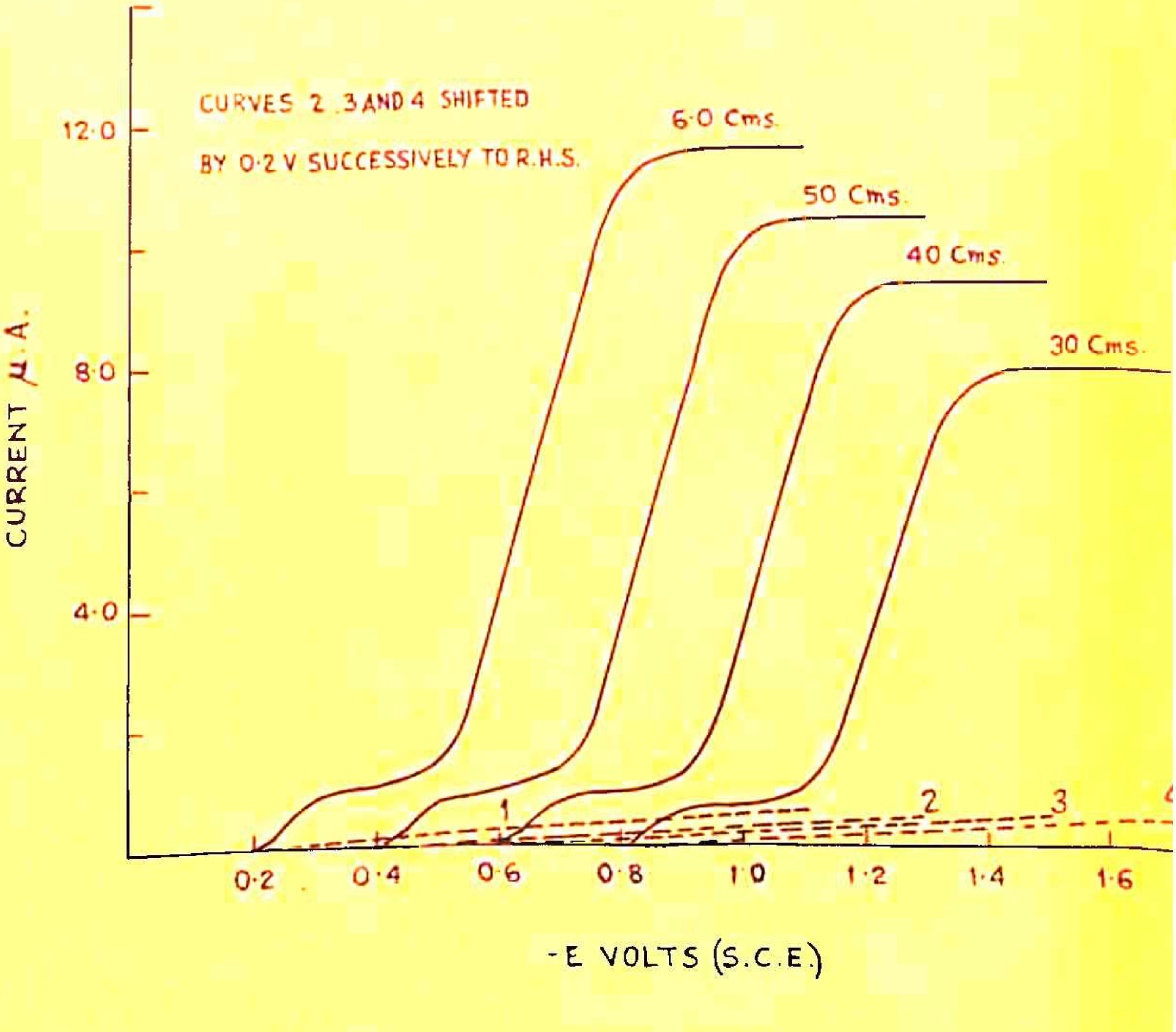
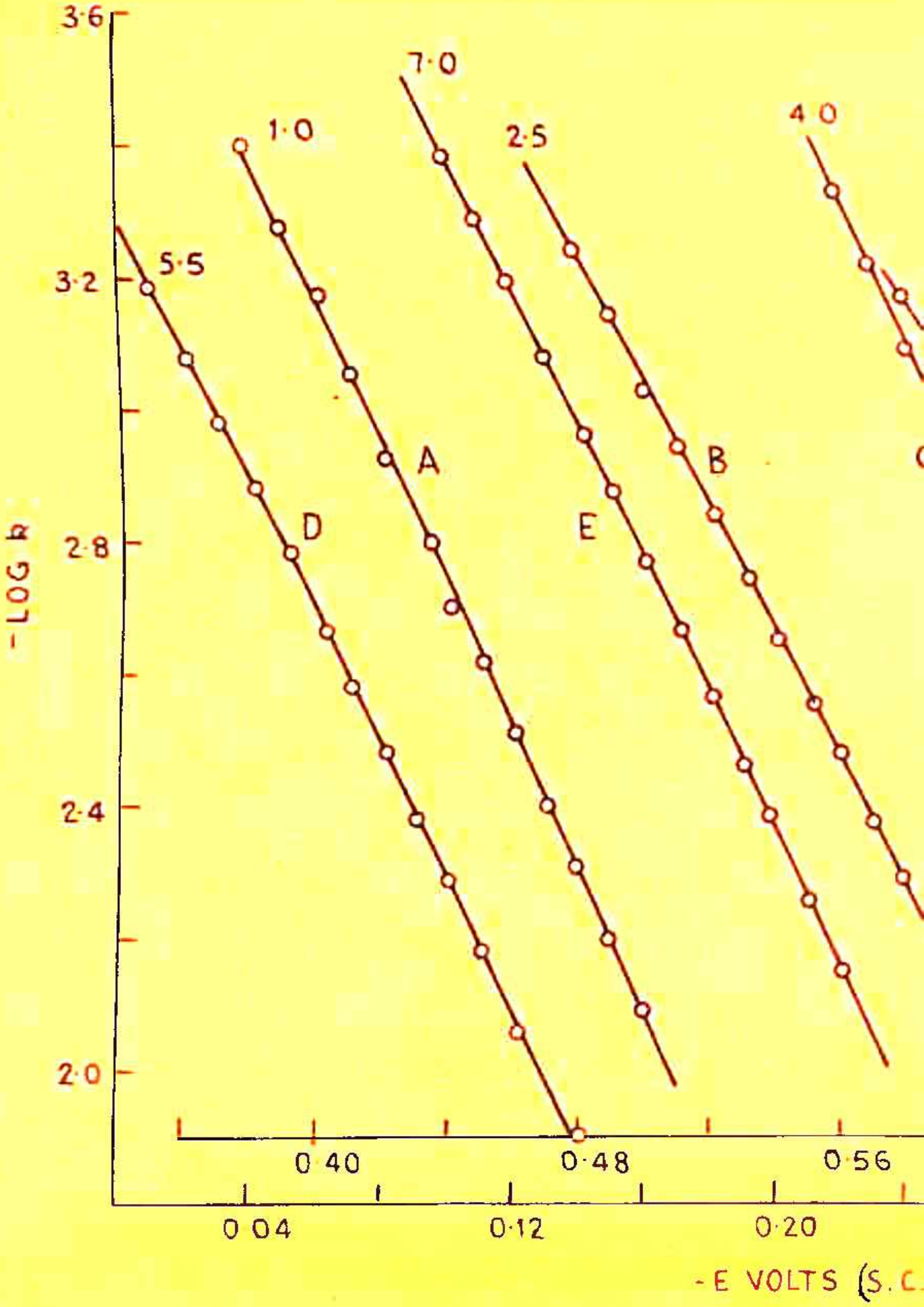
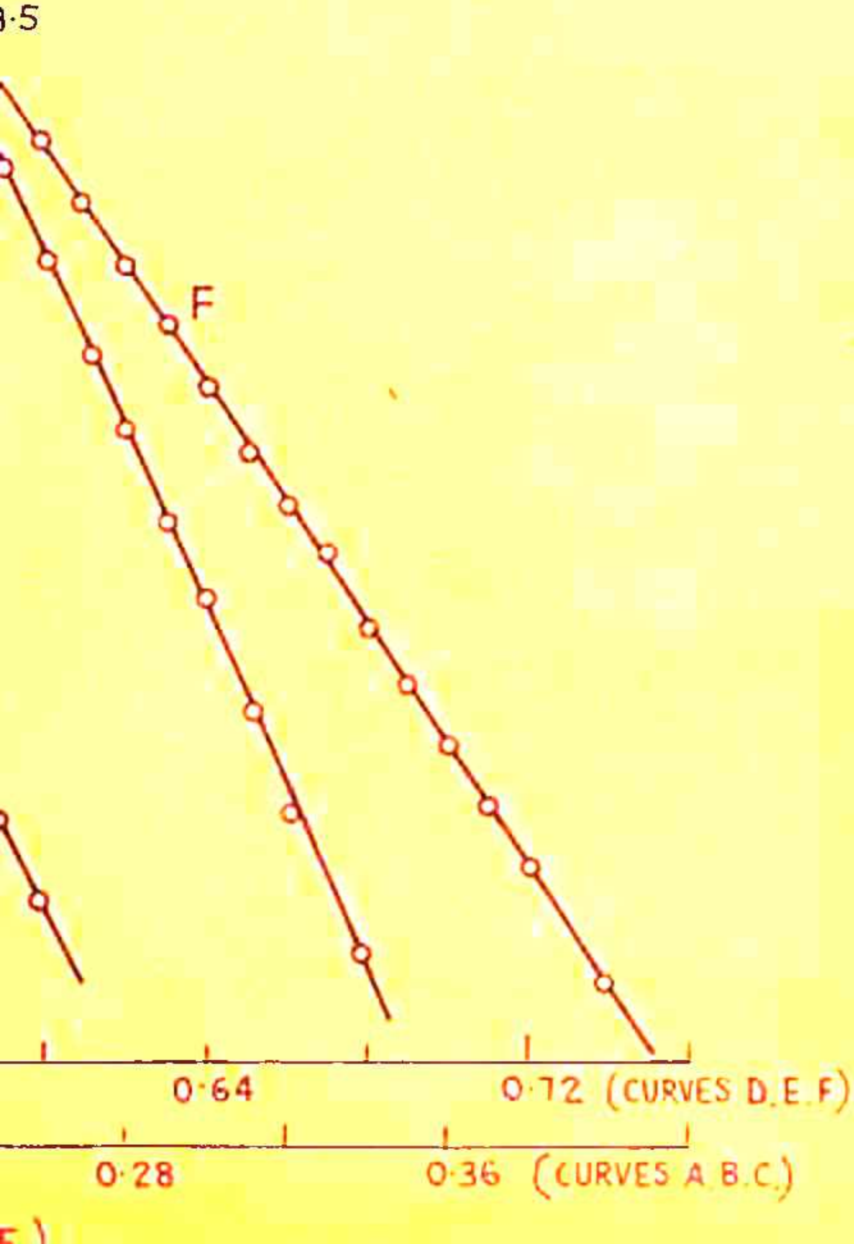

CURVES 2, 3 AND 4 SHIFTED
BY 0·2 V SUCCESSIVELY TO R.H.S.
6·0 Cms.
50 Cms.
40 Cms.
30 Cms.
1
2
3
12·0
8·0
4·0
CURRENT μA.
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
-E VOLTS (S.C.E.)

FIG. 3·9


3·6
3·2
2·8
2·4
2·0
-LOG k
7·0
1·0
2·5
4·0
5·5
A
B
D
E
0·40
0·48
0·56
0·04
0·12
0·20
-E VOLTS (S.C.


·5
F
0·64
0·72 (CURVES D.E.F)
0·28
0·36 (CURVES A.B.C.)

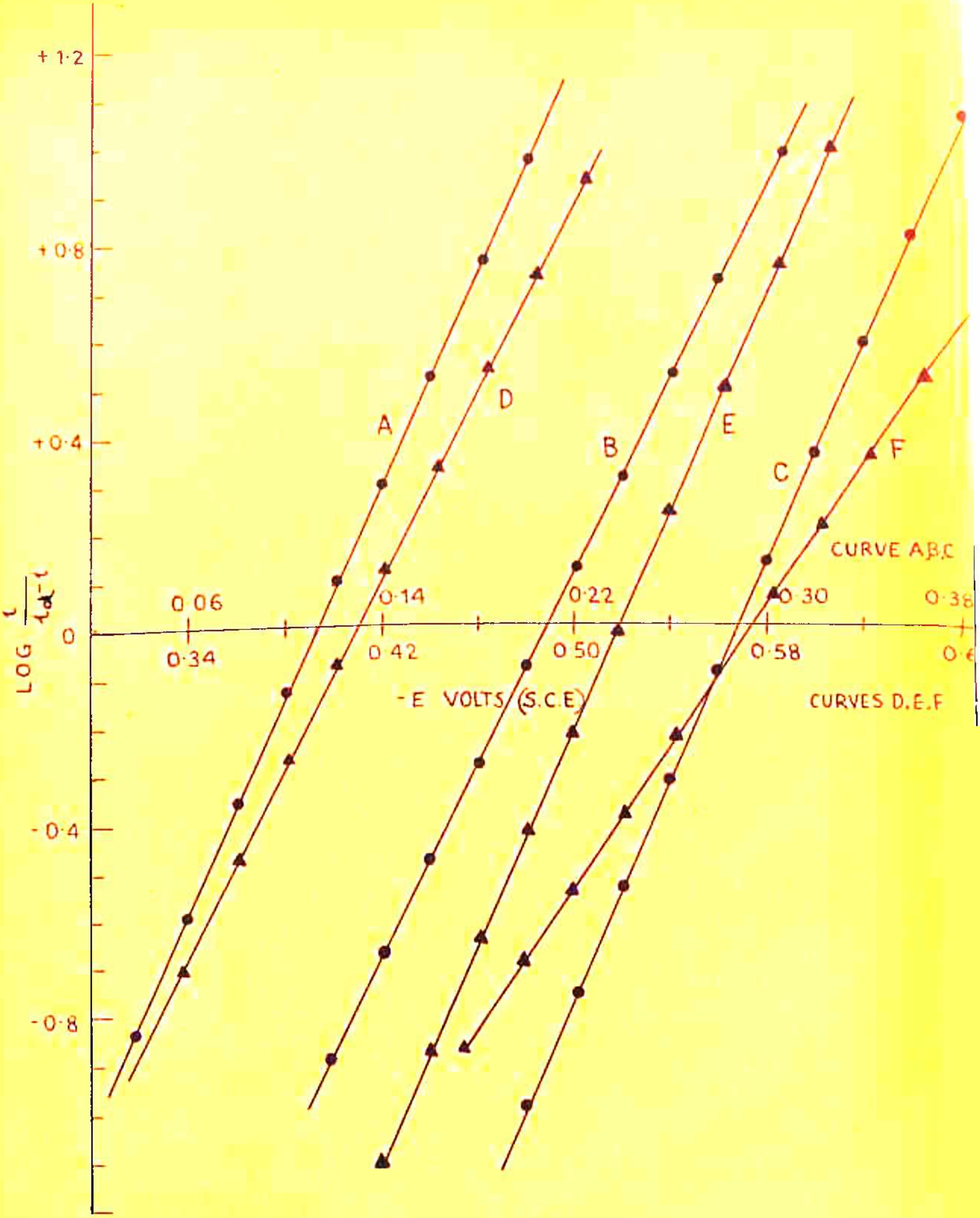
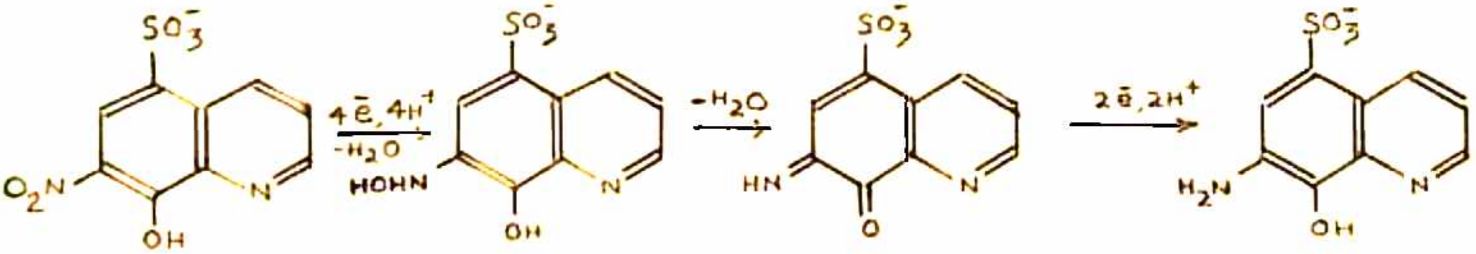


FIG. 3·11 -E VS LOG $\frac{i}{i_d - i}$ AT VARIOUS pH.

accurately. Qualitatively, however, it was seen that it shifted to more cathodic potentials with pH and the magnitude of this shift corresponded to the magnitude of the shift in $E_{0.5}$. The splitting of the wave at high pH may also be due to adsorption phenomena and in these cases only one a.c. peak was observed which may be ascribed to the composite nature of the peak. Similar splitting of the d.c. polarographic wave has also been reported[224] in the study of heterocyclic nitro acids and heterocyclic aldoximes.

The diffusion coefficient of NOSA (5.42×10^{-6} cm^2 s^{-1} at 35°C) was found by using McBain and Dawson cell and applying King-Cathcart equation[148]. Using this value of D in the Ilkovic equation the number of electrons involved in the nitro group reduction was calculated to be $5.93 \doteq 6$.

Koutecky's method[164] was used to calculate the values of kinetic parameters from the data for the polarographic waves at pH 1.0 to 8.5. These results are given in Table 3.7. $-\log k$ vs $-E$ plots yielded straight lines (Fig. 3.10) thus showing that there is only one process which determines the rate of the reduction of the nitro group. Values of αn_a showed a regular decrease from pH 1.0 to 8.5 and $-\log k^o$ showed an increase in the region. $E_{0.5}$ and $-\log k^o$ showed an increase with pH. The electrode processes thus become more irreversible with increase of pH because of the increased difficulty of the availability of the H^+ which are involved in the reduction processes. The probable reduction mechanism (below pH 8.5) when a single $6\bar{e}$ reduction is taking place may be as follows:



Cations such as monovalent Li, Na and K, divalent Mg, Ca and Ba, trivalent La were taken to study the effect of the nature of supporting electrolytes on kinetic parameters at a constant pH. The effect of monovalent anions Cl^-, Br^- and I^- were also examined.

Table 3.8 gives the effect of halide ions on kinetic parameters. It can be seen that $E_{0.5}$ and αn_a do not change appreciably whereas - log k^o showed a decrease on going from Cl^- to I^-. The tendency of the halide ions to increase the apparent reversibility of the electrode process is in conformity with their adsorbabilities[69,70,83,84] on the mercury drop surface. The accelerating effect on the electrode process with increase in adsorbability may be due to some sort of activated complex formed at the electrode surface with the resultant decrease in the activation energy for the electrochemical process.

Table 3.9 gives the effect of Li^+, Na^+ and K^+ on the kinetic parameters. There was no regular variations in $E_{0.5}$ and αn_a whereas -log k^o increased successively in going from Li^+ to Na^+ to K^+. This shows that the electrode process becomes more irreversible as the atomic weight of the cation increases. This is further confirmed by the effect of Mg^{2+}, Ca^{2+}, Ba^{2+} (Table 3.10). However, αn_a did not vary appreciably whereas $E_{0.5}$ showed a cathodic shift. This may be due to the increasing atomic radii of the cations resulting in the enhancement of the thickness of the electrical double layer thereby increasing the value of zeta potential. The increased zeta potential decreases the rate of the electrode process by offering a greater potential barrier.

Table 3.11 gives the results on the study of the effect of Na^+, Ca^{2+} and La^{3+} on the kinetic parameters. There was a slight variation in αn_a and a slight cathodic shift in $E_{0.5}$ on going from Na^+ to Ca^{2+} to La^{3+}. A slight increase in the value of $-\log k^o$ was noticed with increasing valence and increasing atomic weight of the cations. The fact that the increase in $-\log k^o$ is small in solutions of mono-, di- and tri-valent cations as compared to the cations of same valence but different atomic weights (Tables 3.9 and 3.10) may be due to the accelerating effect of increased valence of cations counteracting the retarding effect of increasing atomic weight of these cations.

With the increase in the ionic strength of the supporting electrolyte a decrease in the value of αn_a $-\log k^o$ and a positive shift of $E_{0.5}$ was observed (Table 3.12). This can be attributed to the lowering of the thickness of the electrical double layer, thereby, reducing the zeta potential and accelerating electrode process. Holleck and Kastening[127] made similar observations with m-chloro-nitrobenzene.

Table 3.13 shows the effect of the concentration of the depolarizer on the kinetic parameters. Values of αn_a and $-\log k^o$ show a slight increase as the concentration of NOSA was increased.

With increase in temperature i_d showed a regular increase (Table 3.14). αn_a increased slightly and $-\log k^o$ showed a decrease. $E_{0.5}$ values, not unexpectedly[201], showed a slight positive shift with increase in temperature.

The effect of increasing concentration of ethanol resulted in the decrease in αn_a and increase in $-\log k^o$ values. $E_{0.5}$ exhibited a marked cathodic shift with increasing concentration of ethanol (Table 3.15). The value of i_d, however, first decreased upto about 40% ethanol concentration after which it increased with further increase in the concentration of ethanol. The viscosity of aqueous-ethanolic mixture is shown to increase gradually upto about 50% ethanol after which it decreases regularly[167] with further increase in ethanol content in the mixture. The behaviour of the value of i_d may be ascribed to theseviscosity changes. Shreve and Markhan also encountered similar effects with p-nitroaniline[251]. Similar variation of i_d have also been reported in the study of nitrobenzene[111,265].

The appreciable cathodic shift in the $E_{0.5}$ with increase in ethanol content may be attributed to the adsorption of ethanol on d.m.e. with the result that more activation energy is needed for the reduction processes to take place. The changes in αn_a and $-\log k^o$ may be the result of the adsorbed film of ethanol at the d.m.e. thereby altering the structure of the electrical double layer. The adosrption of ethanol in this potential region has been reported by a.c. polarographic studies[12,102].

Table 3.16 gives the results obtained during the investigations on the kinetic parameters due to the presence of various alcohols (each present in 5% concentration). Four groups of alcohols were taken viz. alcohols of varying length of hydrocarbon chain, various isomeric alcohols, saturated and unsaturated alcohols and alcohols having different number of hydroxyl groups.

With the first group of alcohols it can be seen that $-\log k^{o}$ showed a regular increase with increasing chain length and $E_{0.5}$ showed a cathodic shift. This is to be expected as the reported behaviour of these alcohols[102] indicates that surface activity increased on going from lower to higher member of the series. This renders the reduction process more and more irreversible.

With the second group of alcohols $-\log k^{o}$ decreased on going from normal butyl alcohol to tertiary butyl alcohol. The $E_{0.5}$ showed a positive shift. These are due to the fact that straight chain alcohol possess greater surface activity than branched chain alcohol.[102]

The values of $-\log k^{o}$ in normal or isopropyl alcohol was more than that in allyl alcohol (unsaturated alcohol). Allyl alcohol has been shown[102] to be less surface active than the other two.

The values of $-\log k^{o}$ increased in the order normal propyl alcohol > isopropyl alcohol > propylene glycol > glycerol. The first two being monohydric and the next two are dihydric and trihydric respectively. These observations are consistent with the surface activity of the alcohols[102] and it is seen that the greater the surface acitivity, the stronger the adosrption at the d.m.e. and greater is the barrier for the reduction of the nitro group of NOSA at the electrode. In other words, the reduction process becomes more and more irreversible as the surface activity of the alcohol increases.

TABLE 3.1 : Effect of concentration of NOSA on i_d and $E_{0.5}$ at pH 8.5

NOSA Concn. mM	I Wave			II Wave		
	$-E_{0.5}$ S.C.E.	i_d µA	i_d/c	$-E_{0.5}$ S.C.E.	i_d µA	i_d/c
0.2	0.26	0.35	1.75	0.39	4.30	21.50
0.3	0.27	0.60	2.00	0.62	6.40	21.30
0.4	0.275	0.75	1.90	0.65	8.50	21.30
0.5	0.275	1.00	2.00	0.67	10.60	21.20
0.6	0.275	1.35	2.25	0.685	12.80	21.30
0.8	0.28	1.70	2.10	0.73	16.95	21.20

TABLE 3.2: Effect of mercury column height on i_d and $E_{0.5}$ of NOSA at pH 8.5

h cm	I Wave				II Wave			
	$-E_{0.5}$ S.C.E.	i_d µA	i_d/h	$i_d/\sqrt{h}$	$-E_{0.5}$ S.C.E.	i_d µA	i_d/h	$i_d/\sqrt{h}$
					0.4 mM NOSA			
30	0.255	0.70	0.02333	0.1277	0.630	7.35	0.2450	1.342
40	0.260	0.80	0.02000	0.1265	0.640	8.49	0.2122	1.343
50	0.260	0.88	0.01973	0.1247	0.635	9.52	0.1904	1.346
60	0.265	0.95	0.01583	0.1227	0.665	10.50	0.1750	1.356
					0.2 mM NOSA			
30	0.260	0.30	0.0100	0.0547	0.615	3.82	0.127	0.6974
40	0.260	0.37	0.0092	0.0585	0.615	4.53	0.114	0.7163
50	0.260	0.43	0.0086	0.0608	0.620	5.05	0.101	0.7142
60	0.265	0.48	0.0080	0.0619	0.620	5.53	0.092	0.7141

TABLE 3.3 : Effect of concentration of NOSA on i_d and $E_{0.5}$ at pH 10.0

Concen. mM	I Wave			II Wave			III Wave		
	$-E_{0.5}$ S.C.E.	i_d µA	i_d/c	$-E_{0.5}$ S.C.E.	i_d µA	i_d/c	$-E_{0.5}$ S.C.E.	i_d µA	i_d/c
0.2	0.355	0.45	2.25	0.690	4.10	20.50	0.995	0.90	4.50
0.3	0.360	0.70	2.33	0.720	6.40	21.33	1.025	1.40	4.67
0.4	0.365	1.05	2.62	0.740	8.55	21.37	1.065	1.85	4.62
0.5	0.365	1.30	2.60	0.760	10.10	20.20	1.120	2.20	4.40
0.7	0.370	1.70	2.43	0.810	14.70	21.00	1.170	3.30	4.71

TABLE 3.4 : Effect of mercury column height on i_d and $E_{0.5}$ of 0.2 mM NOSA

h cm	I Wave		II Wave		III Wave	
	$-E_{0.5}$ S.C.E.	i_d µA	$-E_{0.5}$ S.C.E.	i_d µA	$-E_{0.5}$ S.C.E.	i_d µA
30	0.360	0.50	0.710	3.30	1.010	0.75
40	0.360	0.45	0.715	3.80	1.020	1.00
50	0.360	0.45	0.715	4.25	1.020	1.20
60	0.360	0.45	0.720	4.65	1.020	1.45

h cm	I Wave		II Wave		III Wave	
	i_d/h	$i_d/\sqrt{h}$	i_d/h	$i_d/\sqrt{h}$	i_d/h	$i_d/\sqrt{h}$
30	0.01334	0.0912	0.1100	0.6024	0.0250	0.1371
40	0.01125	0.0711	0.0949	0.6009	0.0250	0.1581
50	0.00899	0.0636	0.0850	0.6009	0.0240	0.1697
60	0.00749	0.0581	0.0770	0.6005	0.0241	0.1873

TABLE 3.5 : Effect of concentration of NOSA on i_d and $E_{0.5}$ at pH 11.0

Concn. mM	I Wave			II Wave			III Wave		
	$-E_{0.5}$ S.C.E.	i_d µA	i_d/c	$-E_{0.5}$ S.C.E.	i_d µA	i_d/c	$-E_{0.5}$ S.C.E.	i_d µA	i_d/c
0.3	0.420	0.40	1.33	0.735	3.00	10.00	0.980	3.20	10.66
0.4	0.425	0.65	1.62	0.740	4.15	10.37	0.985	4.30	10.72
0.5	0.430	0.85	1.70	0.755	5.50	11.00	1.015	5.45	10.90
0.6	0.435	1.10	1.83	0.770	6.85	11.40	1.050	6.50	10.80
0.7	0.442	1.35	1.90	0.790	7.55	10.80	1.075	8.45	12.70
0.8	0.453	1.60	2.00	0.820	8.85	10.06	1.115	10.10	12.50

TABLE 3.6 : Effect of mercury column height on i_d and $E_{0.5}$ of 0.4 mM NOSA at pH 11.0

h cm	I Wave				II Wave			
	$-E_{0.5}$ S.C.E.	i_d µA	i_d/h	$i_d/\sqrt{h}$	$-E_{0.5}$ S.C.E.	i_d µA	i_d/h	$i_d/\sqrt{h}$
30	0.420	0.60	0.0200	0.1095	0.755	3.70	0.1231	0.6754
40	0.425	0.75	0.0187	0.1186	0.750	4.15	0.1037	0.6361
50	0.430	0.85	0.0170	0.1201	0.755	4.55	0.0909	0.6435
60	0.430	0.90	0.0150	0.1162	0.750	4.90	0.0816	0.6326
	III Wave							
30	0.985	3.50	0.1167	0.6390				
40	0.990	4.35	0.1087	0.6879				
50	1.010	5.15	0.1030	0.7266				
60	1.020	6.00	0.1000	0.7761				

TABLE 3.7 : Kinetic parameters αn_a, $-\log k^0$ and $E_{0.5}$ of nitro group reduction of NOSA at various pH values.

Temperature = 35°C, h = 40.0 cm,

μ = 0.54 M, Concn. of NOSA = 0.4 mM

pH	i_{d_1}* µA	$-E^1_{0.5}$* S.C.E.	$-\log k^0$ N.H.E.	αn_a*	i_{d_2}** µA	$-E^2_{0.5}$** S.C.E.
1.0	8.20	0.105	1.27	0.5720	-	-
2.5	7.80	0.210	2.34	0.5678	-	-
4.0	8.20	0.295	3.19	0.5654	-	-
5.5	8.30	0.405	4.31	0.5604	-	-
7.0	8.20	0.520	5.47	0.5572	-	-
8.5	8.50	0.650	5.68	0.4362	-	-
10.0	6.95	0.740	-	-	1.35	1.050
11.0	4.15	0.735	-	-	4.20	0.985
12.0	1.40	0.740	-	-	6.90	1.000

* First wave of nitro group reduction

** Second wave of nitro group reduction

TABLE 3.8 : Effect of I^-, Br^- and Cl^- on kinetic parameters.

35°C, h = 40.0 cm, pH = 8.5

Supporting electrolyte	i_d µA	$-E_{0.5}$ S.C.E.	αn_a	$-\log k^o$ N.H.E.
		0.4 mM NOSA		
0.1 M KI	8.80	0.660	0.448	5.732
0.1 M KBr	8.70	0.655	0.445	5.800
0.1 M KCl	8.70	0.655	0.458	5.904
		0.6 mM NOSA		
0.1 M KI	13.20	0.690	0.476	5.231
0.1 M KBr	13.10	0.685	0.481	5.324
0.1 M KCl	13.10	0.685	0.484	5.442

TABLE 3.9 : Effect of Li^+, Na^+ and K^+ on kinetic parameters

35°C, h = 40.0 cm, pH = 8.5, 0.4 mM NOSA

Supporting electrolyte	i_d µA	$-E_{0.5}$ S.C.E.	αn_a	$-\log k^o$ N.H.E.
0.1 M LiCl	8.60	0.650	0.442	5.242
0.1 M NaCl	8.50	0.645	0.463	5.504
0.1 M KCl	8.60	0.645	0.467	5.768

TABLE 3.10 : Effect of Mg^{2+}, Ca^{2+} and Ba^{2+} on kinetic parameters.

35°C, h = 40.0 cm, pH = 5.5

Supporting electrolyte	i_d µA	$-E_{0.5}$ S.C.E.	αn_a	$-\log k^o$ N.H.E.
		0.4 mM NOSA		
0.1 M $MgCl_2$	8.40	0.415	0.431	4.678
0.1 M $CaCl_2$	8.50	0.425	0.446	4.764
0.1 M $BaCl_2$	8.60	0.435	0.442	4.890
		0.6 mM NOSA		
0.1 M $MgCl_2$	13.00	0.460	0.454	4.224
0.1 M $CaCl_2$	13.10	0.475	0.478	4.256
0.1 M $BaCl_2$	13.10	0.485	0.489	4.286

TABLE 3.11 : Effect of Na^+, Ca^{2+} and La^{3+} on kinetic parameters.

35°C, h = 40.0 cm, pH = 5.5

Supporting electrolyte	i_d µA	$-E_{0.5}$ S.C.E.	αn_a	$-\log k^o$ N.H.E.
		0.4 mM NOSA		
0.1 M NaCl	8.20	0.410	0.469	4.281
0.1 M $CaCl_2$	8.10	0.415	0.473	4.290
0.1 M $LaCl_3$	8.10	0.420	0.471	4.312
		0.6 mM NOSA		
0.1 M NaCl	13.20	0.455	0.471	4.421
0.1 M $CaCl_2$	13.20	0.460	0.475	4.430
0.1 M $LaCl_3$	13.10	0.460	0.479	4.440

TABLE 3.12 : Effect of ionic strength on kinetic parameters

35°C, h = 40.0 cm, pH = 8.5, 0.4 mM NOSA

Ionic strength	i_d µA	$-E_{0.5}$ S.C.E.	αn_a	$-\log k^o$ N.H.E.
0.4	8.40	0.660	0.437	5.834
0.7	8.40	0.652	0.435	5.762
1.0	8.50	0.642	0.431	5.623

TABLE 3.13 : Effect of concentration of the depolarizer on kinetic parameters

35°C, h = 40.0 cm, pH = 8.5

Concentration NOSA mM	i_d µA	$-E_{0.5}$ S.C.E.	αn_a	$-\log k^o$ N.H.E.
0.2	4.30	0.590	0.430	5.581
0.3	6.60	0.620	0.434	5.644
0.4	8.60	0.650	0.436	5.682
0.5	11.05	0.670	0.438	5.713
0.6	13.30	0.685	0.439	5.742
0.8	17.70	0.730	0.441	5.761

TABLE 3.14 : Effect of temperature on kinetic parameters

$h = 40.0$ cm, pH = 8.5, 0.4 mM NOSA

Temperature °C	i_d µA	$-E_{0.5}$ S.C.E.	$D \times 10^{+6}$ cm^2 s^{-1}	αn_a	$-\log k^o$ N.H.E.
20	7.40	0.660	3.73	0.423	5.890
27	7.90	0.656	4.56	0.431	5.761
35	8.50	0.650	5.42	0.436	5.682

TABLE 3.15 : Effect of concentration of ethanol on kinetic parameters

35°C, $h = 40.0$ cm, $\mu = 0.30$ M LiCl, 0.4 mM NOSA

Ethanol %	i_d µA	$-E_{0.5}$ S.C.E.	αn_a	$-\log k^o$ N.H.E.
10	8.35	0.675	0.394	5.792
20	8.15	0.710	0.364	5.981
30	7.95	0.750	0.346	6.212
40	7.70	0.785	0.314	6.464
50	7.80	0.805	0.296	6.676
60	8.05	0.820	0.284	6.842
70	8.25	0.845	0.276	7.063
80	8.40	0.865	0.269	7.292

TABLE 3.16 : Effect of various alcohols (5% solutions) on kinetic parameters

35°C, h = 40.0 cm, pH 8.5, 0.4 mM NOSA,
Each alcohol is present in 5% concentration

Alcohol	i_d µA	$-E_{0.5}$ S.C.E.	αn_a	$-\log k^o$ N.H.E.
Alcohols with varying length of hydrocarbon chain				
Methanol	8.40	0.660	0.425	5.741
Ethanol	8.40	0.665	0.418	5.761
n-propanol	8.30	0.680	0.406	6.040
n-butanol	8.15	0.695	0.388	6.222
Isomeric alcohols				
t-butanol	8.40	0.675	0.418	5.841
iso-butanol	8.30	0.680	0.412	5.922
sec-butanol	8.25	0.686	0.401	6.060
n-butanol	8.15	0.695	0.388	6.223
Saturated and unsaturated alcohols				
allyl alcohol	8.40	0.669	0.422	5.853
iso-propanol	8.35	0.674	0.416	5.921
n-propanol	8.30	0.680	0.406	6.041
Alcohols with different number of hydroxyl groups				
n-propanol	8.30	0.680	0.406	6.041
iso-propanol	8.35	0.674	0.416	5.921
propylene glycol	8.40	0.670	0.421	5.892
glycerol	8.40	0.663	0.428	5.824

Legend of the figures

Fig. 3.1 : Polarograms of 0.5 mM oxine at 25°C, $\mu = 0.54$ M

- a. pH 2.5
- b. pH 5.5
- c. pH 7.0
- d. pH 7.0, with gelatin (0.04%)
- e. pH 10.0
- f. pH 12.0

Fig. 3.2 : Polarograms of 0.5 mM oxine-5-sulfonic acid (OSA) at 25°C, $\mu = 0.54$ M

- a. pH 1.0
- b. pH 4.0
- c. pH 7.0
- d. pH 8.5
- e. pH 10.0
- f. pH 11.0

Fig. 3.3 : Polarograms of 0.5 mM 7-nitro-oxine-5-sulfonic acid (NOSA) at 25°C, $\mu = 0.54$ M

- a. pH 4.0
- b. pH 7.0
- c. pH 8.5
- d. pH 10.0
- e. pH 11.0
- f. pH 12.0

Fig. 3.4 : A.C. polarograms of 0.5 mM NOSA at various pH and temperatures

- a. pH 7.0, 25°C
- b. pH 7.0, 30°C
- c. pH 7.0, 35°C
- d. pH 7.0, 40°C
- e. pH 10.0, 25°C
- f. pH 10.0, 30°C
- g. pH 10.0, 35°C

Fig. 3.5 : NOSA, concentration effect (d.c. polarography), pH 8.5, 35°C

Fig. 3.6 : NOSA, concentration effect (d.c. polarography), pH 10.0, 35°C

Fig. 3.7 : NOSA, concentration effect (d.c. polarography), pH 11.0, 35°C

Fig. 3.8 : NOSA, concentration effect (d.c. polarography), pH 12.0, 35°C

Fig. 3.9 : 0.4 mM NOSA, effect of the height of the mercury column, pH 8.5, 35°C

Fig. 3.10 : NOSA, -log k vs -E plots at various pH values, 35°C

Fig. 3.11 : NOSA, log $\frac{i}{i_d - i}$ vs -E plots at various pH values, 35°C.

POLAROGRAPHIC STUDIES ON THE REDUCTION OF SOME NITROPYRIDINES

The present investigation gives the results obtained in the polarographic studies on some nitropyridines of which no data are available in literature.

EXPERIMENTAL

2-hydroxy-5-nitropyridine (A), 3-hydroxy-2-nitropyridine (HNP), 2-amino-5-nitropyridine (ANP) and 6-methyl-2-nitro-3-pyridinol (MNP) (Aldrich, U.S.A.) were used without further purification. Stock solutions were prepared in 10% ethanol. All other chemicals were of analytical reagent grade. Triton X-100 was used as maximum suppressor wherever necessary. HCl/KCl, Na_2HPO_4/citric acid, Boric acid/NaOH and NaOH buffers were used. The ionic strength was adjusted to 0.54 M by KCl. Temperature was maintained at 30±0.1°C.. The capillary characteristics were : $m = 2.931$ mg/s, $t = 3.05$ s in 0.54 M KCl (open circuit) at $h = 40.0$ cm (uncorrected for back pressure) for d.c. polarographic work and $m = 4.564$ mg/s, $t = 1.8$ s in 0.1 M KCl (open circuit) for a.c. polarographic work.

CALCULATION OF KINETIC PARAMETERS BY KOUTECKY'S METHOD USING IBM 1130 COMPUTER

<u>Construction of polynomial equation:</u> Koutecky's table (reproduced by Heyrovsky and Kuta in their book[134]) giving the value of λ (described in Chapter I of this thesis) for different values of i/i_d was utilized to construct a

polynomial equation which fits in these values. The polynomial equation was found to be of sixth order and the values fitted reasonably well as shown by a comparison of Y and Y^* in Table 3.17 which gives the Koutecky's tabulated value of λ and the calculated value of λ using the sixth order polynomial equation as given below.

The polynomial equation was found to be

$$Y = 2.54 - 40.89875\ (F) + 276.7559\ (F^2) - 899.0495\ (F^3) + 1589.541\ (F^4) - 1447.858\ (F^5) + 542.8582\ (F^6)$$

where F denotes i/i_d.

The computer is so programmed as to get the value of i/i_d and λ for each value of the applied potential. These calculated values of λ are more accurate than those read manually from the curve constructed using Table of Koutecky. The factor 0.001153 in the computer program denotes the value of $\sqrt{D/t}$ for the system. The slopes (by the method of least squares) of the plots of $-\log k$ vs E and those of $\log \frac{i}{i_d - i}$ vs E are also furnished in the output. For a set of data the slopes were calculated in eight seconds. The linearity of the plot of $-\log k$ vs E was checked for each set of data by manually plotting a graph. This is necessary because Koutecky's procedure is applicable only if one rate-determining step is involved in the reduction processes.

Computer program for the determination of slope of the plot of -log k vs E and that of log(i/i$_d$-i) vs E

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// JOB T                                                          02605

LOG DRIVE   CART SPEC   CART AVAIL  PHY DRIVE
  0000        0018        0018        0000

V2 M07   ACTUAL 16K  CONFIG 16K

// FOR
*ONE WORD INTEGERS
*LIST SOURCE PROGRAM
      FUNCTION CFIT(X,Y)
      DIMENSION X(10),Y(10)
      SUMX=0.
      SUMY=0.
      SUMXY=0.
      SUMXX=0.
      DO 30 J=1,10
      SUMX=SUMX+X(J)
      SUMY=SUMY+Y(J)
      SUMXX=SUMXX+X(J)*X(J)
   30 SUMXY=SUMXY+X(J)*Y(J)
      T1=SUMX*SUMX
      T2=SUMY*SUMX
      T3=10.*SUMXX
      T4=10.*SUMXY
      CFIT=(T4-T2)/(T3-T1)
      RETURN
      END

FEATURES SUPPORTED
 ONE WORD INTEGERS

CORE REQUIREMENTS FOR CFIT
 COMMON       0  VARIABLES     22  PROGRAM    128

 END OF COMPILATION

// DUP

*STORE      WS  UA  CFIT
CART ID 0018   DB ADDR  365E   DB CNT   0008
```

```
PAGE   1    02605

// JOB T                                                02605

LOG DRIVE   CART SPEC   CART AVAIL   PHY DRIVE
  0000        0018        0018         0000

V2 M07   ACTUAL 16K  CONFIG 16K

// FOR
*ONE WORD INTEGERS
*LIST SOURCE PROGRAM
*IOCS(2501READER,1403PRINTER)
      REAL I(10),LS(10),IO,IONIO
      DIMENSION X(10),E(10),D(10),Y(10)
      FX(F)=+2.5400-40.89875*F+276.7559*F**2-899.0495*F**3+1589.541*F**4
     $-1447.858*F**5+542.8582*F**6
      READ (8,15) NSET
   15 FORMAT (I3)
      N=1
   50 READ(8,10)E,I,IO
   10 FORMAT(10F8.3)
      WRITE(5,12)N,IO
      DO 5 J=1,10
      IONIO=I(J)/IO
      X(J)=FX(IONIO)
      Y(J)=X(J)*.001153
      D(J)=-(ALOG(Y(J)))*.4343
      LS(J)=(ALOG(I(J)/(IO-I(J))))*.4343
   5  WRITE(5,11)I(J),IONIO,X(J)
      WRITE (5,20)
   20 FORMAT (///,22X,'E',35X,'D',30X,'LS',//)
      WRITE (5,21)(E(K),D(K),LS(K),K=1,10)
   21 FORMAT (10X,F15.3,20X,F15.3,20X,F15.3)
      SLOP=CFIT(E,D)
      WRITE(5,22)SLOP
   22 FORMAT(//,10X,'SLOP  E/D  IS ',F10.3,/,29X,'-----',/)
      SLOP=CFIT(E,LS)
      WRITE(5,23)SLOP
   23 FORMAT(10X,'SLOP  E/LS  IS ',F10.3,/,30X,'-----',//)
      N=N+1
      IF (N-NSET) 50,50,51
   11 FORMAT(10X,F15.3,20X,F15.3,20X,F15.3)
   12 FORMAT(/,5X,'SET NO  ',I3,/,21X,'I',32X,'I/IO',31X,'X',7X,'VALUE O
     $F IO IS',F8.4,/,112X,'--------',//)
   51 CALL EXIT
      END

