POLAROGRAPHIC STUDIES ON THE KINETICS AND MECHANISM OF THE ELECTRODE PROCESSES

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SUPERVISOR'S CERTIFICATE

Certified that the research work described in the thesis entitled "Polarographic studies on the kinetics and mechanism of electrode processes" was carried out by Shri Nawal Kishore, M.Sc., during the period from October, 1966 to April, 1970, in the Department of Chemistry under my guidance and supervision.

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C O N T E N T S

PAGE

CHAPTER V

CHAPTER VI

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C H A P T E R I

(A) GENERAL INTRODUCTION

The invention of polarographic technique by Prof. J. Heyrovsky, in 1920 is a landmark in the domain of physical chemistry in general and electrochemistry in particular. Though originally polarography was essentially an electro-analytical technique, it soon found wide applications in electrochemistry and many other branches of science and technology.

The importance of this discovery can be realised by the honour conferred on Prof. Heyrovsky, the discoverer, who was awarded the Nobel Prize in chemistry in the year 1959.

In polarographic studies dropping mercury electrode (dme) occupies a unique position, due to its reproducible character and the ease of operation. The theoretical basis of the current-potential curves given by dme has been thoroughly worked out[1,2].

Quantitative polarography is based on the fact that in a solution containing a small easily polarizable electrode (dme) and the other a large non-polarizable electrode (SCE) a complete concentration polarization is obtained which results in a limiting current over a range of potential. Within this range any material reaching the electrode will be reduced or oxidised immediately and the current will be determined by the rate of supply of this material from the body of the solution. The factors which contribute to the

limiting current are 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 the 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 recognised by observing the dependence of the current upon the variation of the experimental factors as given in the following table[3].

Table I

Characteristics of the important types of polarographic electrolytic currents.

Current	Conc. (c)	h	$\frac{1}{i}.\frac{di}{dT}$	pH	Buffer
Diffusion(i_d)	k c	$k\sqrt{h}$	1.6%	independent	independent
Kinetic (i_k)	kc	kh^0	1.6-20%	dependent	dependent
Adsorption(i_a)	limit.	kh^1	different	independent	independent
Catalytic(i_c)	limit.	different	-	dependent	dependent

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 oxidisable 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

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

The Heyrovsky-Ilkovic equation[4-6], 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[1]:

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

$i_{d_{ave.}} = 607\ ncm^{2/3}t^{1/6}D^{1/2}$ (for mean currents).

In deriving the Ilkovic equation, the curvature of the electrode was neglected and only linear diffusion was considered, this led a few workers[7-14] to take into account the spherical diffusion towards a growing spherical electrode and the following modified equation was suggested :-

$$i_{d_{ave.}} = 607\ nD^{1/2}cm^{2/3}t^{1/6}\left(1 + \frac{AD^{1/2}t^{1/6}}{m^{1/3}}\right)$$

where the numerical constant A is 39 according to Lingane-Loveridge[8] and 19 according to M. Von Stackelberg[9].

The most sophisticated treatment by Koutecky[13,14] gives A = 34.7 and also provides the following equation:-

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

here,

c is concentration of depolarizer in millimole/liter in the body of the solution,

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

t is drop time in seconds,

m is mass of mercury in milligram flowing per second,

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

Diagnostic criteria for the characterisation of polarograms

In a current-voltage curve, on the plateau, electron transfer is so fast that the ions or molecules of the electroactive substance are reduced or oxidized as rapidly as they arrive or are formed at the electrode surface. As the potential moves from the plateau of the wave towards its foot, the rate of the electron-transfer process decreases and the reduction or oxidation becomes less and less complete. It is convenient to divide electrode reactions into two extreme classes.

(i) Reversible - which 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 the variations of current with potential reflect the changing position of the equilibrium, which is described by Nernst equation.

(ii) Totally irreversible - which 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 with slope equal to $-2.3\frac{RT}{nF}$ for a plot of E vs. log $i/(i_d-i)$. If t (drop time) varies appreciably over the range of potentials covered by the rising part of the wave, a correction for this has been suggested by L. Meites[15] and E vs. $\left[\log i/(i_d-i) - 0.546 \log t\right]$ plot is made to test the reversibility.

Another criterion, more rapid and convenient to apply, involving the measurements of $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ from the polarogram

(potentials corresponding to currents equal to ¾ i_d and ¼ i_d, respectively) was originally suggested by Tomes[16]. For a reversible cathodic wave

$$E_{\frac{3}{4}} - E_{\frac{1}{4}} = - \frac{0.0564}{n} .$$

The half-wave potential of a reversible wave is nearly independent of drop time[17], while that of an irreversible cathodic wave becomes more positive, as the drop time is increased[18,19]. 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, as it is 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. And $E_{0.5}$ and t have usual significance.

The irreversibility of the reduction process of the system has also been tested by the observations on the variation of current with the height of the mercury reservoir. From theoretical considerations of Laitinen and coworkers[20] it has been indicated for irreversible processes that the current at the foot of the wave is independent of the height of the mercury reservoir (h), while, the diffusion current (i_d) varies linearly with changes in $\sqrt{h}_{corrected}$.

$E_{0.5}$ is independent of concentration of the depolarizer or that of the supporting electrolyte in case of reversible waves, whereas, for irreversible waves alteration in $E_{0.5}$ is generally encountered. Moreover, temperature coefficient of $E_{0.5}$ is usually small for reversible systems, while, in case of irreversible systems, $E_{0.5}$ usually has positive temperature coefficient and exceeds several millivolts per degree.

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

Organic polarography

The polarographic studies of various organic substances including aldehydes, ketones, unsaturated acids, halogenated compounds, nitro and nitroso compounds, quinones of various types, have been carried out from the early stages. The reduction of the organic compounds generally proceeds in more than one step, one of which is slow. This fact makes the reduction process irreversible in nature. Until recently it was not possible to analyse comprehensively the data on irreversible systems because of the lack of suitable theoretical formulations. In the recent years, however, satisfactory

thecretical treatments of irreversible systems have been developed which have given an impetus to the study of polarography of organic compounds.

The basic problem in organic polarography is pH control. Frequently the pH of the medium has a great effect upon the half-wave potential since hydrogen ions often participate in the electrode process. Thus, it is desirable to work with buffer solutions as in an unbuffered solution the pH at the electrode surface changes considerably and this causes the waves to be drawn-out or sometimes even the appearance of two waves.

The type and concentration of the buffer system may affect the shape of current-voltage curves of irreversible waves and the half-wave potential in the reduction of organic substances[21-23]. It must also be remembered that with a buffer solution there is always the possibility of interaction between the substance under examination and the buffer components[24,25].

(B) THEORY OF IRREVERSIBLE ELECTRODE PROCESSES

A quantitative treatment of the current-potential curves was employed by Randles[26] and Sevcik[27] for reversible processes and by Delahay[28,29] for irreversible processes. Reactions which can be followed from polarographic curves can be divided into three groups:

(1) Electrode reaction.

(2) Chemical reaction occurring close to the electrode surface and caused by perturbation of the chemical equilibria of the system of the electrode reaction.

(3) Homogeneous chemical reactions occurring in the bulk of the solution which are not influenced by the electrode reaction.

The 4th process, which accompanies all polarographic processes, is diffusion and 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[30] for following rapid reactions. In the following section the "Electrode Reaction" will be discussed in detial.

Electrode Processes

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 and equilibria undergo a disturbance, which 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, but there are other cases in which the equilibrium is slow to attain. The interpretation of such electrode processes involves kinetic considerations. For the reaction represented by

$$O + ne^- \rightleftharpoons R \qquad (1.1)$$

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

$$-\frac{dN_O}{dt} = \frac{dN_R}{dt} = k_{f,h}\, C_o - k_{b,h}\, C_R \qquad (1.2)$$

where the C's are the concentrations and the k's are the formal rate constants for the forward and the backward processes. Constants $k_{f,h}$ and $k_{b,h}$ are interpreted by introducing additional kinetic considerations. 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 electric field has to be taken into account. If E is

the electrode potential referred to N.H.E., the fraction αE of this 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;

$$k_{f,h} = k^{o}_{f,h} \exp\left[-\frac{\alpha nF}{RT}.E\right] \qquad (1.3)$$

$$k_{b,h} = k^{o}_{b,h} \exp\left[\frac{(1-\alpha)nF}{RT}.E\right] \qquad (1.3a)$$

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

Once the rate of reaction is known, 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 'O'. Thus

$$i = nFA\left[C_o\, k^{o}_{f,h} \exp\left\{\left(\frac{-\alpha nFE}{RT}\right)\right\} - C_R\, k^{o}_{b,h} \exp\left\{\frac{(1-\alpha)nF}{RT}.E\right\}\right] \qquad (1.4)$$

or

$$i = nFA\, k_{s,h}\left[C_o \exp\left\{\frac{-\alpha nF}{RT}(E-E^{o}_{c})\right\} - C_R \exp.\left\{\frac{(1-\alpha)nF}{RT}(E-E^{o}_{c})\right\}\right] \qquad (1.5)$$

The value of E^{o}_{c} is generally not very different from the standard potential E^{o}, and E^{o}_{c} can often be identified with E^{o}. Comparing equations(1.4)and(1.5),

$$k_{s,h} = k^{o}_{f,h} \exp\left[\frac{-\alpha n F}{RT} \cdot E^{o}_{c}\right] \qquad (1.6)$$

$$k_{s,h} = k^{o}_{b,h} \exp\left[\frac{(1-\alpha) n F}{RT} \cdot E^{o}_{c}\right] \qquad (1.6a)$$

From equation (1.5), current is now a function of the difference of potential $(E-E^{o}_{c})$ whereas in equation (1.4), it depends on E. Therefore, $k_{s,h}$ is truly characteristic of the electrode process whereas the constants $k^{o}_{f,h}$ and $k^{o}_{b,h}$ depend on the difference between the potential E^{o}_{c} and the zero of the scale of potentials. It is, therefore, more advantageous to use $k_{s,h}$ rather than $k^{o}_{f,h}$ and $k^{o}_{b,h}$, in comparing the kinetic characteristics of the electrode processes.