FEATURES SUPPORTED
 ONE WORD INTEGERS
 IOCS

CORE REQUIREMENTS FOR
 COMMON       0  VARIABLES     146  PROGRAM     428

 END OF COMPILATION

// XEQ
```

A known system viz. 7-nitro-8-hydroxyquinoline-5-sulfonic acid was tried to test the validity of the computer program and the results were found to be in good agreement with the manually calculated values.

RESULTS AND DISCUSSION

2-hydroxy-5-nitropyridine (A)

Fig. 3.12 gives the current-voltage curves recorded at various pH at 30°C. Two waves were observed in acidic and weakly alkaline media. The second wave, generally, was ill-defined. Maximum was observed only in solutions of pH 5.0 (curve 1, Fig. 3.12), 6.0 and 7.0 (curve 2, Fig. 3.12). The maximum was suppressed by 0.001% Triton X-100 as shown in Fig. 3.12. Fig. 3.16 gives the a.c. polarograms at various pH. Generally, a broad peak with a small peak height appeared. In some cases, where maximum appeared in d.c. polarograms, the a.c. polarogram showed peaks greater in magnitude to that obtained when no maximum was present in d.c. polarograms. Breyer and Bauer[17] have also reported, in the case of nitrobenzene, the appearance of two different peaks or a single peak with increased wave height where a maximum was present in d.c. polarographic studies. Fig. 3.18, curve 1 gives the a.c. polarogram of (A) at pH 12.0. A peak appeared corresponding to the hump present (curve 1') in d.c. polarogram. This may be attributed to adsorption processes. Similar behaviour was observed in the case of 3-hydroxy-2-nitropyridine (pH 10 and 11) and 6-methyl-2-nitro-3-pyridinol (pH 9.0).

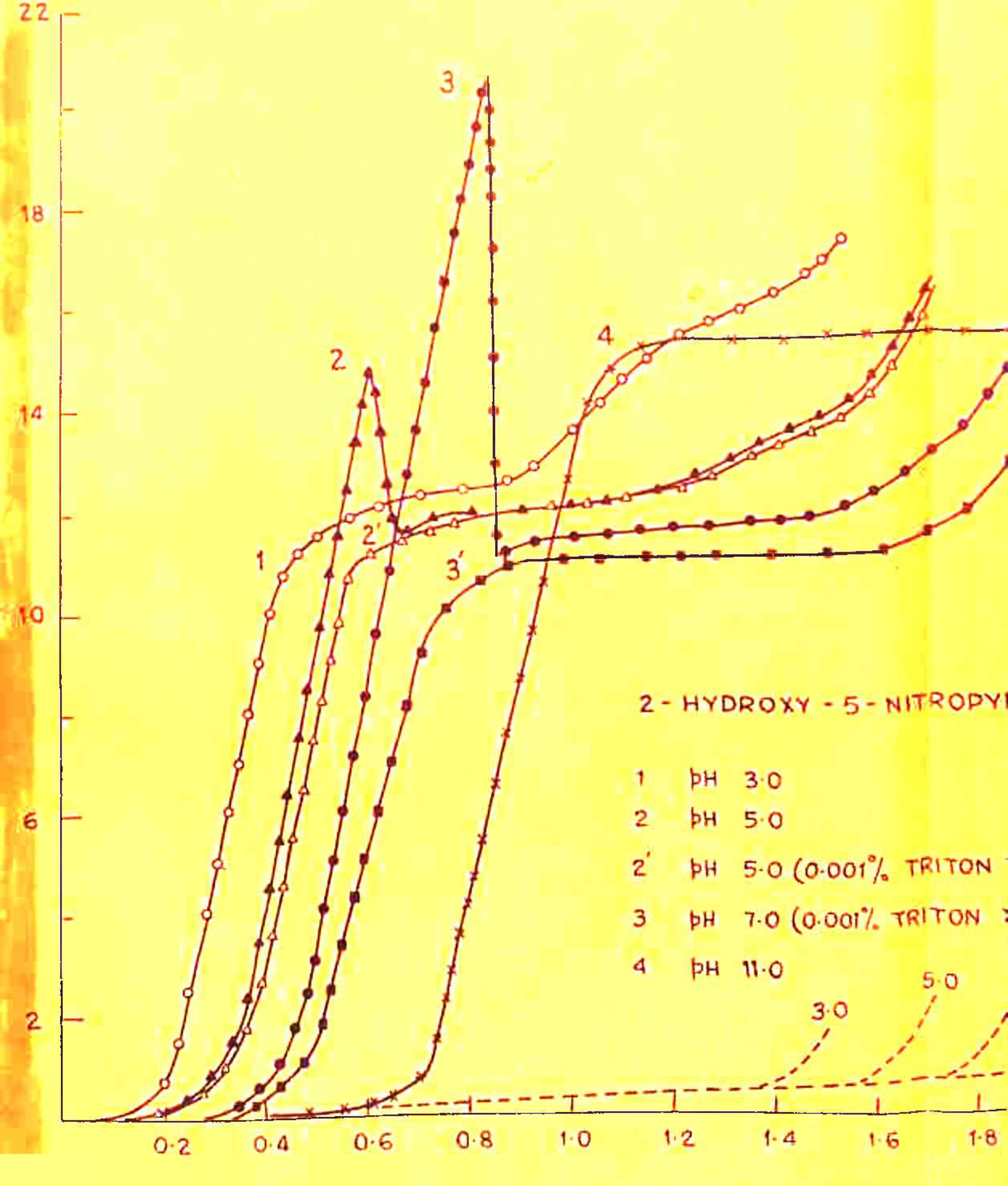

22
18
14
10
6
2
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
-E VOLTS (S.C.E.)
1
2
2′
3
3′
4
3·0
5·0
2 - HYDROXY - 5 - NITROPY
1 þH 3·0
2 þH 5·0
2′ þH 5·0 (0·001% TRITON
3 þH 7·0 (0·001% TRITON
4 þH 11·0

FIG. 3·12

However, the peak was not strictly reproducible which is not unexpected[26]. On addition of maximum suppressor the a.c. polarogram again showed a broad peak.

In order to analyze the nature of the reduction of the nitro group the tests of i_d/c, $i_d/\sqrt{h}$ and negative shift of $E_{0.5}$ with concentration were performed at pH 5.0. Further, $\log \frac{i}{i_d - i}$ vs $-E$ plots (Fig. 3.31) were also made at various pH. All these tests showed that the nitro group underwent diffusion controlled irreversible reduction. The current-voltage curves at various concentration and at various heights of mercury column are shown in Figures 3.19 and 3.23 respectively. It can be seen that the value of i_d decreases with decrease in the height of the mercury column. The fact that $E_{0.5}$ showed a positive shift with decrease in the height of the mercury column, is in accord with the findings of Kivalo et al.[151] and Delahay[36].

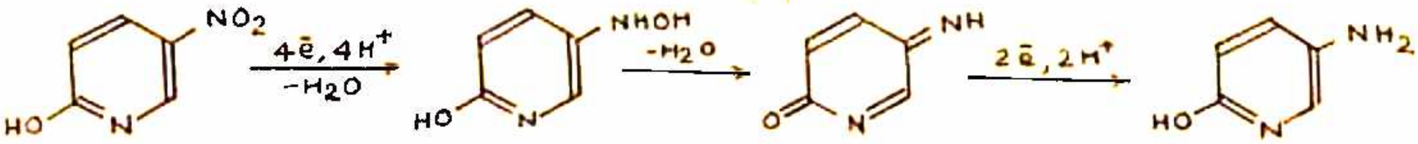
The diffusion coefficient (4.05×10^{-6} cm^2 s^{-1} at 30°C) was found by using McBain Dawson cell applying King Cathcart equation. Using this value of D in Ilkovic equation the number of electrons involved in the nitro group reduction was calculated to be $6.4 \doteq 6$.

The kinetic parameters were calculated with a knowledge of the slope (least squares fit) of the straight line plot of $-\log k$ vs E. It was seen that the plots of $-\log k$ vs $-E$ were straight lines as shown in Fig. 3.27. This indicated that the reduction processes were controlled by a single rate determining step. The values of kinetic parameters are given in Table 3.18.

It can be seen from Table 3.18 that αn_a does not show any regularity whereas -log k^o increases with increase in pH. The increase in -log k^o with increasing pH may be attributed to the difficulty in the availability of the hydrogen ions which are involved in the reduction process with the result that the reduction becomes increasingly irreversible.

The probable reduction mechanism may be represented as:

[illegible]



3-hydroxy-2-nitropyridine (HNP)

Fig. 3.13 gives the current-voltage curves recorded at various pH at 30^{o}C. Two waves were observed in acidic and weakly alkaline media. The second wave as in the case of (A) was ill-defined in most cases. No maximum was observed. A.C. polarograms of ANP showed the presence of a broad peak with a small peak height. The peak potential shifted to more cathodic values with increase in pH.

To analyze the nature of the reduction of the nitro group the tests of i_d/c, $i_d/\sqrt{h}$ and negative shifts of $E_{0.5}$ with concentration were performed at pH 5.0. Further, the $\log \frac{i}{i_d - i}$ plots (Fig. 3.32) were constructed at various pH. All these tests showed that the nitro group underwent diffusion controlled irreversible reduction. Fig. 3.20 gives the current-voltage curves at various concentrations of HNP

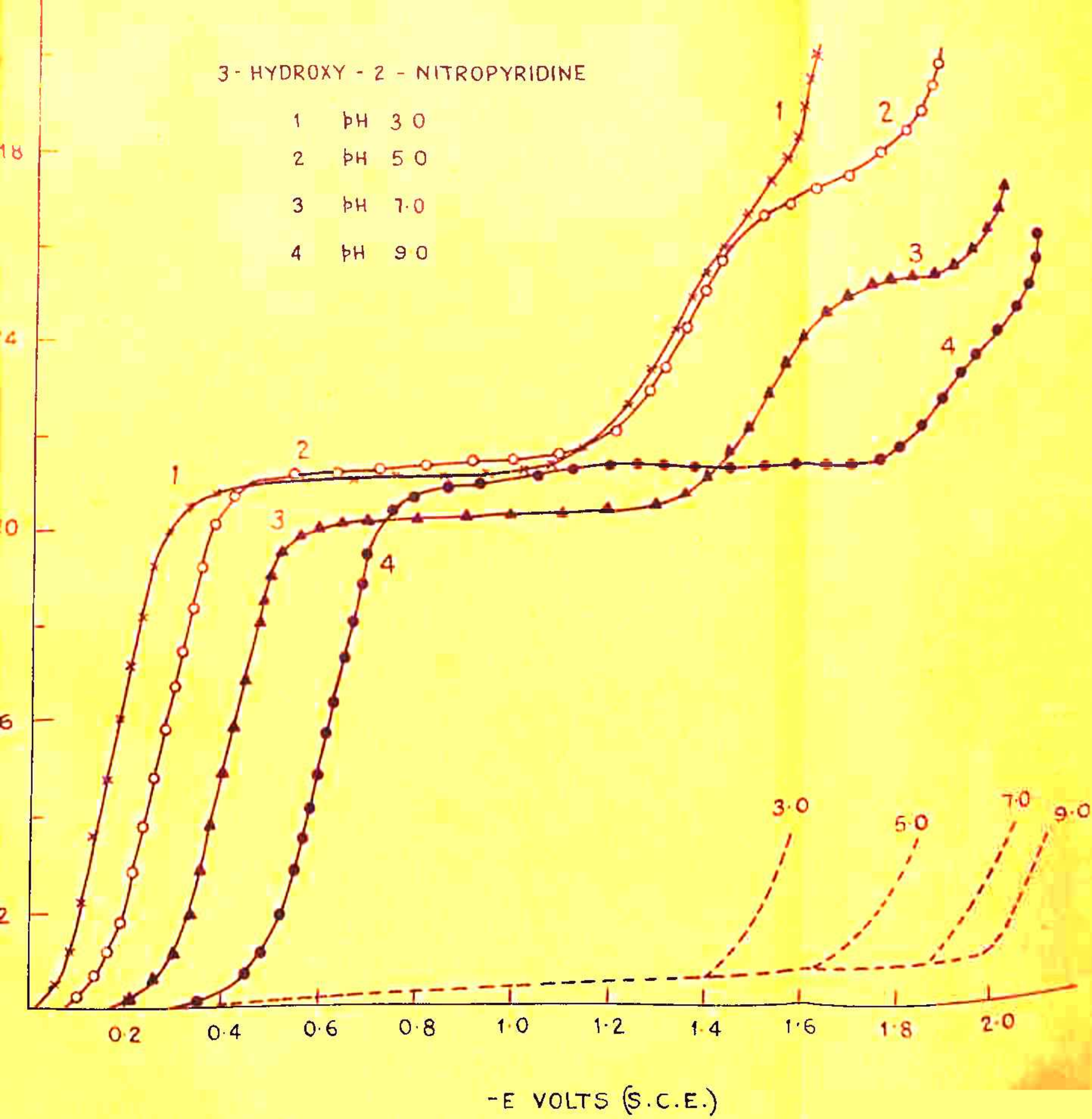
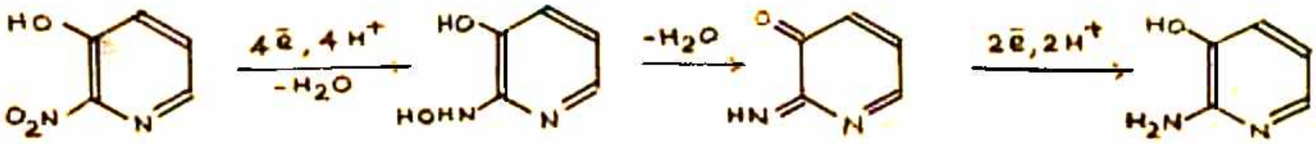

3 - HYDROXY - 2 - NITROPYRIDINE
1 pH 3.0
2 pH 5.0
3 pH 7.0
4 pH 9.0
18
14
10
6
2
1
2
3
4
3.0
5.0
7.0
9.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
-E VOLTS (S.C.E.)

FIG. 3.13

and Fig. 3.24 gives the current-voltage curves at varying heights of mercury column.

The diffusion coefficient (4.12×10^{-6} cm^2 s^{-1} at 30°C) was found in the usual manner and the number of electrons involved in the reduction process was calculated to be 6.09 ≐ 6.

Table 3.19 gives the values of kinetic parameters calculated as mentioned in the case of (A). Fig. 3.27 gives the straight line plots of -log k vs -E for HNP at various pH values. The linearity of the plots indicated that only one slow step, governing the rate of reduction, was involved. An examination of Table 3.19 reveals that αn_a decreases and -log k^o increases with increase in pH. The probable reduction mechanism may be represented by



2-amino-5-nitropyridine (ANP)

Current-voltage curves were recorded at various pH values and some of them are shown in Fig. 3.14. In acidic and weakly alkaline side two waves appeared. The second wave was ill-defined. Maximum was observed in solutions of pH 6.0, 7.0 and 9.0. 0.0005% Triton X-100 was sufficient to eliminate the maximum. The appearance of maximum at pH 7.0 is shown by curve 2 in Fig. 3.14. The same curve is shown by curve 2' (Fig. 3.14) after the addition of 0.0005%

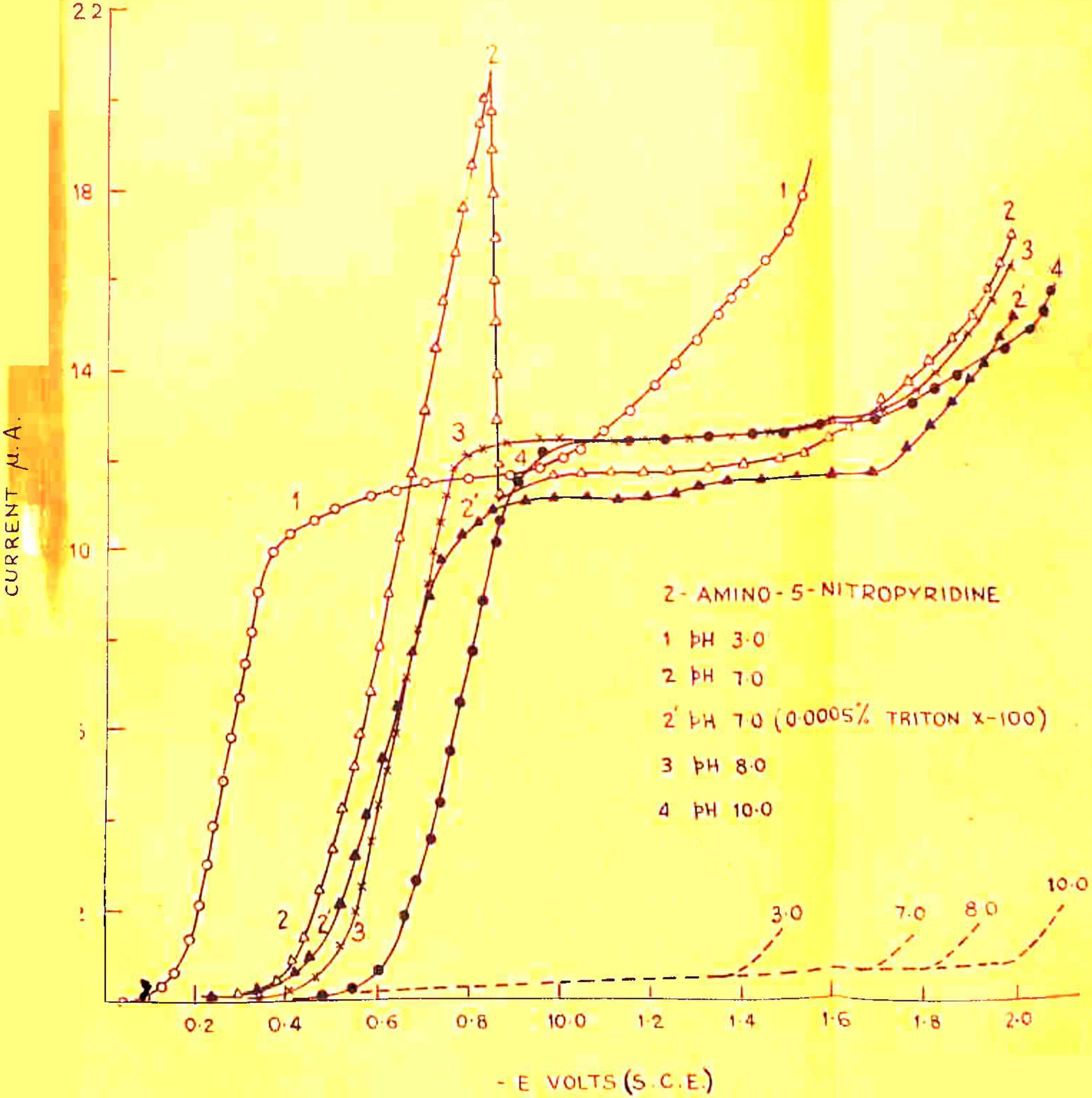

2-AMINO-5-NITROPYRIDINE
1 pH 3.0
2 pH 7.0
2' pH 7.0 (0.0005% TRITON X-100)
3 pH 8.0
4 pH 10.0
CURRENT μA.
- E VOLTS (S.C.E.)
22
18
14
10
6
2
0.2
0.4
0.6
0.8
10.0
1.2
1.4
1.6
1.8
2.0
1
2
2'
3
4
3.0
7.0
8.0
10.0

FIG. 3·14

Triton X-100. Fig. 3.17 contains a.c. polarograms obtained with ANP at different pH values.

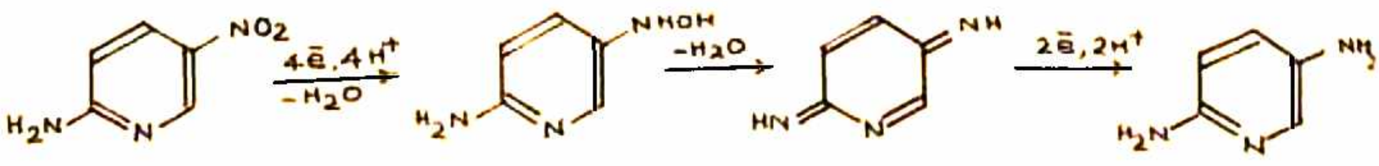
The a.c. polarogram showed a peak in cases where maximum was present in d.c. polarogram. However, on addition of 0.0005% Triton X-100 the peak was suppressed. This type of behaviour was also exhibited by (A) as described earlier.

Figs. 3.21 and 3.25 give the current-voltage curves at various concentrations of ANP and at different heights of the mercury column.

The diffusion coefficient (4.11 × 10^{-6} cm^2 s^{-1} at 30°C) was found in the usual manner. The number of electrons involved in the nitro-group reduction was calculated to be 5.92 ≐ 6.

Table 3.20 gives the values of kinetic parameters calculated as described earlier for (A). The plots of -log k vs -E at various pH are shown in Fig. 3.29. The straight line plot of -log k vs -E shows that only a single rate determining step was involved in the reduction process.

The tabulated values of αn_a and $-\log k^o$ (Table 3.20) show that αn_a does not show any regularity whereas $-\log k^o$ increases with increase in pH. The probable reduction mechanism may be represented by:



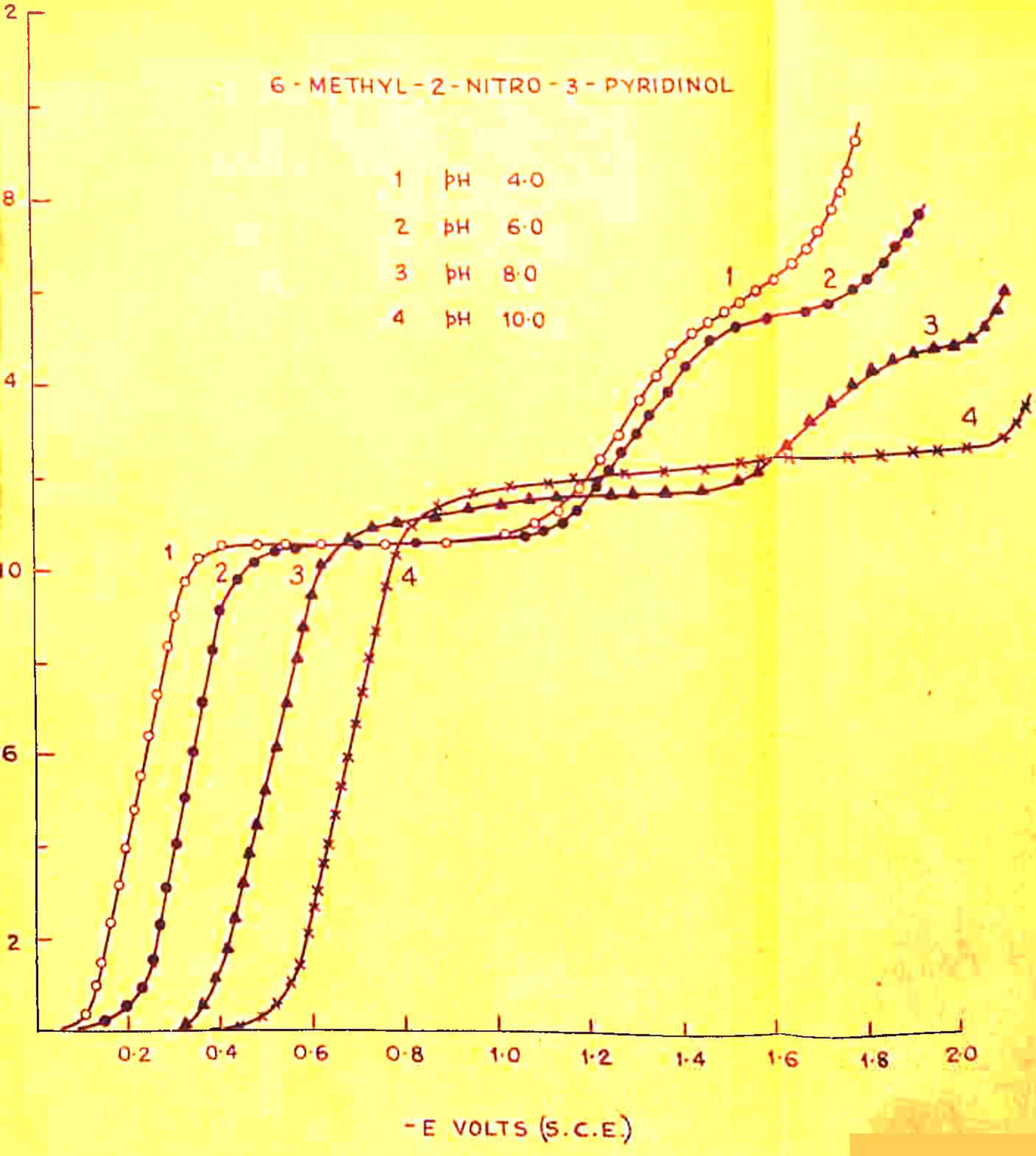

6 - METHYL - 2 - NITRO - 3 - PYRIDINOL
1 pH 4·0
2 pH 6·0
3 pH 8·0
4 pH 10·0
1
2
3
4
1
2
3
4
2
8
4
10
6
2
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
- E VOLTS (S.C.E.)

FIG. 3·15

6-methyl-2-nitro-3-pyridinol (MNP)

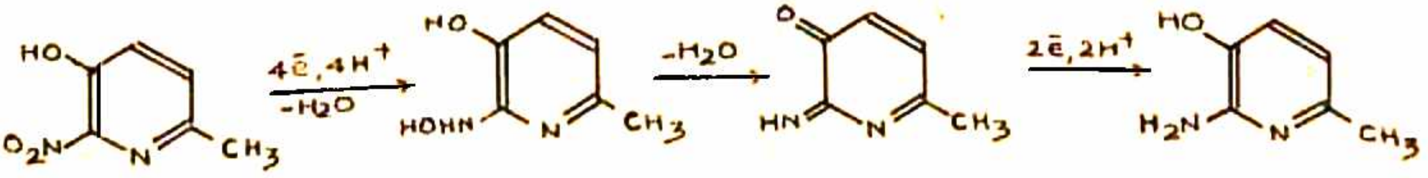
The current-voltage curves recorded at various pH values are given in Fig. 3.15. Two waves were observed in acidic and weakly alkaline media. The second wave was not well-defined. No maximum was observed in this case. A.C. polarograms showed the presence of a small peak.

It was found to undergo diffusion controlled irreversible reduction. For this the tests of i_d/c, $i_d/\sqrt{h}$ and the negative shift of $E_{0.5}$ with concentration were performed at pH 5.0. Further the $\log \frac{i}{i_d - i}$ vs $-E$ plots (Fig. 3.34) were constructed at various pH. Figs. 3.20 and 3.24 give the current-voltage curves by varying the concentration of MNP and height of the mercury column respectively.

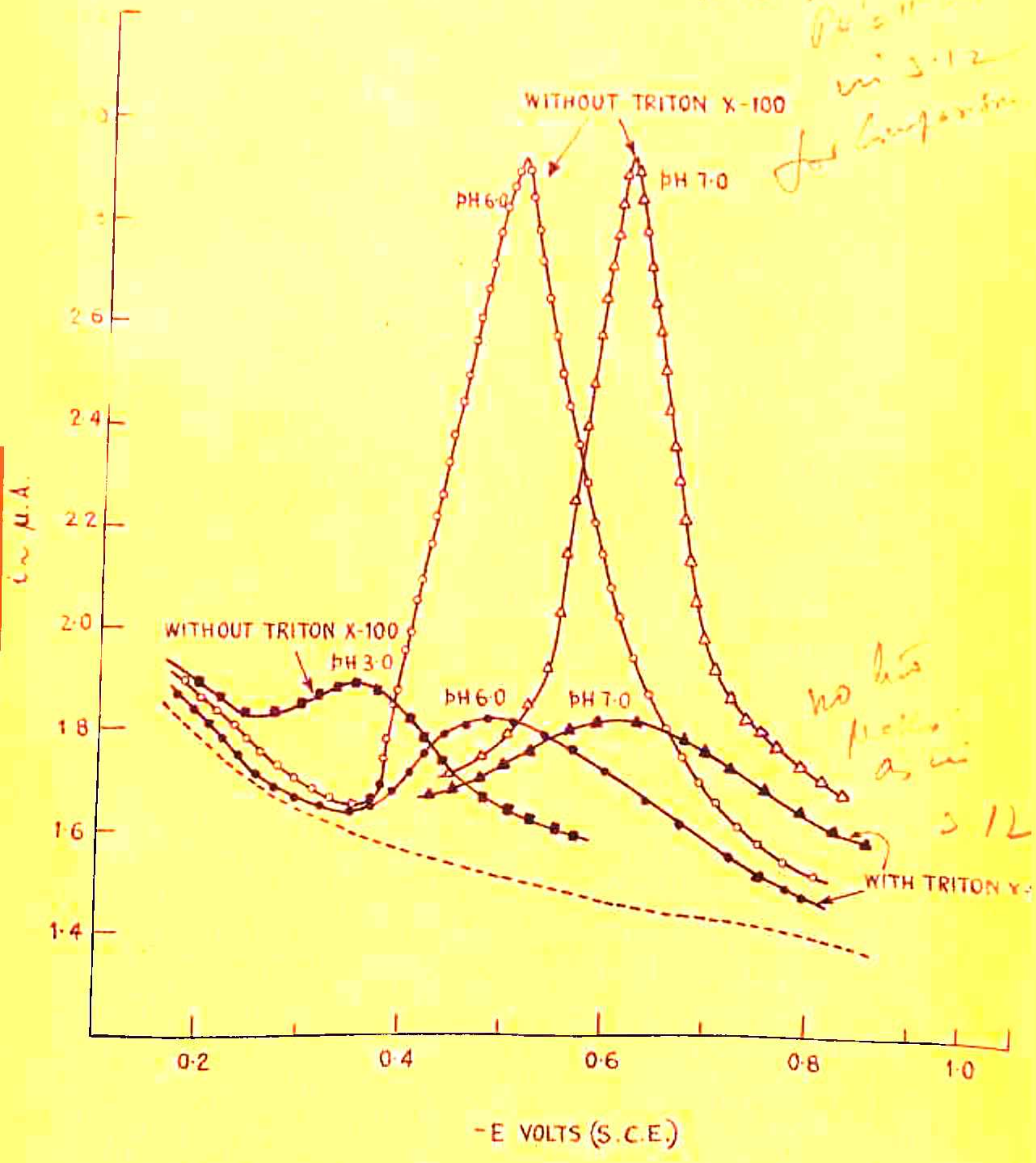
The diffusion coefficient (3.97×10^{-6} cm^2 s^{-1} at 30°C) was found by the usual method as described earlier. The number of electrons was calculated to be $6.09 \approx 6$.

The kinetic parameters are given in Table 3.21. It can be seen that αn_a does not show any regularity but $-\log k^0$ shows an increase with increase in pH.

The probable reduction mechanism may be represented by



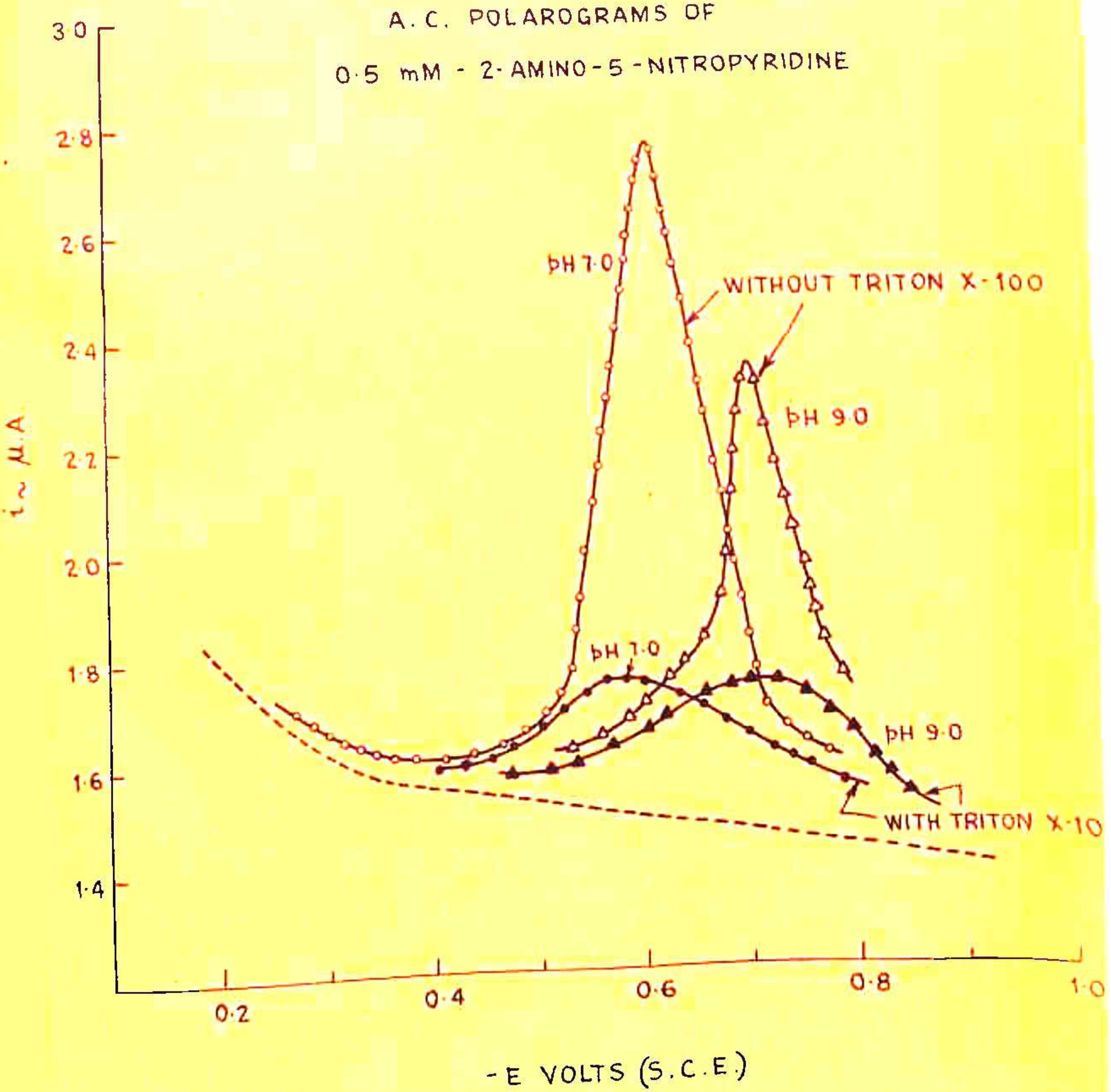
A.C POLAROGRAMS OF 0·5 mM
2 - HYDROXY - 5 NITROPYRIDINE



Why not [illegible]
[illegible]
in 3·12
for comparison

no two
peaks
as in
3·12

FIG. 3·16



A.C. POLAROGRAMS OF

0·5 mM - 2-AMINO-5-NITROPYRIDINE

FIG. 3·17.

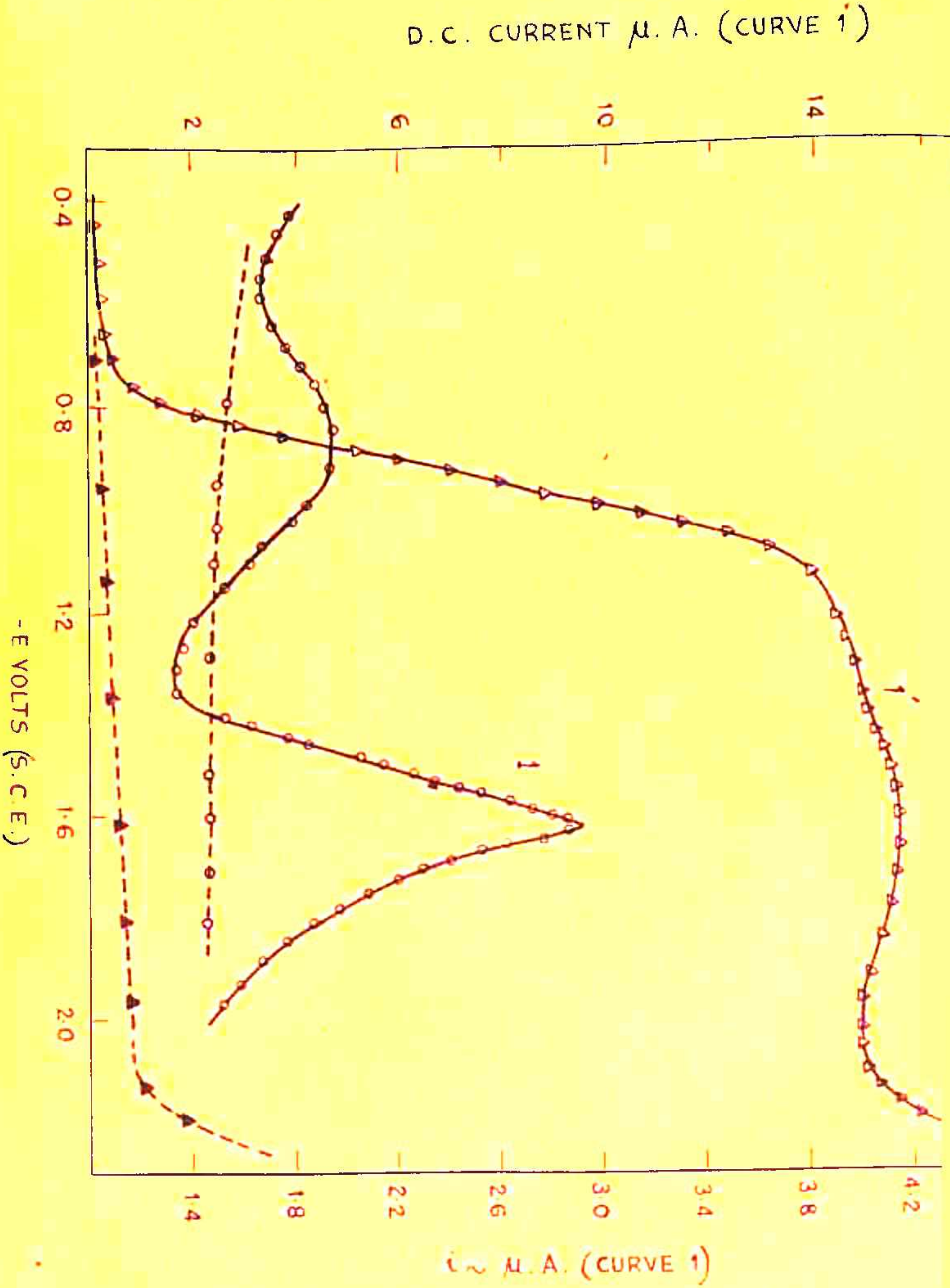

D.C. CURRENT μ.A. (CURVE 1')
2
6
10
14
0.4
0.8
1.2
1.6
2.0
1'
1
1.4
1.8
2.2
2.6
3.0
3.4
3.8
4.2
- E VOLTS (S.C.E.)
i~ μ.A. (CURVE 1)

FIG. 3.18

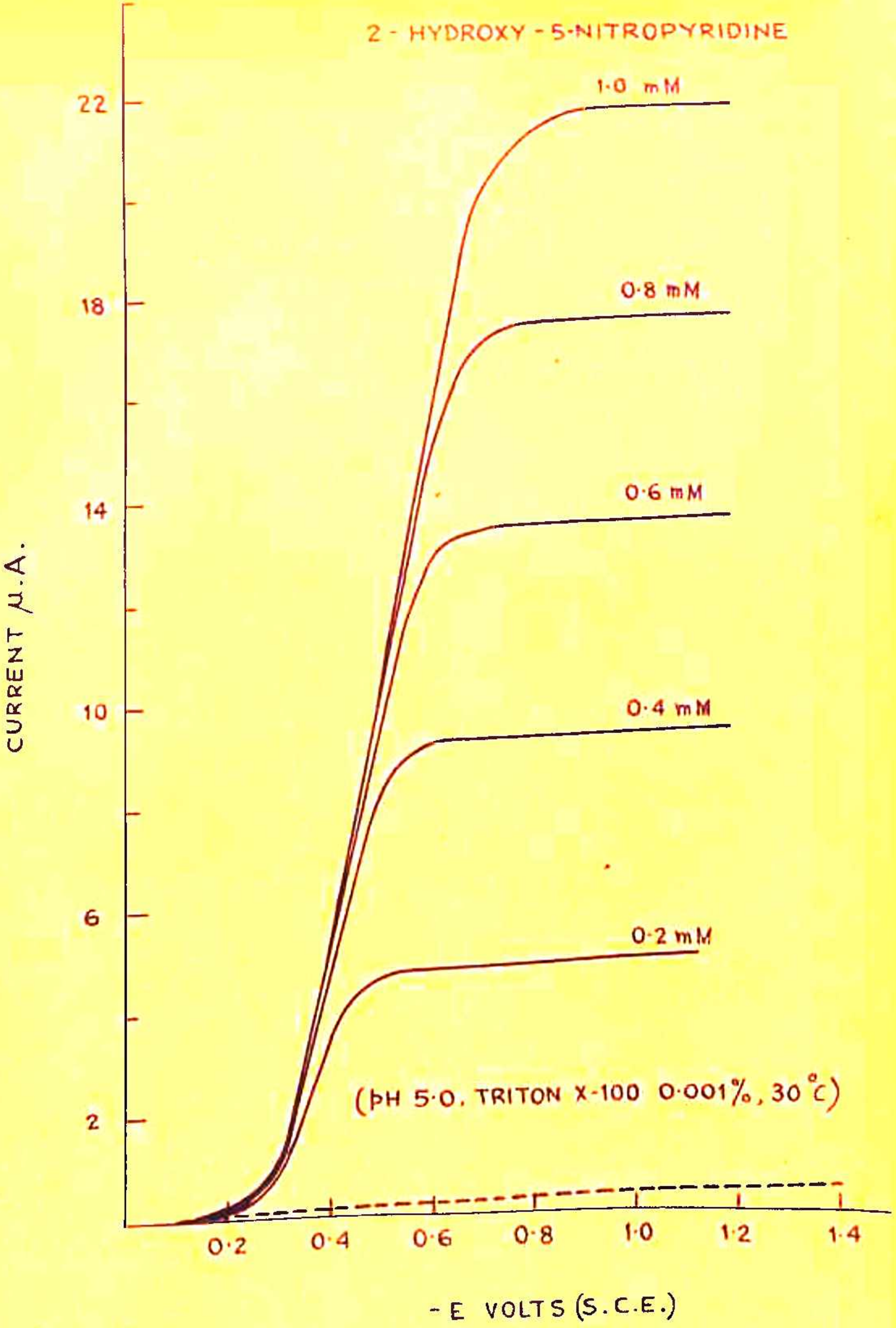

2 - HYDROXY - 5-NITROPYRIDINE
1·0 mM
0·8 mM
0·6 mM
0·4 mM
0·2 mM
(pH 5·0. TRITON X-100 0·001%, 30 °C)
CURRENT μ.A.
22
18
14
10
6
2
0·2
0·4
0·6
0·8
1·0
1·2
1·4
- E VOLTS (S.C.E.)

FIG. 3·19

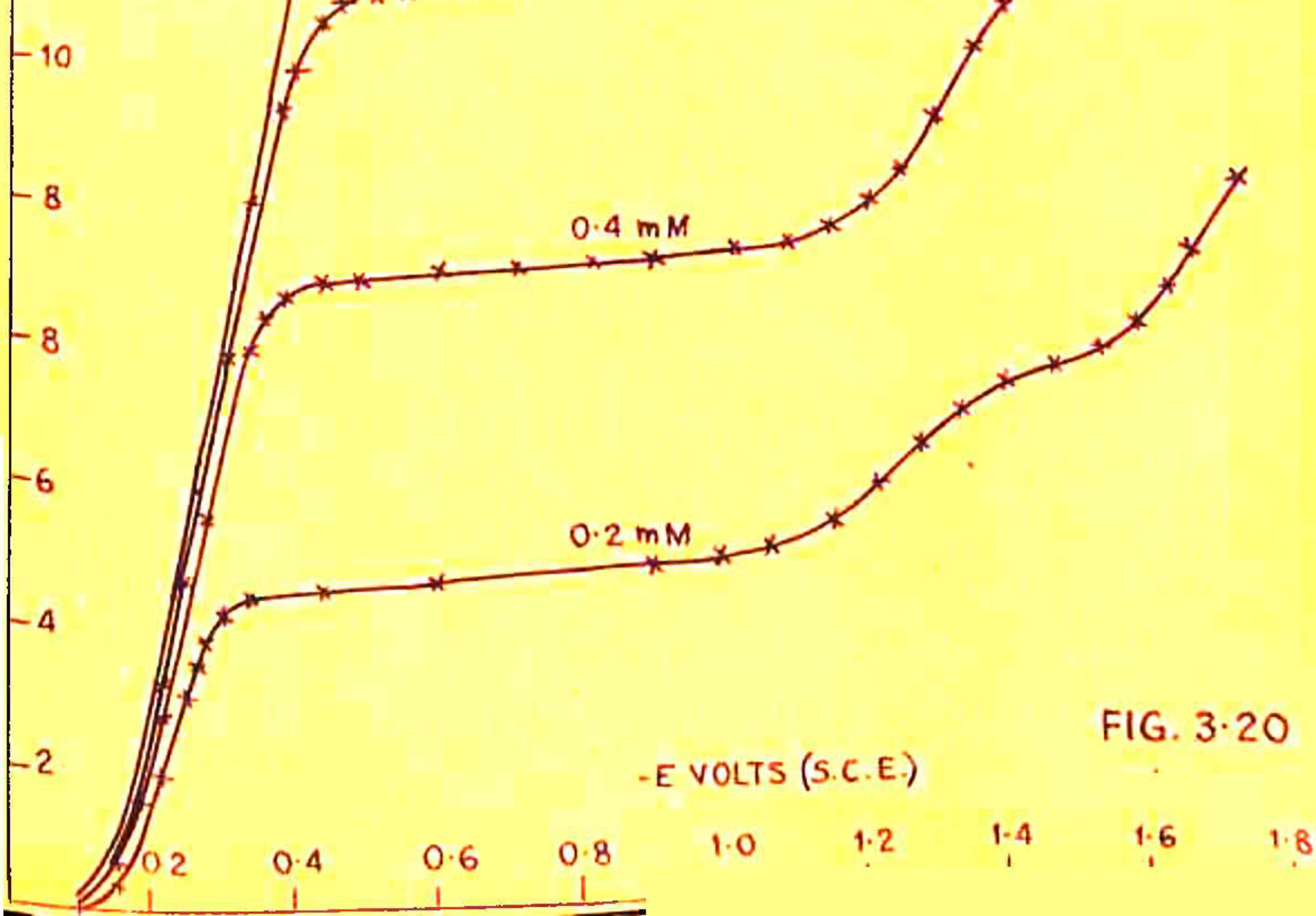
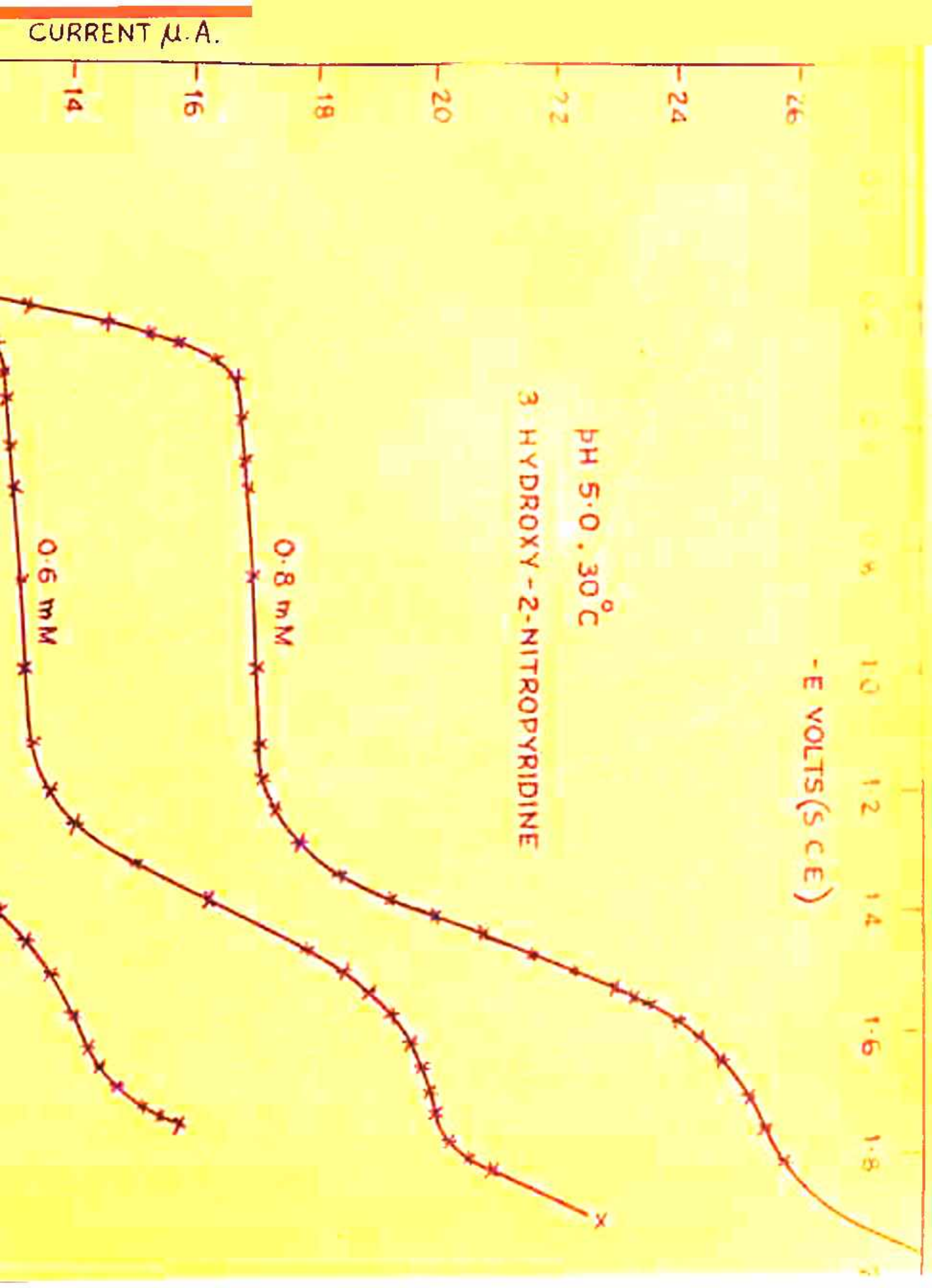


FIG. 3·20


CURRENT μ.A.
14
16
18
20
22
24
26
-E VOLTS(S C E)
1.0
1.2
1.4
1.6
1.8
pH 5.0 . 30°C
3 HYDROXY-2-NITROPYRIDINE
0.8 mM
0.6 mM

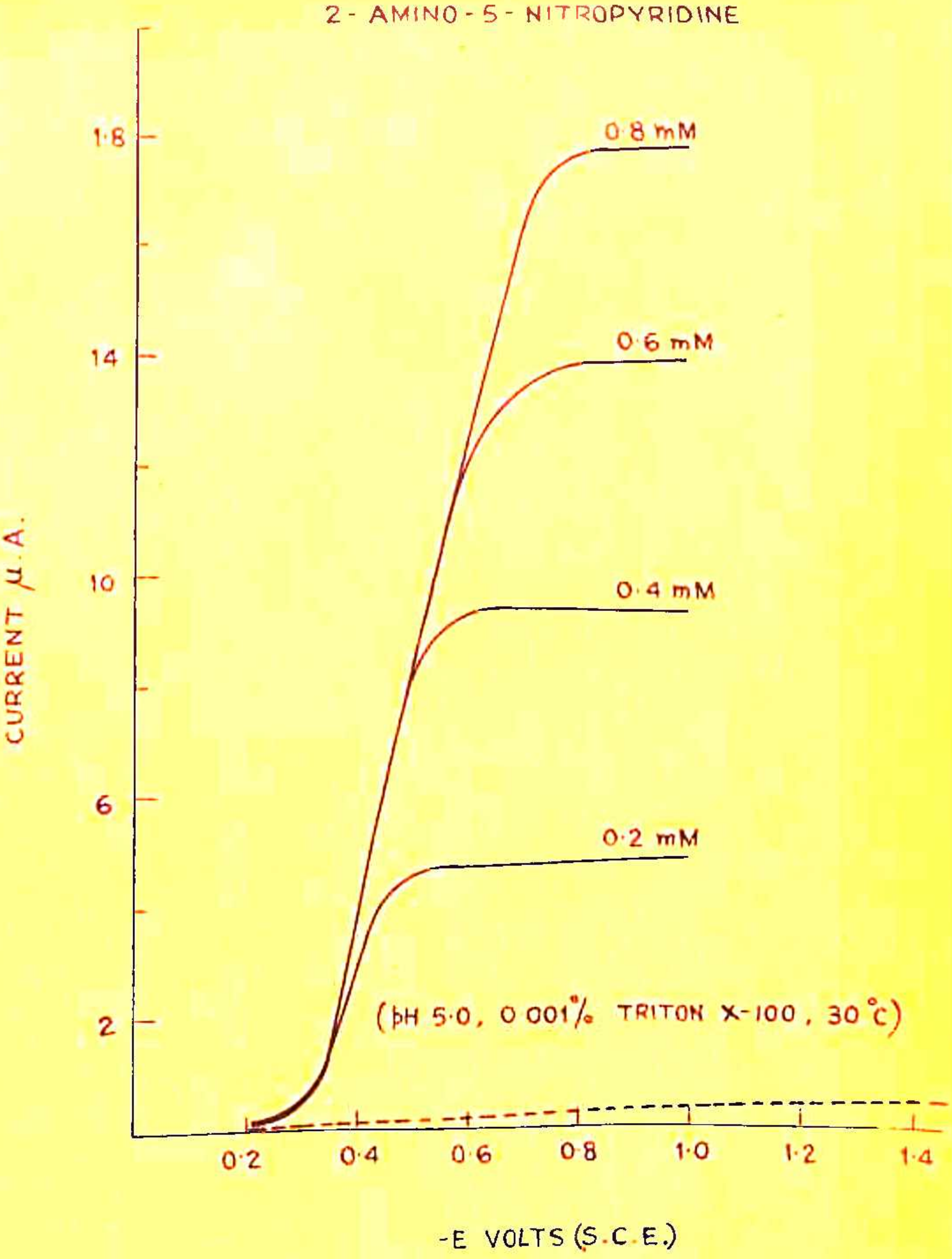
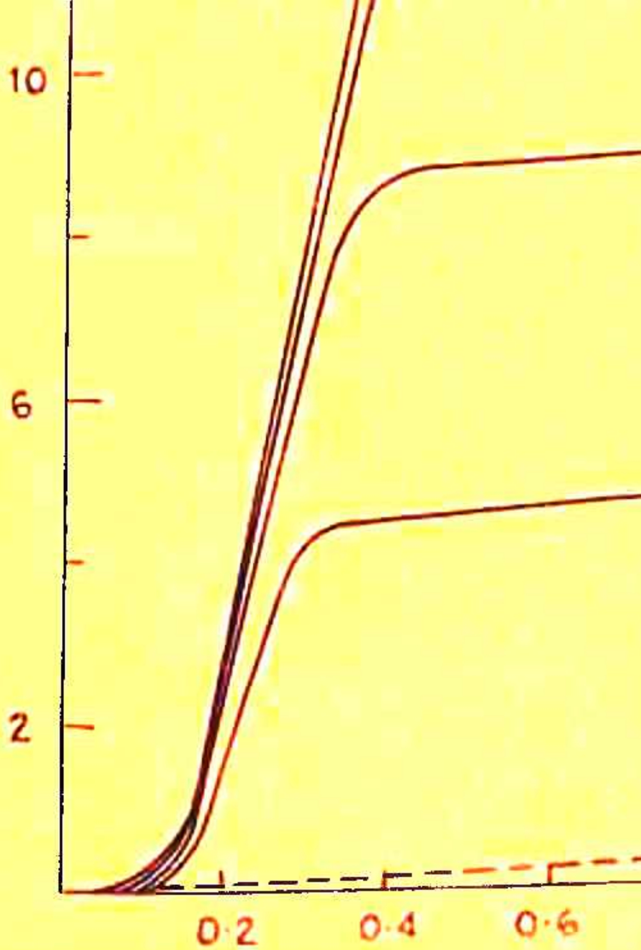
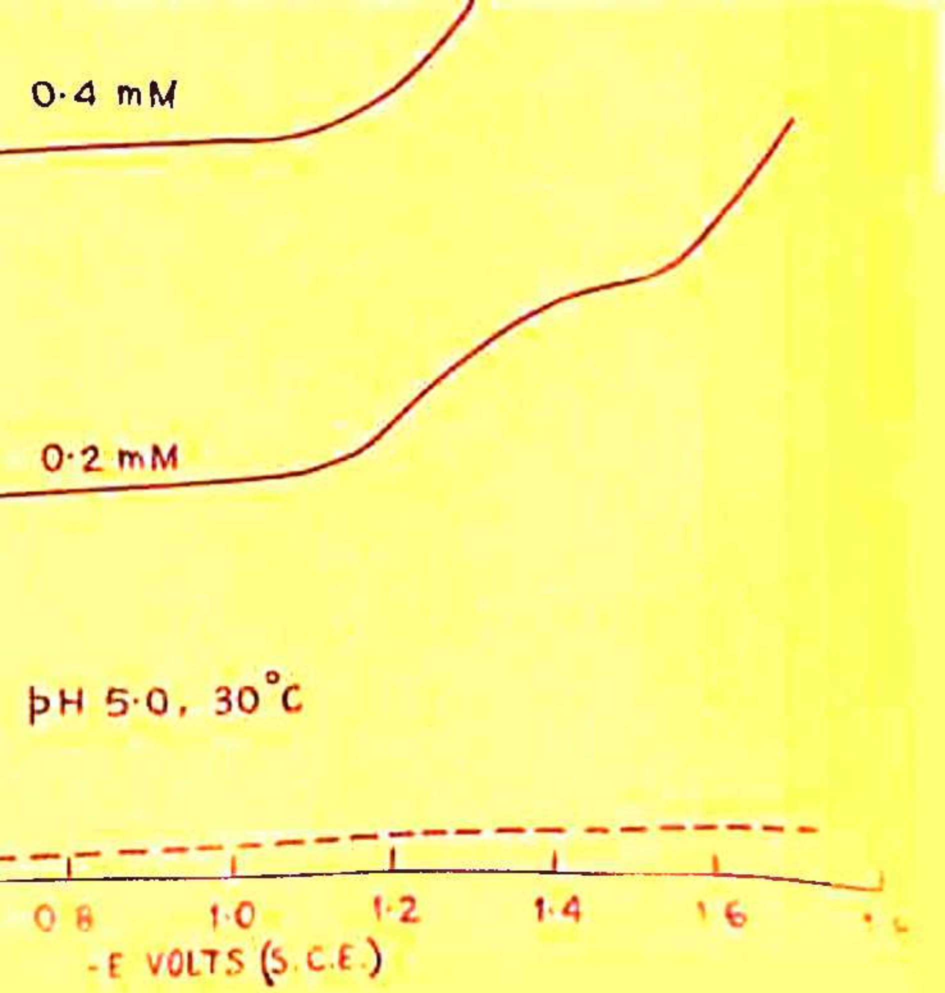
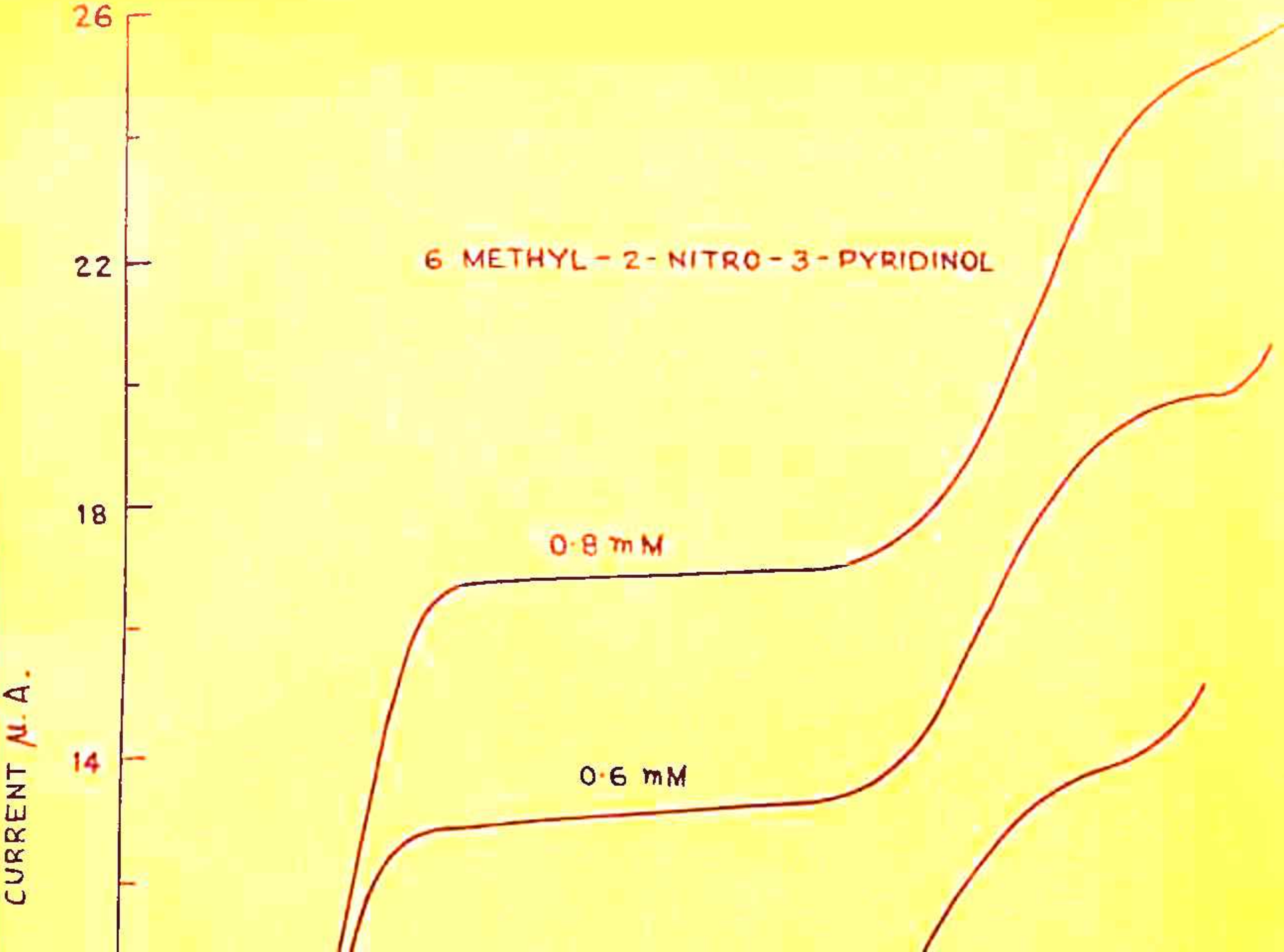

2- AMINO-5- NITROPYRIDINE
CURRENT μ A.
1·8
14
10
6
2
0·8 mM
0·6 mM
0·4 mM
0·2 mM
(pH 5·0, 0·001% TRITON X-100, 30 °C)
0·2
0·4
0·6
0·8
1·0
1·2
1·4
-E VOLTS (S.C.E.)

FIG. 3·21


10
6
2
0·2
0·4
0·6


0·4 mM
0·2 mM
þH 5·0, 30°C
0 8
1·0
1·2
1·4
1 6
-E VOLTS (S.C.E.)



6 METHYL - 2 - NITRO - 3 - PYRIDINOL
0·8 mM
0·6 mM
CURRENT μ.A.
26
22
18
14

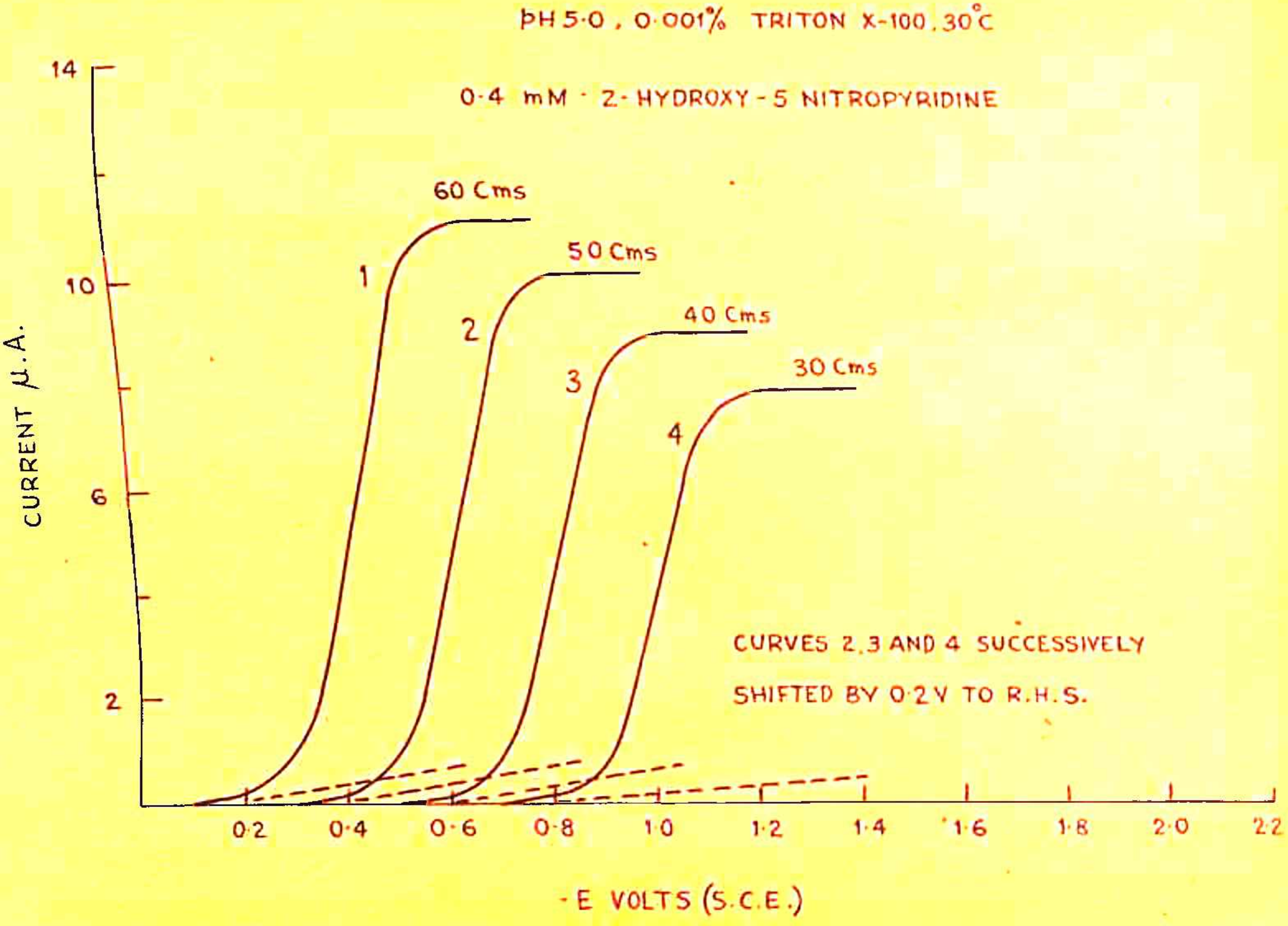
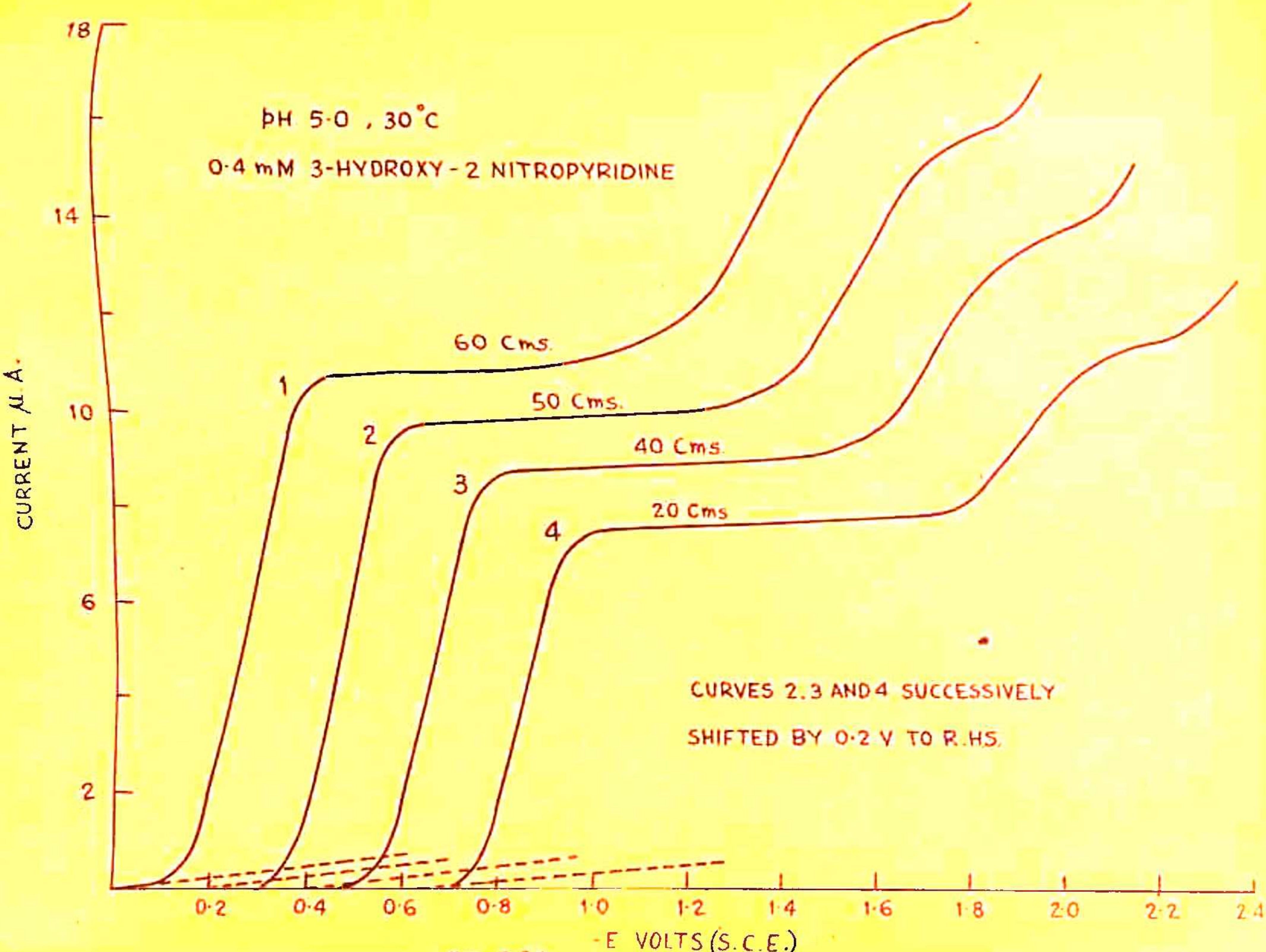

PH 5·0 , 0·001% TRITON X-100, 30°C
0·4 mM · 2-HYDROXY-5 NITROPYRIDINE
CURRENT μ.A.
14
10
6
2
1
60 Cms
2
50 Cms
3
40 Cms
4
30 Cms
CURVES 2,3 AND 4 SUCCESSIVELY
SHIFTED BY 0·2V TO R.H.S.
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
-E VOLTS (S.C.E.)

FIG. 3·23



18
14
10
6
2
CURRENT μ A.
þH 5·0 , 30°C
0·4 mM 3-HYDROXY - 2 NITROPYRIDINE
1
60 Cms.
2
50 Cms.
3
40 Cms.
4
20 Cms
CURVES 2.3 AND4 SUCCESSIVELY
SHIFTED BY 0·2 V TO R.HS.
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
2·4
-E VOLTS (S.C.E.)

FIG. 3·24

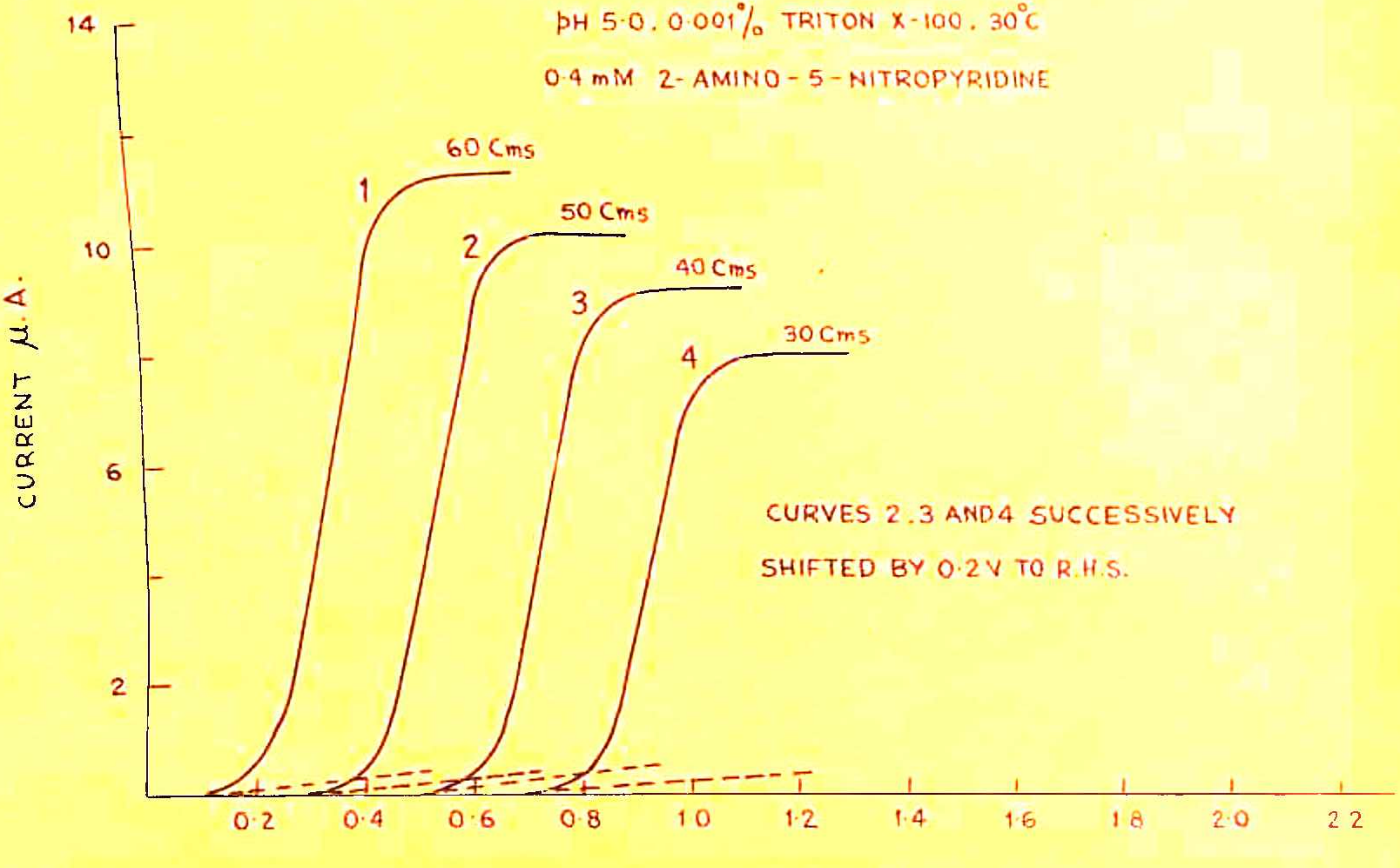

pH 5·0. 0·001% TRITON X-100. 30°C
0·4 mM 2-AMINO-5-NITROPYRIDINE
60 Cms
50 Cms
40 Cms
30 Cms
1
2
3
4
CURVES 2.3 AND4 SUCCESSIVELY
SHIFTED BY 0·2V TO R.H.S.
CURRENT μ.A.
14
10
6
2
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
-E VOLTS (S.C.E)

FIG. 3.25

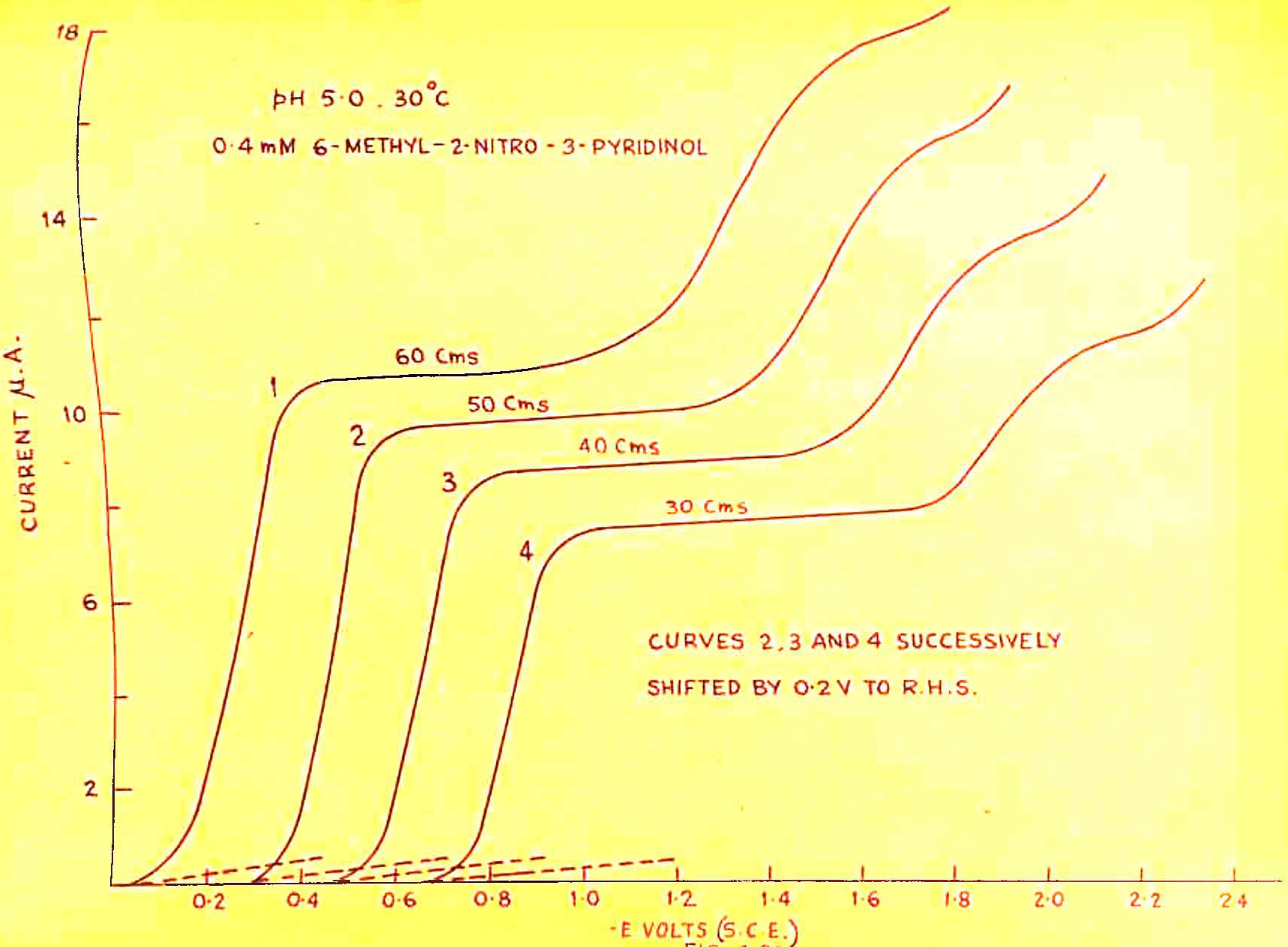

pH 5·0 . 30°C
0·4 mM 6-METHYL-2-NITRO-3-PYRIDINOL
CURRENT μ.A.
18
14
10
6
2
1
2
3
4
60 Cms
50 Cms
40 Cms
30 Cms
CURVES 2, 3 AND 4 SUCCESSIVELY
SHIFTED BY 0·2 V TO R.H.S.
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
2·4
-E VOLTS (S.C.E.)

FIG. 5.26

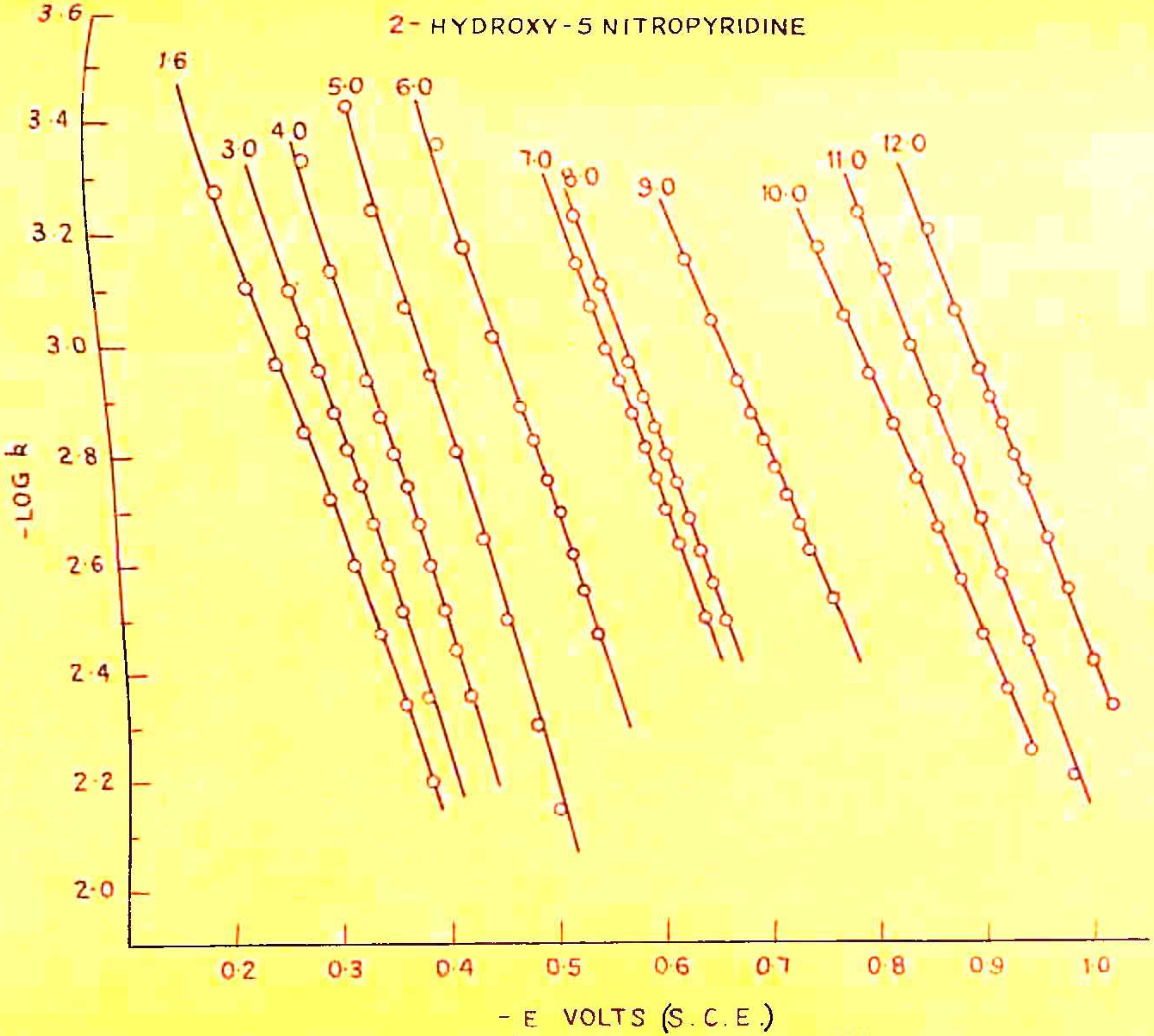


FIG. 3.27 -LOG k vs -E AT VARIOUS pH VALUES

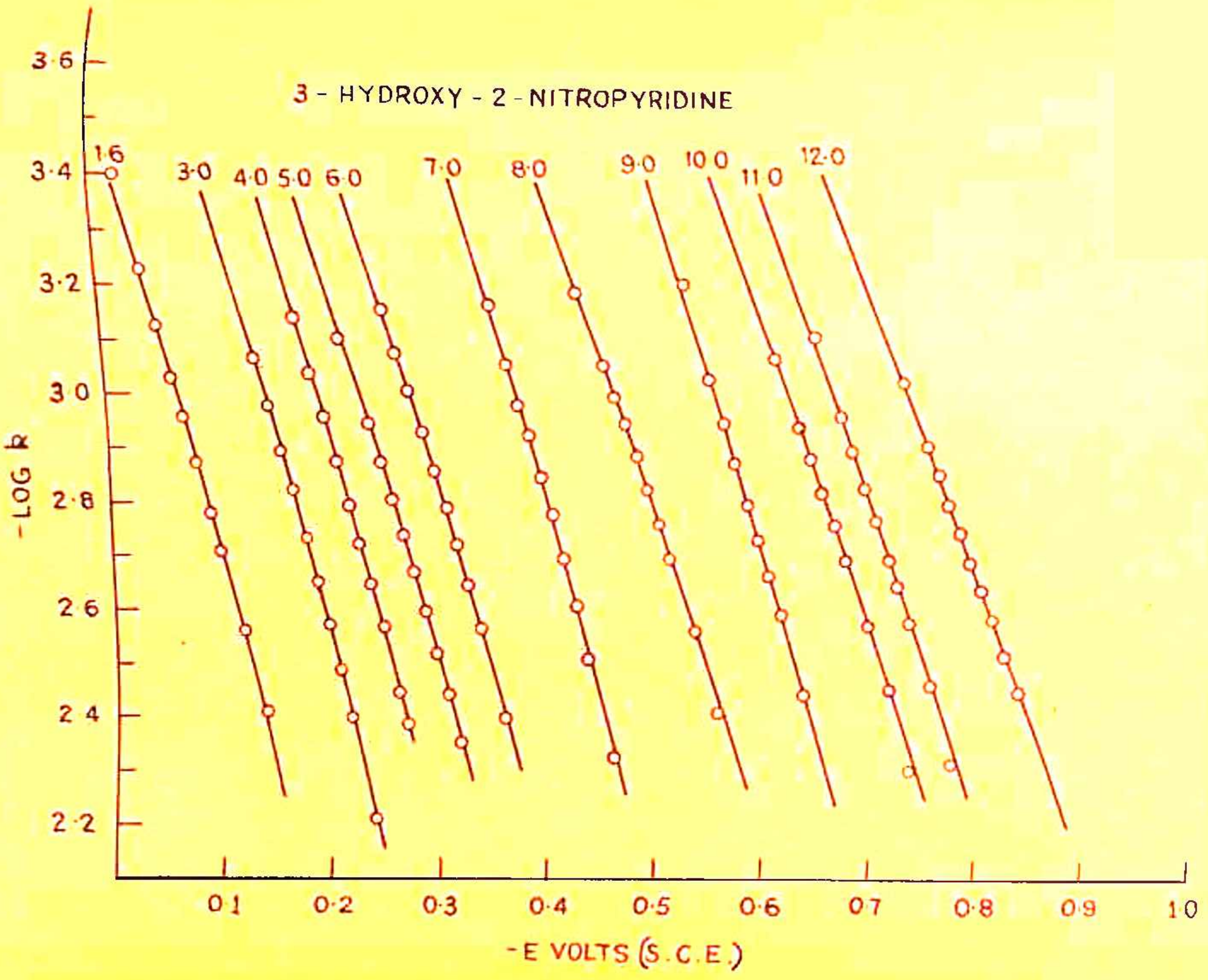


FIG 3.28 -LOG k VS -E AT VARIOUS pH VALUES

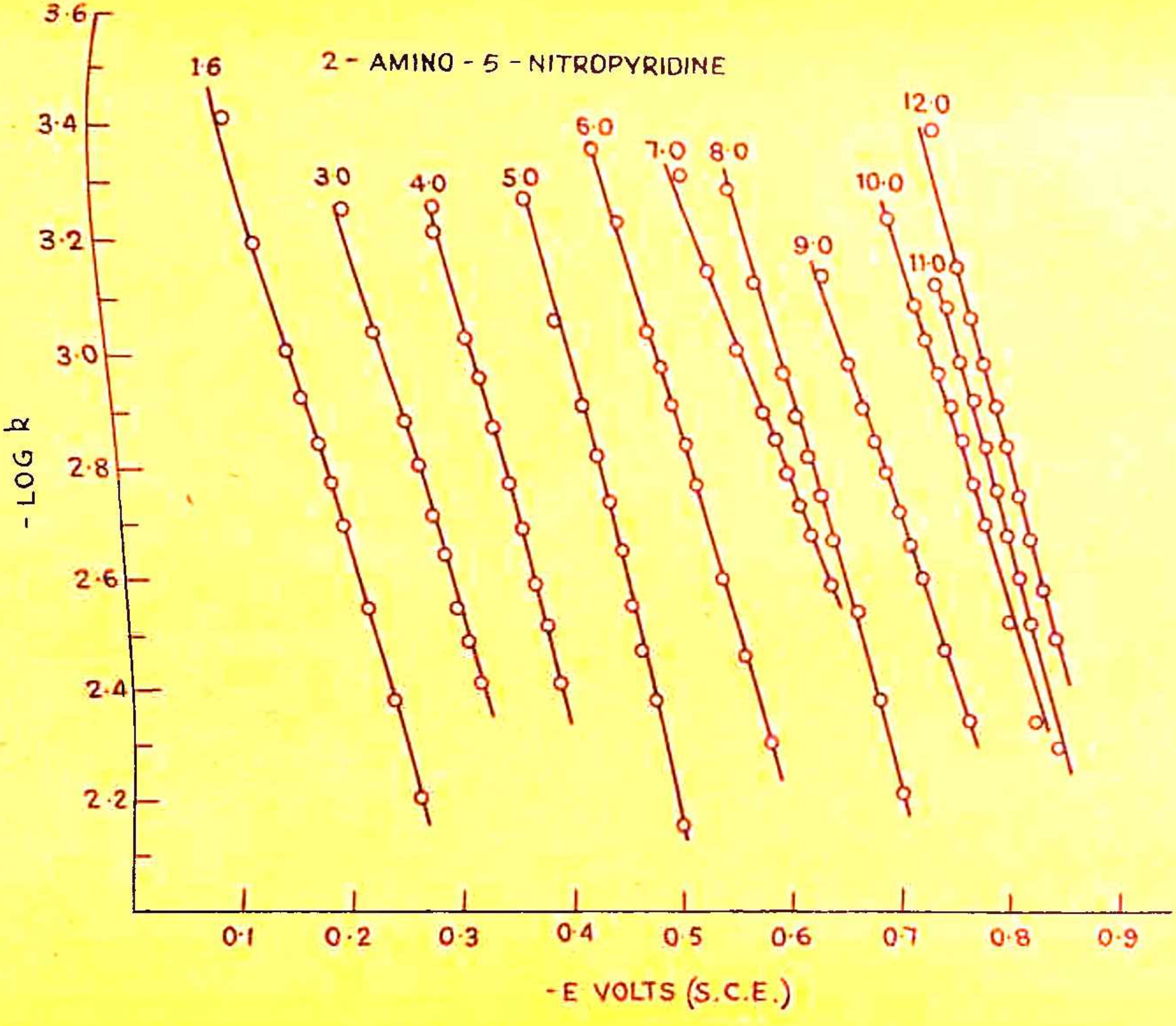


FIG 3·29 -LOG k VS -E AT VARIOUS pH VALUES.

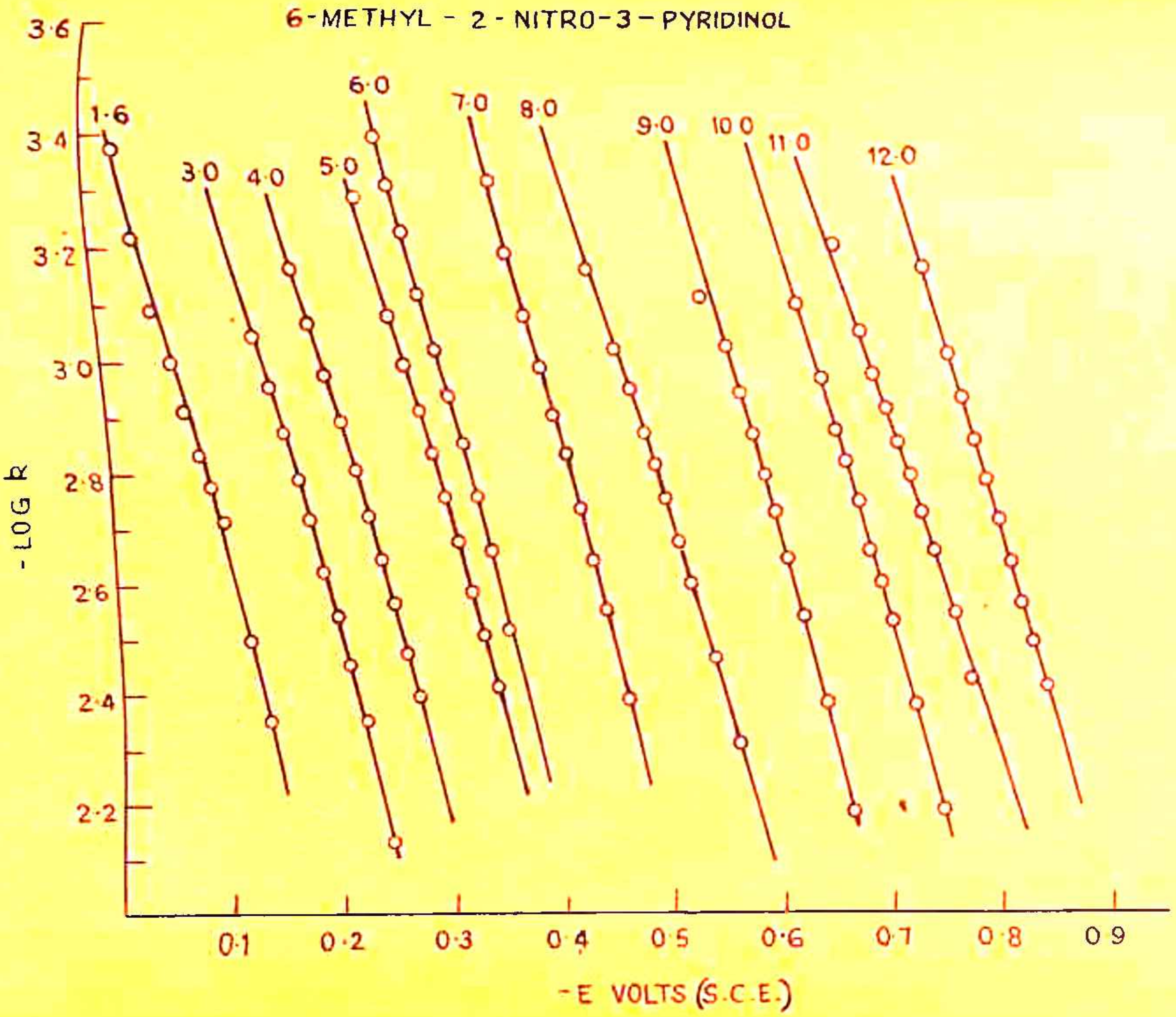


FIG 3.30 -LOG k VS -E AT VARIOUS pH VALUES.

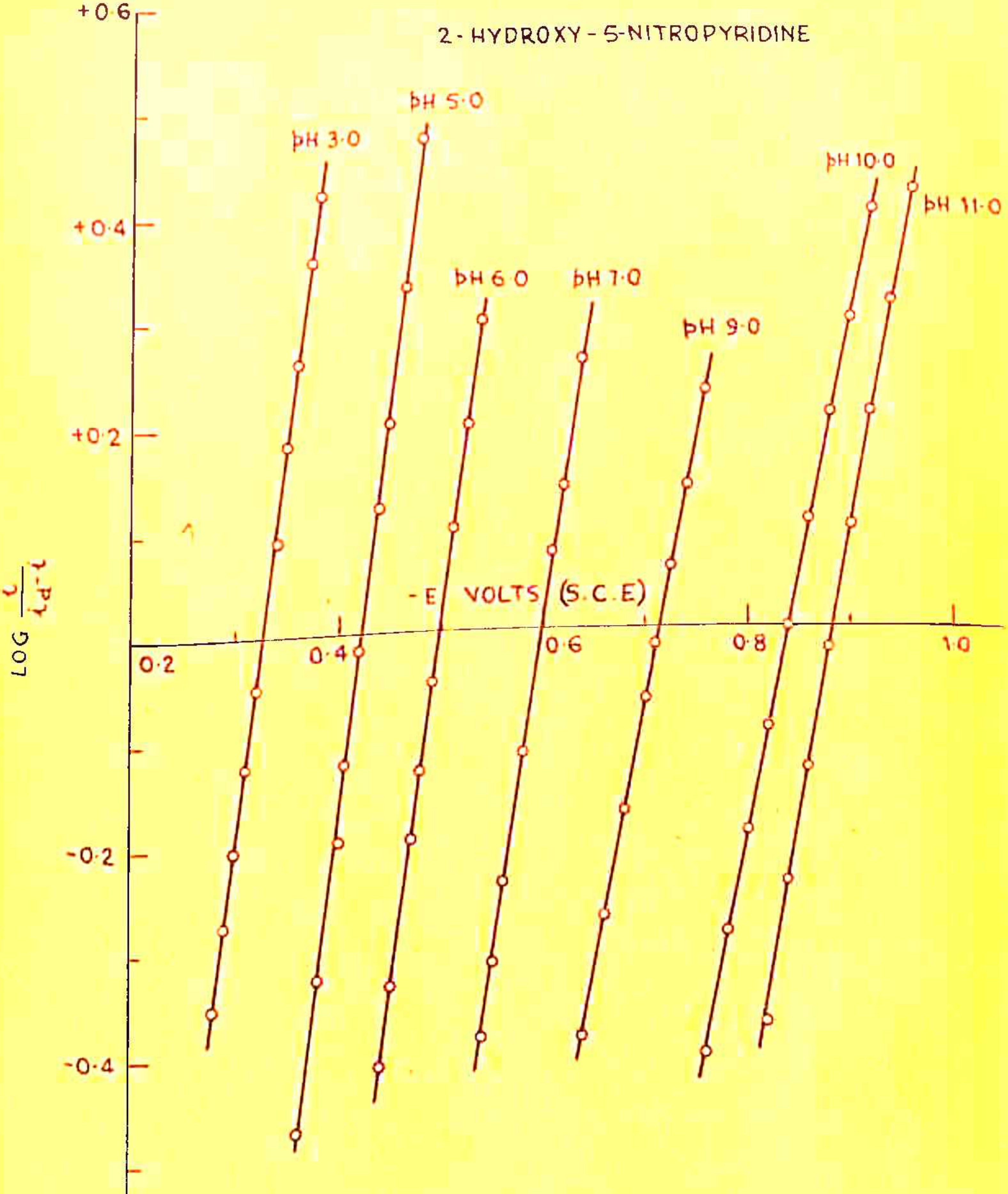


FIG. 3·31 -E VS LOG $\frac{i}{i_d-i}$.

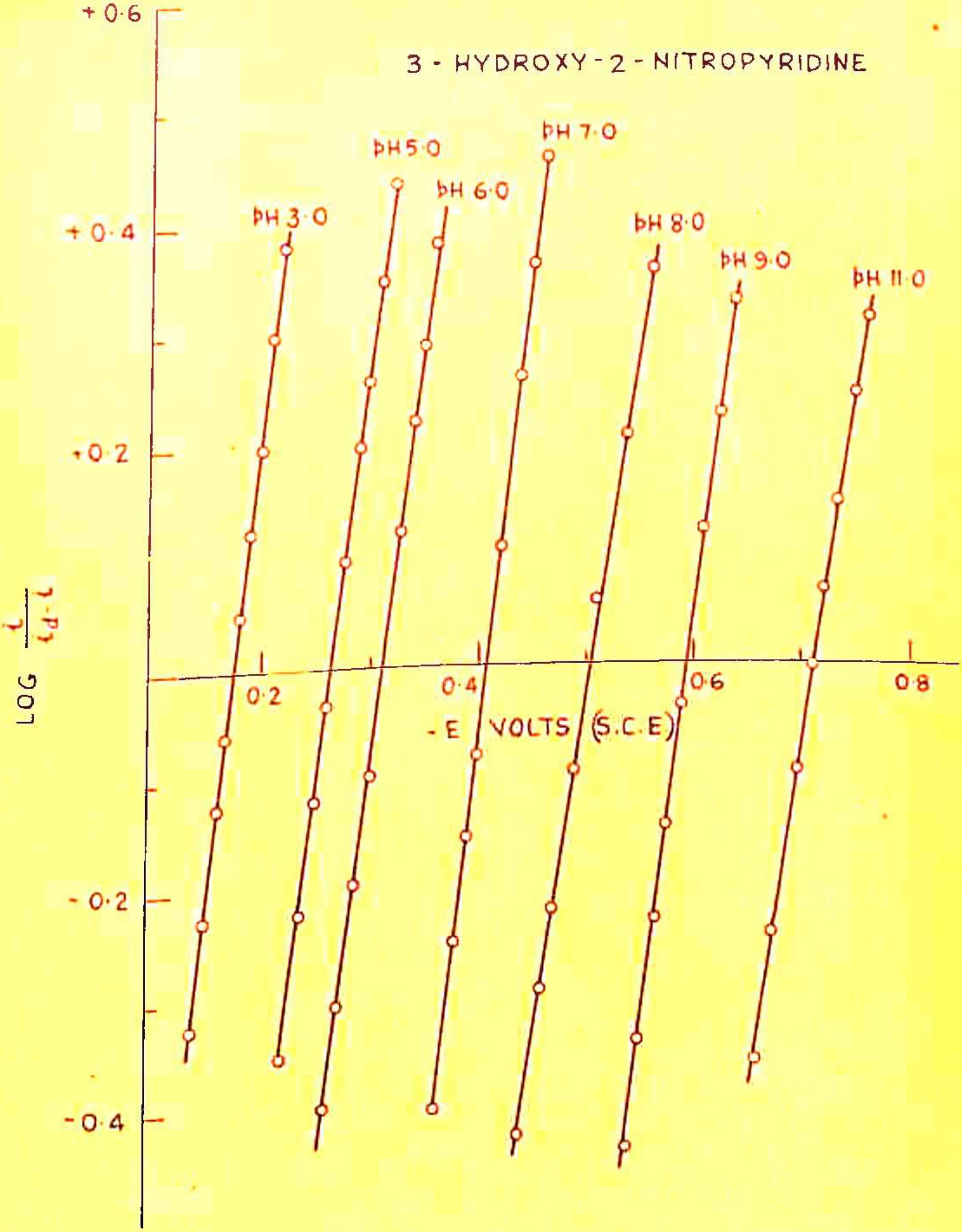


FIG. 3·32 -E VS LOG $\frac{i}{i_d - i}$

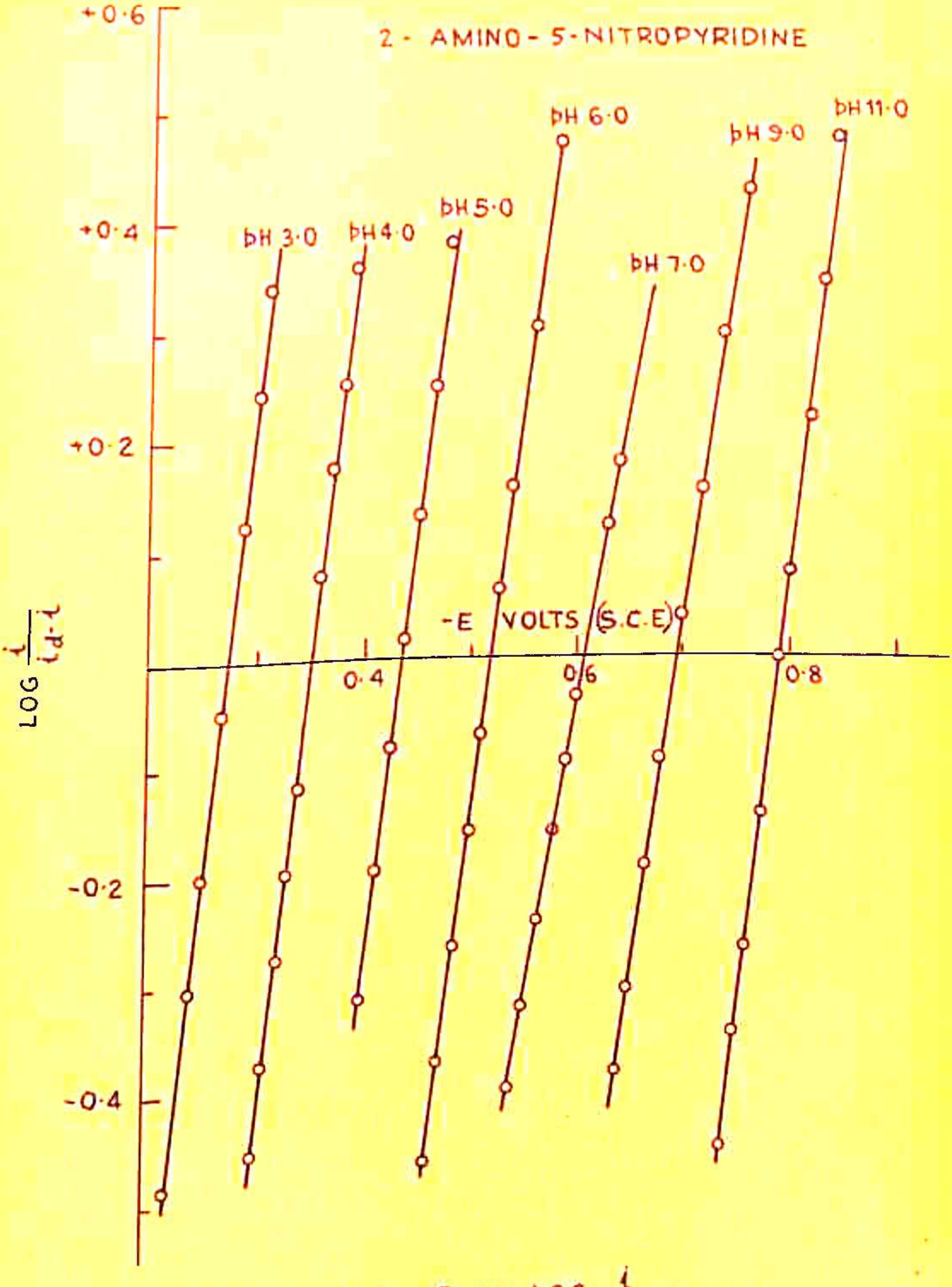


FIG. 3·33 -E VS LOG $\frac{i}{i_d - i}$.

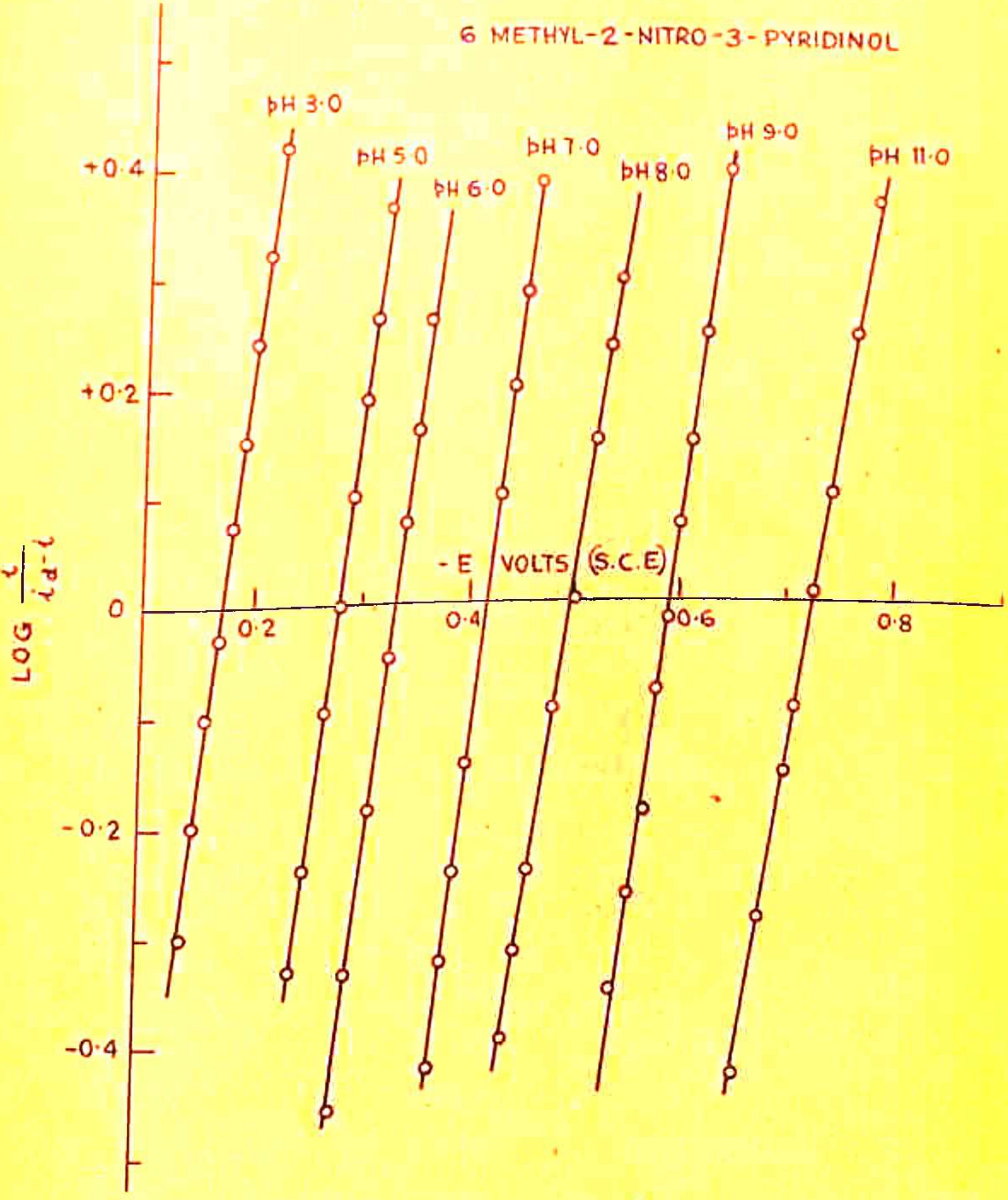


FIG. 3·34 -E VS LOG $\frac{i}{i_d - i}$.

Comparison of the results obtained in the case of nitropyridines

It can be seen from the structures of the different substituted nitropyridines that all of them are capable of forming quinonoid structures. In HNP and MNP the hydroxyl group is in the ortho position to the nitro group whereas in (A) it is in the para position. In ANP the amino group is in the para position.

An examination of Tables 3.18, 3.19, 3.20 and 3.21 reveals that (A) has the most cathodic half-wave potential among the four substituted nitropyridines. It shows that (A) is most difficult to get reduced at the d.m.e., but the values of -log k^o indicate that in the cases of ANP and MNP the extent of irreversibility of the reduction is greater. It seems probable that with amino group in the para position (in ANP) the tendency to form quinonoid structure is greater than the -OH group in the para position in (A). Also in the case of MNP the -OH group in the ortho position increases its tendency to form quinonoid structure thus resulting in its having a more positive $E_{0.5}$ than (A). In the cases of o- and p-nitrophenol[202] and o- and p-nitroanilines[203] also it was seen that the ortho isomer possessed a more positive $E_{0.5}$.

The fact that the $E_{0.5}$ of MNP was only slightly more cathodic than HNP indicates that the methyl group affects the reduction of the nitro group only to a small extent. The value of -log k^o in the cases of HNP and MNP show that the presence of methyl group renders the reduction more irreversible.

TABLE 3.17 : Comparison of the values given in Koutecky's Table[109] and those calculated using the sixth order polynomial equation.

λ	Koutecky's Table	Calculated value
0.16000	0.30000	0.29766
0.23060	0.40000	0.43336
0.24330	0.50000	0.47172
0.27960	0.60000	0.58875
0.31290	0.70000	0.70030
0.34350	0.80000	0.80514
0.37170	0.90000	0.90535
0.39770	1.00000	1.0030
0.44430	1.20000	1.1984
0.48450	1.40000	1.3961
0.51960	1.60000	1.5971
0.55050	1.80000	1.7997
0.57770	2.00000	2.0011
0.63390	2.50000	2.5035
0.67700	3.00000	2.9994
0.73900	4.0000	3.9992
0.78100	5.0000	4.9989
0.81200	6.0000	6.0008

TABLE 3.18 : Kinetic parameters (αn_a and $-\log k^o$) and $E_{0.5}$ of 2-hydroxy-5-nitropyridine (A) at various pH values.

30^oC, $h = 40.0$ cm, $\mu = 0.54$ M, 0.5 mM depolarizer

pH	i_{d_1} μA	$-E^1_{0.5}$ S.C.E.	αn_a	$-\log k^o$ N.H.E.	i_{d_2} μA	$-E^2_{0.5}$ S.C.E.
1.6	14.6	0.300	0.4062	3.106	**	-
3.0	11.6	0.340	0.4493	3.388	3.6	1.060
4.0	11.0	0.380	0.4750	3.750	**	-
5.0*	11.0	0.440	0.4852	4.226	**	-
6.0*	10.6	0.510	0.4320	4.597	**	-
7.0*	10.5	0.615	0.3731	4.961	3.6	1.880
8.0	11.2	0.630	0.3548	4.962	**	-
9.0	11.6	0.710	0.3116	5.191	**	-
10.0	14.0	0.850	0.3152	5.741	**	-
11.0	14.4	0.900	0.3424	6.501	**	-
12.0	14.6	0.935	0.3283	6.547	**	-

* Triton-X-100 (0.001%)

** Ill defined wave

TABLE 3.19 : Kinetic parameters (αn_a and -log k°) and $E_{0.5}$ of 3-hydroxy-2-nitropyridine (HNP) at various pH values

30°C, h = 40.0 cm, μ = 0.54 M, 0.5 mM depolarizer

pH	i_{d_1} µA	$-E^1_{0.5}$ S.C.E.	αn_a	-log k° N.H.E.	i_{d_2} µA	$-E^2_{0.5}$ S.C.E.
1.6	10.7	0.100	0.5200	2.489	**	-
3.0	10.6	0.180	0.5119	2.957	**	-
4.0	10.7	0.230	0.4884	2.902	**	-
5.0	10.8	0.270	0.4454	2.929	5.4	1.370
6.0	10.4	0.320	0.4511	3.282	5.0	1.400
7.0	10.3	0.405	0.4891	4.112	5.1	1.480
8.0	10.1	0.520	0.3196	4.444	**	-
9.0	10.3	0.605	0.4453	5.361	**	-
10.0	10.3	0.670	0.4033	5.627	**	-
11.0	10.2	0.710	0.3952	5.838	-	-
12.0	11.0	0.770	0.3410	5.843	-	-

** Ill-defined wave

TABLE 3.20 : Kinetic parameters (αn_a and $-\log k^o$) and $E_{0.5}$ of 2-amino-5-nitropyridine (ANP) at various pH values

30°C, h = 40.0 cm, μ = 0.54 M, 0.5 mM depolarizer

pH	i_{d_1} µA	$-E^1_{0.5}$ S.C.E.	αn_a	$-\log k^o$ N.H.E.	i_{d_2} µA	$-E^2_{0.5}$ S.C.E.
1.6	10.8	0.200	0.5145	2.335	**	-
3.0	10.6	0.285	0.5381	2.953	**	-
4.0	11.0	0.360	0.5375	3.730	**	-
5.0	11.0	0.450	0.5399	4.495	**	-
6.0*	11.2	0.535	0.4565	4.867	**	-
7.0*	10.7	0.610	0.3634	4.960	**	-
8.0	11.9	0.690	0.4641	5.751	**	-
9.0*	11.9	0.705	0.3914	5.791	-	-
10.0	11.8	0.770	0.4447	6.664	-	-
11.0	11.8	0.800	0.5252	7.539	-	-
12.0	11.4	0.840	0.4714	7.734	-	-

* Triton X-100 (0.0005%)

** Ill-defined wave

TABLE 3.21 : Kinetic parameters (αn_a and $-\log k^o$) and $E_{0.5}$ of 6-methyl-2-nitro-3-pyridinol

30°C, h = 40.0 cm, μ = 0.54 M, 0.5 mM depolarizer

pH	i_{d_1} μA	$-E^1_{0.5}$ S.C.E.	αn_a	$-\log k^o$ N.H.E.	i_d μA	$-E^2_{0.5}$ S.C.E.
1.6	10.8	0.105	0.5249	3.628	**	-
3.0	10.2	0.185	0.5358	2.951	**	-
4.0	10.4	0.235	0.5064	2.612	5.0	1.285
5.0	10.6	0.285	0.5123	3.063	5.1	1.295
6.0	10.2	0.335	0.5414	3.534	4.8	1.320
7.0	10.4	0.430	0.5493	4.334	3.2	1.360
8.0	10.4	0.525	0.4178	4.524	3.1	1.630
9.0	10.6	0.610	0.4763	5.508	**	-
10.0	10.8	0.670	0.4647	6.066	-	-
11.0	11.0	0.735	0.3907	6.902	-	-
12.0	11.6	0.810	0.4535	6.900	-	-

** Ill-defined wave

Legend of the figures

(Temperature 30°C, $\mu = 0.54$ M)

Fig. 3.12 : D.C. polarograms of 0.5 mM 2-hydroxy-5-nitropyridine (A) at various pH

Fig. 3.13 : D.C. polarograms of 0.5 mM 3-hydroxy-2-nitropyridine (HNP) at various pH

Fig. 3.14 : D.C. polarograms of 0.5 mM 2-amino-5-nitropyridine (ANP) at various pH

Fig. 3.15 : D.C. polarograms of 0.5 mM 6-methyl-2-nitro-3-pyridinol (MNP) at various pH

Fig. 3.16 : A.C. polarograms of 0.5 mM (A) at various pH

Fig. 3.17 : A.C. polarograms of 0.5 mM ANP at various pH

Fig. 3.18 : Curve 1. A.C. polarogram of 0.5 mM (A) at pH 12.0

Curve 1'. D.C. polarogram of 0.5 mM (A) at pH 12.0

Fig. 3.19 : (A), concentration effect (d.c. polarography), pH 5.0

Fig. 3.20 : HNP, concentration effect (d.c. polarography), pH 5.0

Fig. 3.21 : ANP, concentration effect (d.c. polarography), pH 5.0

Fig. 3.22 : MNP, concentration effect (d.c. polarography), pH 5.0

Fig. 3.23 : 0.4 mM (A), effect of the height of the mercury column, pH 5.0

Fig. 3.24 : 0.4 mM HNP, effect of the height of the mercury column, pH 5.0

Fig. 3.25 : 0.4 mM ANP, effect of the height of the mercury column, pH 5.0

Fig. 3.26 : 0.4 mM MNP, effect of the height of the mercury column, pH 5.0

Fig. 3.27 : (A), -log k vs -E plots at various pH values

Fig. 3.28 : HNP, -log k vs -E plots at various pH values

Fig. 3.29 : ANP, -log k vs -E plots at various pH values

Fig. 3.30 : MNP, -log k vs -E plots at various pH values

Fig. 3.31 : (A), log $\frac{i}{i_d - i}$ vs -E plots at various pH values

Fig. 3.32 : HNP, log $\frac{i}{i_d - i}$ vs -E plots at various pH values

Fig. 3.33 : ANP, log $\frac{i}{i_d - i}$ vs -E plots at various pH values

Fig. 3.34 : MNP, log $\frac{i}{i_d - i}$ vs -E plots at various pH values

CHAPTER IV

STUDIES ON THE ESTIMATION OF METAL IONS BY AMPEROMETRY AND DETERMINATION OF COMPOSITION AND STABILITY CONSTANTS OF COMPLEXES

(i) POLAROGRAPHIC DETERMINATION OF ZIRCONIUM (IV) AS 7-NITRO-8-HYDROXYQUINOLINE-5-SULFONATE

The solubility products of chelates of divalent ions with 7-nitro-8-hydroxyquinoline-5-sulfonic acid (NOSA) have been determined potentiometrically and spectrophotometrically[213]. However, the reaction of NOSA with tri- and tetravalent metal ions has not received much attention. The present work deals with the use of NOSA as a precipitant in the estimation of zirconium (IV) in the presence of many metal ions, by an indirect d.c. polarographic method.

EXPERIMENTAL

NOSA was prepared from recrystallised oxine (Ward and Blenkinsop and Co., London) as described by Welcher[280]. $ZrOCl_2.8H_2O$ (BDH, AR) was used in the preparation of its stock solution in 0.4 M HCl and the zirconium content was estimated gravimetrically[33]. All other chemicals were of analytical reagent grade. Stock solutions (approximately 0.01 M) of other metal ions were prepared in distilled water taking care to prevent hydrolysis wherever necessary. The d.m.e. had $m = 2.931$ mg/s and $t = 3.05$ s in 0.54 M KCl (open circuit) at $h = 40.0$ cm (uncorrected for back pressure).

RESULTS AND DISCUSSION

The polarographic reduction of NOSA at various pH has been studied and the details are given in Chapter III of this thesis. It would suffice to point out here that upto pH 8.5

a single well-defined wave ($6\bar{e}$) due to the reduction of the nitro group appeared. This wave was preceded by a small wave of adsorption characteristics. At pH 8.5 the diffusion current due to the reduction of the nitro group increased linearly in the range 0.1 mM to 1.1 mM. A typical polarogram of 0.8 mM NOSA is given in Fig. 4.1 and the calibration curve of the nitro group reduction wave at pH 8.5 is shown in Fig. 4.2.

Direct amperometric titrations with NOSA as the titrant were carried out at pH 0.5, 1.0, 1.5 and 2.0 at -0.8 volts. Results were found to be 5 to 8% lower than the theoretically calculated results. An indirect method was employed and this improved the results. A preliminary investigation showed that a pH of 1.5 was most suitable.

The test solution containing zirconium was taken in HCl/KCl buffer of pH 1.5 and NOSA was added till complete precipitation was ensured. The resulting solution containing the precipitate was kept for one hour at 50°C. The yellow precipitate was then filtered and washed with HCl/KCl buffer of pH 1.5. The filtrate was tested for the presence of zirconium by testing portions of the filtrate with Alizarin Red S, Quinalizarin and making a portion alkaline with NaOH (to precipitate zirconium as hydroxide). All these tests showed negative results and thus the quantitativeness of the precipitation was established. The precipitate was dissolved in a minimum volume of 0.1 M NaOH. The pH of the solution was adjusted to 8.5 by boric acid solution. The resulting

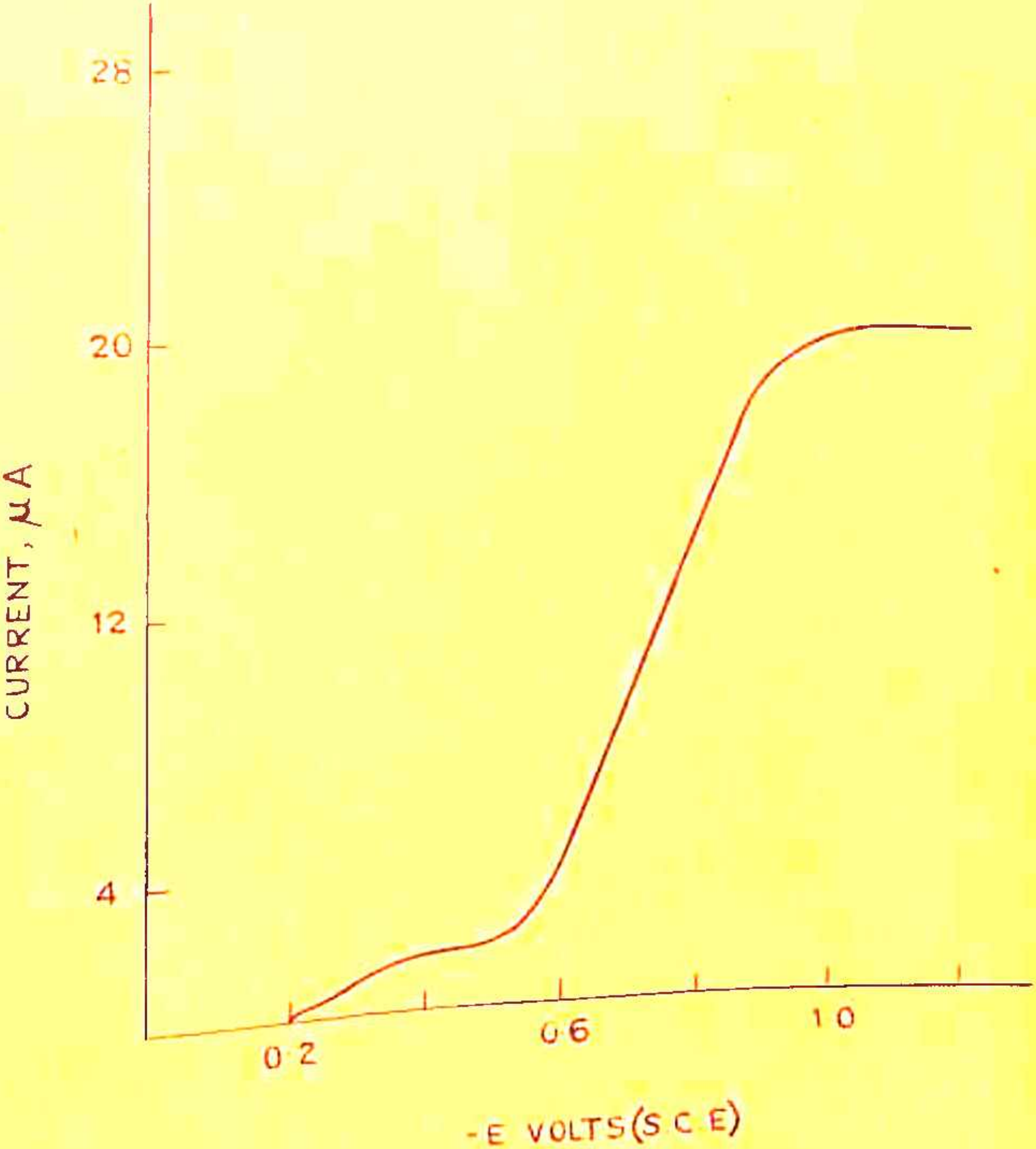


FIG. 4 1

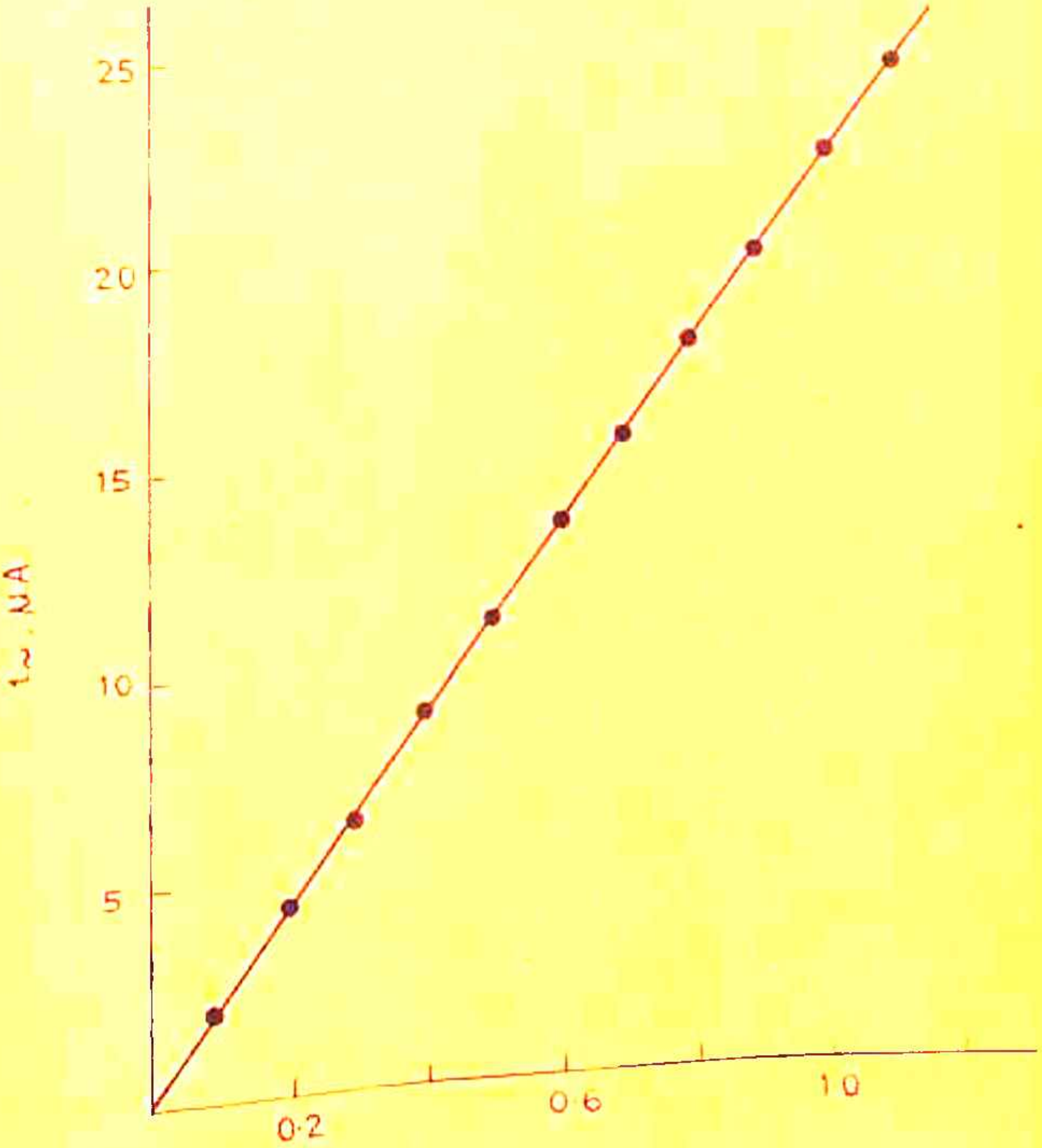


FIG. 4·2

solution was diluted to a volume such that eventually the concentration of NOSA does not exceed 1.1 mM. After adjusting the pH to 8.5 and the ionic strength to 0.54 M by KCl, the solution was deoxygenated and polarographed upto -1.0 volt. In this range of potential zirconium does not exhibit any wave. The concentration of NOSA was found from the calibration curve. Knowing the initial concentration of zirconium, the metal to ligand ratio was established and corresponded very close to 1:4. Table 4.1 depicts the results obtained in the direct amperometric and indirect polarographic methods. The results under indirect polarographic method in Table 4.1 establish the metal to ligand ratio of 1:4 for various concentration of zirconium and thus the precipitate may be assigned the composition Zr $(NOSA)_4$.

Table 4.2 gives the effect of various ions in the estimation of zirconium. It can be seen that UO_2^{++}, trivalent Al, Pr, Sm, La, Lu, Yb, Er, Gd, Nd and tetravalent Th can be tolerated even if present in concentrations 20 times that of zirconium. Interference was caused by divalent Pb, Ba, Ca, Sr, Mn, Cd, Zn, Co, Ni and Cu when present in concentrations greater than or equal to about one-fifth that of zirconium.

TABLE 4.1 : Estimation of zirconium (IV) by direct amperometric and indirect polarographic methods, using 7-nitro-8-hydroxyquinoline-5-sulfonic acid (NOSA)

Concen. of Zr (IV) mM/litre	Direct amperometry*			Indirect polarographic methods**		
	Titre values of M/50 NOSA, ml. Calc.	Found	Error %	Concn. of NOSA, mM/litre Calc.	Found	Error %
0.25	1.25	1.15	-8.0	0.25	0.245	-2.0
0.50	2.50	2.32	-7.2	0.50	0.49	-2.0
0.75	3.75	3.53	-6.0	0.75	0.74	-1.3
1.00	5.00	4.75	-5.0	1.00	0.99	-1.0

* 25 ml, pH 1.5, E = -0.8 V vs S.C.E., 35°C

** Final volume 100 ml.

TABLE 4.2 : Tolerance of various ions in the estimation of zirconium by indirect polarographic method

Conc. of Zirconium 0.001 M

Foreign ions	% Error Concentration (M) of foreign ions present at the time of precipitation						
	0.0001	0.0002	0.0005	0.001	0.01	0.02	0.03
UO_2^{++}	-	-	-	1.0	1.2	1.8	4.0
Al^{3+}	-	-	-	1.0	1.4	1.8	4.5
Pr^{3+}	-	-	-	1.2	1.5	1.8	3.8
Sm^{3+}	-	-	-	1.0	1.5	1.6	5.0
La^{3+}	-	-	-	1.2	1.5	1.8	4.5
Lu^{3+}	-	-	-	1.2	1.6	2.0	4.8
Yb^{3+}	-	-	-	1.2	1.6	2.0	5.0
Er^{3+}	-	-	-	1.2	1.5	1.8	6.0
Cd^{3+}	-	-	-	1.0	1.5	1.6	5.5
Nd^{3+}	-	-	-	1.0	1.5	1.8	5.0
Th^{4+}	-	-	-	1.2	1.6	2.0	5.0
Pb^{2+}	2.0	2.8	6.0	-	-	-	-
Ba^{2+}	2.0	3.0	7.0	-	-	-	-
Ca^{2+}	1.8	2.8	6.5	-	-	-	-
Sr^{2+}	1.8	3.0	8.4	-	-	-	-
Mn^{2+}	1.8	3.2	6.8	-	-	-	-
Cd^{2+}	2.0	3.2	6.8	-	-	-	-
Zn^{2+}	2.0	3.2	8.0	-	-	-	-
Co^{2+}	1.8	2.8	8.4	-	-	-	-
Ni^{2+}	2.0	3.8	6.5	-	-	-	-
Cu^{2+}	2.0	3.4	7.0	-	-	-	-

Legend of the figures

Fig. 4.1 : Nitro group reduction wave of 0.8 mM 7-nitro-8-hydroxyquinoline-5-sulfonic acid (NOSA) at 35°C, $\mu = 0.54$ M, pH 8.5

Fig. 4.2 : Calibration curve for NOSA at 35°C, $\mu = 0.54$ M, pH 8.5.

(ii) ESTIMATION OF THORIUM (IV) AND ZIRCONIUM (IV) WITH METANITROBENZOIC ACID BY A.C. AMPEROMETRY

The determination of Thorium (IV)[65] and Zirconium (IV)[121] by direct polarographic method is difficult. The value of their half-wave potentials being too negative to permit the recording of a wave before hydrogen or other cations of the supporting electrolyte are reduced. Indirect polarographic methods have been proposed which involve the reduction of the organic precipitant associated with Th(IV)[77] and Zr(IV)[78]. The present work deals with the use of m-nitrobenzoic acid both as a precipitant and as polarographic reducible substance in the direct estimation of Th(IV) and Zr(IV) by a.c. amperometry. D.C. amperometric and and indirect polarographic methods have also been carried out for comparison of results.

EXPERIMENTAL

Stock solution of m-nitrobenzoic acid (NBA) which was a recrystallized sample of L. Light and Co. (U.S.A.), was prepared in 70% ethanol. AnalaR grade ethanol was redistilled before use. All other chemicals were of reagent grade. The stock solution of thorium nitrate $Th(NO_3)_4.6H_2O$ and zirconyl chloride ($ZrOCl_2.8H_2O$) were prepared in 2M HNO_3 and 2M HCl respectively. The thorium content[277] and zirconium content[33] in their stock solutions were estimated gravimetrically. The constants of the d.m.e. were: m = 2.931 mg/s, t = 3.05 s in 0.54 M KCl (open circuit) at h = 40 cm (uncorrected for back pressure) for d.c. polarographic work and m = 4.564 mg/s, t = 1.8 s in 0.1 M KCl (open circuit) for a.c. polarographic work. Temperature was maintained at 30±0.1°C.

In the indirect polarographic method excess of NBA was added to solutions (40% in alcohol) containing thorium (IV) and zirconium (IV) and the pH adjusted to 3.4 and 3.0 respectively with ammonia. The solution containing the precipitate was kept at 60°C for one hour. The precipitate was filtered after cooling the solution. The precipitate was then washed with 40% ethanol and dissolved in a minimum volume of 2M $HClO_4$. 0.1M tartaric acid was added to the solution containing thorium (IV) to complex the thorium (IV) and 0.1M Na_2HPO_4 to the solution containing zirconium (IV) to precipitate zirconium (IV) so that subsequent adjustment of pH to 4.0 would not cause their reprecipitation as nitrobenzoates. The solutions were then buffered with 0.1M potassium hydrogen phthalate and finally the pH was adjusted to 4.0 by NaOH. The solutions were diluted to the required volume such that the concentration of NBA eventually did not exceed 1.0 mM. The solution was deoxygenated and polarographed. The concentration of NBA was found from its calibration curve (for the reduction of the nitro group) and thereby the concentrations of thorium (IV) and zirconium (IV) in the original test solutions were calculated from the stoichiometry of the complex i.e. thorium tetranitrobenzoates[121] and zirconium mononitrobenzoate[77] respectively.

In d.c. amperometry the potential applied to the d.m.e. was maintained at -0.8 V vs S.C.E. (which lies on the plateau of the nitro group reduction wave of NBA) and nitrogen gas was passed through the solution for 10 minutes after each addition of titrant.

In a.c. amperometry potential applied to the d.m.e. was maintained at -0.82 V for thorium (IV) and at -0.79 V for zirconium (IV) and better results were obtained for thorium (IV) at pH 3.4 and for zirconium (IV) at pH 3.0. NBA showed a peak at -0.82 V in pH 3.4 and at -0.79 V at pH 3.0 (vide Fig. 4.3). Before taking readings, 10 minutes were allowed to elapse after each addition of the titrant. 50 ml of test solutions were taken and M/30 NBA was used as titrant in amperometric methods.

RESULTS AND DISCUSSION

Table 4.3 gives the comparative results obtained in indirect polarographic, d.c. amperometric and a.c. amperometric methods for the estimation of thorium (IV) and zirconium (IV). It can be seen that a.c. amperometric method is more efficient than the other two methods.

The thorium to NBA ratio at the end point in a.c. amperometry was found to be 1:4 which agrees with the literature value[77] and the formula assigned may be $(m - NO_2C_6H_4COO)_4Th$.[121] It is known that zirconyl ion hydrolyses as follows:[122]

$$ZrO^{2+} + HOH \longrightarrow ZrO(OH)^{+} + H^{+}$$

The end point occurs at the Zr(IV) to NBA ratio of 1:1 which also agrees with the literature and the precipitate may be assigned the formula $(m - NO_2C_6H_4COO)ZrO(OH)$ which agrees with the literature value[78].

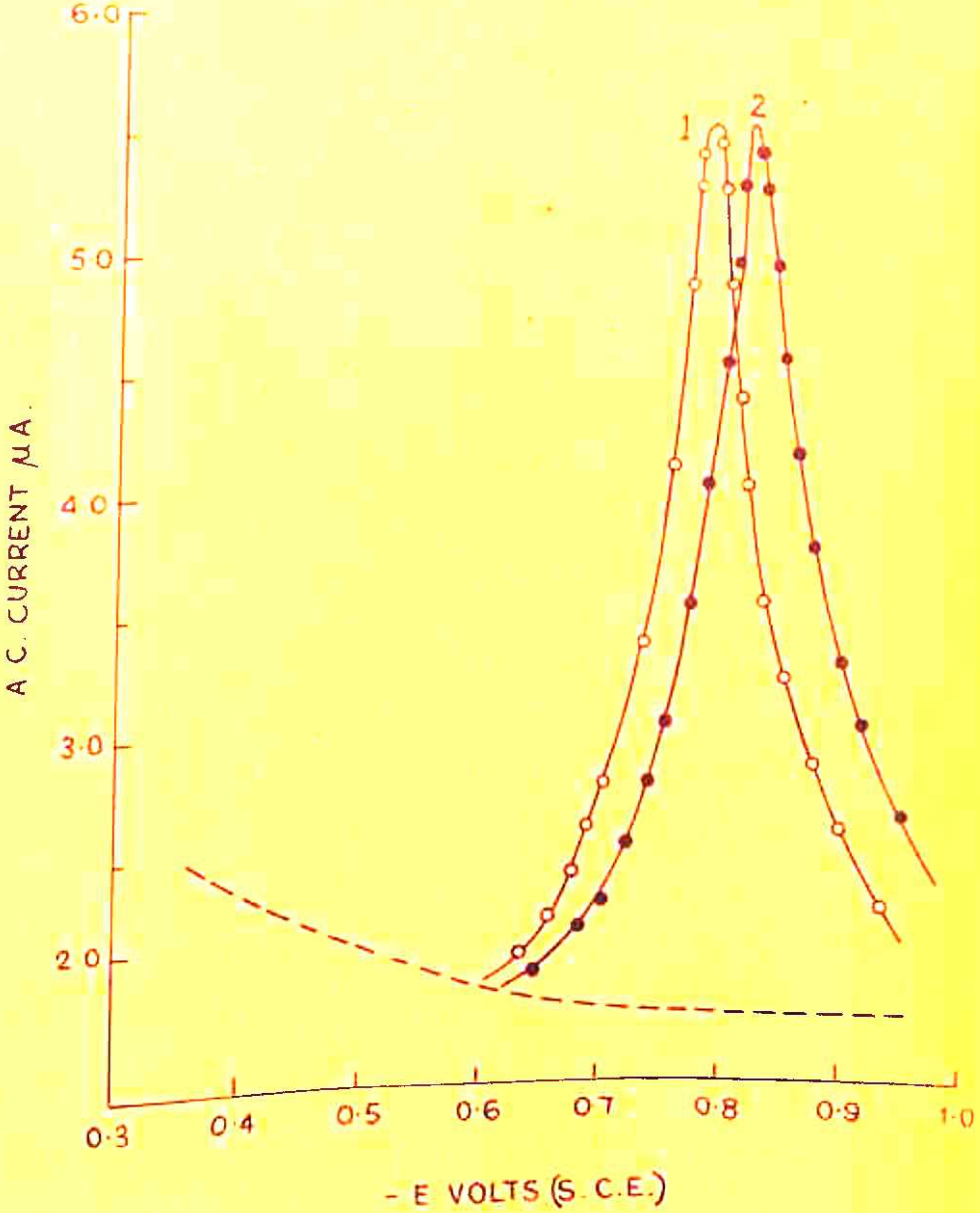


FIG. 4·3