The derivation of the current-voltage relationship for the electrode process has helped much in the understanding of the kinetics of the electrode reactions. It may be pointed out here that the theory of the reversible polarographic process - the Heyrovsky-Ilkovic equation - represents only a limiting case of this more general treatment. The nature of the irreversible processes can be explained quantitatively from the current-voltage curve. In case of irreversible waves, a rather drawn-out wave is obtained which is shifted to more cathodic potentials. The quantitative explanation for this is as follows. In the lower segment of the wave,

the rate of the electrochemical reaction is so slow that virtually no current is observed. As the potential is made more cathodic, the rate of the electrochemical reaction increases and an appreciable current is observed. The flow of current causes concentration polarization, and in the upper 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 over-potential (over-voltage) $\eta_{1/2}$

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

Thus an electrochemical reaction occurring without any measurable over-voltage is said to be reversible. The slow establishment of an equilibrium between the oxidised and reduced form at the electrode surface, i.e., a slow electrode process, is regarded as the cause of irreversibility. The electrode process in this sense refer 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 overall electrode process or depolarization process is used. A slow electrode 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. The values of αn

and k^{o}_{f} can be determined from the wave[31]. The significance of the $E_{0.5}$, the dependences of this on drop-time[32], etc., have been derived from the theory.

Delahay[18] compared the general equation regardless of the degree of irreversibility with Ilkovic equation and deduced a general criterion for polarographic reversibility.

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

$$\frac{i_d - i}{i} = \exp\left[\frac{nF(E-E^{o})}{RT}\right] + \frac{1.13}{k_{s,h}}\sqrt{\frac{D}{t}} \cdot \exp\left[\frac{\alpha nF(E-E^{o})}{RT}\right] \qquad (1.7)$$

Now two limiting cases can be distinguished according to the value of the rate constant $k_{s,h}$. If $k_{s,h}$ is sufficiently high so that the expression $k_{s,h}\sqrt{\frac{t}{D}} \gg 1$ the 2nd term on the right hand side in equation (1.7) can be neglected and the Heyrovsky-Ilkovic equation is obtained,

$$\frac{i_d - i}{i} = \exp\left[\frac{nF(E-E^{o})}{RT}\right] \qquad (1.8)$$

which expresses the shape of the polarographic curves corresponding to a reversible electrode process. In this case the $E_{0.5}$ differs from the standard redox potential E^{o} of a true redox system (both forms in the solution) only by the term $\frac{RT}{nF} \ln \sqrt{\frac{D_{ox}}{D_{red}}}$, which is, in most cases, negligible.

If on the other hand, the value of the rate constant $k_{s,h}$, is lower than about 2×10^{-2} cm.sec^{-1}., the second term in the R.H.S. of the equation (1·7) is no longer negligible and the half-wave potential is measurably shifted to more negative value and the wave is less steep. Such electrode processes are called irreversible. In these reactions the scope of obtaining information is broadened, because in this case the rate of the electrode reaction can be measured with high accuracy.

The theory of the irreversible waves was first developed by Eyring and coworkers[30] and Tanaka and Tamamushi[33], but a more rigorous treatment was made independently by several workers[18,34,35]. Irreversible waves can be divided into two groups according to the magnitude of the rate constant $k_{s,h}$.

(1) If the rate constant ($k_{s,h}$) lies within the limits 2×10^{-2} to 3×10^{-5} cm. sec^{-1}., the reaction is termed quasi-reversible.

(2) If $k_{s,h} \leq 3 \times 10^{-5}$ cm.sec^{-1}., the reaction is termed totally irreversible.

For totally irreversible systems the treatments of Meiman[36], Delahay[29,37], Koutecky[34] and Randles[38] are available whereas for quasi-reversible, Matsuda[39,40], Gelling[41], Koryta[42] and modification of the method of Randles and Stromberg[43] by Sathyanarayana[44] are available.

Case of consecutive electrochemical reaction

Electrochemical reaction involving $n\bar{e}$ can in principle involve up to n consecutive electrochemical steps and possibly subsequent chemical transformation. The rate of the overall chemical reaction obviously depends on the kinetic characteristics of each of these reactions. In the case of an overall electrochemical reaction involving two steps as represented by the equation -

$$O_x \xrightarrow[n_1\bar{e}]{k_1} Z \xrightarrow[n_2\bar{e}]{k_2} \text{Red} . \qquad (1.9)$$

The rate of reduction of O_x to Red. depends upon the kinetics of each step. Since these steps are in series, the corresponding rates are equal but the concentration of Z depends on the kinetics of each step as well as on the rate of transference of substance Z from the electrode towards the bulk of solution.

Electrochemical Reaction involving only one rate determining step:-

It is quite often possible to assume that the overall electrochemical reaction involves only one rate determining step. In this case intermediate products such as Z in equation (1.9) are virtually consumed as soon as they are formed. The number of electrons involved in this rate determining step

will be represented in subsequent discussions by the symbol n_a in order to differentiate it from the total number of electrons (n) involved in the overall reduction (electrochemical). Under such condition equation (1.3) should be written in the form -

$$k_{f,h} = k^{o}_{f,h} \exp\left[\frac{-\alpha n_a F}{RT} .E\right] \qquad (1.10)$$

Thus the kinetics of the electrode process is partially determined by n_a but the current depends upon the total number of electrons n. This is so because the process which follows the rate determining step involves $(n-n_a)$ electrons and is by definition much faster than the rate controlling step. Equation (1.10) can also be written as

$$\log k_{f,h} = \log k^{o}_{f,h} - \frac{\alpha n_a F}{2.3RT} .E \qquad (1.11)$$

According to this equation (1.11) a plot of $\log k_{f,h}$ vs. E yields a straight line whose slope is $-0.434 \frac{\alpha n_a F}{RT}$; the parameter $k^{o}_{f,h}$ and αn_a can thus be determined experimentally for various values of E. This is done by measuring the ratio of current for various points along the wave to the diffusion current (i/i_d) and by determining the corresponding value of the dimensionless parameter Λ which is defined by the equation -

$$\Lambda = k_{f,h} t^{1/2} D^{-1/2} \qquad (1.12)$$

and the ratio i/i_d is related to λ by equation

$$\frac{i}{i_d} = \pi^{1/2} \lambda \exp(\lambda^2) \operatorname{erfc}(\lambda) \qquad (1.13)$$

where $\operatorname{erfc}(\lambda) = 1-\operatorname{erf}(\lambda)$ (1.14)

and erf (λ) is the error integral defined by the formula

$$\operatorname{erf}(\lambda) = \frac{2}{\pi^{1/2}} \int_0^{\lambda} \exp(-Z^2)\, dZ \qquad (1.15)$$

It should be noted that the function erf (λ) is defined under the form of a finite integral having zero as the lower limit and λ as the upper limit of integration. Therefore, values of erf(λ) are determined only by the variable (λ), Z being simply an auxiliary variable in the equation (1.15).

Delahay and Strassner[18,45] were the first who applied this method, measured average currents during the drop-life and obtained $k_{f,h}$ by a graphical integration method[29]. The treatment of linear diffusion being used, Koutecky[46] has computed a table of λ for various values of i/i_d and thus the values of $k_{f,h}$ can be calculated with the help of this table.

In the present investigations the corresponding values of λ for the experimental values of i/i_d has been found from the theoretical plot of $\sqrt{\frac{12}{7}}.\lambda$ v/s i/i_d, as given by

Koutecky[47]. Once λ is known at various potentials it is a trivial matter to calculate $k_{f,h}$ from equation (1.12), since the drop-time (t) can be measured and the diffusion coefficient "D" can be readily calculated from the Ilkovic equation or any other suitable method. αn_a can be calculated from the slope of the line obtained by plotting log $k_{f,h}$ vs. E.