Table 4.4 gives the result of a.c. amperometric estimation of 1.00 mM thorium (IV) and 1.00 mM zirconium (IV) at various pH. It can be seen that a pH of 3.4 is most suited for thorium (IV) estimations and a pH of 3.0 for zirconium (IV) estimations.

Fig. 4.4 shows typical curve obtained by a.c. amperometric titration for the estimation of 0.75 mM thorium (IV) and Fig. 4.5 for that of zirconium (IV) with M/30 NBA respectively.

Reverse titrations have also been carried out using thorium (5 mM) or zirconium (10 mM) as titrants in the estimation of 50 ml of 1.0 mM NBA by the a.c. amperometric method (Table 4.5). Figs. 4.6 and 4.7 show typical curves obtained for the a.c. amperometric titration of NBA by thorium and zirconium respectively. Thorium seems to give better results in the estimation of NBA, which may be due to the lesser solubility of the thorium tetranitrobenzoate.

The a.c. amperometric method is advantageous in that it is quicker and is free from the inherent possibility of precipitate losses in the process of its filtration and dissolution encountered in the indirect polarographic method. In addition, the deoxygenation of the solution before making current measurements was not necessary unlike in indirect polarographic and d.c. amperometric methods.

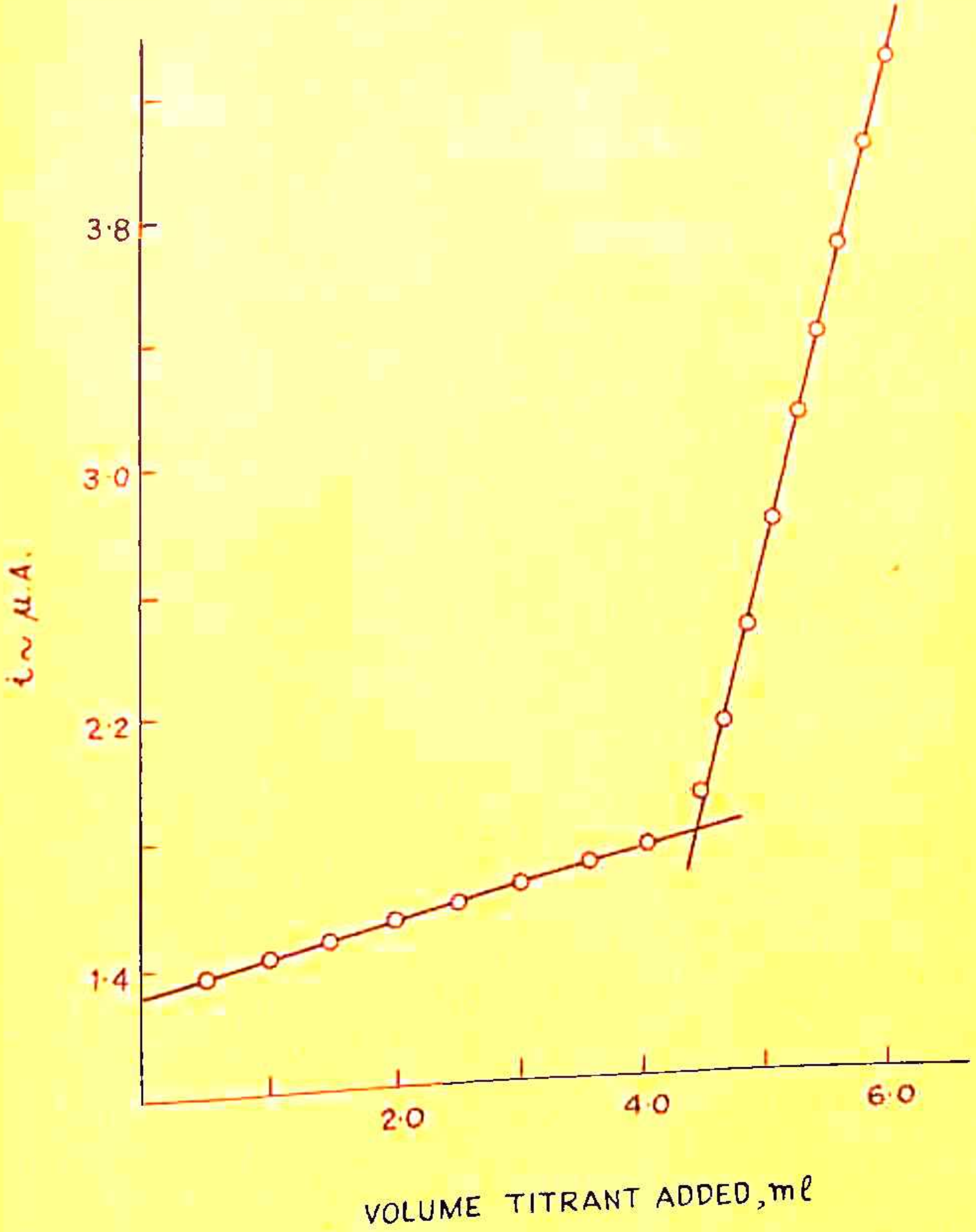


FIG. 4·4

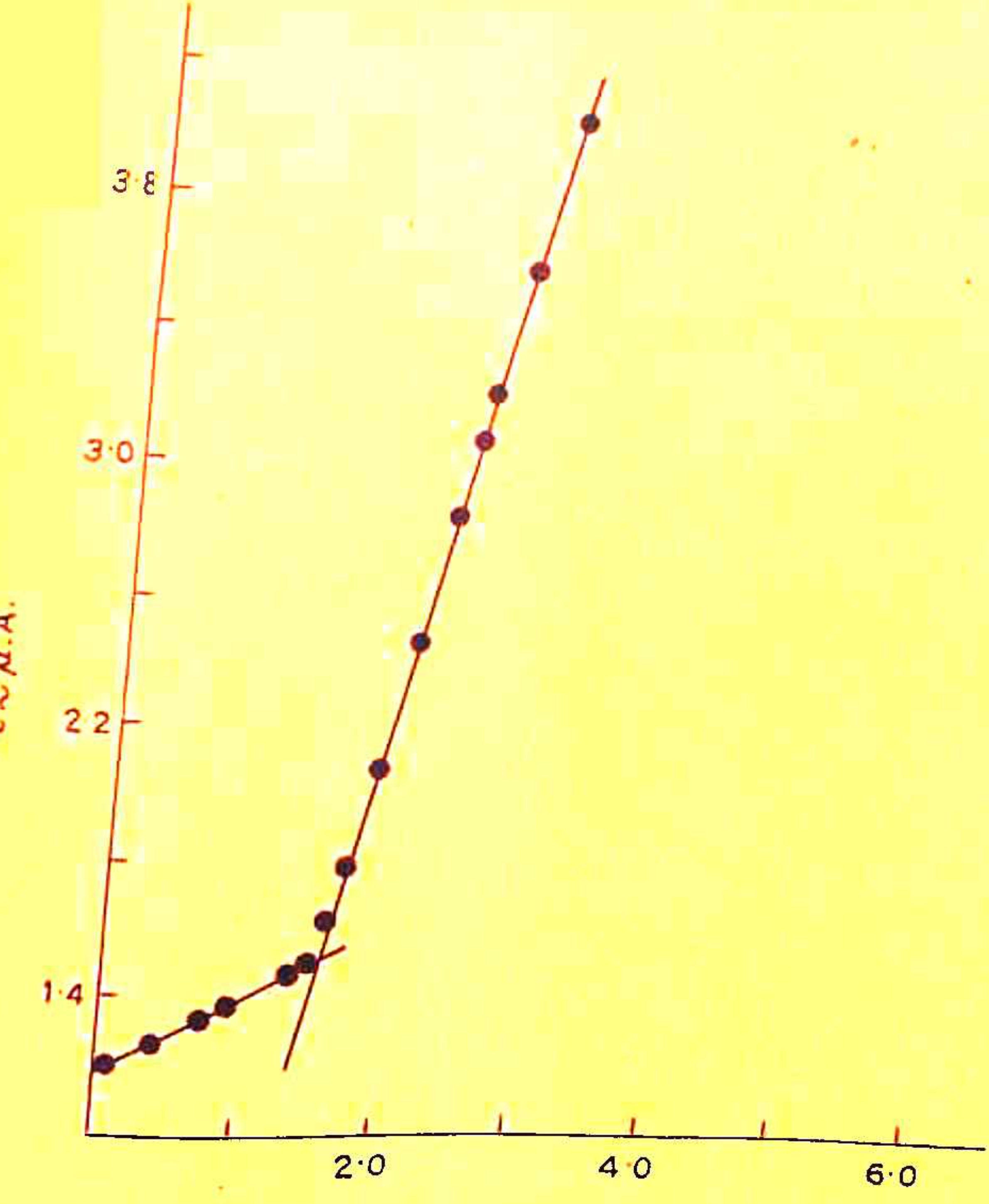


FIG. 4·5

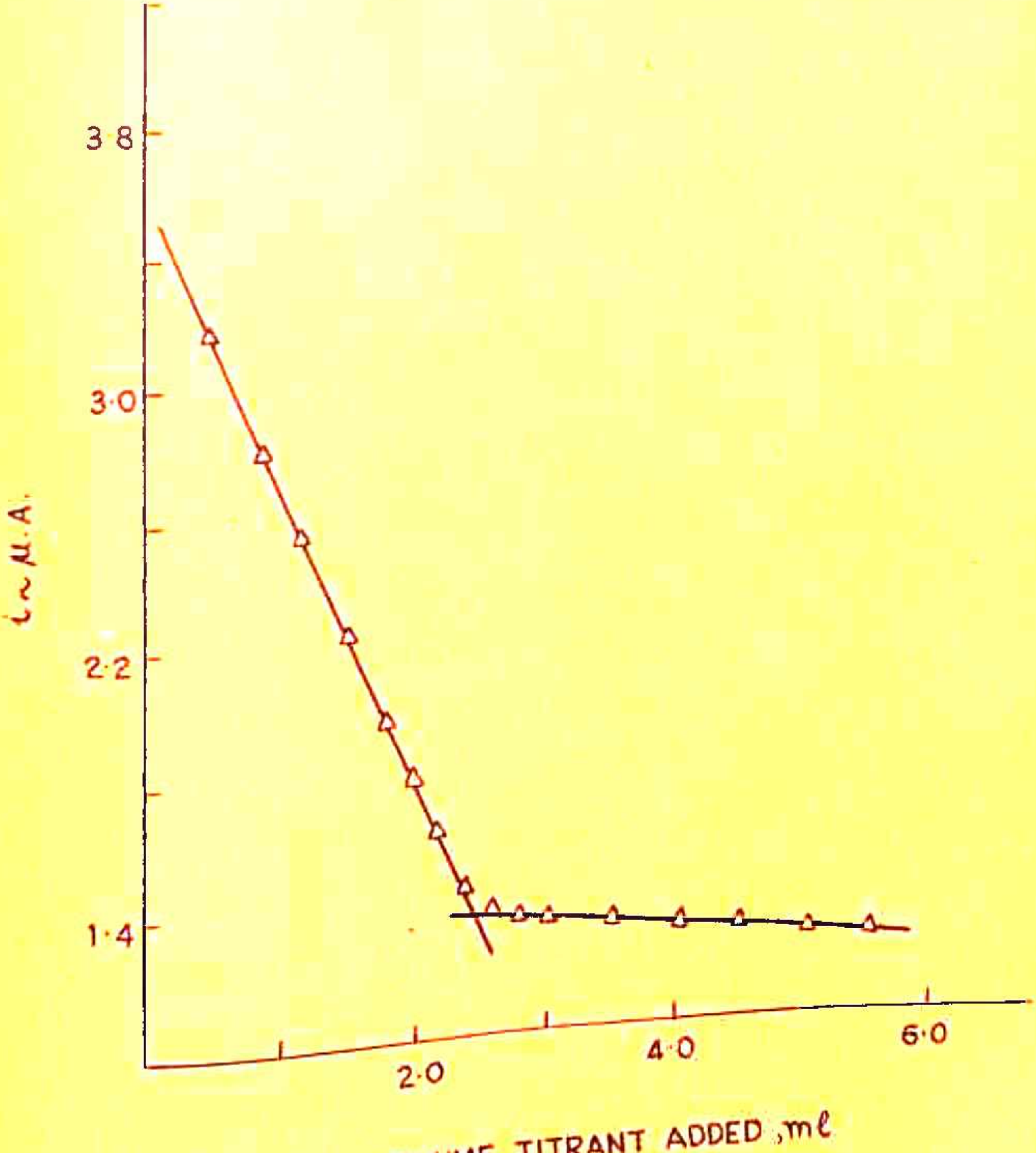


FIG. 4·6

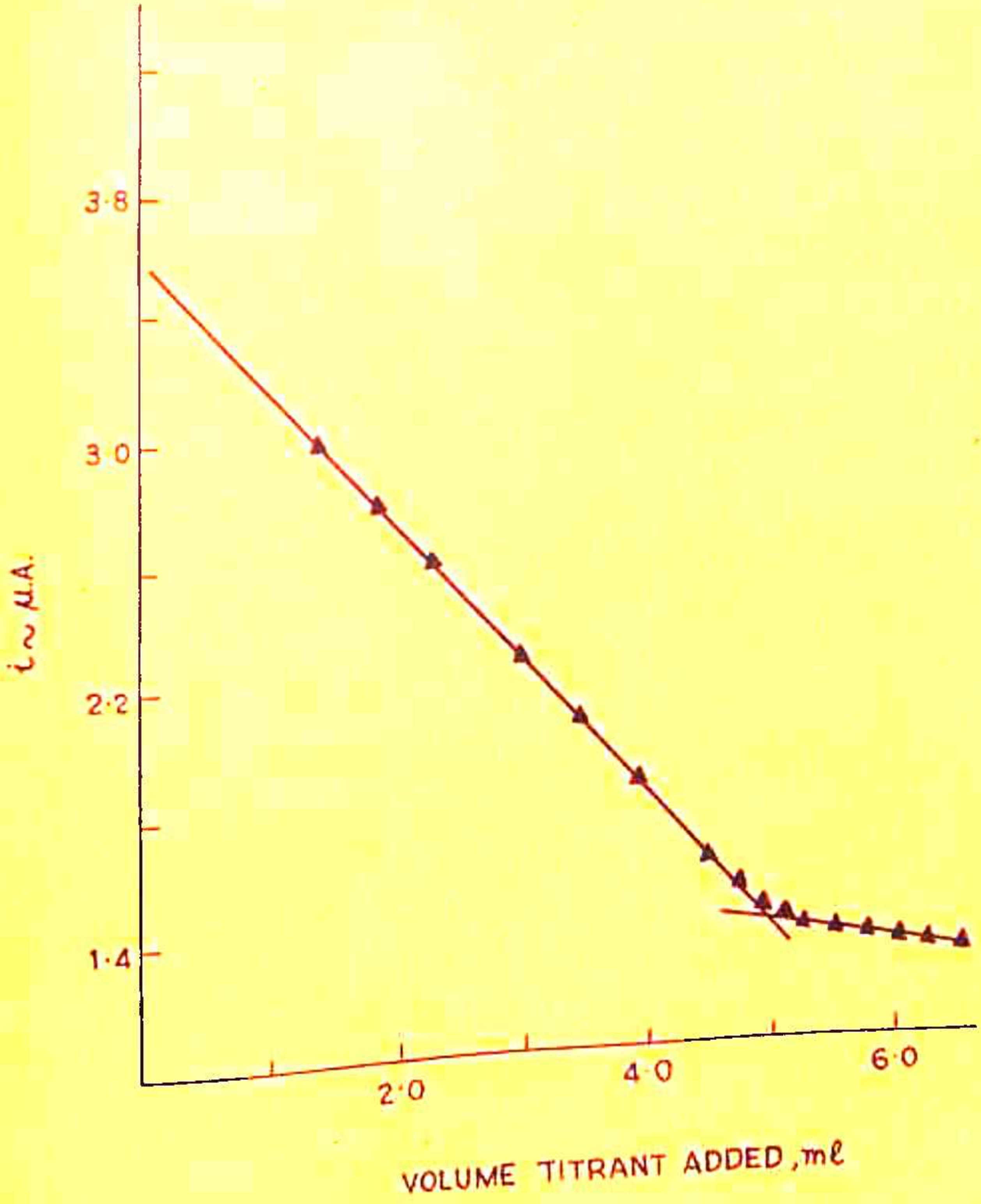


FIG. 4·7

TABLE 4.3 : Comparison of the results obtained by indirect polarographic, d.c. [illegible] amperometric methods in the estimation of Th(IV) and Zr(IV) with m-nitrobenzoic acid

Composition of test soln. mM/litre	% Error		
	Indirect polarographic method	D.C. amperometry	A.C. amperometry
1.00 Th(IV)	-2.4	-3.0	-1.5
0.75 Th(IV)	-3.0	-3.4	-2.0
0.50 Th(IV)	-3.2	-4.0	-2.0
1.33 Zr(IV)	-2.4	-3.2	-1.5
1.00 Zr(IV)	-2.8	-3.8	-2.0
0.67 Zr(IV)	-3.6	-4.6	-3.0

TABLE 4.4 : Effect of pH on the estimation of Th(IV) and Zr(IV) with m-nitrobenzoic acid by a.c. amperometry

pH	(Potential applied to the d.m.e.) peak potential of NBA V vs S.C.E.	% Error	
		Thorium (1.0 mM)	Zirconium (1.0 mM)
2.2	-0.72	-3.8	-4.4
2.6	-0.76	-2.2	-3.2
3.0	-0.79	-1.5	-2.6
3.4	-0.82	-2.0	-2.0
3.8	-0.84	-2.8	-3.0
4.2	-0.86	-4.2	-4.6

TABLE 4.5 : Reverse a.c. amperometric titrations of m-nitrobenzoic acid (NBA) with thorium (IV) and zirconium (IV)

Concentration of NBA mM/litre	% Error	
	5 mM thorium as titrant	10 mM zirconium as titrant
1.00	-1.2	-1.6
0.75	-1.2	-1.9
0.50	-1.6	-2.4

Legend of the figures

Fig. 4.3 : Curve 1. A.C. polarogram of 1.0 mM NBA at pH 3.0
Curve 2. A.C. polarogram of 1.0 mM NBA at pH 3.4

A.C. amperometric titrations

Fig. 4.4 : 50.0 ml, 0.75 mM Th(IV) vs $\frac{M}{30}$ NBA, pH 3.4, E_p = -0.82 V vs S.C.E.

Fig. 4.5 : 50.0 ml, 1.0 mM Zr(IV) vs $\frac{M}{30}$ NBA, pH 3.0, E_p = -0.79 V vs S.C.E.

Fig. 4.6 : 50.0 ml, 1.0 mM NBA vs 5.0 mM Th (IV), pH 3.4, E_p = -0.82 V vs S.C.E.

Fig. 4.7 : 50.0 ml, 1.0 mM NBA vs 10.0 mM Zr(IV), pH 3.0, E_p = -0.79 V vs S.C.E.

(iii) ESTIMATION OF Ba^{++}, Ag^{+} AND Tl^{+} AS CHROMATES BY A.C. AMPEROMETRY

Kolthoff et al.[154,155] estimated barium with chromate ion in aqueous and aqueous-ethanol mixtures by conventional amperometric titration which yielded results that were 2 to 5% low. Many others[276,279] have also studied the precipitation of Ba^{++} as chromate. Kalvoda and Zyka[143] estimated Tl^{+} in the concentration range 10^{-3} to 10^{-2} M in 0.3 M KNO_3 containing 10% acetone using dichromate ion. However, no data are available for such determinations using a.c. polarography. The present investigation therefore, gives the results obtained in the estimation of Ba^{++}, Ag^{+} and Tl^{+} as chromates in aqueous-methanol and aqueous-ethanol mixtures by a.c. amperometry and the comparison of the results by d.c. amperometry.

EXPERIMENTAL PROCEDURE

Pure recrystallised samples of barium chloride ($BaCl_2.2H_2O$), silver nitrate, thallous sulphate (Tl_2SO_4), potassium chromate and indifferent electrolytes (BDH, AR) were used. Methanol, ethanol and acetone were AnalaR grade which were redistilled in an all-glass fractionating column and the middle one-third of the distillate was used for experiments.

The experiments were carried out at a temperature of 30±0.2°C. The constants of the d.m.e. were: m = 4.564 mg/s and t = 1.8 s in 0.1 M KCl, open circuit for a.c. and

$m = 2.931$ mg/s, $t = 3.05$ s in 0.54 M KCl (open circuit) at $h = 40$ cm (uncorrected for back pressure) for d.c. polarographic work. 0.1 M KCl was used as supporting electrolyte for the titration of Ba^{++} whereas 0.1 M KNO_3 solution was used for the titration of Ag^+ and Tl^+.

Gupta and Sharma[103,104,109] estimated different metal ions at their peak potentials with precipitating agents by a.c. amperometric titrations. The above method could not be applied for the estimation of Ba^{++} and Ag^+ as these do not give a.c. peaks. For such estimations, potential at which the electrode is sensitive to the precipitating agent, such as chromate, is employed. However, Tl^+ could be estimated both at its peak potential and at the peak potential of the chromate ion. Chromate ion provides two a.c. peaks around -0.2 V and -1.3 V in aqueous-methanol and aqueous-ethanol using 0.1 M KCl (Fig. 4.8) or 0.1 M KNO_3 as supporting electrolytes. In the case of acetone-water mixtures the peak potentials shifted towards more cathodic side, and the magnitude of the current decreased with increase in acetone concentration. The second peak, was chosen for carrying out titrations as it was more pronounced than the first one. Fig. 4.9 depicts the a.c. polarogram of Tl^+.

A known excess of K_2CrO_4 was added to Ba^{++} test solution of suitable strength containing appropriate amount of alcohol or acetone and the excess of chromate was back titrated with standard barium chloride solution. The back titration was found more suitable for the estimation of Ba^{++}, Ag^+ and Tl^+

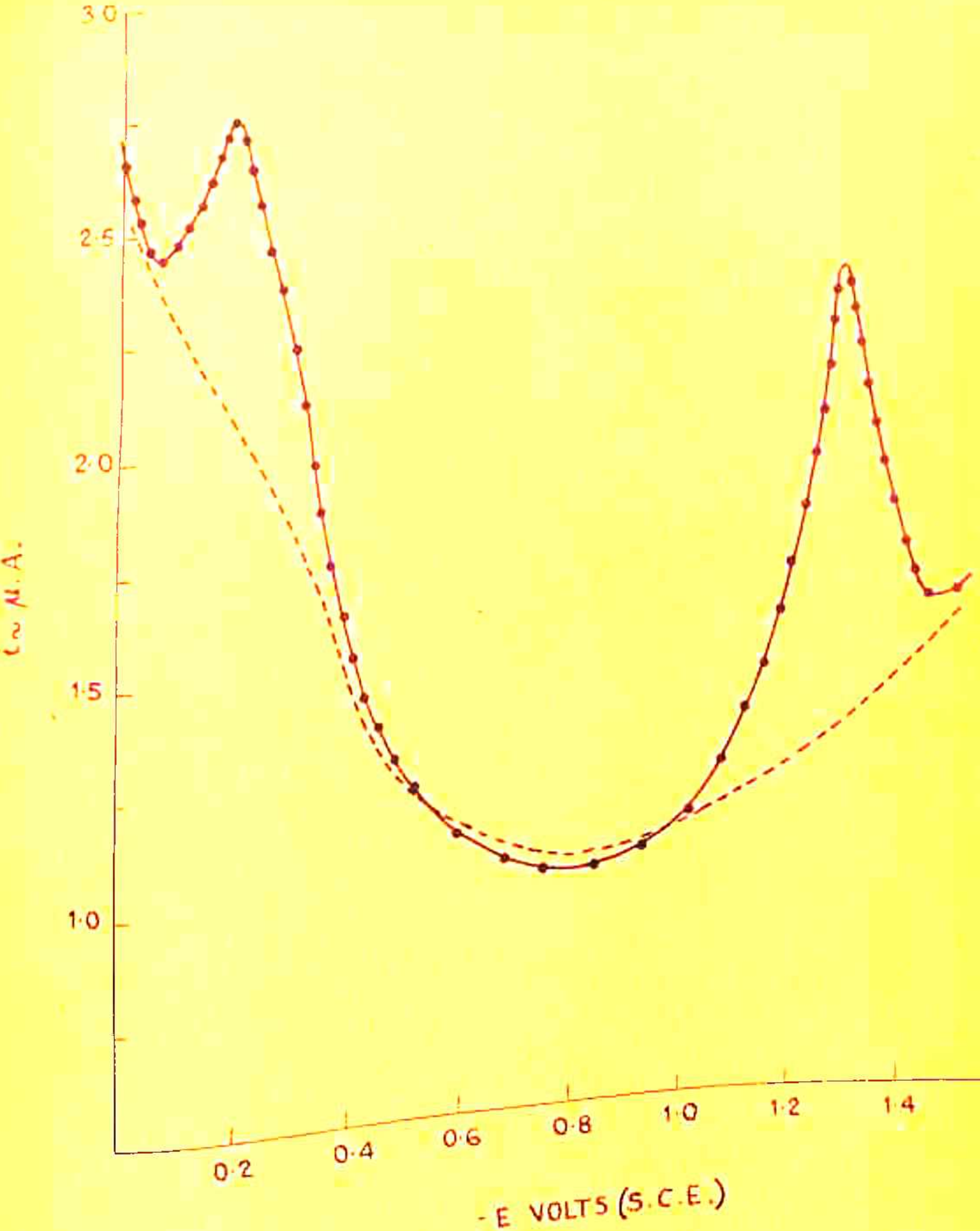


FIG. 4·8 A.C. POLAROGRAM OF CrO_4^{--}.

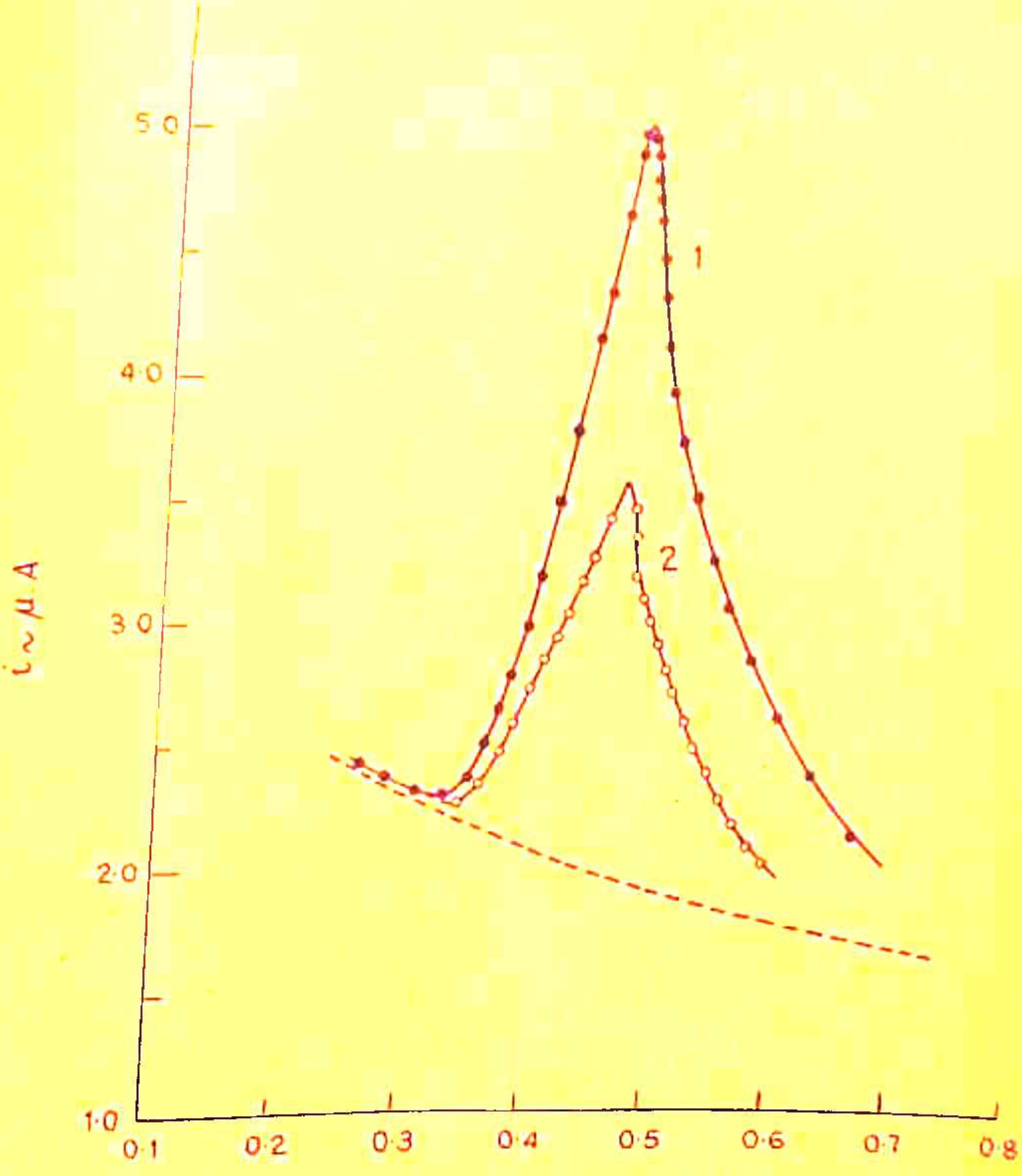


FIG. 4·9 A.C. POLAROGRAMS OF Tl$^+$.

were, however, estimated by direct a.c. amperometric titrations. The potential of the d.m.e. in d.c. amperometry was kept at -1.4 V which lies on the plateau of the current-voltage curves of CrO_4^{--} vide Fig. 4.10. Titrations were carried out at pH 6.8.

RESULTS AND DISCUSSION

A.C. Amperometry

It was found that 0.1 M or 0.2 M KCl gave best results in the case of Ba^{++}. The other supporting electrolytes in which these studies were carried out were 0.1 M solutions of KNO_3, KI, KCNS, NaCl, $NaNO_3$, LiCl, $CaCl_2$, $MgCl_2$ and $AlCl_3$. It was found that in solutions of KI, KCNS, $CaCl_2$, $MgCl_2$ and $AlCl_3$ erroneous results were obtained. This may be ascribed to the surface active nature of I^- and CNS^- ions and to the charge effect in the case of $CaCl_2$, $MgCl_2$ and $AlCl_3$. The optimum pH range was found to be 5.5 to 7.0 in the case of Ba^{++} and 6.0 to 7.0 in those of Ag^+ and Tl^+. It was observed that solutions containing 10% methanol, 20% ethanol or 5% acetone gave fairly good results in the case of Ba^{++}. In the case of Ag^+, solutions containing 20% ethanol were found most suitable. In the case of Tl^+, best results were obtained in solutions containing 10% methanol when titrated at the peak potential of Tl^+ ion viz. -0.47 V and in solutions containing 20% ethanol when titrated at the reduction potential of chromate ion viz. -1.32 V.

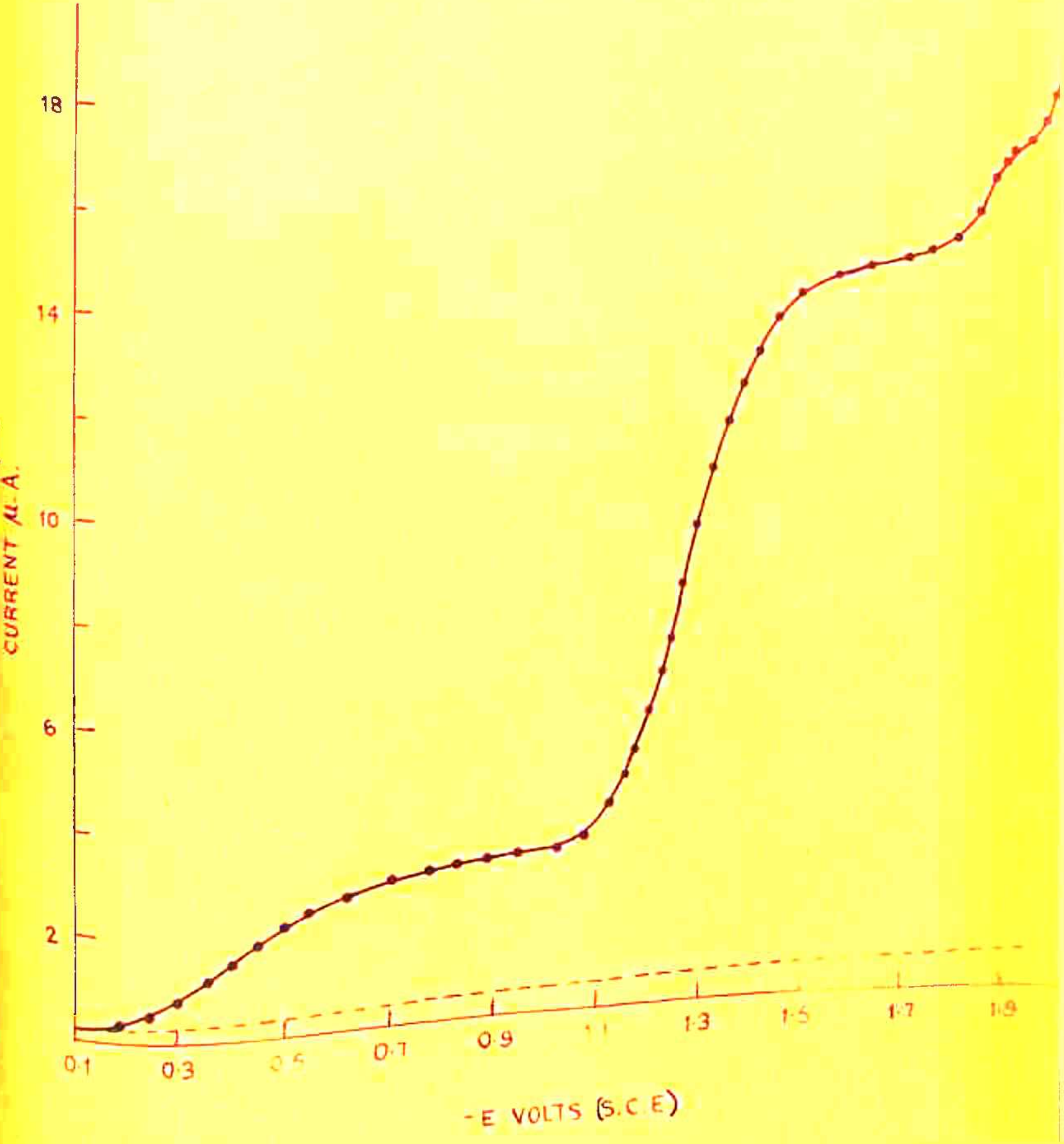
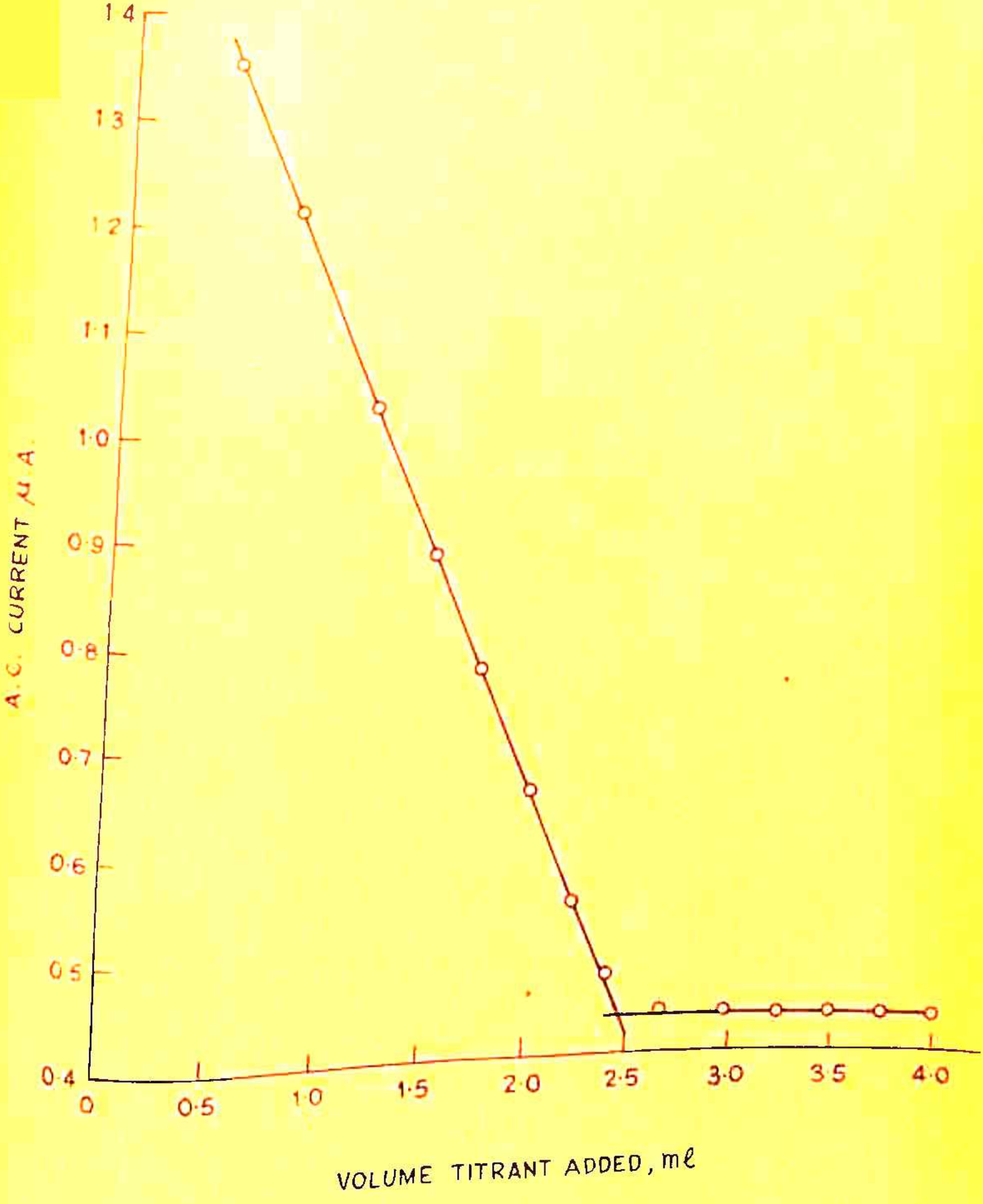


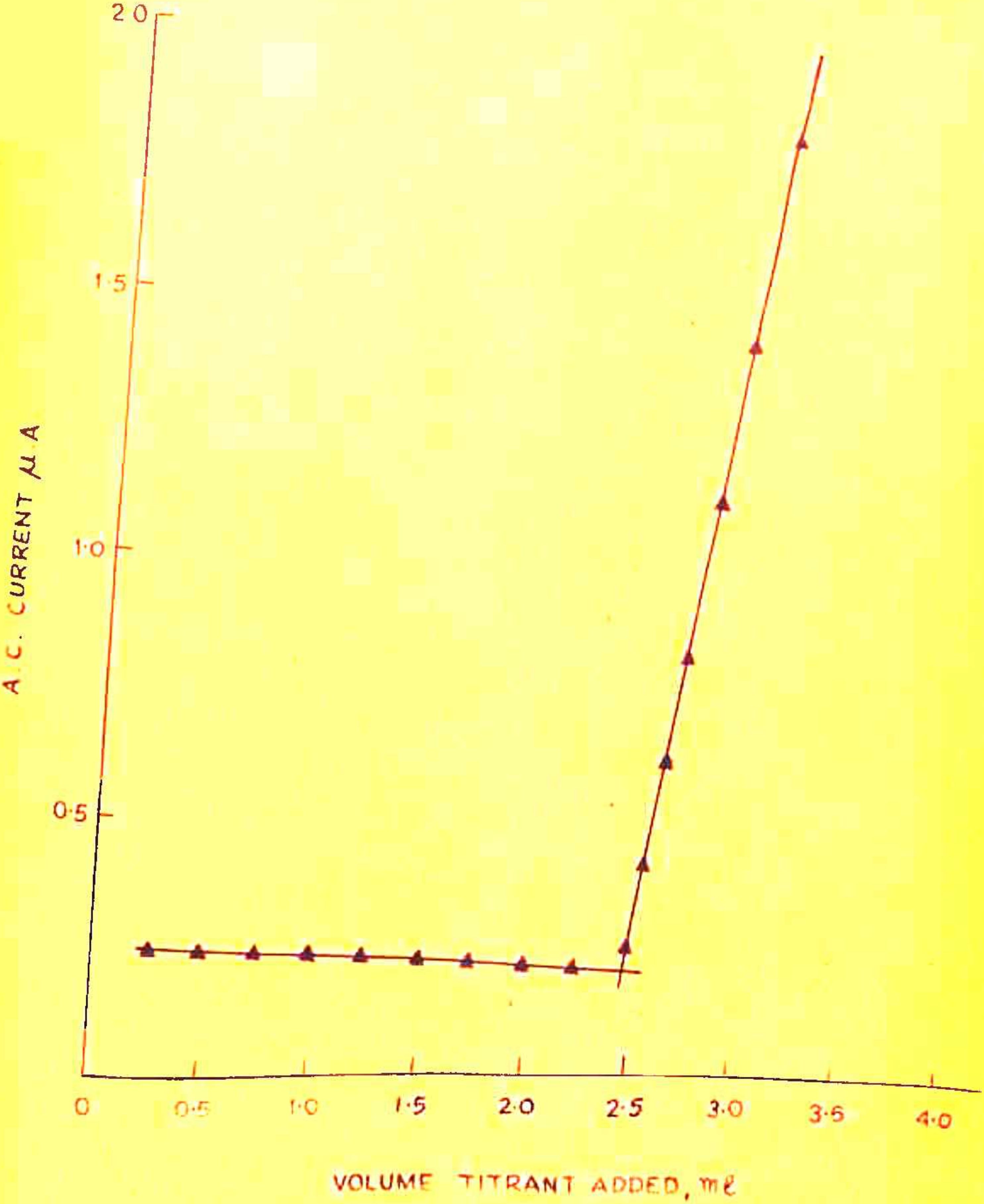
FIG 4·10 D.C POLAROGRAM OF CrO_4^{--}.

Typical a.c. amperometric curve depicting the result obtained in the titration of 0.5 mM excess chromate in each case at -1.32 V are given in Fig. 4.11 and the results are recorded in Table 4.6. Fig. 4.12 depicts the a.c. amperometric curve in the titration of 1.0×10^{-2} M Ag^+ with K_2CrO_4. Figs.4.13 and 4.14 show the results obtained in the a.c. amperometric titration of 0.6 mM Tl^+ at -1.32 V and -0.47 V respectively. It can be seen that concentration of Ba^{++} as low as 2.0×10^{-4} M can be estimated by back titration method with good accuracy. However, the accuracy in the case of Ag^+ (Table 4.7) decreased considerably below the concentration of 8.0×10^{-3} M. The estimation of Tl^+ (Table 4.8) upto 1.0×10^{-3} M could be done with fairly accurate results, though at lower concentrations of Tl^+ the error increased. The error in most cases is within 1.5% in a.c. amperometric titrations. By comepring the results obtained in d.c. amperometric titrations (Tables 4.6, 4.7 and 4.8) it can be seen that a.c. amperometric titrations give better results.



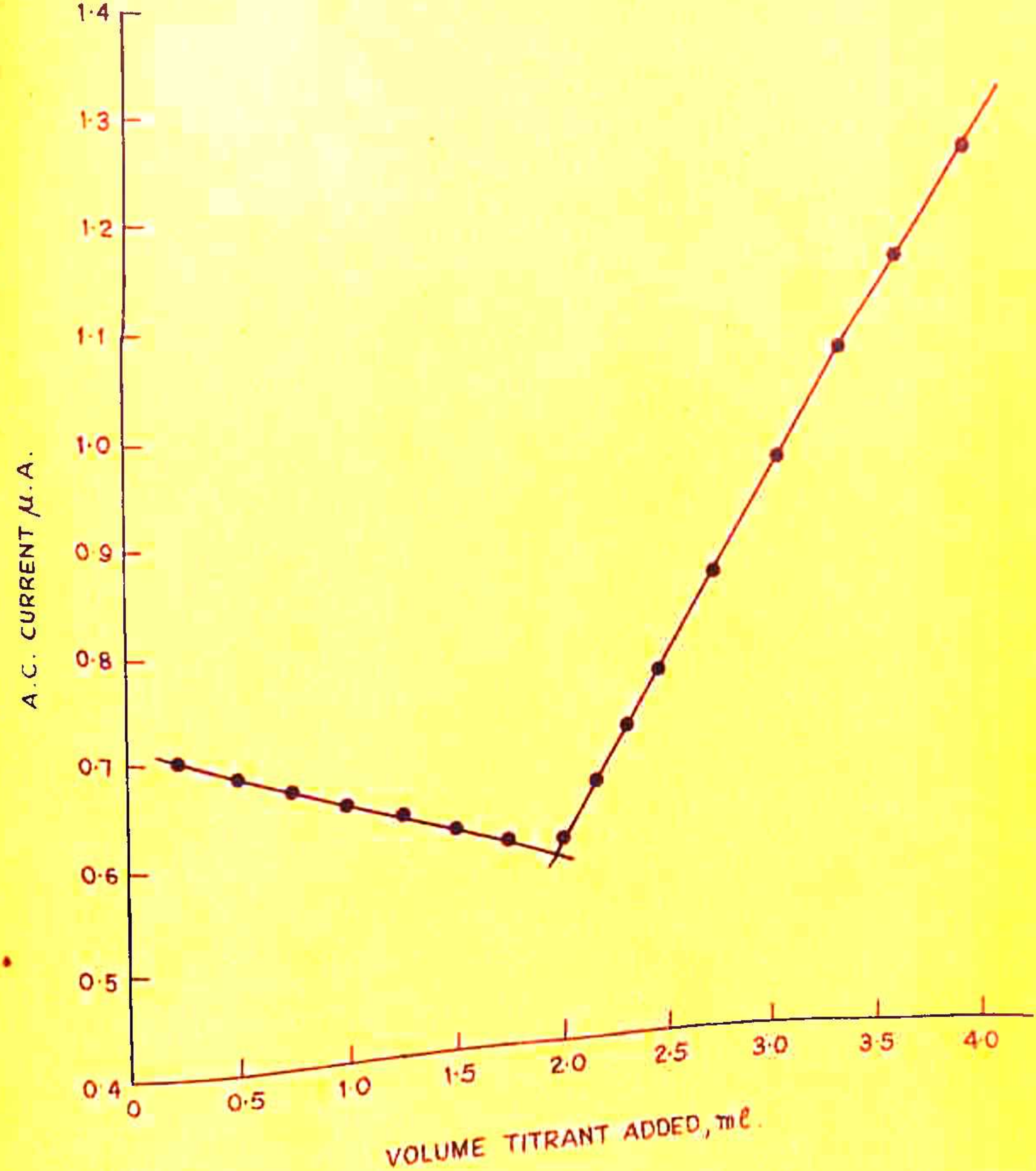
A.C. CURRENT μ.A.
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
VOLUME TITRANT ADDED, ml

FIG. 4·11



2.0
1.5
1.0
0.5
A.C. CURRENT μA
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
VOLUME TITRANT ADDED, mℓ

FIG. 4.12



1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
A.C. CURRENT μ.A.
0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
VOLUME TITRANT ADDED, ml.

FIG. 4·13

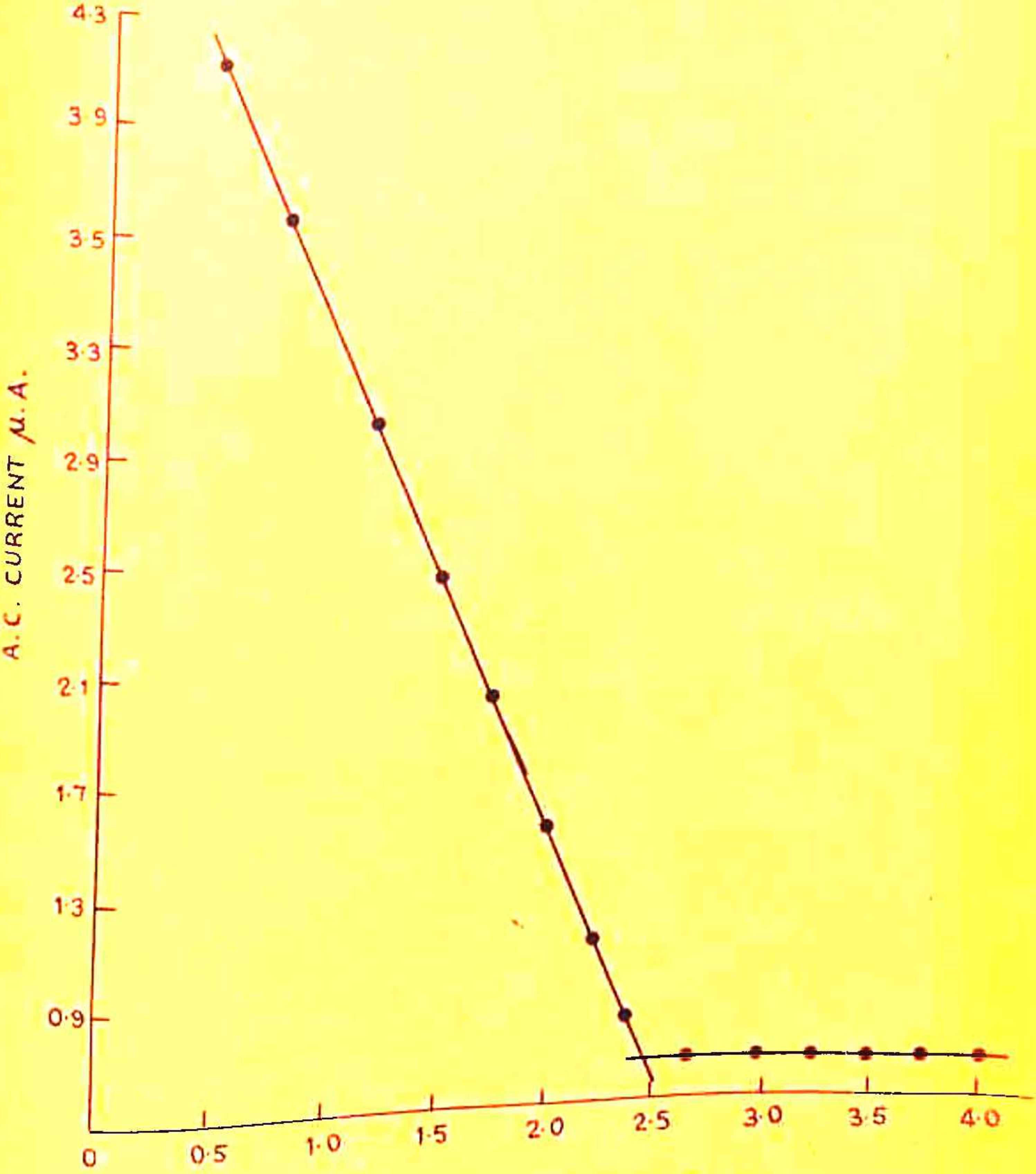

4·3
3·9
3·5
3·3
2·9
2·5
2·1
1·7
1·3
0·9
A.C. CURRENT μ.A.
0
0·5
1·0
1·5
2·0
2·5
3·0
3·5
4·0
VOLUME TITRANT ADDED, ml.

FIG. 4·14

TABLE 4.6 : A.C. and D.C. amperometric titrations of Ba^{++} with potassium chromate

Concentration mole/litre	Titrant and its concentration mole/litre	Error %	
		A.C. Amperometry	D.C. Amperometry
Ba^{++}($BaCl_2$, 0.1 M KCl, Excess CrO_4^{--} 0.5 × 10^{-3}M)*			
1.0 × 10^{-3}	$BaCl_2$,0.01	-0.8	-2.0
0.5 × 10^{-3}	-do-	-0.8	-3.2
0.25 × 10^{-3}	-do-	-1.6	-3.6
Ba^{++}($BaCl_2$, 0.1 M KCl, direct titration)*			
1.0 × 10^{-3}	K_2CrO_4,0.01	-3.0	-3.0
0.5 × 10^{-3}	-do-	-3.4	-3.6
0.25 × 10^{-3}	-do-	-3.8	-4.2

* 50.0 ml, 20% ethanol, pH = 6.8, E_p = -1.32 V or $E_{d.c.}$ = -1.4 V vs S.C.E.

TABLE 4.7 : A.C. and D.C. amperometric titrations of Ag^+ with potassium chromate

Concentration mole/litre	Titrant and its concentration mole/litre	Error %	
		A.C. amperometry	D.C. amperometry
	$Ag^+(AgNO_3$, 0.1 M $KNO_3)^*$		
1.0×10^{-2}	K_2CrO_4,0.1	-1.2	-1.5
0.8×10^{-2}	-do-	-1.5	-2.0
0.5×10^{-2}	-do-	-3.2	-3.2

* 50.0 ml, 20% ethanol, pH = 6.8, E_p = -1.32 V or $E_{d.c.}$ = -1.4 V vs S.C.E.

TABLE 4.8 : A.C. and D.C. amperometric titrations of Tl^+ with potassium chromate

Concentration mole/litre	Titrant and its concentration mole/litre	Error %	
		A.C. amperometry.	D.C. amperometry
	$Tl^+(Tl_2SO_4$, 0.1 M $KNO_3)^*$		
2.0×10^{-3}	K_2CrO_4,0.1	-1.0	-1.5
1.0×10^{-3}	-do-	-1.2	-1.5
0.6×10^{-3}	-do-	-2.7	-3.0
2.0×10^{-3}**	K_2CrO_4,0.01	-1.2	-
1.0×10^{-3}**	-do-	-1.2	-
0.6×10^{-3}**	-do-	-3.3	-
0.4×10^{-3}**	-do-	-5.0	-

* 50.0 ml, 20% ethanol, pH = 6.8, E_p = -1.32 V or $E_{d.c.}$ = -1.4 V vs S.C.E.

** 50.0 ml, 10% ethanol, pH = 6.8, E_p= -0.47 V vs S.C.E.

Legend of tne figures

Fig. 4.8 : A.C. polarogram of 1.0 mM CrO_4^{--}

Fig. 4.9 : A.C. polarograms of 0.6 mM Tl^+ (curve 1) and 0.3 mM Tl^+ (curve 2)

Fig. 4.10 : D.C. polarogram of 0.5 mM CrO_4^{--}

A.C. amperometric titration of Ba^{++}, Ag^+ and Tl^+

50.0 ml of test solution in 20% ethanol

Fig. 4.11 : 1.0×10^{-3} M Ba^{++} + 0.5×10^{-3} M excess CrO_4^{--} vs 0.01 M Ba^{++} at -1.32 V vs S.C.E.

Fig. 4.12 : 1.0×10^{-2} M Ag^+ vs 0.1 M CrO_4^{--} at -1.32 V vs S.C.E.

Fig. 4.13 : 0.8×10^{-3} M Tl^+ vs 0.01 M CrO_4^{--} at -1.32 V vs S.C.E.

Fig. 4.14 : 0.8×10^{-3} M Tl^+ vs 0.01 M CrO_4^{--} at -0.47 V vs S.C.E.

(iv) A.C. POLAROGRAPHIC AND SPECTROPHOTOMETRIC STUDIES ON Fe (III)-7-NITRO-8-HYDROXYQUINOLINE-5-SULFONIC ACID COMPLEX

The conventional polarographic method can be applied to the study of complex metal ions since the half-wave potentials of metal ions are shifted usually to more negative values by complex formation. Quantitative information regarding the formula and stability constant of the complex can be obtained by measuring this shift as a function of the concentration of the complexing agent provided the reduction or oxidation of the metal ion complex takes place reversibly at the d.m.e.

Kolthoff and Lingane[156] have shown that the shift in half-wave potential due to the formation of a metal complex $MX^{(n-pb)+}$ for a solvated cation M^{n+} and a ligand X^{-b} can be given approximately by

$$\Delta E_{0.5} = (E_{0.5})_s - (E_{0.5})_c = \frac{0.0591}{n} \log \beta_p + \frac{0.0591}{n} p \log C_x \tag{18}$$

where $(E_{0.5})_s$ and $(E_{0.5})_c$ are the half-wave potentials for the reduction of the simple and complex ions respectively. C_x is the total concentration of the complexing ligand 'X' and 'β_p' is the stability constant of the complex MX_p. Equation (18) has been derived with the assumption that all the reactions at the d.m.e. are reversible and very rapid as compared with rates of ionic diffusion.

According to Kolthoff and Lingane[157] when the free energies of the various possible oxidation states of a complex metal ion are sufficiently different, reduction from a higher to lower oxidation state can proceed in stages at the d.m.e. to produce a polarogram consisting of two or more separate waves. For a polarogram consisting of two waves they have represented the stepwise reduction of the complex by two equations.

For many systems the plot of $(E_{0.5})_c$ vs log C_x is a nonlinear continuous curve indicating the presence of more than one complex of varying stabilities. Deford and Hume[34,35] have treated such cases adequately by giving the relations between the change in half-wave potential and the free ligand concentration.

Gupta and Chatterjee[110] were the first to apply a.c. polarography to study complexes. They introduced summit potentials in place of half-wave potentials into the Kolthoff and Lingane equation for the reduction wave of a complex ion, and have shown the equation, given below, to be suitable for determining the ligand number and stability constant of the cadmium ammonia complex.

$$\Delta E_p = (E_p)_s - (E_p)_c = \frac{0.0591}{n} \log \beta_p + \frac{0.0591}{n} p \log C_x \qquad (19)$$

where $(E_p)_s$ and $(E_p)_c$ denote peak potentials of simple ion and complex species respectively. It follows from the above equation that a plot of $(E_p)_c$ against log C_x should be a straight line with a slope of $-\frac{0.0591}{n}$ p, with an intercept of $-\frac{0.0591}{n} \beta_p$ wherefrom the values of "p" and "β_p" can be calculated knowing the number of electrons "n" involved in the reduction process.

D.C. polarography has been applied to the study of complexes like cadmium-ammonia[204], cadmium-iodide[275], lead-hydroxide[158], lead-oxalate[205] and many others. A.C. polarography has been used for the study of cadmium-ammonia[110], cupric-β-resorcylic acid[112,113], cadmium-oxalate[114], zinc-thiocyanate[114], all involving one reduction peak. Studies on complexes of copper with ammonia and pyridine[115] and on complexes of copper and ferric ions with sulfosalicylic acid[246] have also been carried out by a.c. polarography.

The present investigation gives the results obtained in the study of the Fe(III)-7-nitro-8-hydroxyquinoline-5-sulfonic acid system on which no polarographic data are available in literature. The same system has also been studied by spectrophotometry for confirmation of results.

EXPERIMENTAL

7-nitro-8-hydroxyquinoline-5-sulfonic acid (NOSA) was prepared as described by Welcher[280]. The stock solution of Iron(III) was prepared by dissolving ferric nitrate (E. Merck) in distilled water and the iron content was estimated by usual methods. Sodium perchlorate was used as the supporting electrolyte and pH was adjusted by HCl. The d.m.e. had the following characteristics: m = 4.564/s and t = 1.8 s in 0.1 M KCl (open circuit). Temperature was maintained at 30±0.1°C. Ionic strength was maintained by $NaClO_4$.

Absorbance measurements were made with a Hilger Uvispec Spectrophotometer (Model H 700-308) equipped with thermoplates to stabilize the temperature of the cell holder.

RESULTS AND DISCUSSION

A.C. Polagraphic Studies

The d.c. polarographic reduction of NOSA at the d.m.e. has been described in Chapter III of this thesis. Spectrophotometric studies revealed that a stable complex was formed in solution in the pH region 2.0 to 3.0. In this pH region NOSA gave a d.c. polarographic wave which seriously interfered with the wave due to Fe(III). Thus the shift in the half-wave potential of Fe(III) could not be determined with d.c. polarography. NOSA did not give a.c. polarographic peak in this pH region whereas Fe(III) gave a peak. This enabled the study of the shift in the peak of Fe(III). Fig.4.15 shows the a.c. polarograms of Fe(III) and Fe(III)-NOSA complex. The peak potential is shifted to more cathodic side thereby showing complex formation.

Fig. 4.16 depicts the plot of $(-E_p)_c$ and log concentration of NOSA, which yields a straight line with a slope of -0.1822 at pH 2.5. From this slope, using equation (20), the value of "p" has been calculated to be $3.083 \simeq 3$ with $n = 1$. This gives the formula of the complex to be $Fe(NOSA)_3$. This agrees with the value obtained spectrophotometrically which will be described later.

$$\frac{\Delta E_{0.5}}{\Delta \log C_x} = - p \frac{0.0591}{n} \qquad (20)$$

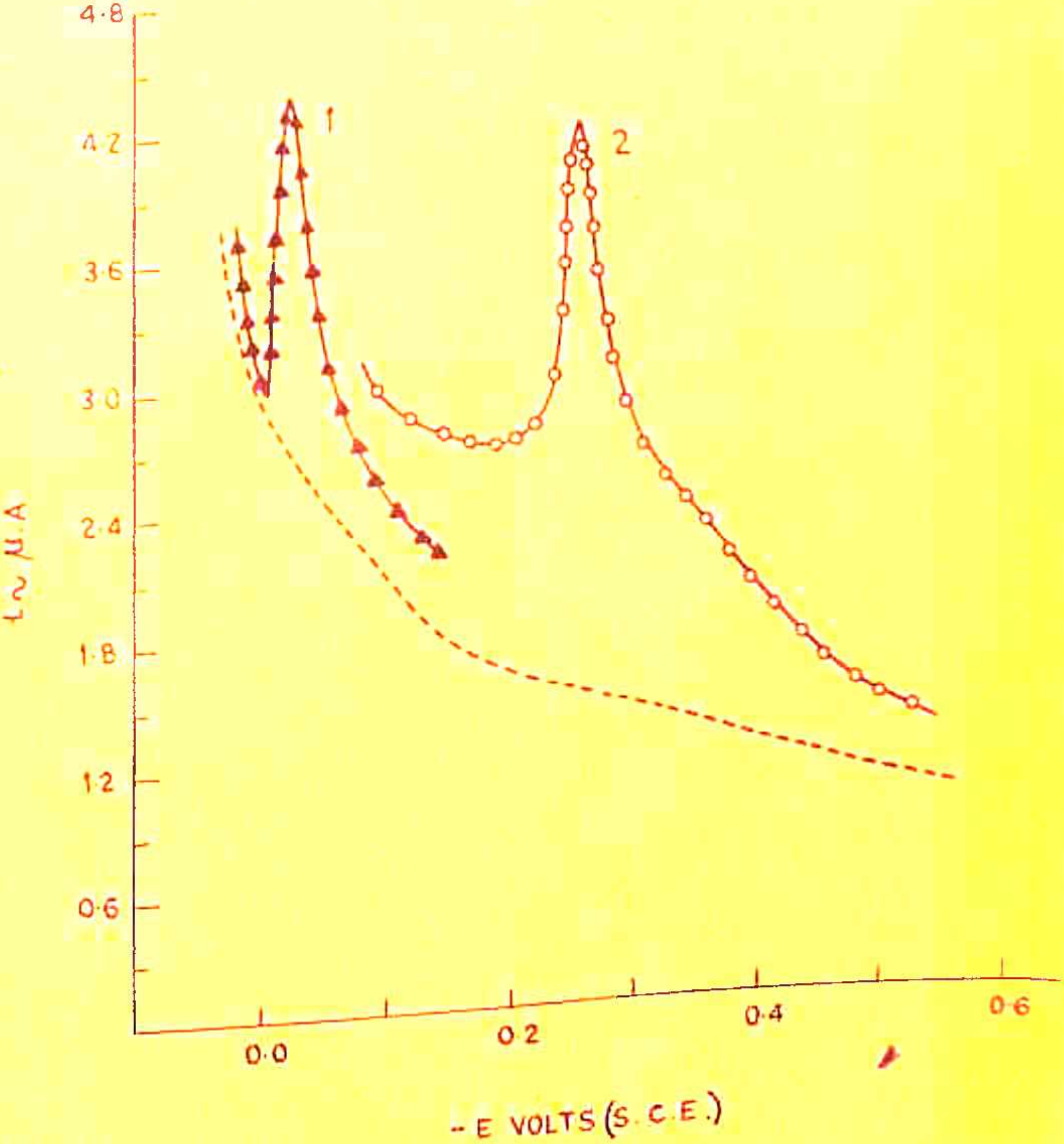


FIG. 4·15

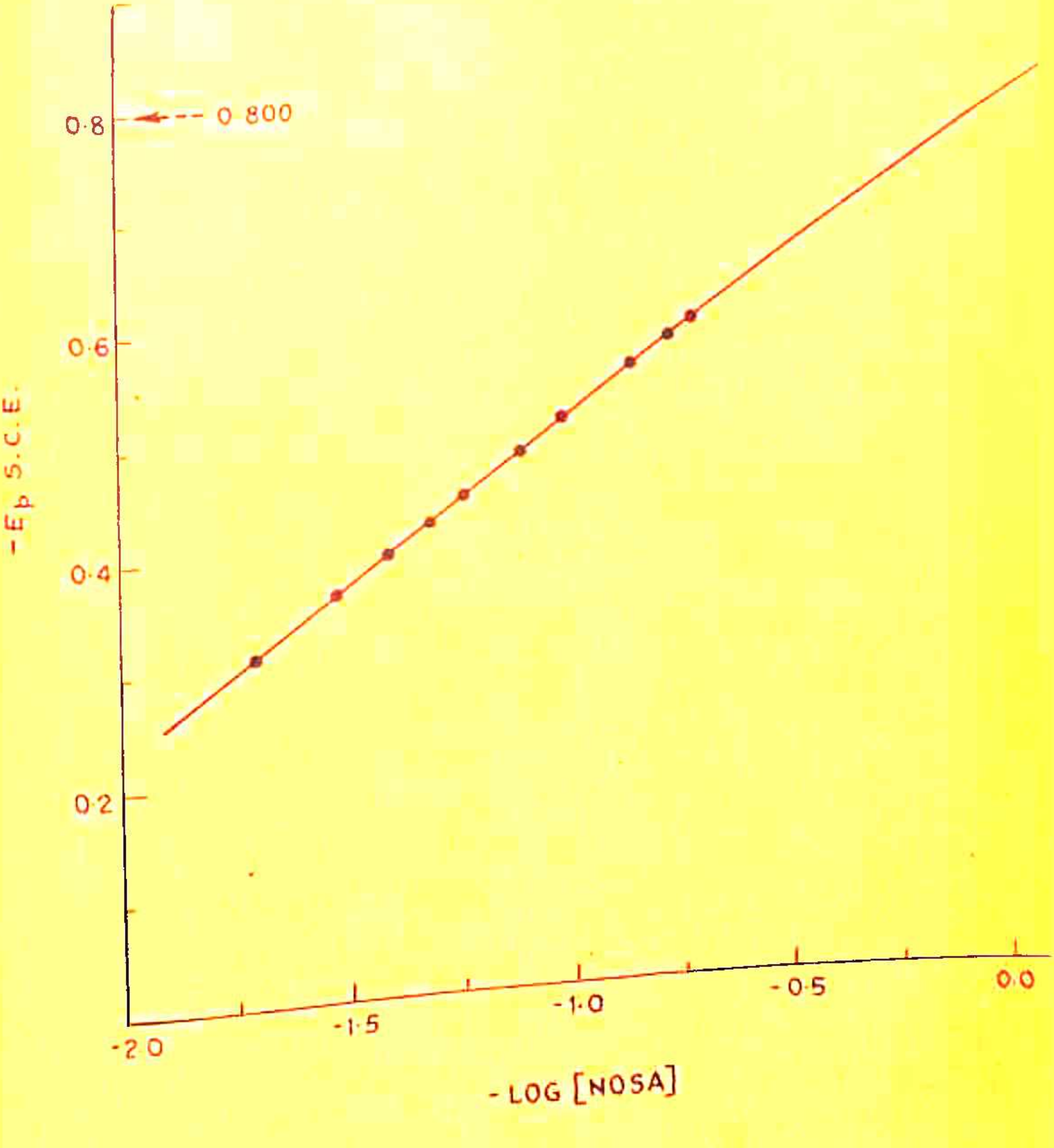


FIG. 4·16

From the Fig. 4.16 the value of $(E_p)_c$ is -0.800 V at NOSA concentration of 1.00 M. From this value andthe measured peak potential of the simple Fe^{+3} in 1.0 M $NaClO_4$ containing no added NOSA (-0.02 V vs S.C.E.), the value of β_p was calculated from equation (19) as 0.513×10^{-13}.

Spectrophotometric Studies

The composition of the complex was established by three independent methods as the continuous variation method of Job[142], the mole-ratio method of Yoe and Jones[282] and the slope ratio method of Harvey and Manning[123].

Fig. 4.17 gives the curve obtained by the Job's method. Fig. 4.18 gives the straight lines obtained by the slope ratio method and the ratio of the slopes was found to be 3. The straight line 1 in Fig. 4.18 is obtained by keeping (NOSA) constant and varying the (Fe^{3+}) and the line 2 is obtained by keeping (Fe^{3+}) constant and (NOSA) varying. Fig. 4.19 gives the curve obtained by the mole-ratio method. These indicate that one mole of Fe(III) combines with three moles of NOSA to form a stable complex in solution in the pH region 2.0 to 3.0 with λ_{max} at 570 nm.

The stability constant (K) of the complex was calculated by molecular extinction coefficient method and mole ratio method. The stability constants were determined at various temperatures at a fixed ionic strength of 0.02 M and pH 2.5 (Table 4.9). From the slope of the plot log K vs $\frac{1}{T}$

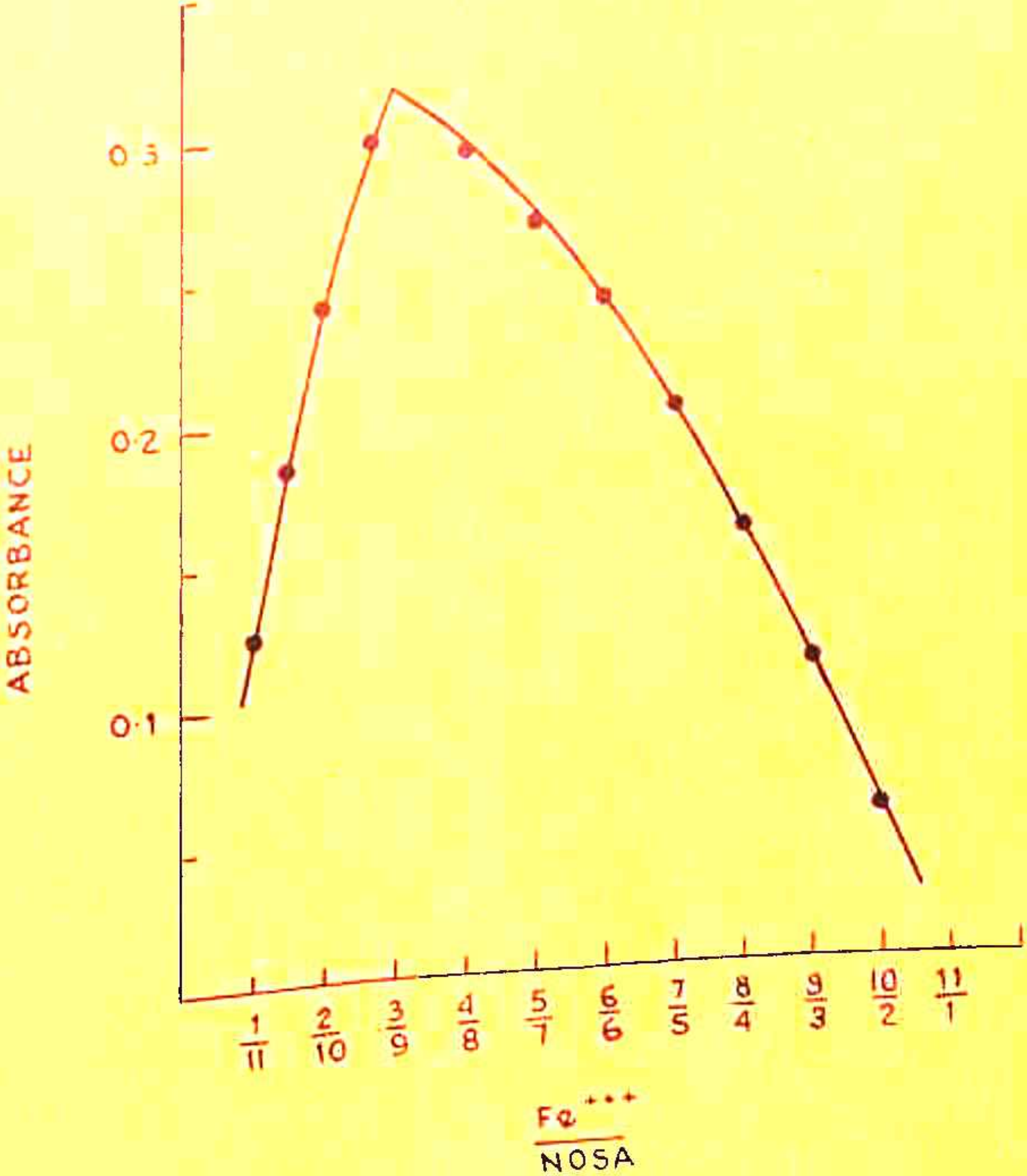


FIG. 4·17 JOB'S METHOD

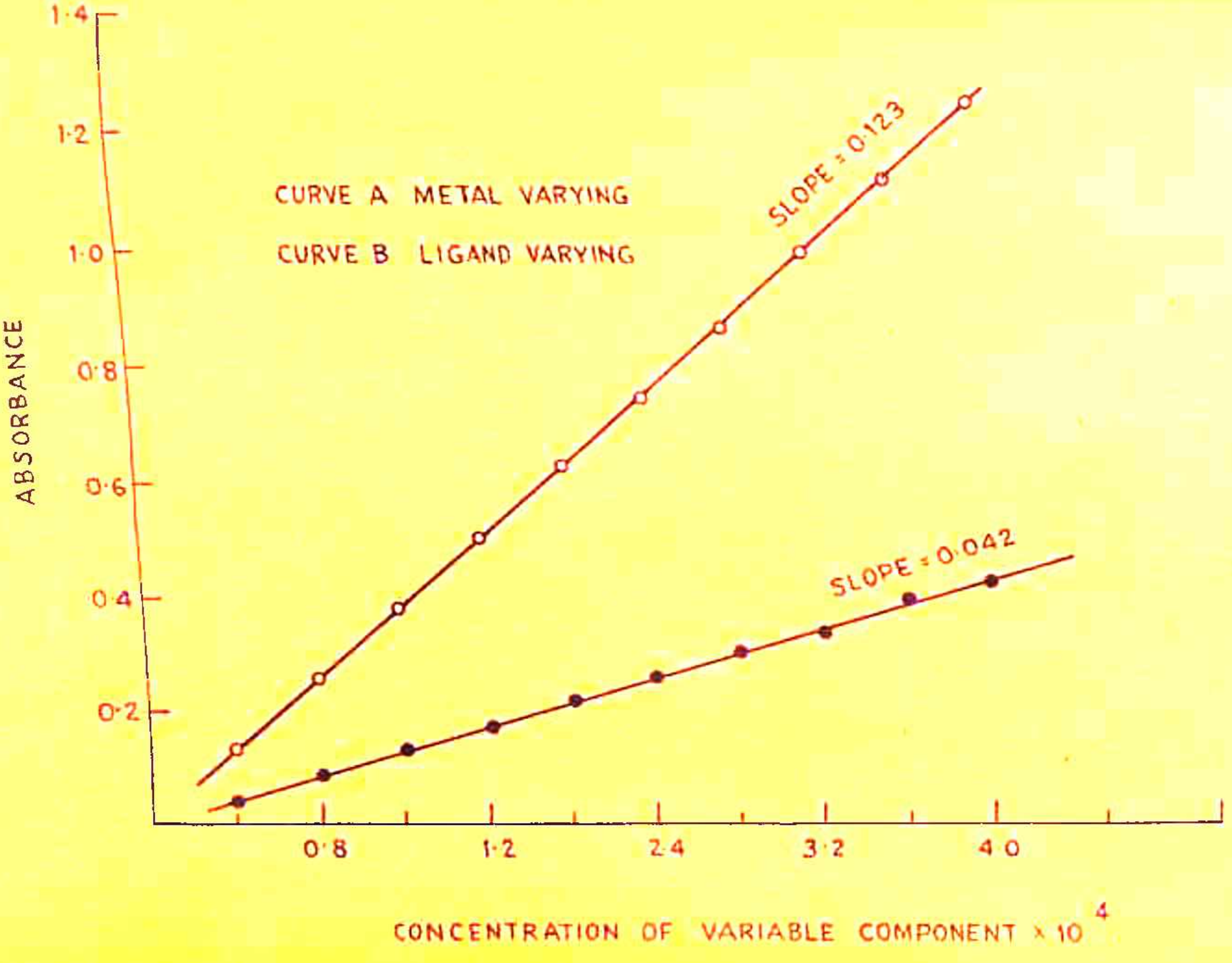


FIG. 4 18 SLOPE RATIO METHOD

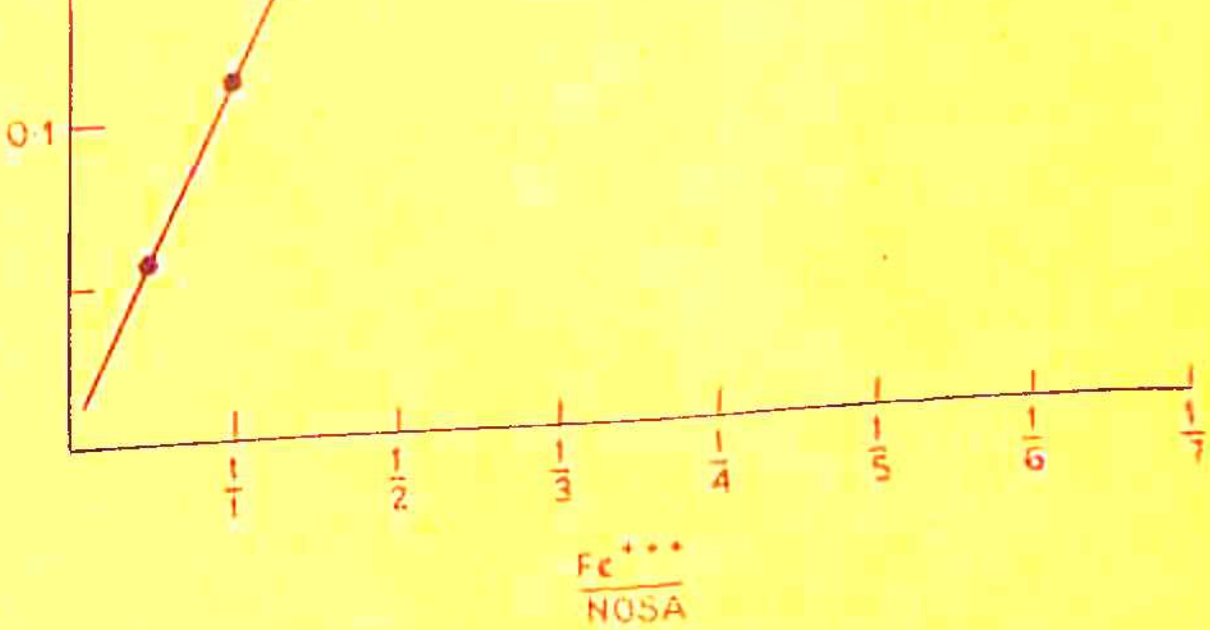
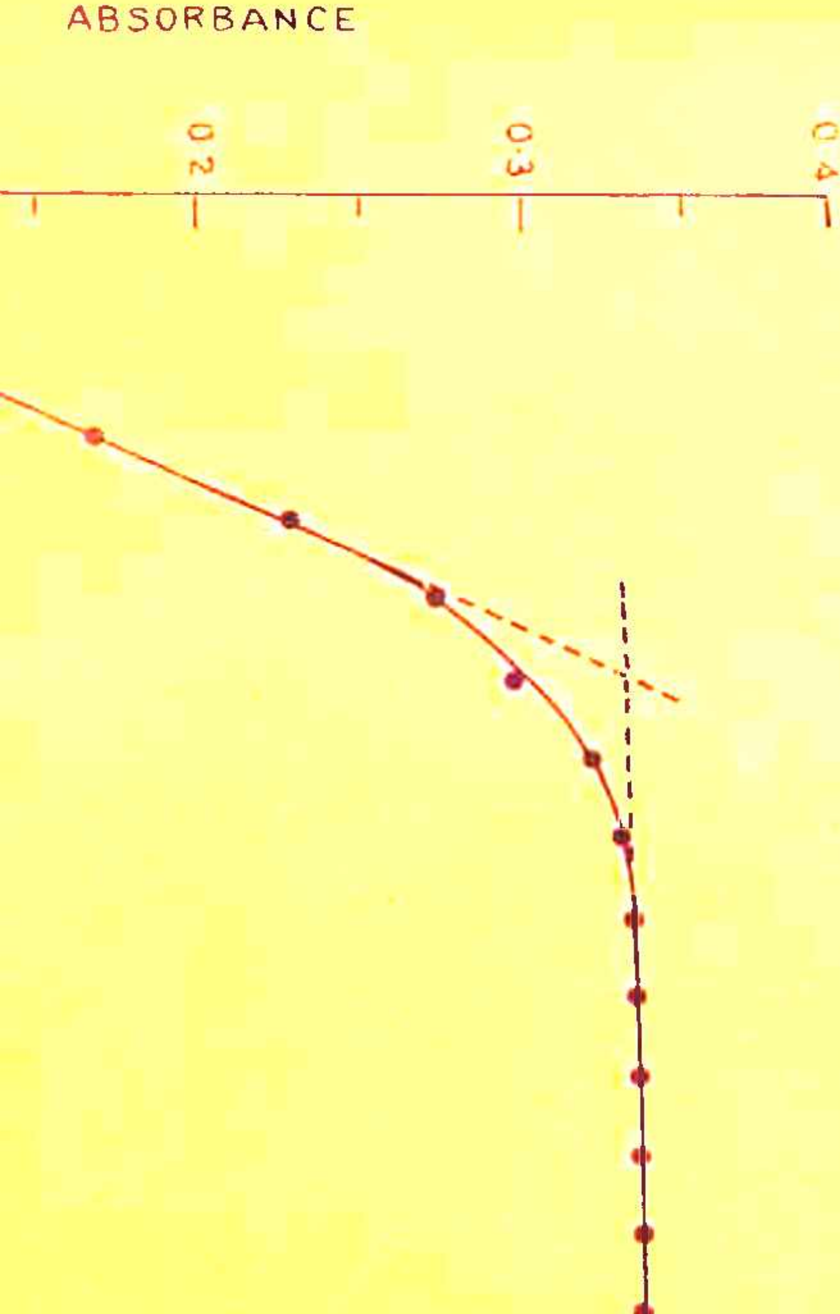


FIG. 4·19 MOLE RATIO METHOD.


ABSORBANCE
0.2
0.3
0.4

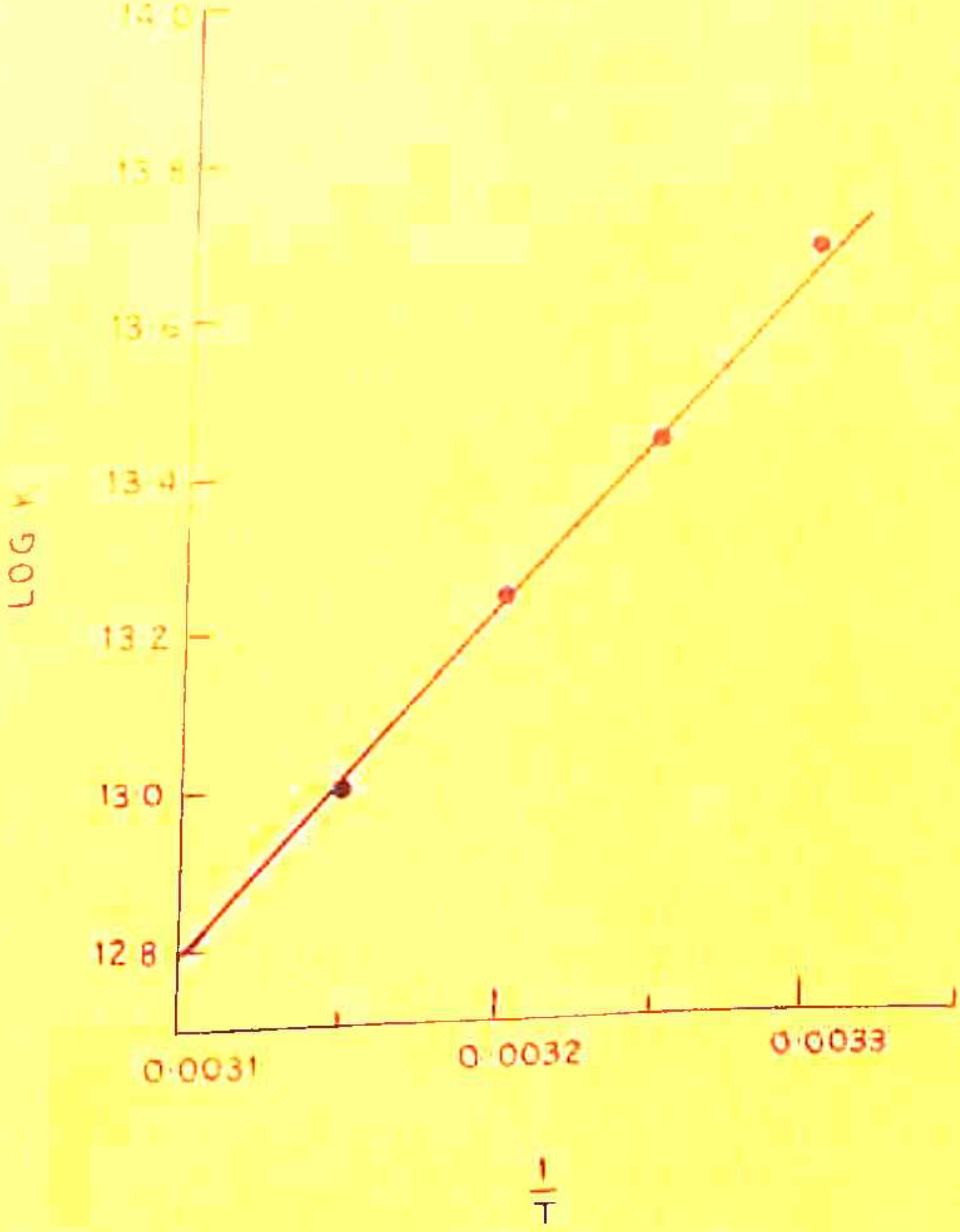


FIG. 4·20 LOG K VS $\frac{1}{T}$ ·

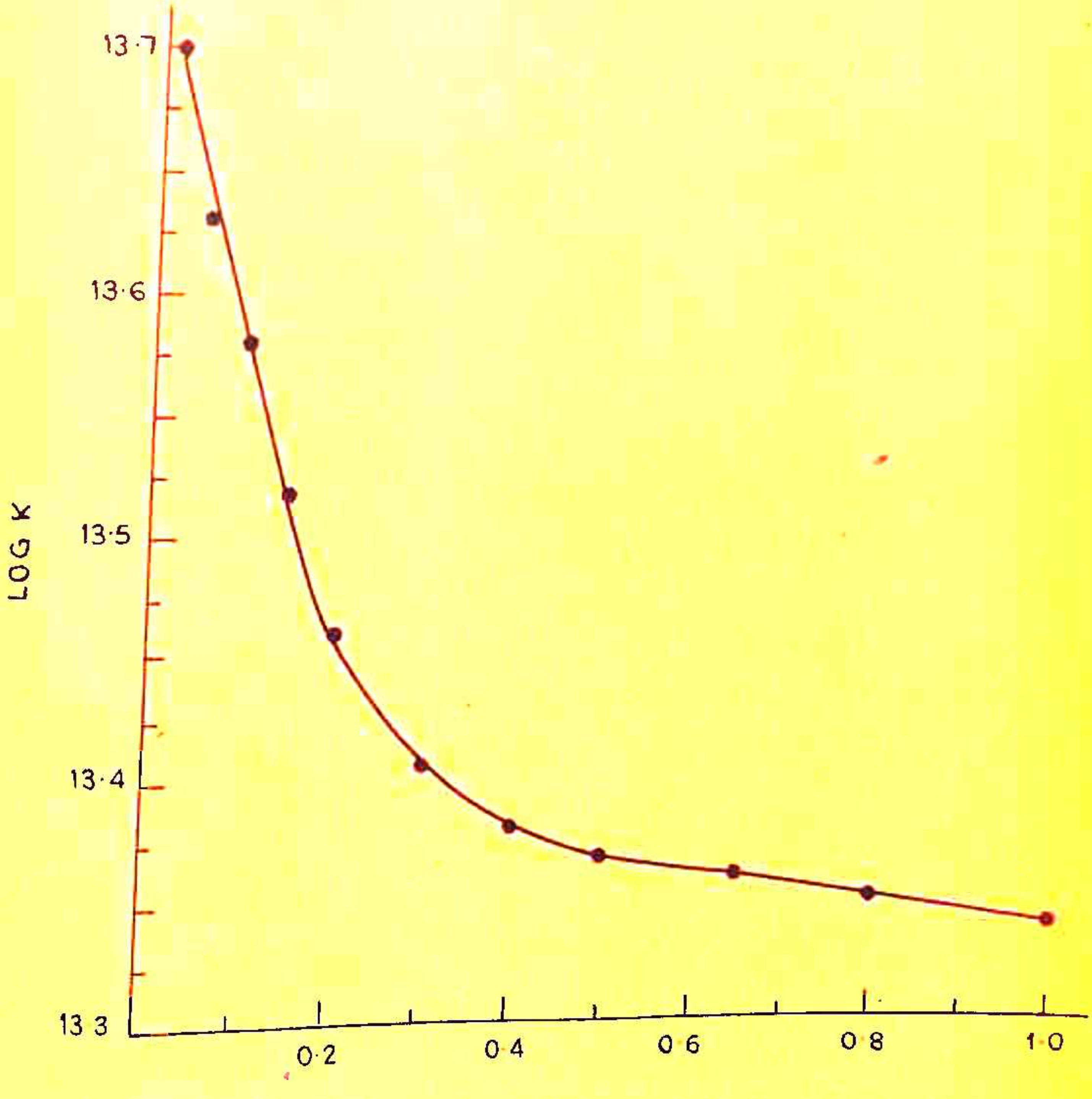


FIG. 4·21

(Fig. 4.20), the enthalpy change ΔH of the reaction was calculated and found to be -23.96 kcal. Assuming this to be constant over a range of experimental temperatures, ΔS of the reaction has also been calculated (Table 4.9).

Determination of stability constants of the complex at various ionic strengths (Fig 4.21) upto 0.4 M shows that the value of K decreases with the increase in ionic strength, as expected, but beyond ionic strength 0.4 M the value of K remains almost constant.

The value of the stability constant of the complex obtained in the spectrophotometric studies was found to be 2.188×10^{13} (log K = 13.34) at ionic strength 1.0 M and temperature 30°C. The reciprocal of this values gives the values of dissociation constant (β_p) to be 0.457×10^{-13}, which agrees fairly well with the value of dissociation constant (0.513×10^{-13}) obtained by using a.c. polarography.

TABLE 4.9 : Effect of temperature on stability constant (K) of the Fe(III)-NOSA complex by spectrophotometry

Temperature °C	log K	$-\Delta G$ (kcal/mole)	$-\Delta S$ cal/deg mole
30	13.70	19.00	16.37
35	13.45	18.65	17.24
40	13.25	18.37	17.85
45	13.01	18.03	18.65
50	12.80	17.76	19.20

Legend of the figures

A.C. Polarography

Fig. 4.15 : Curve 1. A.C. polarogram of 0.5 mM Fe^{3+}

Curve 2. A.C. polarogram of 0.5 mM Fe^{3+} + 0.02 M NOSA

Fig. 4.16 : Effect of NOSA concentration on the peak potential of Fe^{3+} - NOSA complex

Spectrophotometry

Fig. 4.17 : Job's curve for Fe(III)-NOSA complex

Fig. 4.18 : Curve 1. 0.01 M NOSA (fixed) + varying concentration of Fe(III)

Curve 2. 0.01 M Fe(III) (fixed) + varying concentration of NOSA

Fig. 4.19 : Mole ratio method

Fig. 4.20 : Effect of temperature on K

Fig. 4.21 : Effect of ionic strength on K

(v) A.C. POLAROGRAPHIC STUDIES ON THE COMPLEX OF Cd^{++} WITH SOME NITROPYRIDINES

The present investigation gives the results obtained in the study of complexes formed by cadmium and some nitropyridines on which no data are available in literature.

EXPERIMENTAL

2-hydroxy-5-nitropyridine, 3-hydroxy-2-nitropyridine, 2-amino-5-nitropyridine and 6-methyl-2-nitro-3-pyridinol (Aldrich, U.S.A.) were used without further purification. Stock solutions of ligands were prepared in 20% ethanol. Ethanol was distilled in an all-glass fractionating column and the middle one-third portion of the distillate was used for experiments. Stock solution of $3\,CdSO_4.7H_2O$ (B.D.H., A.R.) was prepared in double distilled water. HCl was used to adjust the pH to 2.5 and KCl was used to maintain the ionic strength at 1.0 M. Temperature was maintained at 30±0.1°C and complex studies were carried out in 20% ethanolic medium.

RESULTS AND DISCUSSION

The reduction of the nitropyridines at the d.m.e. has been described in Chapter III of this thesis. It can be seen that the reduction wave due to the nitro group appears at more positive potentials than the reduction wave due to Cd^{++}. Thus the shift in $E_{0.5}$ of the cadmium complex could not be measured accurately. Further at a Cd^{++} concentration of 0.5 mM and varying ligand concentration the wave height due to ligand far exceeded that due to Cd^{++}. Thus d.c. polarography could not be utilized to study these systems.

A.C. polarography, however, could be used to study such systems because the peaks due to nitropyridines and Cd^{++} were distinctly separate and hence the shift in peak potential of Cd^{++} could be measured. Curve 1 in Fig. 4.22 gives the peak due to 2-hydroxy-5-nitropyridine. Curve 3 depicts the a.c. polarogram of the complex. The first peak of curve 3 is due to the ligand and the second peak is due to the reduction of the cadmium complex. The peak potential of cadmium shifted to more cathodic potentials on successive addition of the ligand thereby showing complex formation.

The plot of $(-E_p)_c$ and log concentration of 2-hydroxy-5-nitropyridine (curve 1, Fig. 4.23) yields a straight line with a slope of -0.060 at pH 2.5. From this slope, using equation (20), the value of p was calculated to be $2.04 \doteq 2$ with $n = 2$.

Similar straight lines were obtained with 3-hydroxy-2-nitropyridine (HNP) (curve 2, Fig. 4.23), 2-amino-5-nitropyridine (ANP) (curve 3, Fig. 4.23) and 6-methyl-2-nitropyridine (MNP) (curve 4, Fig. 4.23). The slopes were found to be -0.0625, -0.057 and -0.056 and the coordination number "p" was calculated to be 2.12, 1.94 and 1.90 respectively. The general formula was thus found to be $[Cd(L)_2]^{++}$ where L stands for the ligand.

From Fig. 4.23 the value of $(E_p)_c$ is -0.779 V for 2-hydroxy-5-nitropyridine at a concentration of 1.0 M. From

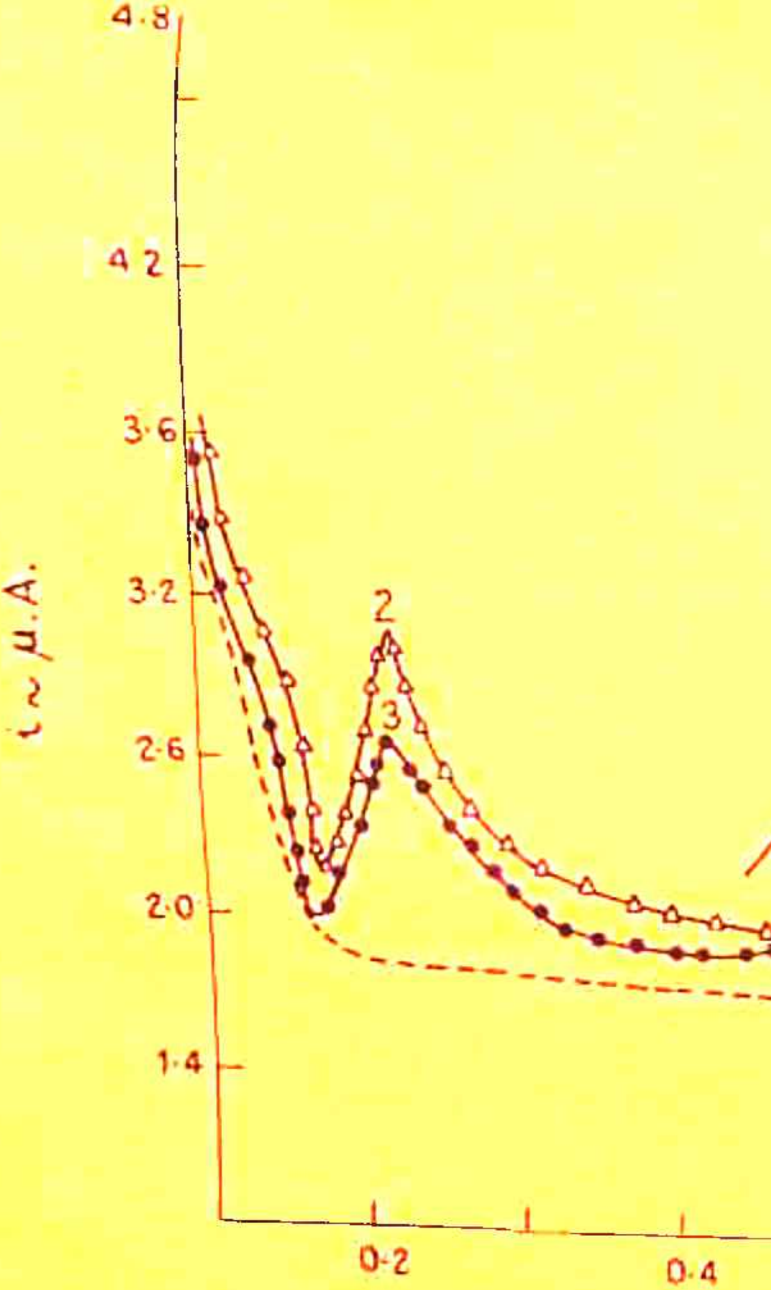

4·8
4·2
3·6
3·2
2·6
2·0
1·4
i ~ μA.
2
3
0·2
0·4

FIG 4·22

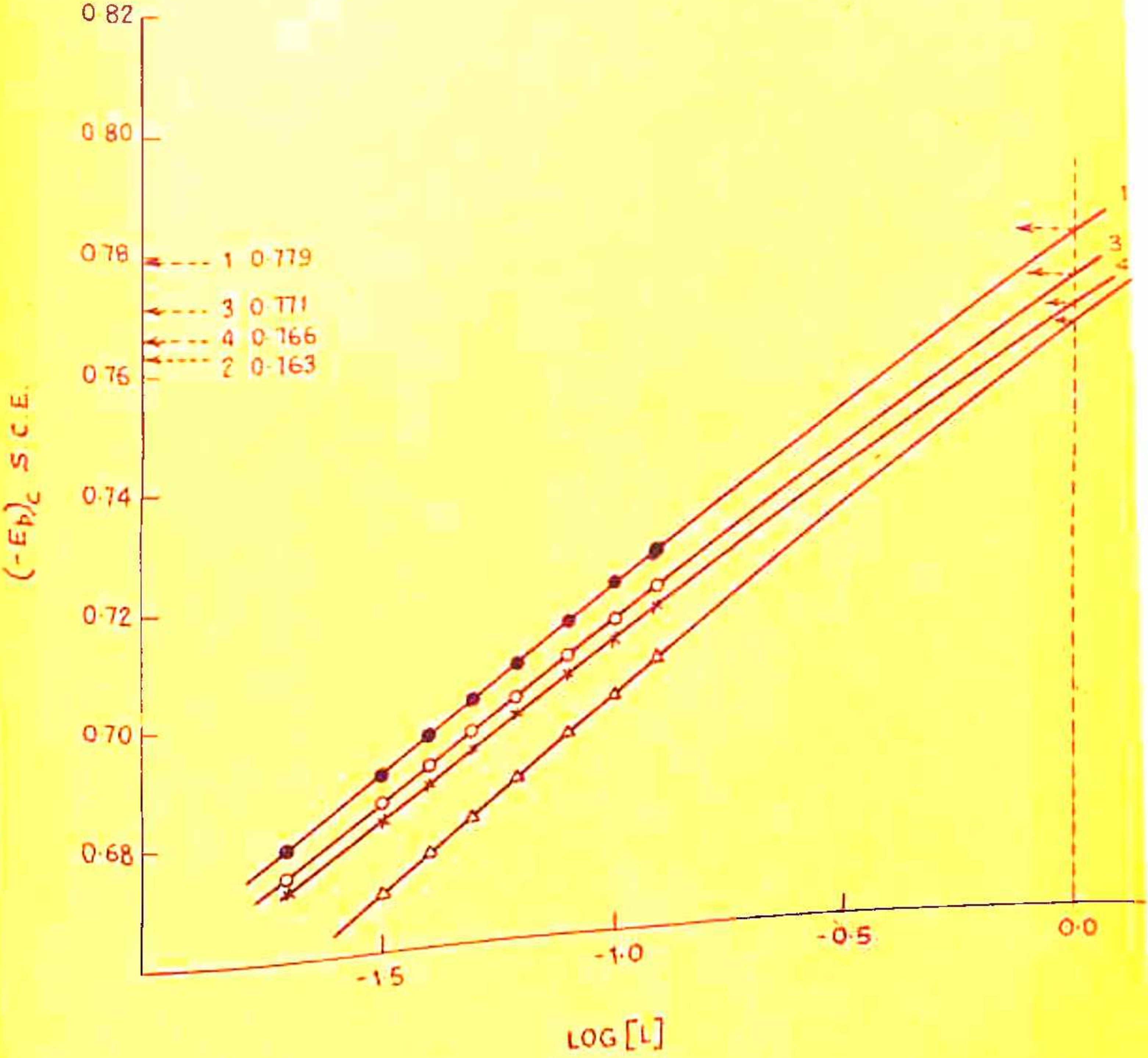

0·82
0·80
0·78
0·76
0·74
0·72
0·70
0·68
1 0·779
3 0·771
4 0·766
2 0·763
(−Ep)c S.C.E.
1
3
4
−1·5
−1·0
−0·5
0·0
LOG [L]

FIG. 4·23

this value and the measured peak potential of Cd^{++} containing no added ligand (-0.62 V vs S.C.E.) the value of β_p was calculated from equation (19), as 4.169×10^{-6}. Similarly β_p for Cd-HNP, Cd-ANP and Cd-MNP was found to be 1.318×10^{-5} 8.185×10^{-6} and 1.146×10^{-5} respectively.

It can therefore be seen that a.c. polarography can be used advantageously for the study of complexes where ligand also gives a reduction wave and conventional polarography cannot be used accurately for such systems.

Legend of the figures

Fig. 4.22 : Curve 1. A.C. polarogram of 0.5 mM Cd^{++}, pH 2.5

Curve 2. A.C. polarogram of 0.04 M ligand

Curve 3. A.C. polarogram of 0.5 mM Cd^{++} + 0.04 M 2-hydroxy-5-nitropyridine, pH 2.5

Fig. 4.23 : Curve 1. Effect of the concentration of 2-hydroxy-5-nitropyridine on the peak potential of Cd^{++} - (2-hydroxy-5-nitropyridine) complex.

Curve 2. Effect of the concentration of 3-hydroxy-2-nitropyridine on the peak potential of Cd^{++} - (3-hydroxy-2-nitropyridine)

Curve 3. Effect of the concentration of 2-amino-5-nitropyridine on the peak potential of Cd^{++} - (2-amino-5-nitropyridine) complex

Curve 4. Effect of the concentration of 6-methyl-2-nitro-3-pyridinol on the peak potential of Cd^{++} - (6-methyl-2-nitro-3-pyridinol) complex.

* * *

CHAPTER V

A.C. POLAROGRAPHIC STUDIES ON REACTION KINETICS IN SOLUTION

A.C. POLAROGRAPHIC STUDIES ON THE KINETICS OF THE NEUTRALIZATION OF SOME PSEUDO ACIDS

The nitroparaffins have been recognised as pseudo acids. They dissolve in alkaline solution through the formation of salts according to the equation

$$RCH_2NO_2 + OH^- \longrightarrow R\text{-}CH{=}NO_2^- + H_2O \qquad (21)$$

This neutralization is a relatively slow process and the rates of neutralization by different bases have been investigated by Maron and LaMer[185] and later by Pearson[221]. In both investigations the reaction rate was followed conductometrically. De Vries and Iwett[278] reported that the wave heights for the reduction of nitroparaffins were proportional to the concentration of the nitroparaffin when 0.05 molar sulfuric acid was used as the supporting electrolyte but this relationship was not linear when 0.05 molar sodium sulfate was used in place of sulfuric acid. When sodium sulfate was used as the supporting electrolyte the pH increased as the reduction progressed because hydrogen ions were used up in the reduction process. This increase in pH caused a shift in the equilibrium between the normal and aci form which was not reducible at the dropping mercury cathode. As the concentration of the nitroparaffin was increased the pH became still greater resulting in still more of the aci-nitroparaffin being formed and consequently the wave height was not proportional to concentration. The nitroparaffin could not be reduced in 0.1 N sodium hydroxide or 0.1 N tetramethylammonium hydroxide. This investigation would indicate that polarography would make possible the determination of the normal nitroparaffin - which is the form present in acid solution - in the presence of aci-form and that the rate of this transformation could be determined in a buffered solution where the hydroxyl ion concentration is maintained at a constant value. Turnbull and Maron[272] represented the tautomeric equilibrium between the normal nitroparaffins and its aci-nitro form as

$$RCH_2NO_2 \rightleftarrows R\bar{C}H - NO_2 \rightleftarrows RCH = N\bar{O}_2 \rightleftarrows RCH = NO_2H$$

The latter three molecules are collectively called 'aci-nitroparaffin'.

The use of polarographic analysis in the field of reaction kinetics has been reviewed by Semerano[243]. The applicability of the method depends on the direct or induced polarographic activity of one or more of organic substances taking part in the reaction. The use of polarographic technique as a tool to evaluate the rate of tautomeric inter-conversion depends on the fact that the aci-form is not reduced polarographically even at the most negative potentials available for ordinary aqueous solutions.

Miller et al.[209] employed d.c. polarography to study the rate of aci-transformation of nitroparaffins in buffered solutions. Jannakoudakis et al.[141] studied the aci-conversion of phenyl-nitromethane and nitrocyclohexane. Recently Gupta and Nawal Kishore have investigated the kinetics of aci-conversion of β-nitropropionic acid[116], 1-chloro-1-nitropropane[11 and 5-nitro-acenaphthene[118]. However, no such studies are available by using a.c. polarography. The present investigation, therefore, gives the results obtained in the study of the kinetics of the neutralization of some pseudo acids with the view to see if this technique could be applied successfully for such investigations.

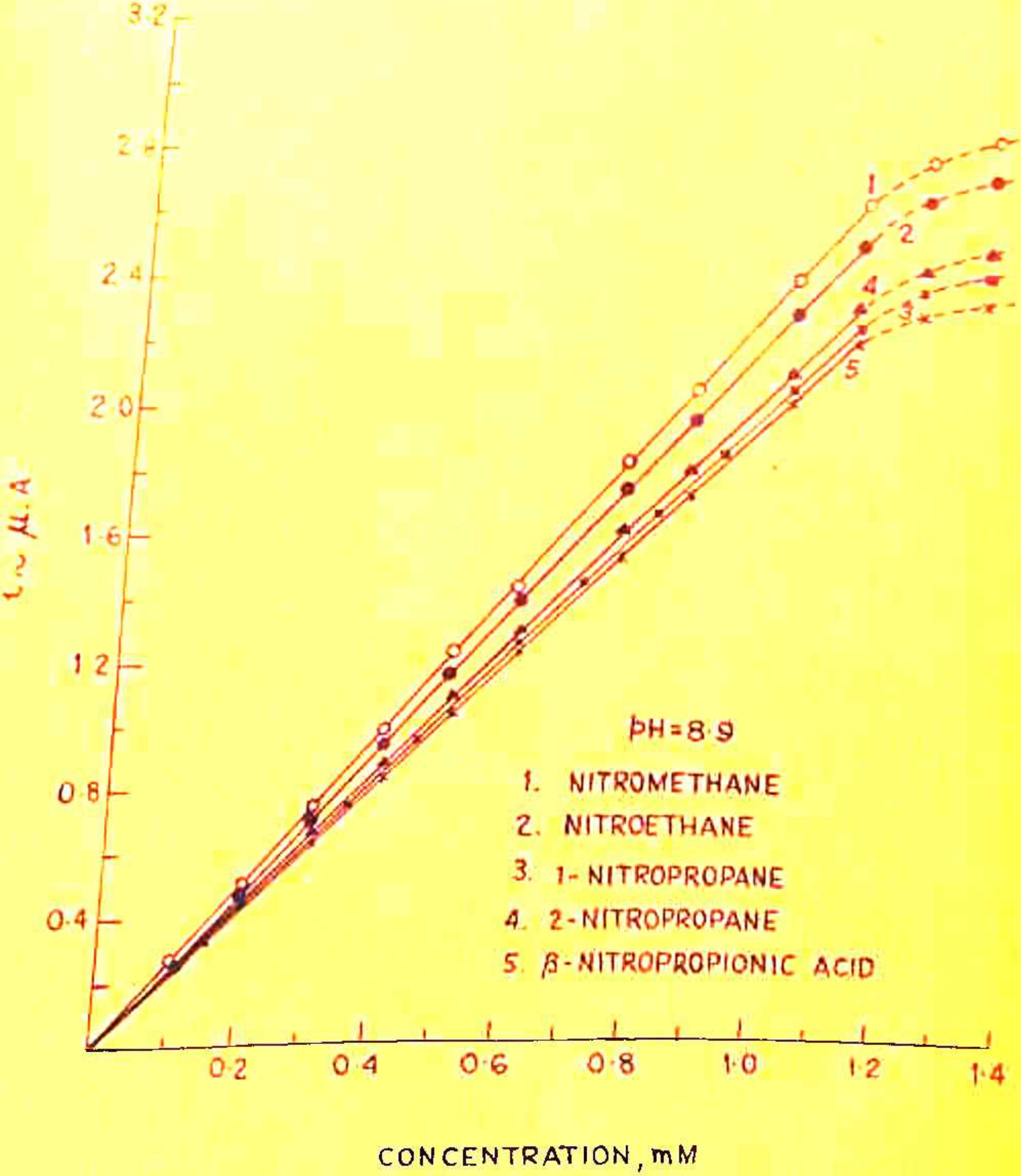
EXPERIMENTAL

Nitromethane, nitroethane and 1-nitropropane, 2-nitropropane (Fluka) were distilled in all-glass fractionating column and a fraction was collected having a boiling range of less than 1° which included the boiling point of the respective nitroparaffin. β-nitropropionic acid (Aldrich, USA) was used without further purification. All other chemicals used were of B.D.H., A.R. quality. The buffers used were HCl/KCl, Na_2HPO_4/citric acid and boric acid/NaOH. Ionic strength was adjusted to 0.54 by KCl. All pH measurements were made with Beckmann model H2 pH meter. Oxygen did not interfere in the studies. Temperature was maintained with an accuracy of ±0.1°. The constants of the d.m.e. were: $m = 2.32$ mg/s, $t = 3.75$ s in 0.1 M KCl (open circuit).