At the half-wave potential ($E_{0.5}$) the current (i) is by definition equal to one-half of diffusion current i_d. It follows from equation (1.12) that the parameter λ can be replaced by $\lambda_{1/2}$ at potential $E = E_{0.5}$; then $k_{f,h}$ at $E_{0.5}$ will be

$$\lambda_{1/2} D^{1/2} / t^{1/2}$$

By introducing $E = E_{0.5}$ in equation (1.3), we get

$$k_{f,h} = k^{o}_{f,h} \exp \left[\frac{-\alpha n_a F}{RT} \cdot E_{0.5} \right]$$

$$= \lambda_{1/2} D^{1/2} / t^{1/2}$$

or

$$E_{0.5} = \frac{RT}{\alpha n_a F} \cdot \frac{\ln k^{o}_{f,h}}{\lambda_{\frac{1}{2}} D^{1/2}} + \frac{RT}{2 \alpha n_a F} \cdot \ln t \qquad (1.16)$$

It follows from the equation (1.16) that $E_{0.5}$ depends on the quantities t, D, $k^{o}_{f,h}$ and αn_a.

It should be kept in mind that in organic polarography

it is customary to plot $E_{0.5}$ for a series of substances against some parameter which characterizes the substances being studied. Half-wave potential for reversible waves are related in a simple manner to the free energy change for the reaction, but this is not so for irreversible processes. In comparing substances which are reduced irreversibly in a reaction involving one rate determining step it is the value of the rate constant $k^{\circ}_{f,h}$ which is significant.

The foregoing discussion for the irreversible electrochemical reaction involving only one rate determining step can be summarized on the following lines. If we assume that the reduction process is controlled by diffusion and by only one rate determining step and that the backward reaction can be neglected, the heterogeneous rate constant $k_{f,h}$ for the forward reaction can be calculated from the relation

$$k_{f,h} = \lambda D^{1/2}/t^{1/2}$$

where D is the diffusion coefficient of the reducible species, t is drop-time and λ a complicated function of i/i_d (i is a current along the wave and i_d is the diffusion current). A table of λ for different values of i/i_d is available from the Koutecky's original paper[34].

Further $k_{f,h}$ is related to the electrode potential (E) by the equation (1.11)

$$\log k_{f,h} = \log k^{o}_{f,h} - \frac{\alpha n_a F}{2.3RT} \cdot E$$

The symbols have usual meanings. Plot of $\log k_{f,h}$ vs. E should be straight line with slope equal to $-\frac{\alpha n_a F}{2.3RT}$, from which the value of αn_a can be calculated, and the intercept at E = zero should give the value of $\log k^{o}_{f,h}$.

Irreversible reactions involving more than one rate determining step:-

When a plot of $-\log k_{f,h}$ vs. E does not yield a straight line it indicates that the assumption that the electrode process involves only one rate determining step, is not valid. This indicates the possibility that the apparent single electrode reaction involves two or more slow consecutive reactions.

TH167

The theoretical treatment of two consecutive irreversible electrochemical reactions in the case of semi-infinite linear diffusion has been developed by Berzius and Delahay[28]. Suzuki and Elving[48] have constructed the polarographic waves for more general conditions and reached the general conclusion that, when the $\log k_{f,h}$ vs. E plot is a bent line, the electrode process very likely involves two rate determining consecutive reactions, whose kinetic parameters cannot be evaluated by analyzing each segment of the plot.

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C H A P T E R II

(A) EXPERIMENTAL TECHNIQUE

Experimental Technique

The major part of the work embodied in this thesis emplcyed a manual polarograph assembled in the laboratory. This consists 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. CL02A, Sr.No. 083) for applying potentials to the dropping mercury electrode, dme, (M).

3. Lead accumulators (C).

4. Standard resistance (D), 10,000 Ω.

5. Weston standard cadmium cell (F).

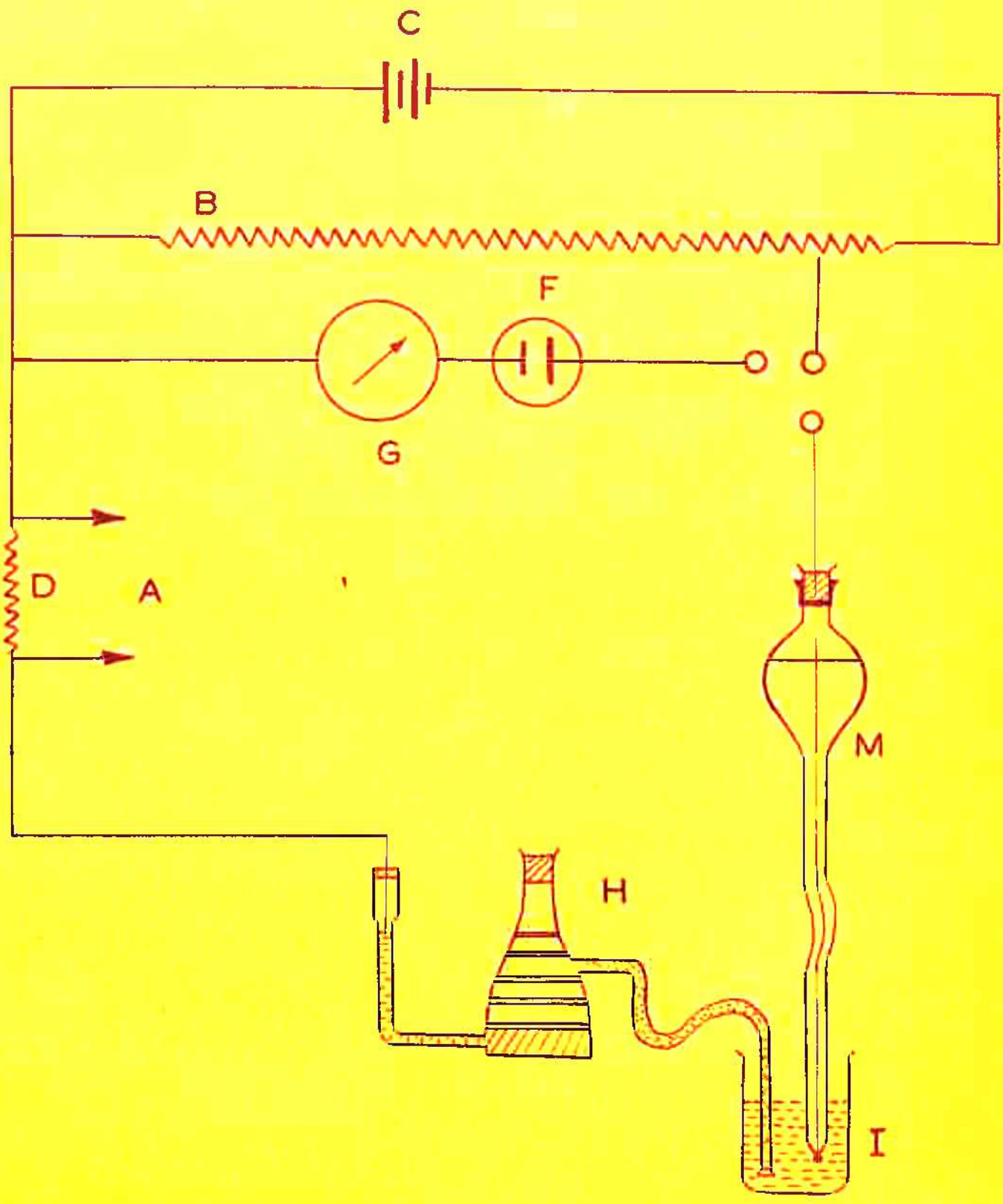
6. Spot Galvanometer of long period, (G), (Cambridge Instrument Co. Ltd. England).

7. Saturated calomel electrode, SCE, (H).

8. Reaction cell (I).

The electrical circuit employed is given in figure. The potentiometer B connected to a 4 volt lead accumulator "C" gave potential (V) of the desired magnitude. B was

POLAROGRAPHIC CIRCUIT



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

The potentiometer A was also calibrated against the standard cell F and was employed for measuring potential (E) across the resistance "D" in series with the dme. The current (i) passing through the system, at a particular applied potential V, due to the electro-chemical reaction occuring in the reaction cell (I) 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.

In the early stages of the work Type "LP60" polarograph (made in Czechoslovakia) was used for the current-voltage curves manually. This polarograph is attached with EZ2 compensating type electronic line recorder. The accuracy of the polarizing voltage is $\pm$ 1.5 mV and the current is recorded with an accuracy of 0.2%.

The procedure employed for the determination of m and t was the same as recommended by Meites and others[1].