The a.c. polarograms were taken after the test solution (which initially contained 1 mM of nitro compound) was allowed to stand for 12 hours for the attainment of equilibrium. It was found that the peak potential, E_s, was independent of the concentration of the nitro-compound. For checking the linearity of the current vs concentration plot the following method was adopted. Initially a known concentration of nitro compound was taken and the current-time curve recorded keeping the applied potential (E_p) respectively constant. From the curve the current at zero time was found out. By taking different concentrations of the nitro compound the current was found out at zero time. A plot of this current and initial concentration of the nitro-compound showed linearity in the range 0.2 mM to 1.1 mM as shown in Fig. 5.1. Initial concentration of each nitro-compound was kept at 1.0 mM in kinetic studies.

RESULTS AND DISCUSSION

Fig. 5.2 shows the nature of a.c. polarograms of nitromethane recorded after the attainment of equilibrium at different pH values. Similar a.c. polarograms are shown in Fig. 5.3 (nitroethane), Fig. 5.4 (1-nitropropane), Fig.5.5 (2-nitropropane) and Fig. 5.6 (β-nitropropionic acid). Tables 5.1, 5.2, 5.3, 5.4 and 5.5 contain the peak potentials and the initial and final alternating current ($i_\sim$) values for nitromethane, nitroethane, 1-nitropropane, 2-nitropropane and β-nitropropionic acid respectively. E_p values shifted to more cathodic potential with increase in pH and ultimately the peak potentials became almost constant in alkaline media. D.C. polarographic studies also showed similar behaviour of $E_{0.5}$ values[116,209]. From the Tables it can be seen that $i_\sim$ increased upto about pH 7 and then decreased in alkaline media and beyond pH 9.5 no peak could be observed. The increase in



3.2
2.8
2.4
2.0
1.6
1.2
0.8
0.4
i_d μA
0.2
0.4
0.6
0.8
1.0
1.2
1.4
CONCENTRATION, mM
1
2
3
4
5
pH = 8.9
1. NITROMETHANE
2. NITROETHANE
3. 1-NITROPROPANE
4. 2-NITROPROPANE
5. β-NITROPROPIONIC ACID

FIG. 5·1

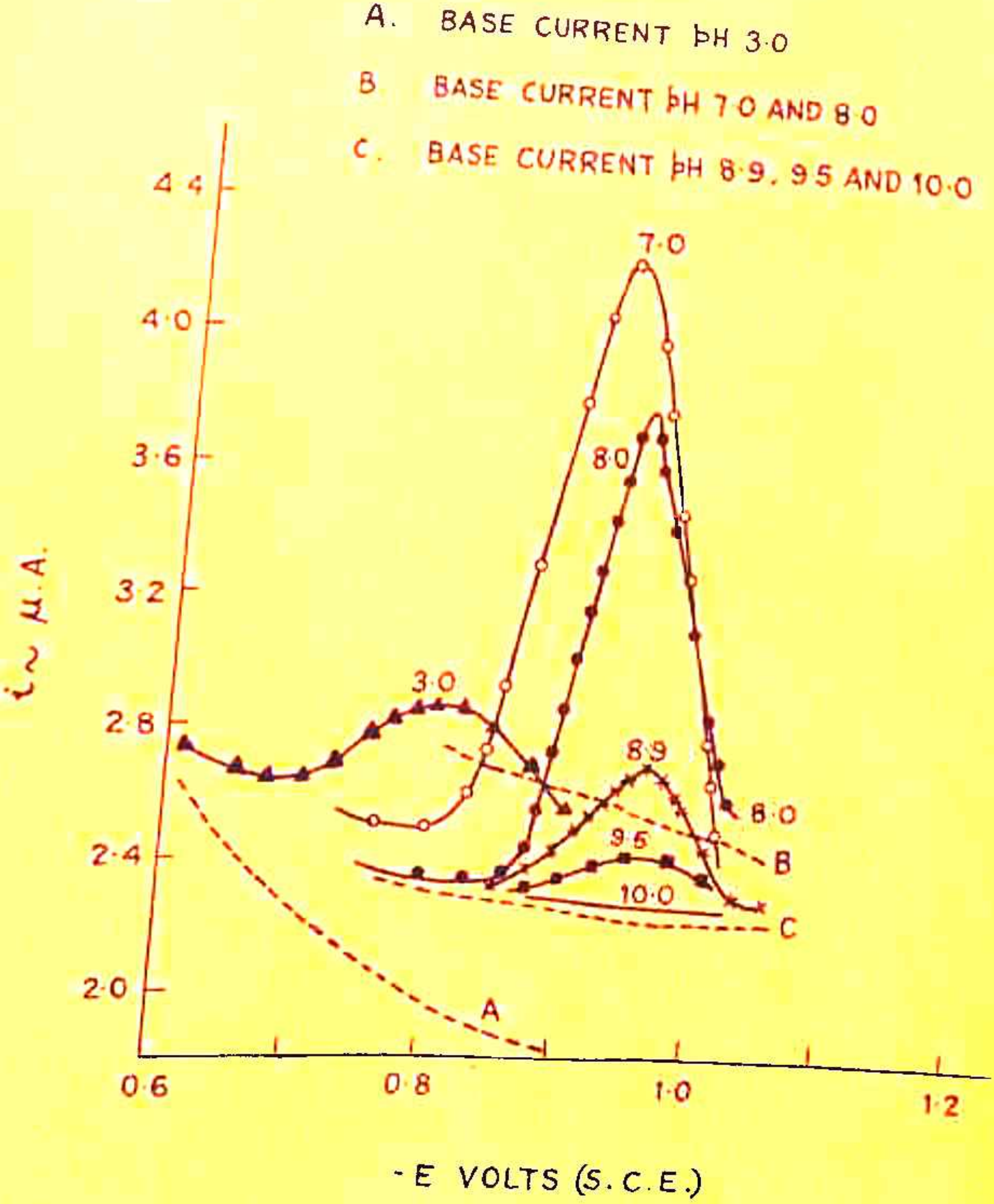


FIG. 5·2 A.C. POLAROGRAMS OF NITROMETHANE AT VARIOUS þH.

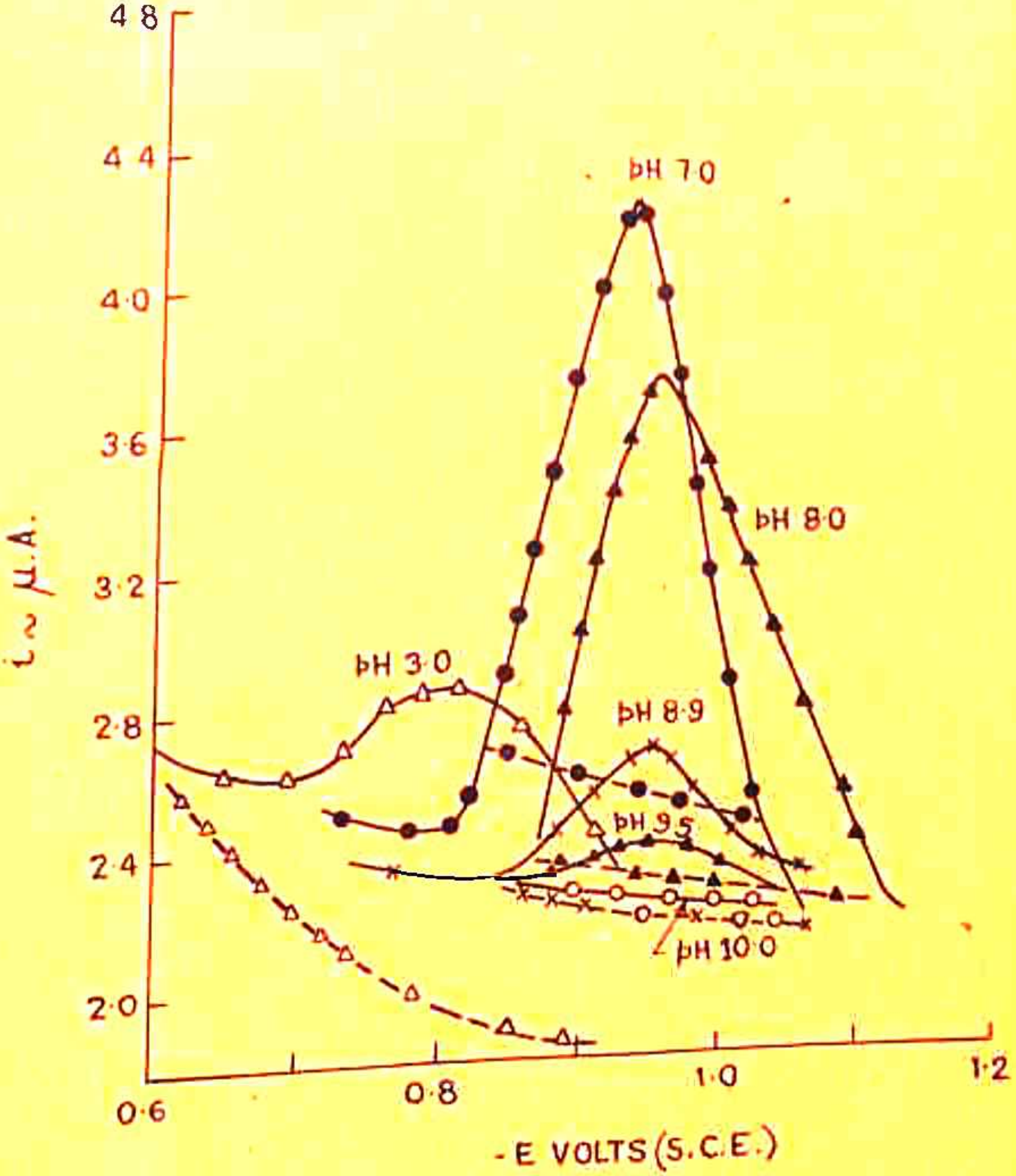


FIG. 5·3 A.C. POLAROGRAMS OF NITROETHANE AT VARIOUS pH VALUES.

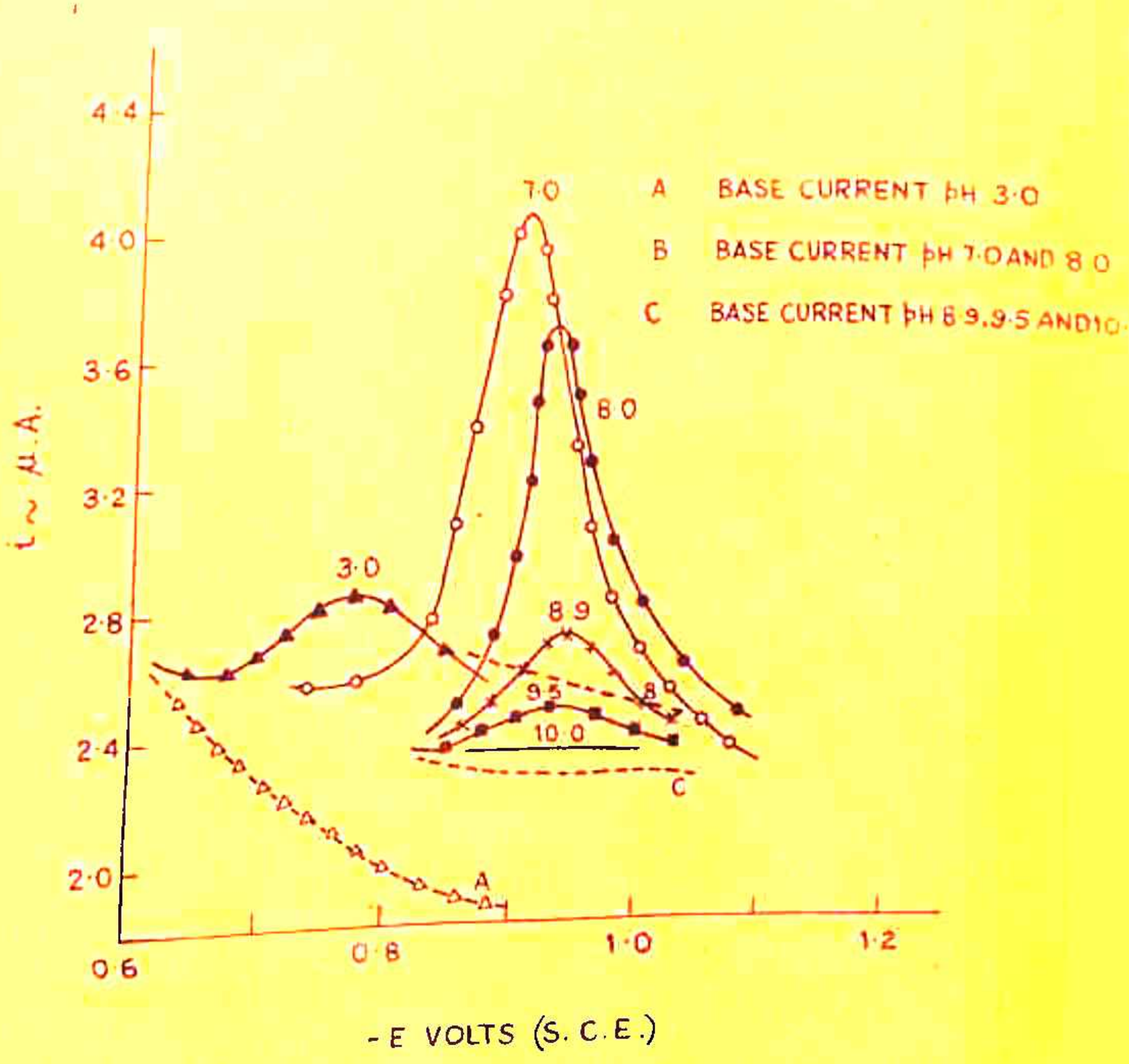


FIG. 5·4 A.C. POLAROGRAMS OF 1-NITROPROPANE AT VARIOUS pH.

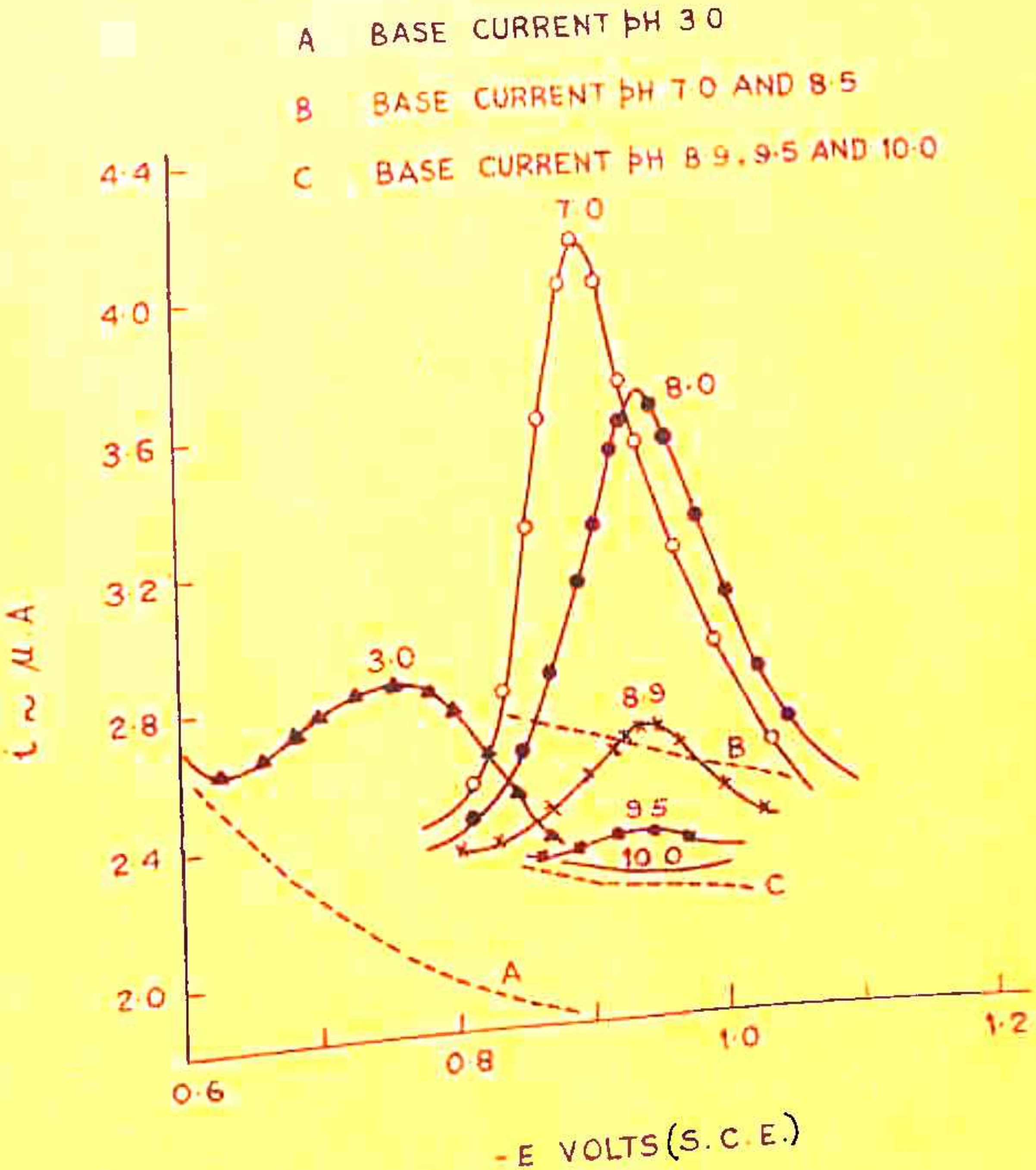


FIG. 5·5 A.C. POLAROGRAMS OF 2-NITROPROPANE AT VARIOUS pH.

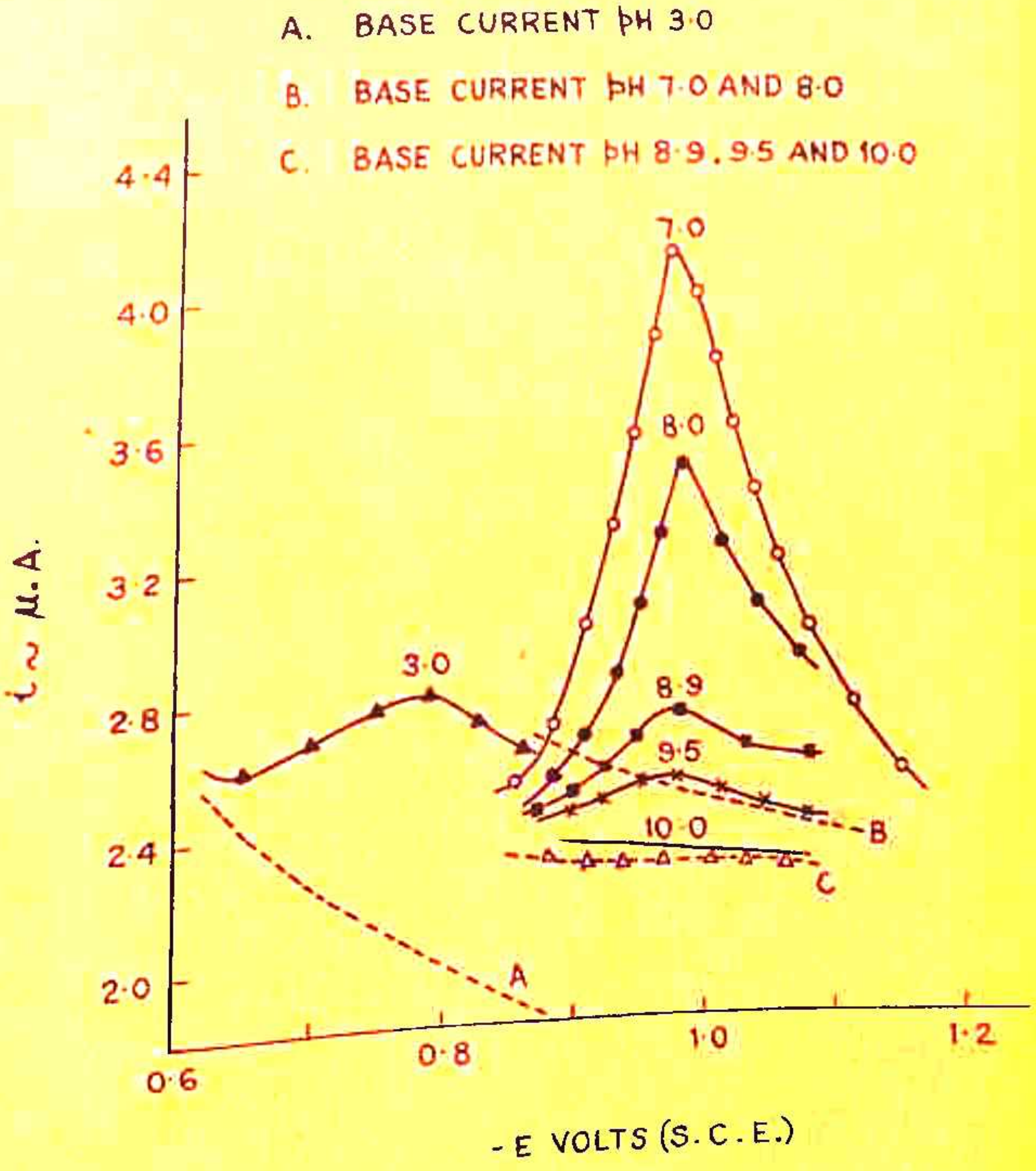


FIG. 5·6 A.C. POLAROGRAMS OF β-NITROPROPIONI ACID AT VARIOUS pH.

$i_\sim$ upto about pH 7 may be ascribed to the greater extent of reversibility of the reduction process. It is known that the height of the a.c. wave decreases as the reduction process becomes more irreversible from d.c. polarographic point of view[16]. However, the decrease in $i_\sim$ (final) after about pH 7 is due to the conversion of the normal nitro-compound into the polarographic inactive aci-form. Beyond pH 9.5 the absence of a peak indicated that the equilibrium had shifted almost completely in favour of the aci-form.

The dissolution of pseudo acids in alkaline solution through the formation of salts may be represented by equation (21). The rate of transformation will depend upon

(a) the concentration of the active nitro-compound, and

(b) the concentration of the OH^- ions.

The buffer solution ensures the constancy of $[OH^-]$ and hence the rate of transformation will depend on the concentration of the active nitro-compound only. Fig. 5.7 gives the variation in the magnitude of $i_\sim$ with time of nitroethane at 35°C (pH 9.5).

The rate of reaction is given by

$$\frac{dx}{dt} \propto (a - x) \propto i_\sim$$

where 'a' is the initial concentration of the nitro-compound, 'x' is the fraction converted to the aci-form in time t and $i_\sim$ the alternating current corresponding to the amount of nitro-compound left in the solution.

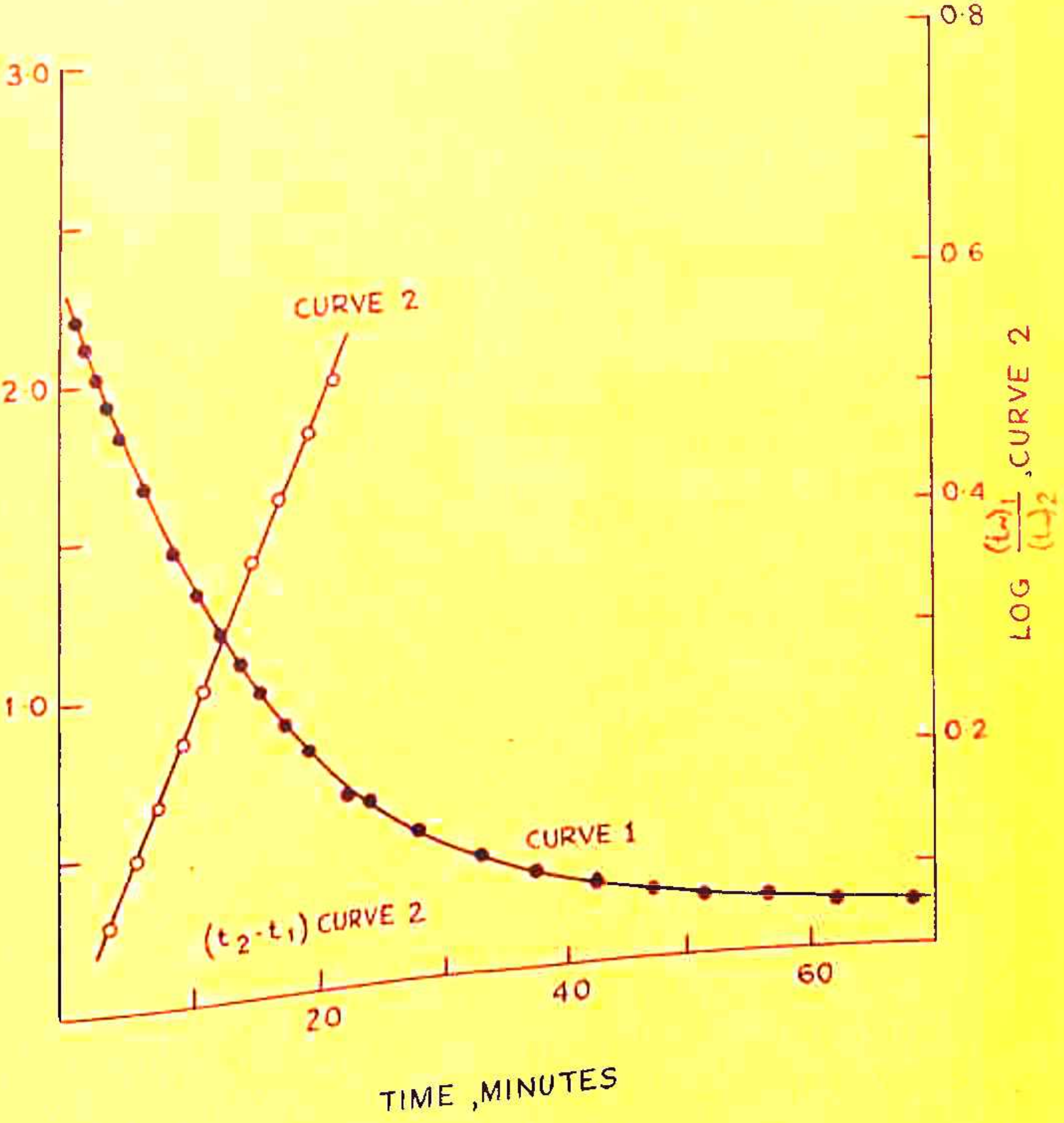

3·0
2·0
1·0
$i_{\sim}$, μA. CURVE 1
0·8
0·6
0·4
0·2
LOG $\frac{(i_{\sim})_1}{(i_{\sim})_2}$, CURVE 2
CURVE 2
CURVE 1
$(t_2 - t_1)$ CURVE 2
20
40
60
TIME, MINUTES

FIG. 5·7

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

$$\text{or} \quad k = \frac{2.303}{t_2 - t_1} \log \frac{a - x_1}{a - x_2}$$

When $(a - x_1)$ and $(a - x_2)$ are substituted by $(i_{\sim})_1$ and $(i_{\sim})_2$ respectively, the values of k can be calculated directly from the knowledge of the $i_{\sim}$ values. Thus

$$k = \frac{2.303}{t_2 - t_1} \log \frac{(i_{\sim})_1}{(i_{\sim})_2}$$

where $(i_{\sim})_1$ and $(i_{\sim})_2$ are the alternating current values (μA) after time t_1 and t_2 respectively.

Excellent constant values of rate constants were obtained for each nitro-compound when the first order equation was used. This is further confirmed from the plot of $\log \frac{(a-x_1)}{(a-x_2)}$ vs (t_2-t_1), in terms of current by $\log \frac{(i_{\sim})_1}{(i_{\sim})_2}$ vs (t_2-t_1), which yielded a straight line as shown in Fig. 5.7, curve 2 for nitroethane. The constancy of the values of the rate constant is shown in Tables 5.6, 5.7, 5.8, 5.9 and 5.10 for the five nitro-compounds. Tables 5.11, 5.12, 5.13, 5.14 and 5.15 show the value of all rate constants of the above said nitro-compounds at various pH values. The thermodynamic parameters ΔG, ΔH and ΔS for the activated complex formed during the transformation process have been calculated at 35°C using Eyring's theory[62,72] and are tabulated in Tables 5.11 through 5.15.

In the case of 1-chloro-1-nitropropane, d.c. polarographic studies[117] showed that the aci-conversion commenced at acidic pH values. However, in this case a.c. polarography could not be applied as good peaks were not recorded.

Although the rate of reaction increases with pH there was no direct relationship between the rate of reaction and the hydroxyl ion concentration of the solution. This might arise from the fact that hydroxyl ion is not the only base present in the solution and that the bases used as buffers may play an important role in controlling the rate of reaction[205].

It can therefore be concluded, in general, that a.c. polarography can be used advantageously for the study of the reaction kinetics in solution.

TABLE 5.1 : Effect of pH on peak potentials (volts vs S.C.E.) and $i_\sim$ of 1 mM solution of nitromethane at 25°C, μ = 0.54 M.

pH	$-E_p$	$i_\sim$ μA Initial*	Final**
1.0	0.72⊕	1.05	1.05
2.0	0.76⊕	1.10	1.10
3.0	0.80⊕	1.15	1.15
4.0	0.83⊕	1.25	1.20
5.0	0.86	1.30	1.20
6.0	0.89	1.50	1.30
7.0	0.92	2.05	1.55
8.0	0.94	2.45	1.40
8.9	0.95	2.45	0.40
9.5	0.95	2.45	0.10
10.0	0.95	2.45	No peak
11.0	No peak could be recorded		

* Current values taken immediately after the test solution and buffer solution were mixed

** Current values taken after 12 hours

⊕ $E_p \pm 15$ mV

TABLE 5.2 : Effect of pH on peak potentials (volts vs S.C.E.) and $i_{\sim}$ of 1 mM solution of nitroethane at 25°C, μ = 0.54 M.

pH	$-E_p$	$i_{\sim}$ µA	
		Initial*	Final**
1.0	0.76⊕	0.95	0.95
2.0	0.72⊕	1.00	1.00
3.0	0.80⊕	1.05	1.00
4.0	0.81⊕	1.11	1.05
5.0	0.85	1.25	1.20
6.0	0.88	1.45	1.25
7.0	0.93	1.95	1.60
8.0	0.95	2.34	1.40
8.9	0.95	2.34	0.50
9.5	0.95	2.34	0.15
10.0	0.95	2.30	No wave
11.0	No wave could be recorded		

* Current values taken immediately after the test solution and buffer solution were mixed

** Current values taken after 12 hours

⊕ E_p ± 15 mV

TABLE 5.3 : Effect of pH on peak potentials (volts vs S.C.E.) and $i_{\sim}$ of 1 mM solution of 1-nitropropane at 25°C, μ = 0.54 M.

pH	$-E_p$	$i_{\sim}$ μA	
		Initial*	Final**
1.0	0.72●	0.85	0.85
2.0	0.75●	0.90	0.90
3.0	0.78●	0.95	0.90
4.0	0.80●	1.05	0.86
5.0	0.81●	1.51	1.12
6.0	0.84	1.80	1.35
7.0	0.90	1.91	1.40
8.0	0.93	2.10	1.50
8.9	0.94	2.10	0.40
9.5	0.94	2.10	0.25
10.0	0.94	2.15	No peak
11.0	No wave could be recorded		

* Current values taken immediately after the test solution and buffer solution were mixed

** Current values taken after 12 hours

● E_p ± 15 mV

TABLE 5.4 : Effect of pH on peak potentials (volts vs S.C.E.) and $i_{\sim}$ of 1 mM solution of 2-nitropropane at 25°C, μ = 0.54 M

pH	$-E_p$	$i_{\sim}$ μA Initial*	Final**
1.0	0.70$^{\oplus}$	0.85	0.85
2.0	0.74$^{\oplus}$	0.95	0.95
3.0	0.77$^{\oplus}$	1.00	1.00
4.0	0.80$^{\oplus}$	1.05	0.90
5.0	0.82$^{\oplus}$	1.55	1.15
6.0	0.85	1.85	1.40
7.0	0.89	1.95	1.40
8.0	0.93	2.10	1.55
8.9	0.95	2.15	0.35
9.5	0.95	2.15	0.15
10.0	0.95	2.15	No peak
11.0	No wave could be recorded		

* Current values taken immediately after the test solution and buffer solution were mixed

** Current values taken after 12 hours

$^{\oplus}$ E_p ± 15 mV

TABLE 5.5 : Effect of pH on peak potentials (volts vs S.C.E.) and $i_{\sim}$ of 1 mM solution of β-nitropropionic acid at 25°C, $\mu = 0.54$ M

pH	$-E_p$	$i_{\sim}$ µA Initial*	Final**
1.0	No wave could be recorded		
2.0	No wave could be recorded		
3.0	$0.79^{\bullet}$	0.60	0.60
4.0	$0.82^{\bullet}$	0.65	0.65
5.0	$0.87^{\bullet}$	1.00	0.90
6.0	$0.94^{\bullet}$	1.25	1.00
7.0	0.97	1.86	1.40
8.0	0.98	2.00	1.53
8.5	0.98	2.05	1.42
8.9	0.98	2.05	0.82
9.5	0.98	2.05	0.31
10.0	0.99	2.05	No peak
11.0	No wave could be recorded		

* Current values taken immediately after the test solution and buffer solution were mixed

** Current values taken after 12 hours

● $E_p \pm 15$ mV

TABLE 5.6 : Rate constant for the transformation of nitromethane into its aci-form

Temperature 25°C, 1.0 mM nitromethane
μ = 0.54 M and pH = 9.5

Time min.	Rate constant $k \times 10^2$ min^{-1}
8.0	1.921
10.0	1.922
12.0	1.910
14.0	1.908
17.0	1.920
20.0	1.908
24.0	1.910
28.5	1.914
33.5	1.920
40.0	1.910
48.0	1.912
54.0	1.914
$k_{average}$	1.914

TABLE 5.7 : Rate constant for the transformation of nitroethane into its aci-form

Temperature 25°C, 1.0 mM nitroethane, $\mu = 0.54$ M and pH = 9.5

Time min.	Rate constant $k \times 10^{2}$ min^{-1}
8.5	2.300
10.0	2.341
12.5	2.411
14.0	2.433
17.0	2.404
20.0	2.328
24.0	2.374
28.5	2.389
33.5	2.383
39.5	2.402
47.5	2.371
54.5	2.331
$k_{average}$	2.373

TABLE 5.3 : Rate constant for the transformation of 1-nitropropane into its aci-form

Temperature 25°C, 1.0 mM 1-nitropropane, $\mu = 0.54$ M and pH = 9.5

Time min.	Rate constant $k \times 10^2$ min^{-1}
8.5	1.852
10.0	1.838
12.0	1.841
14.0	1.847
17.5	1.854
20.0	1.835
23.0	1.842
27.0	1.858
31.5	1.840
35.0	1.839
39.0	1.842
44.5	1.820
$k_{average}$	1.842

TABLE 5.9 : Rate constant for the transformation of 2-nitropropane into its aci-form

Temperature 25°C, 1.0 mM 2-nitropropane, $\mu = 0.54$ M and pH = 9.5

Time min.	Rate constant $k \times 10^2$ min^{-1}
8.5	0.864
10.0	0.852
12.0	0.850
14.0	0.848
17.0	0.851
20.0	0.856
23.0	0.845
27.0	0.858
31.5	0.850
35.0	0.844
39.0	0.850
45.0	0.840
$k_{average}$	0.850

TABLE 5.10 : Rate constant for the transformation of β-nitropropionic acid to aci-form

Temperature $25^{o}C$, 1.0 mM β-nitropropionic acid, $\mu = 0.54$ M and pH = 9.0

Time min.	Rate constant $k \times 10^2$ min^{-1}
9.0	1.612
12.0	1.628
15.0	1.630
17.5	1.631
21.0	1.655
24.0	1.645
27.5	1.601
31.5	1.621
36.0	1.627
41.0	1.628
44.0	1.604
50.0	1.612
$k_{average}$	1.622

TABLE 5.11 : Rate constants and thermodynamic parameters (for the activated complex) for the transformation of nitromethane into its aci-form

1.0 mM nitromethane, $\mu = 0.54$ M

pH	Rate constant $k \times 10^{2}$ min^{-1}	
	25°C	35°C
8.9	1.59	3.28
9.5	1.914	4.05
10.0	3.94	8.36

pH	Thermodynamic parameters 35°C		
	ΔH k cal/mole	ΔG k cal/mole	ΔS cal/deg. mole
9.5	13.77	19.99	-20.2

TABLE 5.12 : Rate constants and thermodynamic parameters (for the activated complex) for the transformation of nitroethane into its aci-form

1.0 mM nitroethane, $\mu = 0.54$ M

pH	Rate constant $k \times 10^{2}$ min^{-1}	
	25°C	35°C
8.9	1.980	3.848
9.5	2.373	5.917
10.0	8.230	17.550

pH	Thermodynamic parameters 35°C		
	ΔH k cal/mole	ΔG k cal/mole	ΔS cal/deg.mole
9.5	16.63	19.77	-10.11

TABLE 5.13 : Rate constants and thermodynamic parameters (for the activated complex) for the transformation of 1-nitropropane into its aci-form

1.0 mM 1-nitropropane, $\mu = 0.54$ M

pH	Rate constant $k \times 10^2$ min^{-1}	
	25°C	35°C
8.0	1.680	3.129
9.5	1.842	4.789
10.0	4.926	10.260

	Thermodynamic parameters 35°C		
	ΔH kcal/mole	ΔG kcal/mole	ΔS cal/deg. mole
9.5	17.43	19.90	-8.05

TABLE 5.14 : Rate constants and thermodynamic parameters (for the activated complex) for the transformation of 2-nitropropane into its aci-form

1.0 mM 2-nitropropane, $\mu = 0.54$ M

pH	Rate constant $k \times 10^2$ min^{-1}	
	25°C	35°C
8.9	0.764	1.42
9.5	0.850	1.81
10.0	0.984	2.06

	Thermodynamic parameters 35°C		
	ΔH kcal/mole	ΔG kcal/mole	ΔS cal/deg. mole
9.5	13.79	20.48	-21.72

TABLE 5.15 : Rate constants and thermodynamic parameters (for the activated complex) for the transformation of β-nitropropionic acid into its aci-form

1.0 mM β-nitropropionic acid, $\mu = 0.54$ M

pH	Rate constant $k \times 10^{2}$ min^{-1}	
	25°C	35°C
9.0	1.622	2.634
9.5	5.227	8.762

pH	Thermodynamic parameters 35°C		
	ΔH k cal/mole	ΔG k cal/mole	ΔS ca/deg. mole
9.5	8.86	16.10	-37.16

LEGEND OF FIGURES

Fig. 5.1. Concentration vs alternating current for different nitro-compounds

Fig. 5.2. A.C. polarogram of nitromethane (1 mM) after equilibrium is attained between the normal nitro-compound and its aci-form at 25°C, $\mu = 0.54$ M. (Broken lines indicate base current.)

Fig. 5.3. A.C. polarogram of nitroethane (1 mM) after equilibrium is attained between the normal nitro-compound and its aci-form at 25°C, $\mu = 0.54$ M. (Broken lines indicate base current.)

Fig. 5.4. A.C. polarogram of 1-nitropropane (1 mM) after equilibrium is attained between the normal nitro-compound and its aci-form at 25°C, $\mu = 0.54$ M. (Broken lines indicate base current.)

Fig. 5.5. A.C. polarogram of 2-nitropropane (1 mM) after equilibrium is attained between the normal nitro-compound and its aci-form at 25°C, $\mu = 0.54$ M. (Broken lines indicate base current.)

Fig. 5.6. A.C. polarogram of β-nitropropionic acid (1 mM) after equilibrium is attained between the normal nitro-compound and its aci-form at 25°C, $u = 0.54$ M. (Broken lines indicate base current.)

Fig. 5.7. Curve 1. Variation of $i_{\sim}$ of nitroethane (1 mM) with time at pH 9.5, 35°C.

Curve 2. Plot of $\log \frac{(i_{\sim})_1}{(i_{\sim})_2}$ vs $(t_2 - t_1)$ for nitroethane at pH 9.5, 35°C.

CHAPTER VI

TENSAMMETRIC STUDIES ON THE INTERACTION BETWEEN SURFACE ACTIVE SUBSTANCES

INTRODUCTION