The significance of the purity of mercury to be used in polarographic work, is well known. Slight contamination of the mercury leads to series of erratic and irreproducible features during polarographic studies and sometimes the choking up of the capillary. Initial treatment with nitric acid, followed by thorough washing with distilled water, drying, pinholing and finally distilling under reduced pressure, appeared to give mercury of suitable purity for polarographic work.

The potentials applied to the dme were measured directly against saturated calomel electrode (SCE) or otherwise mentioned. SCE was prepared in the conventional manner and was connected to the experimental cell by means of a agar - KCl salt bridge.

A polarographic cell of capacity about 100 ml convenient for our purpose was constructed. The lid to cover the mouth of the cell had an arrangement for the inlet and outlet of the N_2 gas and for insertion of capillary of the dme and the salt bridge.

Nitrogen gas with oxygen content less than 0.5% was used for removing the dissolved oxygen. The gas was further purified by passing through alkaline pyrogallol solution and

distilled water bottles connected serially with the polarographic cell. In case of higher percentage of the solvent, or pure solvent (other than water), the N_2 gas was also pre-saturated by passing through a portion of test solution before leading it into the polarographic cell. An atmosphere of N_2 was maintained in the cell during the recording of the current-voltage curves.

The current-voltage curves were recorded at a constant temperature ($\pm 0.2^{\circ}C$) maintained with the help of a Towson and Mercer thermostat.

Phillips (PR9400 Model) pH meter/Beckman (Model H2) pH meter were employed in pH measurements.

The assembled manual polarographic unit was examined for its accuracy by studying the Cd-system and comparing the values of half-wave potential and diffusion coefficient (D)with the values reported in literature[2] . Determination of the diffusion coefficient and the number of electrons involved in the reduction process:—

The knowledge of the number of electrons (n) involved in the reduction process is of marked significance especially for understanding 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 $E_{\frac{3}{4}}$-$E_{\frac{1}{4}}$ values are applicable only to reversible systems. It is the limi-

tation of Heyrovsky-Ilkovic Equation that it cannot be applied to irreversible reduction processes.

The number of electrons can be calculated from Ilkovic equation provided along with the polarographic data employed in this equation, the diffusion coefficient of the reducible species is also known. Diffusion coefficient of the depolarizer was determined using McBain-Dowson cell[3]. This was a symmetrical double cell. Both the lower and the upper compartments were fitted with the pyrex stop-cocks so that either compartment could be filled or emptied without disturbing the liquid in the other compartment. The diaphragm in between was made of pyrex sintered glass of medium porosity[4] (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 King and Cathcard equation[5]

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

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 concentration and C the concentration in the lower compartment after diffusion.

The cell constant "β" was found as follows. The lower compartment of the cell was filled with blank (buffer) and the upper compartment with the same buffer having C_o mM/L of depolarizer (nitrobenzene). The cell was kept vertical in the constant temperature air thermostat. The amount of nitrobenzene (C mM/L) diffused into the lower compartment in time (t) was determined by finding the value of diffusion current (i_d) from the polarographic current/voltage curves recorded for the solution of the lower compartment. Using this value of (i_d) corresponding concentration of nitrobenzene was computed from the calibration curve (i_d vs concentration, obtained polarographically). Also the value of diffusion coefficient (D) for nitrobenzene 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 for our cell was 2.63.

Using this value of β and finding the amount of depolarizer diffused in certain time (from calibration curve i_d vs. concentration from polarographic measurements), the value of "D" for the depolarizer was obtained and thus (n) from Ilkovic equation.

(B) PROPOSED WORK AND RESULTS

Proposed work by the candidate

During the last two decades oxidation or reduction of a large number of organic compounds has been studied by the application of this technique and has proved useful 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 and the correlation between the structure and reactivity, etc.

The influence of adsorption on electrode processes, involving organic depolarizers, has also been studied by this technique. It has been found that the presence of surface active substances affect the electrode processes in a number of ways.

Although considerable work has been done on the conventional polarographic studies of organic nitro-compounds, there are still many aspects of the problem which need systematic and detailed investigations. This thesis, therefore, contains the results obtained in the systematic and detailed study of the following investigations on which very little or no data are available in literature.

(A) Reduction mechanism of some organic nitro-compounds at the dme and the effect of various physical factors on their kinetic parameters:

Polarographic studies of the following nitro-compounds with the idea to gain information on the mechanism of their reduction at dme and to evaluate the kinetic parameters ($-\log k^{o}$ and αn_a), under the influence of various physical factors:

I. 5-nitro-ace-naphthene.
II. 5-nitro-orotic acid.
III. Ortho and para nitro-cinnamic acids.
IV. 2-[N-methyl-N-(5-nitro-2-pyridyl)-amino]-ethanol.
V. Nitrobenzene.

(B) Influence of substituents on the polarographic reduction of aromatic nitro-compounds:

Polarographic studies of the influence of substituents on the reduction of aromatic nitro-compounds, taking the values of rate constants at $E_{0.25}$, $E_{0.5}$ and $E_{0.75}$, instead of the half-wave potentials, as the basic quantity to study substitution effect and its applicability to Hammett equation have been made.

(C) Polarographic studies on the kinetics of the reactions in solution:

Polarographic studies on the kinetics of the conversion of normal nitro-compounds into polarographically inactive aci-form taking place in the solution. The following compounds

have been used:

I. 1-chloro-1-nitro-propane.

II. β-nitro-propionic acid.

III. 5-nitro-ace-naphthene.

(D) Studies on the influence of surface active substances on electrode processes:

The effect of certain nonionic, cationic and anionic s.a.s. has been investigated on the reduction of nitro-group, in the following aromatic nitro-compounds:

I. 2-[N-methyl-N-(5-nitro-2-pyridyl)-amino-]-ethanol.

II. 5-nitro-ace-naphthene.

III. 5-nitro-orotic acid.

It is expected that these studies will throw more light in the elucidation of the electrode process at the dme in the presence and absence of the adsorbed films.

RESULTS

(A) Reduction mechanism of some organic nitro-compounds at the dme and the effect of various physical factors on their kinetic parameters:

This work deals with detailed and systematic studies on -

I. Polarography of 5-nitro-ace-naphthene.

II. Polarography of 5-nitro-orotic acid.

III. Polarography of ortho and para nitro-cinnamic acid in aqueous-methanolic medium.

IV. Polarography of 2-[N-methyl-N(5-nitro-2-pyridyl)-amino]-ethanol in different supporting electrolytes.

V. Polarographic studies of the effect of various physical factors on the kinetic parameters of the reduction of nitrobenzene at dme.

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

Polarography of 5-nitro-ace-naphthene has been carried out in the pH range 1.7 to 11.35 using different buffer systems, in 40% ethyl alcohol medium, at a constant temperature (33± 0.2°C) and ionic strength, 0.27 M. It gave a single step

reduction below pH 3 and two steps above pH 3. Number of electrons ($6\bar{e}$) involved in the reduction process over the whole pH range was found by using McBain-Dowson's Cell. Above pH 5.7, the lowering of the total current (i_d) was due to the conversion of normal nitro-compound into polarographic inactive aci-form. Kinetic parameters ($-\log k^o$ and αn_a) have been reported using Koutecky's method. Mechanism for the electrode reaction has been proposed for its reduction at dme.

Polarography of 5-nitro-orotic acid in aqueous medium has been carried out in the pH range 1 to 10, using different buffer systems. It gave well defined two steps up to pH 9.0, the 1st step was purely diffusion controlled, ($6\bar{e}$) reduction, at all pH values. The 2nd step involved $4\bar{e}$ and was purely diffusion controlled in acidic range. Above pH 9, the compound was reduced in three steps. The first was purely diffusion controlled, $4\bar{e}$, reduction. 2nd ($4\bar{e}$) and 3rd ($2\bar{e}$) steps had adsorption character. However, at pH greater than 11, although the reduction involved three steps, the wave heights were not reproducible. The number of electrons involved in the diffusion controlled process was determined by comparing the wave-height with that of the 1st step of nitrobenzene under identical conditions. It was also confirmed by finding the diffusion coefficient (D) with the help of McBain-Dowson's cell.

Kinetic parameters (αn_a and $-\log k^o$) have been

determined for the diffusion controlled 1st step at all pH values (1 to 10), using Koutecky's method. Plots of $-E_{0.5}$ and $-\log k^{o}$ vs. pH (pH 1 to 9) for the 1st step, resulted in identical S-shaped curve. Plot of -log k vs. E at all pH values for the 1st step (pH 1 to 10) and the same plot for the 2nd step (pH = 1.0) resulted in straight lines - thus showing single rate determining step. The effect of various physical factors such as concentration of depolarizer and height of the Hg column on αn_a and $-\log k^{o}$ has been studied, for the 1st step (pH 1,9 and 10) and also for the 2nd step at pH 1.0. The reduction mechanism has been explained on the basis that below pH 9, there are two species in equilibrium (i) neutral and (ii) singly charged - which undergo $6\bar{e}$ (1st step) and $4\bar{e}$ (2nd step) reduction, respectively. Above pH 9, there may be singly and doubly charged species in equilibrium - each giving a $4\bar{e}$ reduction wave and the hydroxylamine of the singly charged species further undergoing a $2\bar{e}$ reduction (3rd step, pH 10.0) to the amine stage.