The behaviour of the electrocapillary curve of mercury in the presence of surface active organic compounds was first examined by Gouy[120] who observed that generally the amount of substance adsorbed at the mercury electrode decreased with increasing field strength. Theoretical interpretations of these phenomena were attempted by various workers[28,65] who derived general equations for the variations of the amount of substance adsorbed with the potential difference at the interface of the electrode. The picture at which these authors arrived was that of the existence of layers of polar molecules (most commonly monolayers) of sparingly soluble organic substances at the electrode boundary. Frumkin and coworkers[66,67,74,232] studied the effect of surface active substances (s.a.s.) on the differential capacity of electrodes in solutions of indifferent electrolytes, using a mercury pool electrode. They also pointed out the relationship between the capacity effects and the electrocapillary curves. All the experimental evidence indicates that if the potential of the mercury electrode is made strongly positive or strongly negative, the adsorbed polar molecules at the mercury surface are displaced by the ions of the supporting electrolyte. The displacement frequently occurs over a small range of potential and a sudden change in the charge density of the double layer results. This in turn leads to a large value of the dynamic capacitance (dq/dE). Frumkin and Proskurnin[232] thus observed two maxima with a strong depression in the middle part in the capacity potential curve of sodium sulphate saturated with octyl alcohol. The extreme anodic and cathodic ends of the curve coincided with those obtained with sodium sulphate alone. Grahame[81] repeated these experiments witn similar results. The technique employed by Grahame consisted in balancing out the double layer capacity with a set of variable capacitors suitably arranged in a Wheatstone network, whilst a small a.c. voltage was superimposed on the d.c. potential. The process of balancing was laborious and frequently the peaks of the capacity-voltage curves were not sharply defined although the results were very precise.

When electrolytes containing small amounts of surface active substances (e.g., aniline, pyridine, phenol, cresol, benzoic acid, octyl alcohol, etc.) were subjected to a.c. polarography[23-25], current-voltage curves similar to the capacitance-voltage curves of Proskurnin and Frumkin[232] and of Grahame[81] were observed. Studies on surface active substances have also been carried out extensively by Gupta and Sharma[245]. But whereas the waves in a.c. polarography are produced as a consequence of depolarization processes occurring at the d.m.e. (by virtue of the applied d.c. potential), the a.c. waves obtained in the presence of surfactants are produced without corresponding d.c. current flow[11]. In other words, the electrode is depolarized with respect to a.c. only and remains polarized with respect to d.c. It was proposed to distinguish this type of electrode process, which is fundamentally different from a.c. polarography. Breyer and Hacobian[11] termed it "tensammetry".

Breyer and Hacobian observed that when a mixture of two s.a.s. was present in a solution of an indifferent electrolyte, only one tensammetric wave was obtained, corresponding to the substance with a more cathodic peak potential. They also found that certain depolarizers freely penetrate surface films and yield good a.c. waves even after the addition of surfactant such as p-nitrophenol in presence of octyl alcohol[14]. Gupta et al.[64,65] reported the interaction between two surfactants to form a complex which is more surface active than the individual surfactants. Infrared and conductometric studies support these observations[119].

The present work deals with the studies on the interaction of phenol with some organic bases by tensammetry in aqueous medium. The composition of the complexes have also been confirmed by conductometric measurements in aqueous medium. Infrared spectrophotometry has been used to establish, qualitatively, the existence of hydrogen bonded interaction in the formation of these complexes. However, no data are available in literature on such studies.

EXPERIMENTAL

All organic compounds (AnalaR, BDH) were redistilled before use. 0.1 M KCl (BDH, AR) was used as the supporting electrolyte. All solutions were prepared in double distilled water. The constants of d.m.e. were: m = 4.564 mg/s, and t = 1.8 s in 0.1 M KCl, open circuit. Conductometric measurements were made using a conductivity meter type LBR of Wissenschafflich-Technische, Werkstatten, Germany with a titration cell type LTI. Perkin Elmer IR 237B Grating Spectrophotometer with NaCl optics was employed for the studies in CCl_4. All experiments were performed at 25±0.2°C.

RESULTS AND DISCUSSION

A study of the tensammetric peak potentials of the individual surface active substances and that of the peak potentials of the mixture of the phenol with pyridine, phenol with o-toluidine, phenol with m-toluidine and phenol with aniline resulted in the appearance of a new peak in the case of the mixtures and the disappearance of the individual peaks. The new peak appeared at a more cathodic potential than that of the individual peaks of the surfactant and the peak height ~~height~~ also increased. Fig. 6.1 shows the individual peak of phenol and pyridine and that of the mixture of phenol and pyridine. Such a behaviour may be due to the formation of a complex which is more surface active than the individual surfactants[64,65].

Fig. 6.2 gives the curves showing the shift of the peak potential of the mixture of phenol and pyridine to more negative potential by keeping the concentration of phenol fixed (curve 1) and varying the concentration of pyridine in the mixture and vice versa (curve 2). A break in the curve, independent of the way in which the ratio between the surfactants has been reached, is observed corresponding to the ratio of 1:1 between phenol and pyridine. Further curve 1 (Fig. 6.3) shows the change in alternating current after successive

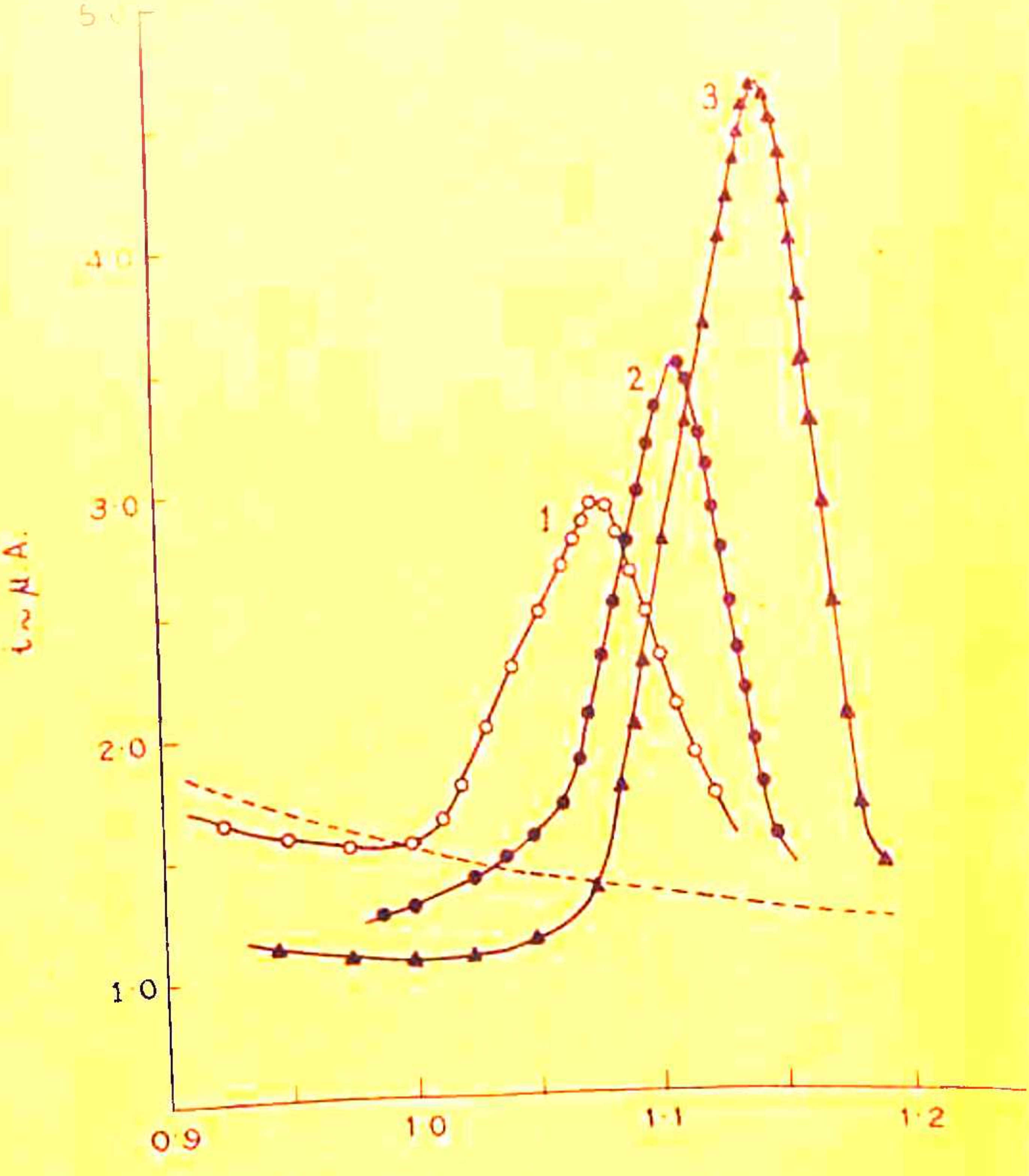


FIG. 6·1

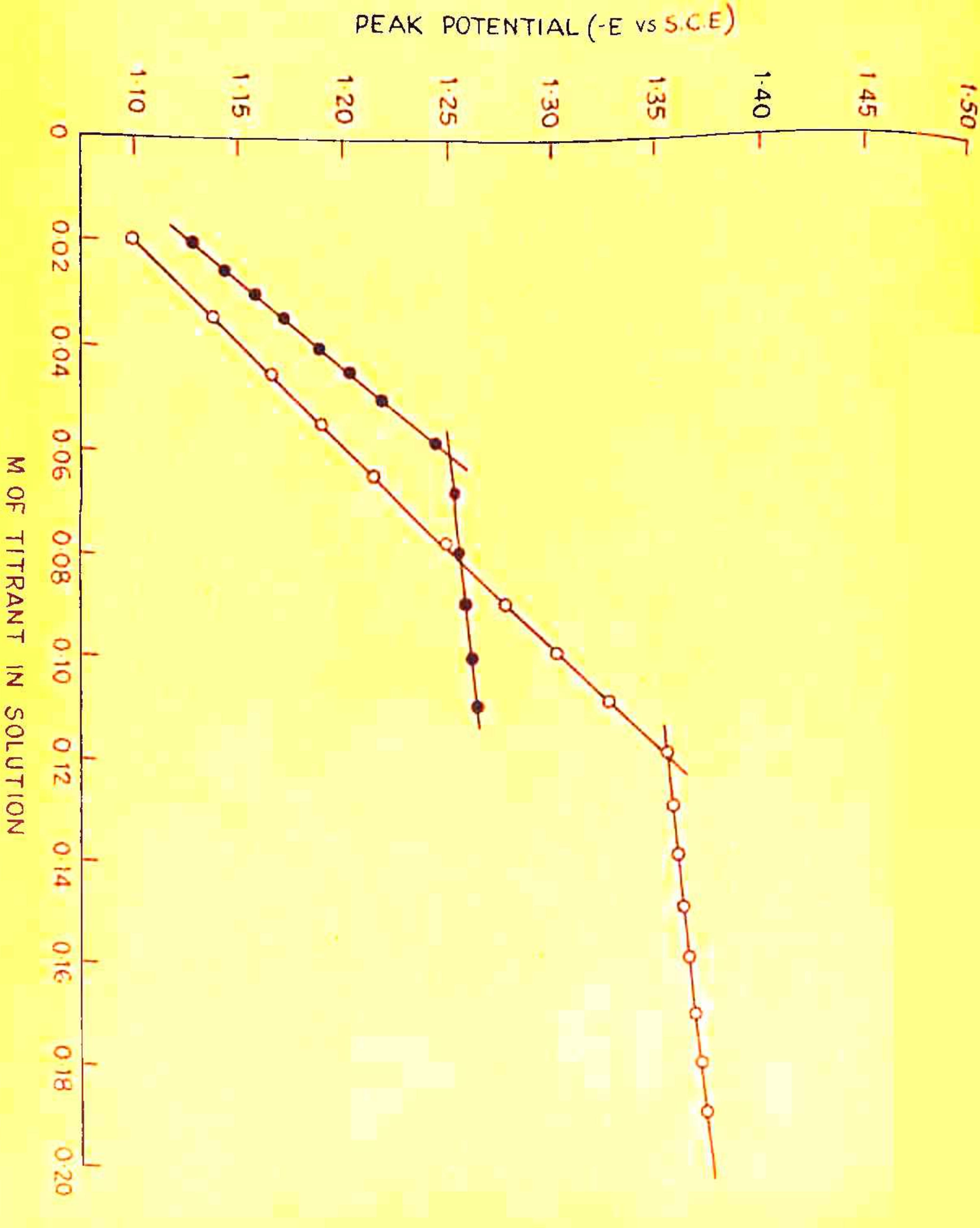

PEAK POTENTIAL (-E vs S.C.E)
1·10
1·15
1·20
1·25
1·30
1·35
1·40
1·45
1·50
0
0·02
0·04
0·06
0·08
0·10
0·12
0·14
0·16
0·18
0·20
M OF TITRANT IN SOLUTION

FIG 6.2

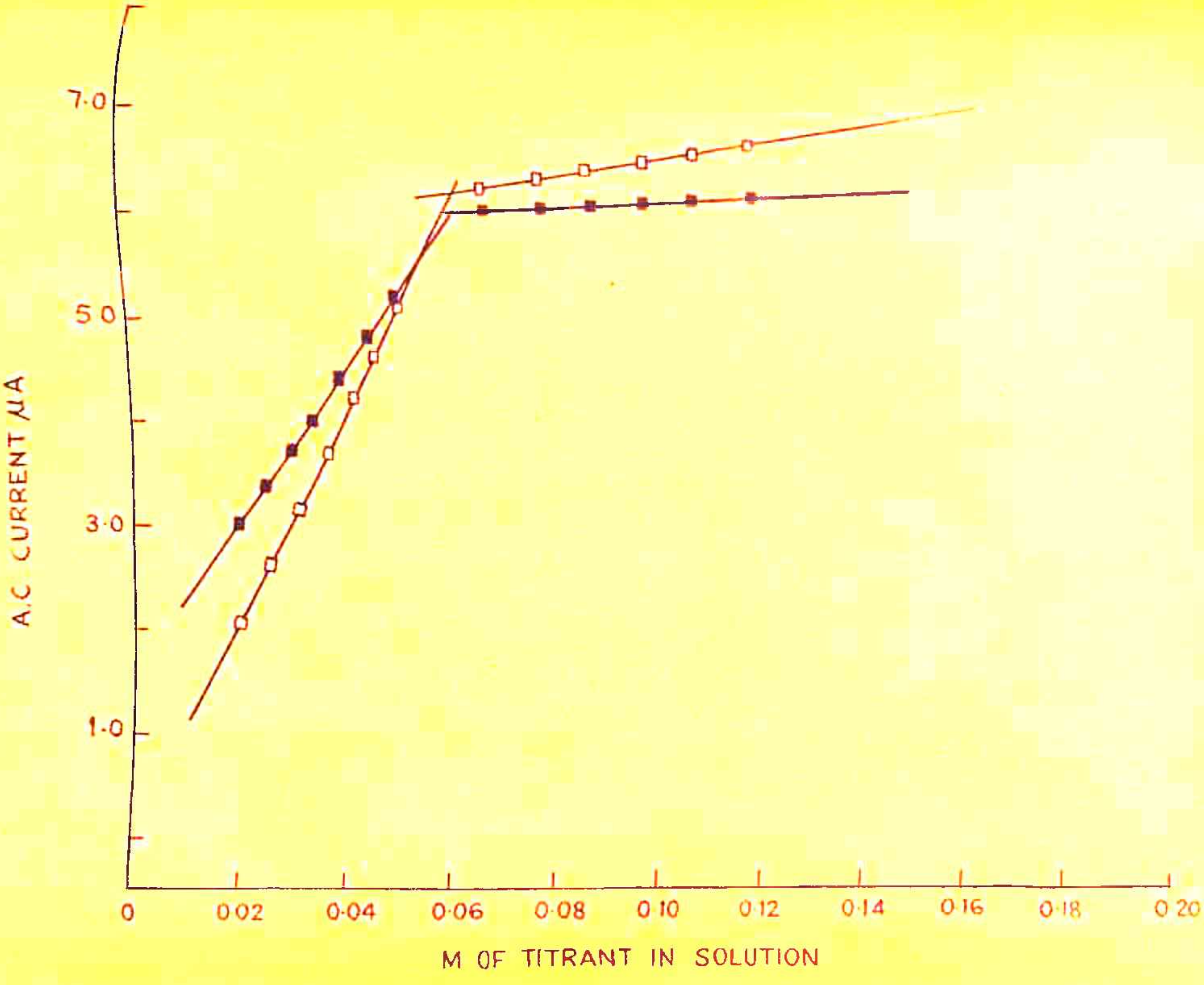

A.C CURRENT μA
7·0
5·0
3·0
1·0
0
0·02
0·04
0·06
0·08
0·10
0·12
0·14
0·16
0·18
0·20
M OF TITRANT IN SOLUTION

FIG. 6·3

addition of pyridine to a fixed concentration of phenol and vice versa (curve 2, Fig. 6.3). It can be noticed that a break occurs similar to the breaks in the curves 1 and 2 of Fig. 6.2. Curve 1 in Fig. 6.4 shows the conductometric curve obtained with successive additions of pyridine to a fixed concentration of phenol and vice versa (curve 2, Fig. 6.4). In this case also a break is observed corresponding to phenol to pyridine ratio of 1:1.

The results of the studies on phenol-(ortho-toluidine) system are shown in Fig. 6.5. The concentration of phenol was fixed and the effect of varying the concentration of o-toluidine on the peak potential (curve 1, Fig. 6.5), peak current (curve 2, Fig. 6.5) and conductance (curve 3, Fig. 6.5) of the mixture were studied. The composition of the complex of phenol with o-toluidine was found to be 3:1.

Similarly the studies on the composition of the complex of phenol with m-toluidine showed a ratio of phenol to m-toluidine as 3:1 (Fig. 6.6) and the composition of the complex of phenol to aniline as 1:1 (Fig. 6.7).

There are several reports in the literature where hydrogen bonded interaction of organic bases with hydroxylic compounds have been investigated employing IR Spectrophotometry[5,231,236]. A qualitative study in CCl_4 of the systems mentioned in this chapter was made by IR spectrophotometry. The frequency shifts and the change in the intensity of the O-H stretching band of phenol pointed to hydrogen bonded interaction.

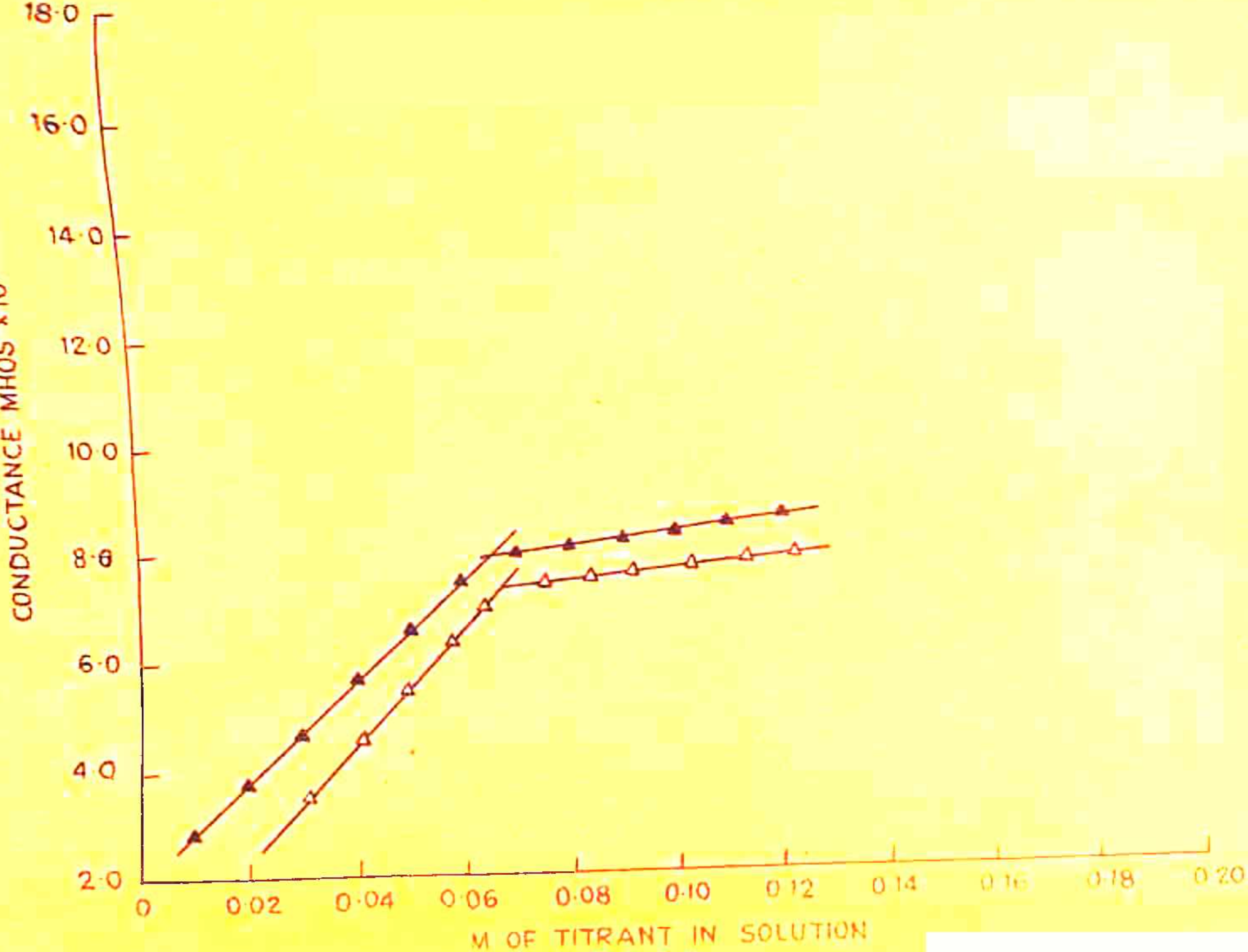

CONDUCTANCE MHOS x10⁵
18·0
16·0
14·0
12·0
10·0
8·0
6·0
4·0
2·0
0
0·02
0·04
0·06
0·08
0·10
0·12
0·14
0·16
0·18
0·20
M OF TITRANT IN SOLUTION

FIG. 6.4

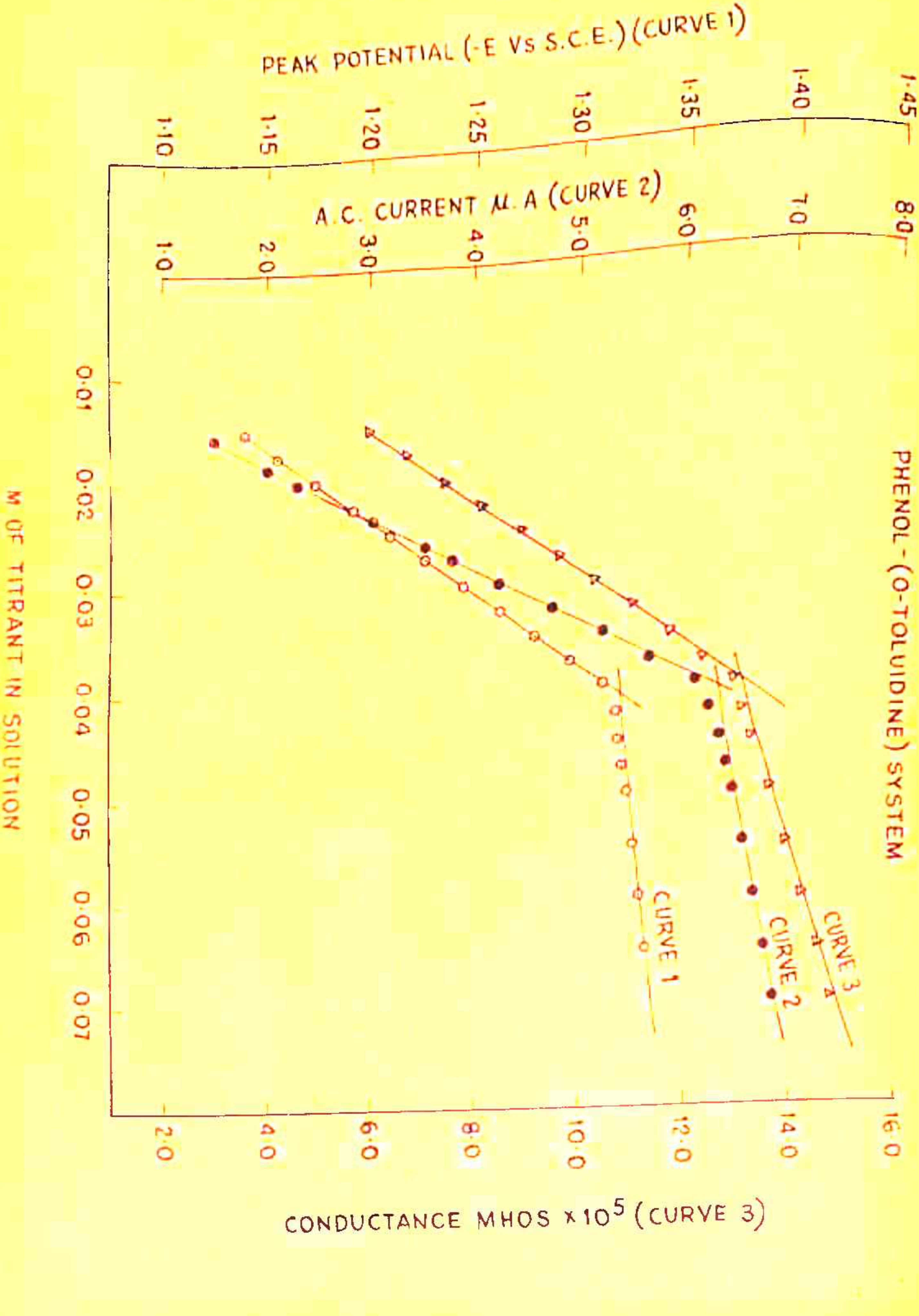

PHENOL-(O-TOLUIDINE) SYSTEM
PEAK POTENTIAL (-E Vs S.C.E.) (CURVE 1)
1·10
1·15
1·20
1·25
1·30
1·35
1·40
1·45
A.C. CURRENT μA (CURVE 2)
1·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
CONDUCTANCE MHOS × 10^5 (CURVE 3)
2·0
4·0
6·0
8·0
10·0
12·0
14·0
16·0
M OF TITRANT IN SOLUTION
0·01
0·02
0·03
0·04
0·05
0·06
0·07
CURVE 1
CURVE 2
CURVE 3

FIG. 6.5

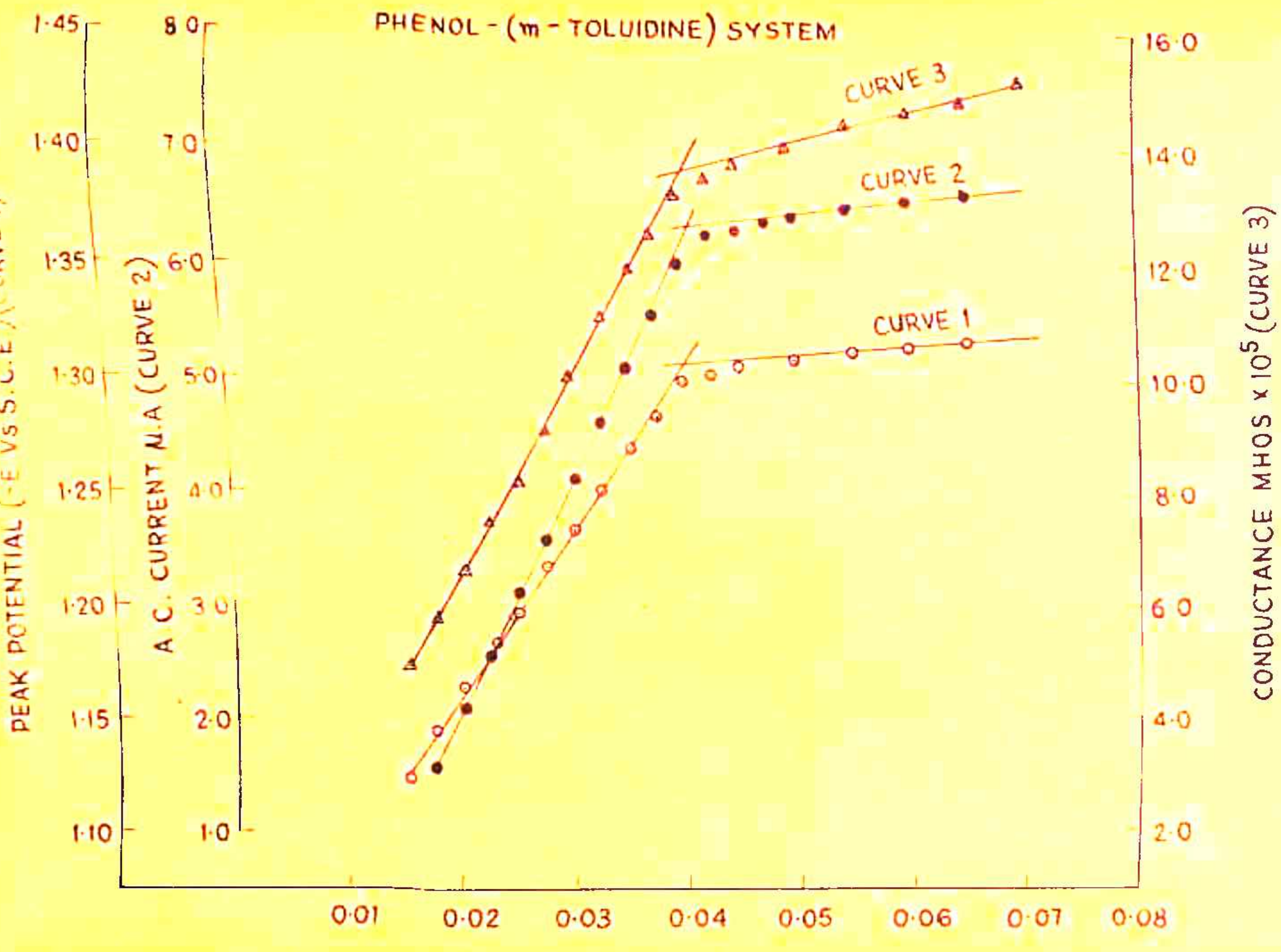

PHENOL - (m - TOLUIDINE) SYSTEM
CURVE 3
CURVE 2
CURVE 1
PEAK POTENTIAL (-E Vs S.C.E)(CURVE 1)
1·45
1·40
1·35
1·30
1·25
1·20
1·15
1·10
A.C. CURRENT μA (CURVE 2)
8·0
7·0
6·0
5·0
4·0
3·0
2·0
1·0
CONDUCTANCE MHOS × 10^5 (CURVE 3)
16·0
14·0
12·0
10·0
8·0
6·0
4·0
2·0
0·01
0·02
0·03
0·04
0·05
0·06
0·07
0·08
M OF TITRANT IN SOLUTION

FIG. 6·6

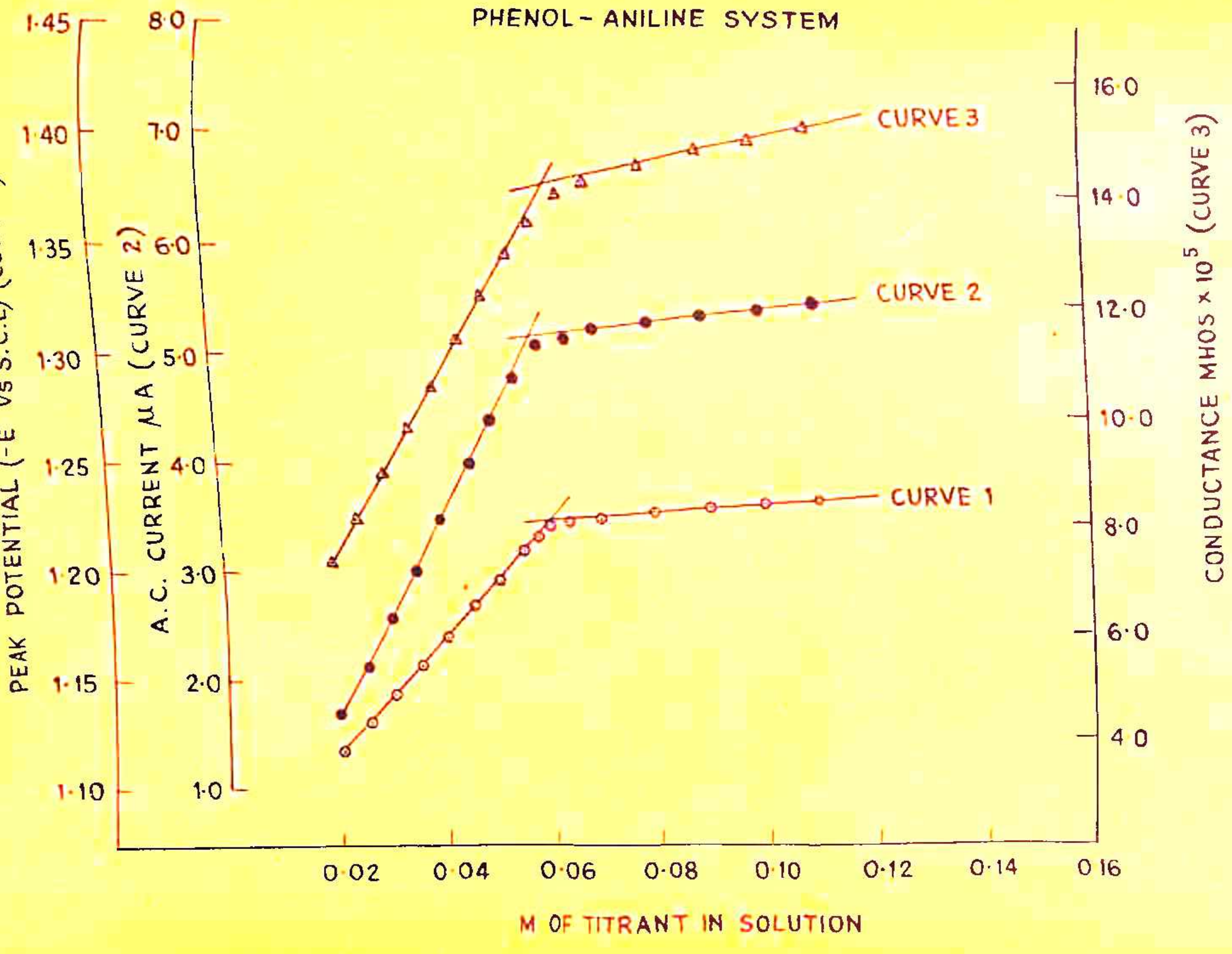

PHENOL - ANILINE SYSTEM
PEAK POTENTIAL (-E Vs S.C.E) (CURVE 1)
1·10
1·15
1·20
1·25
1·30
1·35
1·40
1·45
A.C. CURRENT μA (CURVE 2)
1·0
2·0
3·0
4·0
5·0
6·0
7·0
8·0
CURVE 3
CURVE 2
CURVE 1
CONDUCTANCE MHOS × 10^5 (CURVE 3)
4·0
6·0
8·0
10·0
12·0
14·0
16·0
0·02
0·04
0·06
0·08
0·10
0·12
0·14
0·16
M OF TITRANT IN SOLUTION

FIG. 6·7

Legend of the figures

Fig. 6.1 : Curve 1. A.C. polarogram of 0.12 M phenol.

Curve 2. A.C. polarogram of 0.04 M pyridine.

Curve 3. A.C. polarogram of 0.12 M phenol + 0.04 M pyridine.

Fig. 6.2 : Tensammetric titrations (peak potential vs concentration).

Curve 1. 50.0 ml 0.12 M phenol vs pyridine.

Curve 2. 50.0 ml 0.06 M pyridine vs phenol.

Fig. 6.3 : Tensammetric titrations (peak current vs concentration)

Curve 1. 50.0 ml 0.064 M phenol vs pyridine.

Curve 2. 50.0 ml 0.064 M pyridine vs phenol.

Fig. 6.4 : Conductometric titrations

Curve 1. 50.0 ml 0.064 M phenol vs pyridine.

Curve 2. 50.0 ml 0.064 M pyridine vs phenol.

Fig. 6.5 : Curve 1. 50.0 ml 0.12 M phenol vs o-toluidine (peak potential vs concentration)

Curve 2. 50.0 ml 0.12 M phenol vs o-toluidine (peak current vs concentration)

Curve 3. 50.0 ml 0.12 M phenol vs o-toluidine (conductometric titration)

Fig. 6.6 : Curve 1. 50.0 ml 0.12 M phenol vs m-toluidine (peak potential vs concentration)

Curve 2. 50.0 ml 0.12 M phenol vs m-toluidine (peak current vs concentration)

Curve 3. 50.0 ml 0.12 M phenol vs m-toluidine (conductometric titration)

Fig. 6.7 : Curve 1. 50.0 ml 0.06 M phenol vs aniline (peak potential vs concentration)

Curve 2. 50.0 ml 0.06 M phenol vs aniline (peak current vs concentration)

Curve 3. 50.0 ml 0.06 M phenol vs aniline (conductometric titration)

REFERENCES

REFERENCES

1. Adams, R.N., J. Phys. Chem., 72, 4336 (1968).

2. Astle, M.J. and McConnell, W.A., J. Am. Chem. Soc., 65, 35 (1943).

3. Astle, M.J. and Copper, W.P., J. Am. Chem. Soc., 65, 2395 (1943).

4. Astle, M.J. and Stephenson, S.P., J. Am. Chem. Soc., 65, 2399 (1943).

5. Bellamy, L.J., "Infrared spectra of complex molecules", Mathuen and Co., London (1961).

6. Bodor, N., Fey, L. and Kovendi, A., Rev. Chim. (Bucharest), 19, 552 (1968).

7. Boeke, J. and van Suchtelen, H., Z. Electrochem., 45, 753 (1939).

8. Breyer, B. and Bauer, H.H., "Alternating current polarography and tensammetry", Interscience, New York (1963).

9. Breyer, B. and Gutmann, F., Trans. Faraday Soc., 42, 650 (1946).

10. Breyer, B., Aust. J. Sci., 16, 109 (1953).

11. Breyer, B. and Hacobian, S., Aust. J. Sci. Res., A5, 500 (1952).

12. Idem, Aust. J. Chem., 9, 7 (1956).

13. Idem, Anal. Chim. Acta, 16, 497 (1957).

14. Breyer, B., Bauer, H.H. and Hacobian, S., Aust. J. Chem., 7, 305 (1954).

15. Breyer, B., Bauer, H.H. and Hacobian, S., Aust. J. Chem., 8, 312 (1955).

16. Breyer, B. and Bauer, H.H., ibid., 8, 472 and 480 (1955)

17. Idem, ibid., 9, 425 (1956).

18. Idem, "Alternating current polarography and tensammetry", Interscience, pp. 258 (1963).

19. Idem, Aust. J. Chem., 8, 467 (1955).

20. Idem, ibid., 9, 437 (1956).

21. Breyer, B., Gutmann, F. and Bauer, H.H., Osterr. Chemiker-Ztg., 57, 67 (1956).

22. Breyer, B. and Bauer, H.H., "Alternating current polarography and tensammetry", Interscience, New York, pp. 271 (1963).

23. Breyer, B. and Gutmann, F., Trans. Faraday Soc., 42, 645 (1946).

24. Idem, Discuss. Faraday Soc., No.1, 19 (1947).

25. Breyer, B., Gutmann, F. and Hacobian, S., Aust. J. Sci. Res., A3, 558 (1950).

26. Breyer, B. and Bauer, H.H., "Alternating current polarography and tensammetry", Interscience, New York, pp. 132 (1963).

27. Britz, D. and Bauer, H.H., Electrochim. Acta, 13, 347 (1968).

28. Butler, J.A.V., Proc. Roy. Soc., A122, 399 (1929).

29. Chambers, J.Q., Dissertation Abstr., 26, 52 (1965).

30. Chatterjee, M.K., Ph.D. Thesis, Birla Institute of Technology and Science, Pilani, India (1967).

31. Cheah, E.P.T., Hacobian, S. and Harle, A.I., Aust. J. Chem., 19, 1117 (1966).

32. Idem, ibid., 19, 1609 (1966).

33. Cumins, C.A., Anal. Chem., 19, 376 (1947).

34. DeFord, D.D. and Hume, D.N., J. Am. Chem. Soc., 73, 5321 (1951).

35. DeFord, D.D., Hume, D.N. and Cave, G.C.B., ibid., 73, 5323 (1951).

36. Delahay, P., J. Am. Chem. Soc., 75, 1430 (1957).

37. Idem, ibid., 73, 4944 (1951).

38. Delahay, P. and Strassner, J.E., ibid., 73, 5219 (1951).

39. Delahay, P. and Mattax, C.C., ibid., 76, 5314 (1954).

40. Delahay, P., J. Am. Chem. Soc., 75, 1190 (1953).

41. Delahay, P. and Strassner, J.E., ibid., 74, 6232 (1952).

42. Delahay, P. and Berzins, T., ibid., 75, 5716 (1953).

43. Delahay, P., "New Instrumental Methods in Electrochemistry", Interscience, New York, pp. 81 (1954).

44. Dennis, S.F., Powell, A.S. and Astle, M.J., J. Am. Chem. Soc., 71, 1484 (1949).

45. Deswarte, S., Compt. Rend., 263, 628 (1966).

46. Deswarte, S. and Souchay, P., ibid., 262, 981 (1966).

47. Idem, ibid., 266, 84 (1968).

48. Doss, K.S.G. and Kalyanasundaram, A., Curr. Sci., 20, 199 (1951).

49. Idem, Proc. Indian Acad. Sci., 35, 27 (1952).

50. Doss, K.S.G. and Kalyanasundaram, Proc. Indian Acad. Sci., 35, 173 (1952).

51. Doss, K.S.G. and Gupta, S.L., ibid., 36, 493 (1952).

52. Idem, Bull. Central Electrochem. Res. Inst., 1, No.2, 9 (1954).

53. Idem, Proc. Deccan Eng. Tech. Assocn., India, 11, 235 (1954).

54. Idem, Sci. and Cult., 22, 102 (1956).

55. Doss, K.S.G., Gupta, K.K. and Rao, D.L.N., Proc. Sugar Tech. Assocn., India, No. 21, 9 (1952).

56. Doss, K.S.G., Indian Soap Journal, 18, 12 (1952).

57. Doss, K.S.G. and Venkatesan, V.K., Proc. Indian Acad. Sci., 49, 129 (1959).

58. Doss, K.S.G. and Kalyanasundaram, A., Proc. Indian Acad. Sci., 33, 298 (1951).

59. Elofson, R.M. and Atkinson, J.G., Can. J. Chem., 34, 4 (1956).

60. Elving, P.J., J. Am. Chem. Soc., 72, 3241 and 5183 (1950).

61. Idem, ibid., 73, 947 (1951).

62. Eyring, H., Chem. Rev., 17, 65 (1935).

63. Eyring, H., Marker, L. and Kwoh, T.C., J. Phys. and Colloid Chem., 53, 187 (1949).

64. Field, M., Valle, C. and Kane, M., J. Am. Chem. Soc., 71, 421 (1949).

65. Frumkin, A.N., Z. Phys., 35, 792 (1926).

66. Frumkin, A.N. and Gorodetskaya, A., C.R. Acad. Sci., U.R.S.S., 18, 639 (1928).

67. Frumkin, A.N., Gorodetskaya, A. and Chugunov, P., Acta Physiochem., U.R.S.S., 1, 12 (1934).

68. Fujinaga, T., Arai, T. and Kitazawa, C., Nippon Kagaku Zasshi, 85, 811 (1964).

69. Gaur, J.N. and Goswami, N.K., Electrochim. Acta, 12, 1483 (1967).

70. Idem, J. Indian Chem. Soc., 46, 1030 (1969).

71. Gelling, P.J., Z. Electrochem. Ber. Bunsenges. Physik. Chem., 66, 477, 481 and 799 (1962); 67, 167 (1963).

72. Glasstone, S., Laidler, K.J. and Eyring, H., "Theory of Rate Processes", McGraw-Hill, New York, pp. 148 (1940).

73. Gorodetzkeys, A. and Frumkin, A.N., Compt. Rend. Acad. Sci., U.R.S.S., 18, 639 (1938).

74. Gorodetskaya, A., Acta Physiochim., U.R.S.S., 12, 309 (1940).

75. Gorokhovski, V.M. and Ponomarova, N.M., Z. Obshch. khim., 29, 3535 (1959).

76. Goward, G.W., Bricker, C.F. and Wildman, W.C., J. Org. Chem., 20, 378 (1955).

77. Graham, R.P. and Larrabee, G.B., Analyst, 82, 415 (1957).

78. Graham, R.P., Van Dalen, E. and Upton, A.M.C., Can. J. Chem., 30, 1069 (1952).

79. Grahame, D.C., J. Am. Chem. Soc., 63, 1207 (1941).

80. Idem, ibid., 80, 1736 (1958).

81. Idem, ibid., 68, 301 (1946).

82. Idem, Chem. Rev., 41, 441 (1947).

83. Idem, J. Am. Chem. Soc., 80, 4201 (1958).

84. Grahame, D.C. and Parsons, R., ibid., 83, 1291 (1961).

85. Grimaldi, F.S. in "Treatise on Analytical Chemistry", Edited by Kolthoff, I.M. and Elving, P.J., Interscience, Part II, Section A, Volume 5, pp. 188 (1961).

86. Gupta, S.L., J. Sci. and Ind. Res., 12B, 84 (1953).

87. Idem, Kolloid-Z, 132, 21 (1953).

88. Idem, ibid., 137, 86 (1954).

89. Idem, Proc. Indian Acad. Sci., 39, 282 (1956).

90. Idem, Kolloid-Z, 141, 100 (1955).

91. Idem, ibid., 141, 102 (1955).

92. Idem, Proc. Nat. Inst. Sci., India, 24, 377 (1958).

93. Gupta, S.L., Saraswati, L. and Sharma, S.K., Indian J. Chem., 1, 283 (1963).

94. Gupta, S.L. and Sharma, S.K., Talanta, 11, 105 (1964).

95. Idem, J. Indian *Chem. Soc., 41, 385 (1964).*

96. Idem, J. Indian Chem. Soc., 41, 663 (1964).

97. Idem, ibid., 41, 668 (1964).

98. Idem, Electrochim. Acta, 10, 151 (1965).

99. Idem, ibid., 10, 549 (1965).

100. Idem, J. Indian Chem. Soc., 43, 51 (1966).

101. Idem, ibid., 43, 183 (1966).

102. Idem, Kolloid-Z, 190, 40 (1963).

103. Idem, J. Indian Chem. Soc., 42, 855 (1965).

104. Idem, J. Electroanal. Chem., 8, 478 (1964).

105. Gupta, S.L., Chatterjee, M.K. and Sharma, S.K., J. Electroanal. Chem., 7, 81 (1964).

106. Gupta, S.L. and Chatterjee, M.K., Proc. Nat. Acad. Sci., India, 31A, No. 4 (1965).

107. Idem, Jour. Birla Inst. Tech. and Sci., 1, 105 (1967).

108. Idem, Trans. S.A.E.S.T., Karaikudi, India, 3, 1 (1968).

109. Gupta, S.L. and Sharma, S.K., Indian J. Chem., 4, 166 (1966).

110. Gupta, S.L. and Chatterjee, M.K., J. Electroanal. Chem., 8, 245 (1964).

111. Gupta, S.L. and Nawal Kishore, J. Inst. of Chemists, India, 61, 210 (1969).

112. Gupta, S.L., Soni, R.N. and Jaitly, J.N., J. Indian Chem. Soc., 43, 331 (1966).

113. Idem, ibid., 42, 384 (1965).

114. Gupta, S.L. and Chatterjee, M.K., Rev. Polarog. (Japan), 14, 198 (1967).

115. Idem, Indian J. Chem., 4, 22 (1966).

116. Gupta, S.L. and Nawal Kishore, Convention of Chemists, I.I.T., Kharagpur, India, January (1970).

117. Idem, Trans. S.A.E.S.T., Karaikudi, India, 1, 21 (1970).

118. Idem, Electrochim. Acta, Communicated.

119. Gupta, S.L. and Soni, R.N., ibid., 14, 1313 (1969).

120. Guoy, G., Ann. Chim. Phys., 29, 145 (1903); 8, 231 (1906); 9, 75 (1906).

121. Hahn, R.B. in "Treatise on Analytical Chemistry", Edited by Kolthoff, I.M. and Elving, P.J., Interscience, Part II, Section A, Volume 5, pp. 99 (1961)

122. Idem, ibid., pp. 78.

123. Harvey, A.E. and Manning, D.L., J. Am. Chem. Soc., 72, 4488 (1950).

124. Hiidmaa, S., Pihl, A. and Talvik, A., Reakts, Sposobnost Org. Soedin., Tartu. Gos. Univ., 3, 62 (1966).

125. Holleck, L. and Exner, H., Z. Electrochem., 56, 677 (1952).

126. Holleck, L. and Herman, S., Naturwiss., 41, 87 (1954).

127. Holleck, L. and Kastening, B., Rev. Polarog. (Japan), 11, 129 (1963).

128. Holleck, L., Vavricka, S. and Heyrovsky, M., Z. Naturforsch., B22, 1226 (1967).

129. Idem, J. Electroanal. Chem., 17, 293 (1968).

130. Heyrovsky, J., Czech. Patent No.9, 4672-46, 2, 10,(1947); Chem. Listy, 45, 149 (1949).

131. Heyrovsky, J. and Ilkovic, D., Coll. Czech. Chem. Comm., 7, 198 (1935).

132. Heyrovsky, J., Sorm, F. and Forejt, J., Coll. Czech. Chem. Comm., 12, 11 (1947).

133. Heyrovsky, J. and Kuta, J., "Principles of Polarography", Academic Press, New York, pp. 206 (1966).

134. Idem, ibid., pp. 211.

135. Ibarz, I. and Pladellorens, J., Anales Fis. Quim., 50B, 257 (1964).

136. Ilkovic, D., Coll. Czech. Chem. Comm., 6, 498 (1934).

137. Jain, P.C. and Kapoor, R.C., J. Polarog. Soc., 14, 27 (1968).

138. Idem, ibid., 14, 101 (1968).

139. Idem, ibid., 14, 145 (1968).

140. Jannakoudakis, D., Naturwiss., 49, 57 (1962).

141. Jannakondakis, D., Stalidis, G. and Mavridis, P.G., Chim. Cronika Athens, Greece, 31, 11 (1966).

142. Job, P., Ann. Chimie., X(9), 113 (1928); (XI)6, 97 (1936).

143. Kalvoda, R., and Zyka, J., Coll. Czech. Chem. Comm., 15, 630 (1950); Chem. Listy., 45, 82 (1951).

144. Kambara, T. and Tachi, I., Bull. Chem. Soc., Japan, 25, 135 (1952).

145. Kastening, B. and Holleck, L., Z. Electrochem., 64, 823 (1960).

146. Idem, Vort. Origi. Intern. Kongr. Grenze, Stoffe, Cologne, 2, 288 (1962).

147. Kemula, W. and Chodhowska, A., Rocz. Chem., 41, 1373 (1967).

148. King, C.V. and Cathcart, W.H., J. Am. Chem. Soc., 58, 1639 (1936).

149. Kivalo, P., Suomen Kem., B27, 93 (1954).

150. Kivalo, P., Oldham, K.B. and Laitinen, H.A., J. Am. Chem. Soc., 73, 1448 (1953).

151. Idem, ibid., 75, 4148 (1953).

152. Kolthoff, I.M. and Lingane, J.J., "Polarography", Vol. I, Interscience (1952).

153. Kolthoff, I.M. and Bovey, F.A., J. Am. Chem. Soc., 70, 791 (1948).

154. Kolthoff, I.M. and Gregor, H.P., Anal. Chem., 20, 541 (1948).

155. Kolthoff, I.M. and Pan, Y.D., J. Am. Chem. Soc., 61, 340 (1939).

156. Kolthoff, I.M. and Lingane, J.J., "Polarography", Interscience, New York, Vol. 1, pp. 214 (1952).

157. Idem, ibid., pp. 218 and 227.

158. Idem, ibid., pp. 215.

159. Kolusheva, A., Nino, N. and Vulkova, A., Farmatsiya (Sifia), 18, 22 (1968).

160. Korshunov, I.A. and Kirillova, A.S., J. Gen. Chem., U.S.S.R., 18, 785 (1948).

161. Koryta, J., Chem. Zvesti., 8, 644 (1954).

162. Koutecky, J., Czech. Cas. Fys., 2, 50 (1953).

163. Koutecky, J. and Von Stackelberg, M., "Progress in Polarography", Vol. I, Interscience, pp. 21 (1962).

164. Koutecky, J., Coll. Czech. Chem. Comm., 18, 597 (1953); 21, 836 (1956).

165. Idem, Chem. Listy., 47, 327 (1953).

166. Laitinen, H.A. and Kolthoff, I.M., J. Am. Chem. Soc., 61, 3344 (1939).

167. Lange, N.A., "Handbook of Chemistry", 20th Edn., McGraw-Hill, New York, pp. 1667 (1961).

168. Laviron, E., Fournari, P. and Greusard, J., Bull. Soc. Chim., France, p. 1255 (1967).

169. Laviron, E. and Fournari, P., ibid., p. 518 (1966).

170. Leibzon, V.N., Belikov, V.M. and Kozlov, L.M., Electrokhimiya, 3, 305 (1967).

171. Idem, Tr. Kazan. Khim. Tekhnol. Inst., No.34, 381 (1965).

172. Leibzon, V.N., Belikov, V.M. and Mairanovskii, S.G., Electrokhimiya, 4, 290 (1968).

173. Lingane, J.J., J. Am. Chem. Soc., 67, 1916 (1945).

174. Lingane, J.J. and Loveridge, B.A., ibid., 72, 138 (1950).

175. Loveland, J.W. and Elving, P.J., J. Phys. Chem., 56, 250 (1952).

176. Idem, ibid., 56, 255 (1952).

177. Idem, ibid., 56, 935 (1952).

178. Idem, ibid., 56, 941 (1952).

179. Idem, ibid., 56, 945 (1952).

180. MacAleavy, C., Belgian Patent, 443, 003 (1941).

181. Idem, French Patent, 886, 848 (1942).

182. MacGillavery, D. and Rideal, E.K., Rec. Trav. Chim., 56, 1013 (1937).

183. Mairanovskii, S.G. and Dolgaya, O.M., Electrokhimiya, 4, 879 (1968).

184. Malinovskii, M.S., Yurko, D.G., Yudasina, A.G. and Korchagina, A.M., Ukr. Khim. Zh., 34, 1202 (1968).

185. Maron, S.H. and LaMer, V.K., Annals of New York Academy of Sciences, 39, 355 (1940); J. Am. Chem. Soc., 60, 2588 (1938).

186. Matsuda, H., Bull. Chem. Soc., Japan, 26, 342 (1953).

187. Idem, Z. Electrochem. Ber. Bunsenges. Physik. Chem., 61, 489 (1957); 62, 977 (1958); 63, 1164 (1959).

188. Matsuda, H. and Ayabe, Y., Bull. Chem. Soc., Japan, 28, 422 (1955).

189. McBain, J.W. and Dawson, C.R., Proc. Royal Soc., 32, 152A (1935).

190. McCord, T.G., Hung, H.L. and Smith, D.E., J. Electroanal. Chem., Interfacial Electrochem., 21, 5 (1969).

191. McCord, T.G. and Smith, D.E., Anal. Chem., 40, 1959 (1968).

192. Idem, ibid., 41, 116 (1969).

193. Idem, ibid., 41, 131 (1969).

194. Idem, ibid., 40, 289 (1968).

195. Idem, ibid., 40, 1967 (1968).

196. Idem, ibid., 41, 1423 (1969).

197. Meites, L., "Polarographic Techniques", II Ed., Interscience, pp. 244 (1965).

198. Idem, ibid., pp. 254.

199. Idem, ibid., pp. 246.

200. Idem, ibid., pp. 82.

201. Idem, ibid., pp. 229.

202. Idem, ibid., pp. 702.

203. Idem, ibid., pp. 682.

204. Idem, ibid., pp. 273.

205. Meites, L., Polarographic Techniques", I Ed., Interscience, pp. 127 (1955).

206. Melik-Gaikzian, V.I., J. Phys. Chem., U.R.S.S., 26, 550 (1952).

207. Idem, ibid., 26, 1184 (1952).

208. Meiman, N.N., Zh. Fix. Khim., 22, 1454 (1948).

209. Miller, E.W., Arnold, A.P. and Astle, M.J., J. Am. Chem. Soc., 70 3971 (1948).

210. Miller, I.R. and Grahame, D.C., J. Am. Chem. Soc., 78, 3577 (1956).

211. Idem, ibid., 79, 2093 and 3006 (1957).

212. Müller, R.H., Garman, R.L., Droz, M.E. and Petras, J., Ind. Eng. Chem. (Anal. Ed.), 10, 339 (1938).

213. Näsänen, R. and Uusitalo, E., Suomen Kem., 28B, 17 (1955).

214. Novikov, E.G. and Pozdeva, A.G., Zh. Prikl. khim., 40, 217 (1967).

215. Page, J.E., Smith, J.W. and Waller, J.G., J. Phys. Colloid Chem., 53, 545 (1949).

216. Palyi, G., Kolor. Ert., 10, 182 (1968).

217. Pearson, J., Trans. Faraday Soc., 44, 683 (1948).

218. Idem, ibid., 44, 692 (1948).

219. Idem, ibid., 45, 199 (1949).

220. Pearson, J. and Maurice, , Bull. Soc. Chim., France, 6, 1832 (1966).

221. Pearson, R.C., J. Am. Chem. Soc., 70, 204 (1948).

222. Penttinen, K. and Lindberg, J.J., Suomen Kem., 42, 203 (1969).

223. Person, M. and Laviron, E., Bull. Soc. Chim., France, p. 2669 (1968).

224. Person, M. and Tirouflet, J., Compt. Rend., 258 (20), 4979 (1964); Bull. Soc. Chim., France, 183 (1966).

225. Peter, F., Palko, I. and Lorinc, A., Magy. Kem. Folyoirat, 72, 187 (1965).

226. Idem, ibid., 71, 192 (1965).

227. Idem, ibid., 72, 56 (1966).

228. Petru, F., Coll. Czech. Chem. Comm., 12, 620 (1947).

229. Pflegel, P. and Petzold, I., Z. Chem., 274 (1968).

230. Philips, J.P. and Fernando, Q., J. Am. Chem. Soc., 74, 4459 (1952).

231. Pimentel, G.C. and McClellan, A.L., "The Hydrogen Bond", Freeman, San Francisco (1960).

232. Proskurnin, M. and Frumkin, A.N., Trans. Faraday Soc., 31, 110 (1935).

233. Ramanathan, C.S. and Subrahmania, R.S., Proc. Ind. Acad. Sci., 47A, 379 (1958).

234. Randles, J.E.B., Trans. Faraday Soc., 44, 322 and 327 (1947).

235. Idem, Can. J. Chem., 37, 238 (1959).

236. Rao, C.N.R., "Chemical application of Infrared Spectroscopy", Academic Press, New York (1964).

237. Rita, J., Chem. Listy, 46, 189 (1951); Coll. Czech. Chem. Comm., 16/17, 479 (1951/52).

238. Runner, M.E., Kilpatrick, M.L. and Wagner, E.C., J. Am. Chem. Soc., 69, 1406 (1947).

239. Sample, G.H., British Patent, 599, 409 (1945).

240. Sathyanarayana, S., J. Electroanal. Chem., 7, 403 (1964).

241. Sayo, H. and Masin, M., Rev. Polarog. (Japan), 14, 358 (1967).

242. Seely, G.R., J. Phys. Chem., 73, 117 (1969).

243. Semerano, G., 1st International Polarog. Cong., Prague, 1, 300 (1951).

244. Sevcik, A., Coll. Czech. Chem. Comm., 13, 349 (1948).

245. Sharma, S.K., Ph.D. Thesis, Birla Inst. of Tech. and Sci., Pilani, India (1965).

246. Sharma, S.K., Jour. Birla Inst. Tech. and Science, 1, 119 (1967).

247. Shikata, M., Trans. Faraday Soc., 21, 42 and 53 (1925).

248. Shikata, M. and Watanabe, M., J. Agric. Chem. Soc. (Japan), 49, 924 (1928).

249. Shikata, M. and Nozaki, N., Mem. Coll. Agric. Kyoto, 17, 21 (1931).

250. Shikata, M. and Taguchi, E., ibid., 29, 1 (1934).

251. Shreve, O.D. and Markhan, E.C., J. Am. Chem. Soc., 71, 2993 (1949).

252. Slamnik, M., Kajfez, F. and Sunjic, V., J. Polarog. Soc., 13, 83 (1968).

253. Souchay, P. and Deswarte, S., Compt. Rend., 260, 6379 (1965).

254. Smith, D.E. and McCord, T.G., Anal. Chem., 40, 474 (1968).

255. Von Stackelberg, M. and Strehlow, H., Z. Electrochem., 54, 51 (1950).

256. Stewart, P.E. and Bonner, W.A., Anal. Chem., 22, 793 (1950).

257. Stocesora, D., Coll. Czech. Chem. Comm., 14, 615 (1949).

258. Stock, J.T., J. Chem. Soc., 586 (1949).

259. Stradins, J., Electrokhimiya, 1, 955 (1965).

260. Stradins, J. and Hillers, S., Proc. International Sym. Warsaw, pp. 409 (1964).

261. Stradins, J. and Reichmanis, G.O., Electrokhimiya, 3, 178 (1967).

262. Stromberg, A.G. and Randles, J.E.B., Zh. Fiz. Khim., 36, 2714 (1962).

263. Su, T.Y., Dissertation Abstr., B28, 603 (1967).

264. Subrahmania, R.S. and Vijayalakshamma, S.K., J. Electroanal. Chem., 23, 99 (1969).

265. Suzuki, M. and Elving, P.J., Coll. Czech. Chem. Comm., 25, 3202 (1960).

266. Suzuki, M., Coll. Agr., Kyoto Univ., Chem. Ser., 28, 67 (1954).

267. Tallec, A., Ann. Chim. (Paris), 3, 347 (1968).

268. Tanaka, N. and Tamamushi, R., Bull. Chem. Soc., Japan, 22, 187 and 227 (1949); 23, 110 (1950).

269. Taylor, J.K. and Smith, S.W., J. Res. Natl. Bur. Stds., 42, 387 (1949).

270. Tewari, R.D., Ph.D. Thesis, Agra Univ., India (1961).

271. Tomes, J., Coll. Czech. Chem. Comm., 9, 12 (1937).

272. Turnbull, D. and Maron, S.H., J. Am. Chem. Soc., 65, 212 (1943).

273. Turnham, D.S., J. Electroanal. Chem., 9, 440 (1965).

274. Idem, ibid., 10, 19 (1965).

275. Turyan, Y.I. and Serova, G.F., Zhur. Neorg. Khim., 2, 336 (1956).

276. Vasilev, A.M. and Popel, A.A., Trudy Komissii, Anal. Khim. Akad. Nauk SSSR, Otd. Khim. Nauk, 4, No.7, 126 (1952); Chem. Abstr., 48, 1881d (1954).

277. Vogel, A.I., "Quantitative Inorganic Analysis", III edn.. E.L.B.S., pp. 541 (1964).

278. D.Vries, T. and Iwett, R.W., Ind. Eng. Chem. Anal. Ed., 13, 339 (1941).

279. Warshowsky, B., Shook, T.E. and Schantz, E.J., Anal. Chem., 26, 1051 (1954).

280. Welcher, F.J., "Organic Analytical Reagents", D. Van Nostrand, New York, pp. 341 and 343 (1948).

281. Winkel, A.C. and Proske, G., Ber., 71, 1785 (1938).

282. Yoe, J.H. and Jones, A.L., Ind. Eng. Chem. Anal. Ed., 16, 111 (1944).

283. Zuman, P., "Organic Polarographic Analysis", Pergamon, New York, pp. 25 (1964).

284. Idem, "Substituent Effects in Organic Polarography", Plenum Press, New York, pp. 274 (1967).

285. Idem, "Organic Polarographic Analysis", Pergamon, New York, pp. 62 (1964).

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