Polarographic study of ortho and para nitrocinnamic acids (Transforms) have been carried out at various pH values using acetate buffers in 80% methyl alcohol. Nitro-group showed the normal behaviour, i.e., two steps ($4\bar{e}$, $2\bar{e}$) reduction in acidic medium and single step ($4\bar{e}$) at all other pH values. In highly alkaline pH (0.1 M-NaOH, 80% methyl alcohol, pH = 11.5) another wave appeared which was for the saturation

of the double bond (-C=C-). Analysis of these waves indicated that the processes were irreversible, for which kinetic parameters (αn_a and -log k^o) have been reported using Koutecky's method.

The nitro-group in 2-[N-methyl-N(5-nitro-2-pyridyl)-amino]-ethanol, gave the usual two steps ($4\bar{e}$, $2\bar{e}$) reduction in acidic pH and single step ($4\bar{e}$) in higher pH values. In the acidic range the height of the first step was fairly constant but at further pH values it increased with pH. Also the height of the first step was independent of the nature of the cations or anions and the ionic strength of the supporting electrolyte. The electrode process became more irreversible with the increased atomic weight of the cations and was accelerated with the increased adsorbabilities of halide ions. Increase in ionic strength of the supporting electrolyte also facilitated the electrode process. The results have been explained on the basis of the theory of electrical double layer.

The effect of various physical factors, such as, drop-time, concentration of depolarizer, temperature, concentration of solvent, nature of solvent and pH on the kinetic parameters (αn_a and -log k^o) for the irreversible nitrobenzene reduction were investigated by analysing the 1st polarographic reduction wave of nitrobenzene, using Koutecky's theory of the slow electrode reaction. The results obtained indicated that (a)

the kinetic parameters were independent of the nitrobenzene concentration and of drop-time (b) these parameters decreased with the increase in temperature both in aqueous and methanolic media, (c) with the increase of ethyl alcohol percentage in aqueous-alcoholic mixture, the reaction rate seems to be retarded by a film of ethanol adsorbed on electrode surface, (d) plots of -log k vs. E in protic media resulted in a straight line whereas in aprotic media this plot gave one inflection indicating that there were two slow processes which determine the rate of reduction and (e) in weakly acidic, neutral and alkaline medium (both aqueous and methanolic), -log k vs. E plot gave straight line, thus showing single rate determining process, whereas, in highly acidic aqueous as well as methanolic media this plot showed a break indicating that more than one rate determining step were involved. Probable reduction mechanism has been discussed to support the observed facts.

(B) Influence of substituents on the polarographic reduction of aromatic nitro-compounds:

Nitrobenzene was taken as the parent compound. The theory of irreversible reaction rates as developed by Koutecky was applied. The rate constants were determined at different potentials. These obeyed the Eyring equation $k = k_o e^{-\alpha n_a F/RT}$ From the data, the values of rate constants at $E_{0.25}$, $E_{0.5}$

and $E_{0.75}$ were determined. The influence of substituents on rate constants was studied. Hammett's rule was applied to the values of rate constants at $E_{0.25}$, $E_{0.5}$ and $E_{0.75}$ which gave satisfactory results.

(C) Polarographic studies on the kinetics of the reactions in solution:

Polarography has been used as a tool to study the tautomeric conversion of certain nitro-compounds into polarographic inactive aci-form. The following systems were taken up for detailed and systematic studies:

I. Polarography of 1-chloro-1-nitropropane.
II. Polarography of β-nitropropionic acid.
III. Polarographic study on the kinetics of the conversion of 5-nitro-ace-naphthene into aci-form.

The following are the main results:

Polarography of 1-chloro-1-nitropropane has been carried out over a wide pH range, using different buffer systems in aqueous medium, at a constant temperature 25°C and ionic strength (μ = 0.54 M). The test solution after allowing to stand for 24 hours to attain equilibrium, gave two steps ($4\bar{e}$, $2\bar{e}$) reduction wave over a wide pH range. The total wave height decreased with increase in pH and no wave

could be recorded above pH 8, due to the conversion of the whole of the normal nitro-compound into polarographic inactive aci-form. Kinetic parameters (αn_a and $-\log k^o$) for its reduction at dme (for 1st step) and the rate constant of its conversion into aci-form in solution have been reported. The rate of conversion was found to be of first order.

Polarography of β-nitropropionic acid has been carried out over a wide pH range, using different buffer systems, in aqueous medium, at a constant temperature (35°C) and ionic strength (0.54 M). It gave a single step reduction over the whole pH range. Number of electrons ($4\bar{e}$) involved in the reduction process was found by McBain-Dowsons cell using King-Cathard equation. Above pH 6, the appreciable lowering of the wave height was due to the conversion of normal nitro-compound into polarographic inactive aci-form. No wave was recorded beyond pH 10, as whole of it was converted into inactive aci-form. Kinetic parameters ($-\log k^o$ and αn_a) for its reduction at dme and the rate constants of its conversion into aci-form in solution have been reported. The rate of conversion was found to be of first order. The thermodynamic parameters are derived for the activated complex formed during the transformation into aci-form.

The kinetics of the conversion of 5-nitro-ace-naphthene into polarographic inactive aci-form have been investigated

and found to be of second order. The presence of two final products was confirmed by thin layer chromatography. The thermodynamic parameters are derived for the activated complex formed during the transformation into aci-form.

(D) Studies on the influence of surface-active-substances on electrode processes:

The effect of certain nonionic, cationic and anionic surface active substances, has been investigated on the reduction of nitro-group, in the following aromatic nitro-compounds:

I. 2-[N-methyl-N-(5-nitro-2-pyridyl)-amino]-ethanol.
II. 5-nitro-ace-naphthene.
III. 5-nitro-orotic acid.

The following are the main results obtained:

The nitro-group in 2-[N-methyl-N-(5-nitro-2-pyridyl)-amino]-ethanol, gave the usual two steps ($4\bar{e}$, $2\bar{e}$) in acidic pH and single step ($4\bar{e}$) in alkaline pH. Study of s.a.s. on this compound was taken up at two pH's acidic (1.85) and alkaline (0.05 M - NaOH + 0.2 M - KCl). Gelatin, Triton X-100 and camphor (nonionic), cetyl pyridinium bromide and methylene blue (cationic) and Aerosol OT (anionic) were used as s.a.s. in acidic pH. In case of all these s.a.s., with increase of their concentration, both the steps shifted to more cathodic

side, second one to the extent that it was completely removed at higher concentration. In case of Triton X-100 and Aerosol OT, the first wave indicated a inflection in the lower portion of the wave (height of this new step decreased with increase in concentration of s.a.s.) indicating the increased stability of the intermediate anion radical. Methylene blue gave a pre-wave of adsorption characteristics, which appeared due to the adsorption of the reduced form of the methylene blue at dme.

In basic solutions - gelatin, Triton X-100, camphor, Tween 20, Tween 40 and Tween 80 (nonionic), bromocresol purple and Aerosol OT (anionic) and methylene blue and cetyl pyridinium bromide (cationic) s.a.s. were used. In case of gelatin the single step was shifted to more cathodic side with increased concentration of s.a.s. and the diffusion current showed a decrease, whereas, in case of the remaining nonionic s.a.s., the step split into two and a decrease in the total wave height was noticed with increase in concentration of s.a.s. This split was due to the increased stability of the ($R\text{-}NO_2^-$) anion radical. Bromocresol purple and aerosol OT both showed a cathodic shift of the wave, lowering of its height and a pre-wave of adsorption characteristics, at higher concentration of s.a.s. Cetyl pyridinium bromide at higher concentration distorted the wave in upper portion, while methylene blue, along with its usual adsorption pre-wave,

split the main step into two indicating the stability of the anion radical. Values of rate constants for the electrode process have been computed in presence of varied concentration of s.a.s.

5-nitro-ace-naphthene gave single step ($6\bar{e}$) reduction below pH 3, and two steps ($4\bar{e}$, $2\bar{e}$) above pH 3. No appreciable change in the total wave height was observed up to pH 5.7, beyond which the lowering of wave height was due to the conversion of the normal nitro-compound into polarographic inactive aci-form. PH's 1.85 and 5.7 were chosen to study the effect of Triton X-100, Tween 20, Tween 40 and Tween 80, camphor and gelatin (nonionic), Aerosol OT, sodium lauryl sulphate and bromocresol purple (anionic) and cetyl pyridinium bromide and methylene blue (cationic) surfactants. At pH 1.85, camphor could not remove the polarographic maximum even up to 0.12% of its concentration, whereas, 0.012% gelatin could remove the same. In case of remaining s.a.s. (except for methylene blue and bromocresol purple) a well defined single step ($6\bar{e}$) was observed even up to 0.04% concentration of s.a.s. In case of methylene blue the main step preceded by a pre-wave of adsorption nature, which was due to adsorption of the reduced form of methylene blue. Bromocresol purple with concentration $>$ 0.0048% indicated a sharp maximum on the limiting current region of the main wave, which may be due to the desorption of the s.a.s.

At pH 5.7, Triton X-100, Tween 80, cetyl pyridinium bromide showed similar results, i.e., removal of the second step at higher concentration of s.a.s. Both the steps existed in case of camphor, sodium lauryl sulphate and Aerosol OT. The second step showed a marked increase in magnitude at higher concentrations of Aerosol OT, which may be probably due, at least in part, to catalytic hydrogen evolution and presumably the Aerosol OT serves to accelerate the catalytic step. Behaviour of bromocresol purple was more interesting, i.e., fusion of the two steps and increase in height of the thus resulted single step, with increased concentration of s.a.s. Methylene blue gave a pre-wave of adsorption nature and removed the second reduction step at its higher concentration. Values of rate constant for the electrode process have been computed in presence of varied concentration of s.a.s.

During the polarographic studies on 5-nitro-orotic acid it was observed that it gave two reduction steps ($6\bar{e}$, $4\bar{e}$) up to pH 9. Two pH's 3.0 (acidic) and 9.0 (basic) were chosen to study the effect of Triton X-100 and Tween 20 (nonionic), Aerosol OT and bromocresol purple (anionic) and methylene blue and cetyl pyridinium bromide (cationic) surfactants. In acidic pH Triton X-100 and Tween 20 behaved similarly, i.e., shifting of both the waves to more cathodic side and at higher concentration of s.a.s. only first step remained. In case of Aerosol OT both the steps existed; the first showed

a greater shift to cathodic side with no change in wave height. The second step was not much affected even at higher concentration of s.a.s. Fusion of the two steps in case of bromocresol purple was noticed, along with the appearance of a pre-wave of adsorption characteristics.

Cetyl pyridinium bromide shifted both the steps to more cathodic side and the second step vanished at its higher concentration. Behaviour of methylene blue was more interesting. Appearance of a pre-wave (adsorption character) and removal of the second step was accompanied by splitting of the first step ($6\bar{e}$) into two ($4\bar{e}$, $2\bar{e}$), i.e., the hydroxylamine intermediate stage was stablished by the presence of s.a.s.

Again the behaviour of Triton X-100 and Tween 20 was identical in alkaline pH, i.e., shift of the first step to the extent that it got fused into the second step, thus resulting in a single step only. At higher concentration of Aerosol OT no reduction steps could be recorded. Both the steps, along with a pre-wave, were observed with methylene blue and bromocresol purple. Cetyl pyridinium bromide shifted the first step to more cathodic potential with no appreciable change in wave height, while the second step was deformed into peak at higher concentration of cetyl pyridinium bromide.

Rate constant for the electrode process have been computed in presence of varied concentration of s.a.s.

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List of research papers communicated/published

1. Polarography of 5-nitro-ace-naphthene. Electro-chim. Acta, 15, 1498, 1970.

2. Polarography of 5-nitro-orotic acid. (communicated)

3. Polarographic study of ortho and para nitrocinnamic acid in aqueous-methanolic medium. Jour. B.I.T.S., Vol.II, 1968.

4. Polarography of 2-[N-methyl-N-(5-nitro-2-pyridyl)-amino]-ethanol in different supporting electrolytes. (communicated)

5. Polarographic studies of the effect of various physical factors on the kinetic parameters of the reduction of nitrobenzene at dme. Jour. Inst. of Chemists, India. LXI, 210, 1969.

6. Polarographic study on the influence of substituents on the reduction of aromatic nitro-compounds. Jour. Inst. of Chemists, India (In press).

7. Polarography of 1-chloro-1-nitropropane. Trans. SAEST, Karaikudi, India (In press).

8. Polarography of β-nitropropionic acid. Convention of Chemists held at I.I.T. Kharagpur, India, Dec. 1969.

9. Kinetics of the conversion of 5-nitro-ace-naphthene into the aci-form. (communicated)

10. Effect of nonionic, cationic and anionic surface-active-substances on the reduction of nitro-group in

    (a) 2-[N-methyl-N-(5-nitro-2-pyridyl)-amino]-ethanol.

    (b) 5-nitro-ace-naphthene.

    (c) 5-nitro-orotic acid.

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C H A P T E R III

REDUCTION MECHANISM OF SOME ORGANIC NITRO-COMPOUNDS AT THE dme AND THE EFFECT OF VARIOUS PHYSICAL FACTORS ON THEIR KINETIC PARAMETERS.

I N T R O D U C T I O N

The polarographic behaviour of nitro-compounds has attracted considerable attention. The nitro group is a powerful electron seeking group, it is therefore to be expected that its ability to capture an electron and hence its reducibility at d.m.e. will be affected by the nature and position of other electron donating or electron seeking substituents in the molecule.

Nitrobenzene was the first organic substance to be studied polarographically. M. Shikata[1] measured its reduction potential at various pH values and subsequently, with the help of his collaborators, studied the nitrophenols[2], dinitrobenzenes, dinitrophenols[3] and nitroanilines[4]. A. Winkel[5] et al. later investigated the effect of pH on the reduction potential of nitrobenzene.

Since the earlier work does not contain information on the nature of the electrode reactions, and as arbitrary "Reduction" potentials were quoted rather than $E_{0.5}$'s, the investigation has been repeated and additional nitro-compounds have been examined, mainly by M.J. Astle and P.J. Elving in America, by L. Holleck in Germany, and by J. Pearson and by J.E. Page and his colleagues in England. The substances

studied include the mono, di, tri- nitrobenzenes[6-12], nitrotoluenes, nitrophenols[13,14], nitroresorcinols[15,16], p-nitroaniline, mono-nitrocresols[17] nitroanisoles and nitrobenzoic acids and the methyl nitrobenzoates.

Below pH 4, nitrobenzene gives a $4\bar{e}$ and $2\bar{e}$ step, representing reduction to the hydroxylamine and aniline respectively. The 2nd step is not well defined and disappears above pH 4. Addition of alcohols, however, shifts the steps to more negative potentials and makes the 2nd step more distinct. The nitrotoluenes, nitroanisoles, and methyl nitrobenzoates differ from nitrobenzene in the pH value at which the 2nd wave disappears.

Dinitrobenzenes and dinitrotoluenes undergo a $12\bar{e}$ reduction in acid and a $10\bar{e}$ (or less) reduction in alkaline solution. Trinitrobenzene and trinitrotoluene undergo a greater than $12\bar{e}$ reduction in acid and a $12\bar{e}$ reduction in alkaline solution. Thus mono, di and tri- nitrobenzene and nitrotoluene in neutral and alkaline solutions are reduced to the corresponding hydroxylamine, but at acid pH the reduction proceeds stepwise through the hydroxylamine to the amine. At pH between 3 and 6 a mixture of the hydroxylamine and the amine is formed. $E_{0.5}$'s vary linearly with pH, but the slope of the curves changes in the pH range (i.e. about pH = 4.0) in which the reduction process changes.

L. Holleck[18,19] et al. reported that p-nitrobenzene

gave very peculiar multistage curves caused by two concurrent processes. In acid solution one nitro group was reduced to -NHOH group($4\bar{e}$) and the 2nd to $-NH_2$ group ($6\bar{e}$). But 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 2nd reaction was inhibited over a wide pH range.

L. Holleck and B. Kastening[20] suggested the following mechanism of the polarographic reduction of aromatic nitrocompounds in alkaline solution and in the solution of low concentration of proton;

$$(R\text{-}NO_2)_{ads.} \underset{Rev.}{\overset{1\bar{e}}{\rightleftharpoons}} (R\text{-}NO_2^-)_{ads.} \rightleftharpoons (R\text{-}NO_2^-)_{soln.}$$

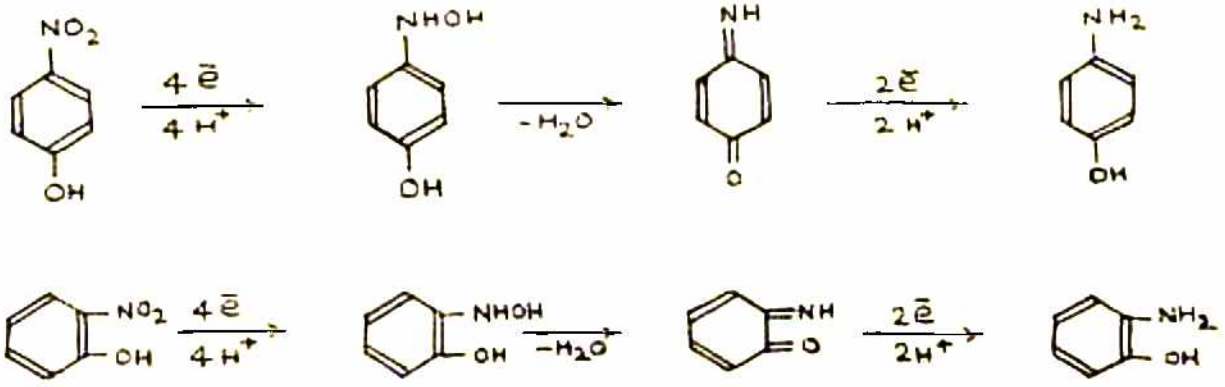
$$(R\text{-}NO_2^-)_{ads.} \xrightarrow{1\bar{e}} (R\text{-}NO_2^{-2}) \xrightarrow{Fast} Product.$$

where the rate determining step is the 2nd electron transfer process. The rate of the electrode reaction is affected by the substituents of the benzene ring, the component of the solution and the nature of the electrode surface especially in the presence of surface active substances. In acid solution containing inhibitors such as 0.1% camphor, the overall reduction process is represented by

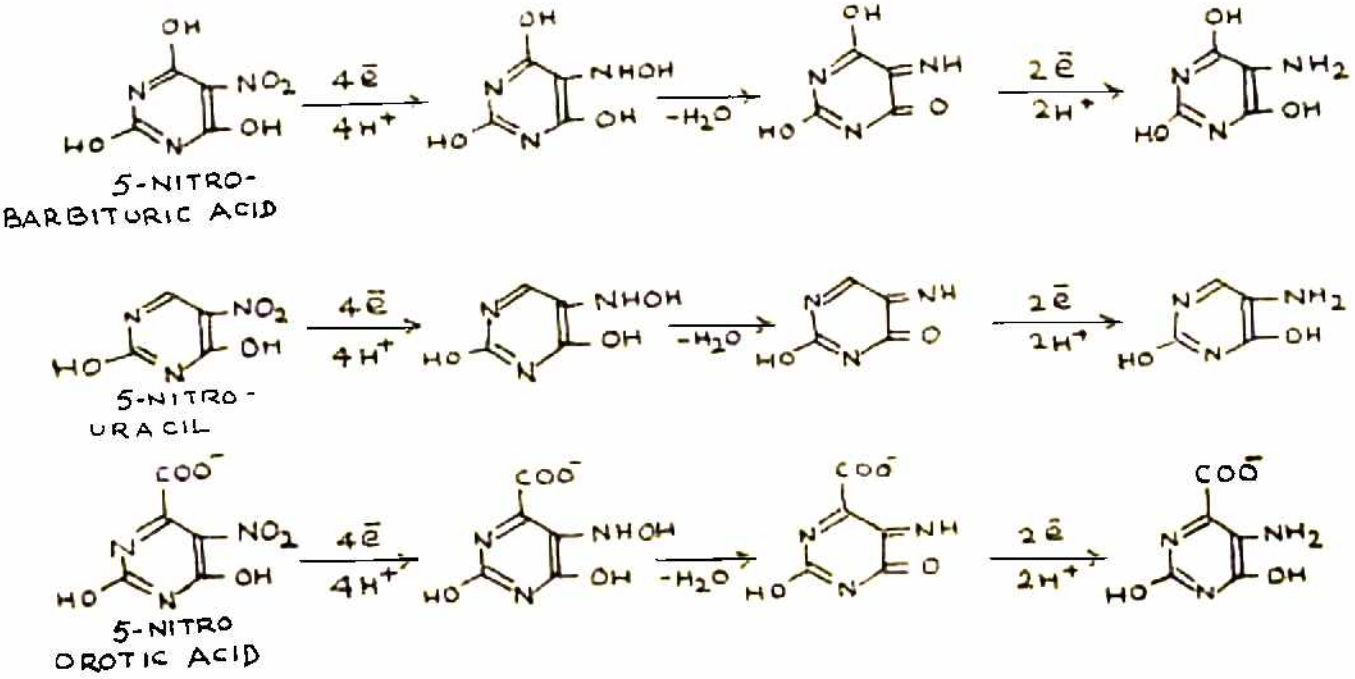
$$R\text{-}NO_2 + H^+ \longrightarrow R\text{-}NO_2H^+ \xrightarrow{1\bar{e}} R\text{-}NO_2H \xrightarrow{Fast} Product$$

$$R\text{-}NO_2H^+ \xrightarrow{2\bar{e}} R\text{-}NO_2H^- \longrightarrow Product.$$

Ortho, meta and para- nitrophenols resemble nitrobenzene in forming two steps in acid solution, but the ortho and para isomer differ from nitrobenzene in that the $4\bar{e}$ step increases to a $6\bar{e}$ step with increase in pH. Ortho and para- nitroaniline also gave similar behaviour at higher pH values. 2-nitro-resorcinol behaves differently than ortho and para nitro-phenols and ortho and para nitroanilines, as in its case a single $6\bar{e}$ wave was observed over a pH range 2 to 12. Their reduction pattern should obviously be different due to the formation of such phenylhydroxylamines which can be converted into rapidly reducible quinonoid form as -



Nitropyrimidines containing (-OH) group at positions suitable for a single $6\bar{e}$ reduction step - through quinonoid form, were 5-nitrobarbituric acid, 5-nitrouracil and 5-nitro-orotic acid. These were taken up by P.C. Jain and R.C.Kapoor[21] and it was shown that they undergo $6\bar{e}$, single step reduction over a wide pH range.



An interesting behaviour is of 4-nitrocatechol[15] for which the reduction of the intermediate nitroso-compound occurs at a more negative potential than the reduction of the nitro-form. The wave for the hydroxylamine is well developed only in acid medium up to pH 2.0. The wave becomes more drawnout and decreases in height with increasing pH. It finally disappears at pH 6.3. This behaviour indicates that the cation corresponding to the aryl hydroxylamine is the reducible form and that the unionised hydroxylamine is usually not polarographically active.

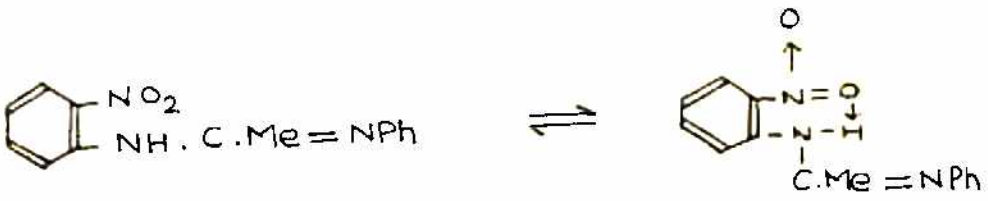
2:4 and 2:6 dinitrophenols resemble the dinitrobenzenes, but picric acid showed a 17$\bar{e}$ reduction and probably is reduced to bis - 3:5 diamino-4-hydroxyphenyl hydrazine which rearranges

in acid to give a benzidine[22]. Styphnic acid also behaves like picric acid in giving a 17$\bar{e}$ step[15].

Polarographic reduction of 2-nitro-, 2:4-dinitro- and 2:6-dinitroresorcinol[15] is simpler than that of nitrobenzenes and nitrophenols; the appropriate amine is formed at all pH values. The ortho, meta and para nitro-derivatives of anisole, benzoic acid and methyl benzoate form characteristic polarograms. The nitrobenzoic acids yield two reduction steps in both acid and alkaline solution. Their half-wave potentials do not change with concentration, but vary linearly with pH over a limited pH range[23].

Polarographic reduction of o- and p- nitrobenzoic acids, p-nitrosalicylic acid, 5-nitroanthranilic acid and 5-nitroaniline was studied over the pH range 2 to 10 by V.M. Gorokhovski[24] et al. The variation of $E_{0.5}$ with pH was shown graphically for these compounds. At low pH value p-COOH group facilitated the reduction of the $-NO_2$ group but at higher pH the reduction of the latter is retarded possibly owing to the negative charge of the ionised carboxyl group.

M.E. Runner[25] et al. have shown that o-nitroisomer of N-nitrophenyl-N'-phenylacetamide is reduced more readily than the meta or para isomer, indicating that internal hydrogen bonding takes place.



Ramaiah and Tewari[26], on polarographic studies of α-nitroso-β-naphthol, have established, that it forms an intra-molecular hydrogen bonding.

Polarographic reduction of 5-nitro-5-phenylcyclohexane and a number of its derivatives has been carried out by G.M. Goward[27] et al.

Very few nitro-compounds derived from the heterocyclic ring systems have been studied polarographically, 2-nitrofuran[28-30] is significant among those studied. At dme the reduction of this compound occurs with a $4\bar{e}$ transfer process. With increase in the molarity of alcohol in water-alcohol mixture the $4\bar{e}$ wave decreased to a $1\bar{e}$ wave. The decrease in the wave was caused by the slowing of the rate of protonation of the nitro-group and the formation of its anion radical. It has been suggested that the nitro-group is reduced via a protonised $R\text{-}NO_2H^+$ to 2-hydroxylamino furan and to 2-amino furan occurred via the 2-hydroxyl ammonium cation.

Polarographic reduction of nitro-derivative of pyrrole and thiophene were investigated by Maurice and

Pearson[31]. E.G. Novikov[32] et al. took 4-nitro-derivatives of N-oxides of pyridine, picolines, lutidines, quinolines and quinaldines for polarographic studies.

Nitro and nitroso derivatives of guanidine and urea were studied polarographically by E. Laviron[33] et al. at pH1-14. Nitroguanidine was reduced to aminoguanidine in a single $6\bar{e}$ step (or two poorly defined steps) in acid media; in alkaline media (pH > 8) two $2\bar{e}$ reductions led successively to nitrosoguanidine and guanidine. Nitrourea and N-nitro-N-methylurea were reduced in a single $6\bar{e}$ step to the semi-carbazides in acid media (pH < 2). At pH 2-6, a two step $6\bar{e}$ reduction was observed. In neutral solution, a two step $4\bar{e}$ reduction took place. At pH < 8, a single step $4\bar{e}$ reduction took place and probably led to the formation of urea and methyl urea as a result of breaking of $N-NO_2$ bond. Mechanism proposed were confirmed by controlled potential electrolysis.

Kyosti Penttinen[34] et al have used nitro-derivatives of guaiacol, vanillin, o-vanillin, vanilli acid and o-vanillic acid in buffered organic-water solutions for d.c. polarographic studies and have discussed ortho effects of substituents.

Ralph N. Adams[35] has reported electrochemical and E.P.R. spectroscopic measurements of several p-nitro-triphenylamine compounds. Polarographic investigation of nitro-

furazone (2-nitrofurfural-semicarbazone) has been taken up by W. Kemula[36] et al. between pH 2 to 12.4 in water and ethyl alcohol solution. An intermediate product is formed in the reduction process. An increase of ethyl alcohol concentration from 8 to 25 volume per cent increases the polarographic product. The latter is probably an azoxy derivative (at NO_2 group) of nitrofurazone.

G. Palyi[37] during the polarographic investigations on 3-nitro-4-chloro-benzene sulfonic acid observed that the nitro-group is irreversibly reduced to hydroxylamine by a $4\bar{e}$ process at dme.

Recently preparative electrochemical reduction of substituted mono-nitro-benzenes with a controlled potential on a Hg cathode was carried out in acid medium by M. Le. Guyader. Hydroxylamines and corresponding amines were thus prepared. In some cases hydroxylamines underwent Gattermann rearrangement to give amino phenols. By using a mercury cathode at the appropriate potential the reduction could be controlled to get yields up to 80%. Five types of general reactions were observed[38].

Nitroparaffins in strongly acid solution yield one polarographic step, which has been attributed to the formation of the alkyl-hydroxylamine; in weakly acid solution, a 2nd step that has been attributed to the alkyl-amine, appears[39].

According to P.E. Stewart and W.A. Bonner[40], however, in well buffered solutions only one $4\bar{e}$ step appears at all pH values.

M. Suzuki and P.J. Elving[41] observed that nitromethane is reduced in a single step, $4\bar{e}$, at all pH values. They analysed the wave by Koutecky's theory of slow electrode reaction. Effect of various physical factors such as pH, concentration of depolarizer, drop-time, concentration of solvent and temperature on kinetic parameters (αn_a and $-\log k^o$) were evaluated. In acidic and neutral media there is a single slow process which controls the rate of the reduction but below pH three the rate determining step seems to involve two consecutive irreversible electron transfer reactions. This process has been interpreted as due to two consecutive single electron transfer processes followed by the addition of two protons and decomposition of the resulting $CH_3NO_2H_2$ to H_2O and CH NO which undergoes further reduction.

Reduction of hydroxy nitrobutanes and their esters and others has been discussed by P.J. Elving[42]. 1-phenyl-2-nitroethanol, 1-(p-bromphenyl)-2-nitroethanol, and 1-phenyl-2-nitroethanol methylate have been studied by V.N.Leibzon[43,44] et al.

M.J. Astle[45] et al. were able to use polarography to study the kinetics of the conversion of the nitroparaffins

into their aci-form. Recently H. Sayo and M. Masui[46] have done polarographic investigations on alkaline decomposition of several aliphatic tertiary-nitro-compounds. Kinetics of the conversion phenyl-nitromethane and nitrocyclohexane into aci-form were studied by D. Jannakoudakis[47].

Anion radicals are formed in the reduction of aliphatic[48] and aromatic[49] nitro-compounds in acetonitrile and dimethyl formamide[50]. The formation of the anion radical has been verified by electron spin resonance studied for both aliphatic and aromatic nitro-compounds and the aliphatic radical was found to be unstable.

Although considerable work has been done on the polarographic studies of organic nitro-compounds, there are still many aspects of the problem which need systematic and detailed investigations.

This chapter, therefore, contains the studies on the following systems on which very little or no data are available in literature, with a view to study their reduction mechanism and the effect of various physical factors on their kinetic parameters.

I. Polarography of 5-nitro-ace-naphthene.

II. Polarography of 5-nitro-orotic-acid.

III. Polarography of ortho and para nitrocinnamic acid in aqueous methanolic medium.

IV. Polarography of 2-[N-methyl-N-(5-nitro-2-pyridyl)-amino] -ethanol in different supporting electrolytes.

V. Polarographic studies of the effect of various physical factors on the kinetic parameters of the reduction of nitrobenzene at dme.

I. Polarography of 5-nitro-ace-naphthene

No data are available in literature for the reduction of 5-nitro-ace-naphthene at the dme. The present investigation, therefore, gives the results obtained in the reduction of this compound, which contains both aliphatic and aromatic characters, with a view to elucidate the mechanism of electrode processes.

Experimental

Stock solution of 5-nitro-ace-naphthene (Aldrich Chemical Comp., U.S.A., mp 102°C) was prepared in redistilled absolute alcohol. Other chemicals used for buffer systems and supporting electrolytes were analytical reagent grade. Double strength stock solutions of HCl/KCl, Na_2HPO_4/citric acid, boric acid/NaOH and NaOH buffers were used. The ionic strength (μ = 0.54 M) of these buffers was brought to a definite value by adjusting the amount of supporting electrolyte. The pH in 40% ethanol was always found higher than in aqueous medium. Triton X-100 (0.001%) was used as maximum suppressor. Experiments were carried out at 33°C. The capillary used for dme had m = 2.931 mg/sec., t = 3.05 sec/drop in 0.54 M KCl (open circuit) at h = 40.0 cms (uncorrected for back pressure).

The current/voltage curves were recorded with using a manual setup, after the test solution had stood for 24 hours.

This was necessary as the current values changed with time but gave a reproducible curve after 24 hours.

Results and Discussion

(A) Current/voltage curves at various pH values

The test solution after attaining the equilibrium gave the current/voltage curves shown in Fig. (1). Below pH 3, a single step reduction took place and pH above 3, the reduction involved two steps which became more and more well defined with the increase of pH. No appreciable change in the value of total current (i_d) was observed up to pH 5.7, but further increase of pH was accompanied by a regular decrease in the total height ($i_{d_1} + i_{d_2}$) of the waves. The height of the first step (i_{d_1}), above pH 3, gradually decreased with increase in pH, whereas no regularity was observed for the height of the second step (i_{d_2}). The $E_{0.5}$ values for the single step (below pH 3) and for the first step (above pH 3) became more negative up to pH 10.4, whereas, for the second step, the shift occurred only up to pH 8.25. Values of i_d/c within the concentration range 0.1×10^{-3} to 1.25×10^{-3} M, $i_d/\sqrt{h}$, the negative shift of $E_{0.5}$ with concentration of the depolarizer, and plots of $\log i/(i_d - i)$ vs. E (all at pH 1.17) showed that it was a diffusion-controlled irreversible reduction.

(B) Determination of number of electrons involved in the reduction:

Comparison of the wave-height for the reduction of 5-nitro-ace-naphthene with that of the 1st wave (four electrons) of nitrobenzene recorded under identical conditions, showed that the present reduction involved four electrons. But as no suitable mechanism could be proposed to explain the two-step reduction above pH 3, the number of electrons involved was confirmed by another method. The number of electrons can be calculated from Ilkovic equation provided that along with the polarographic data the diffusion coefficient (D) of the reducible species is also known.

The diffusion coefficient of the depolarizer was determined by the McBain-Dawson cell with the King-Cathard equation[51]. The value of D for this compound was calculated as 5.53×10^{-6} cm^2/sec. This value of D in Ilkovic equation gives the number of electrons as $5.97 \simeq 6$.

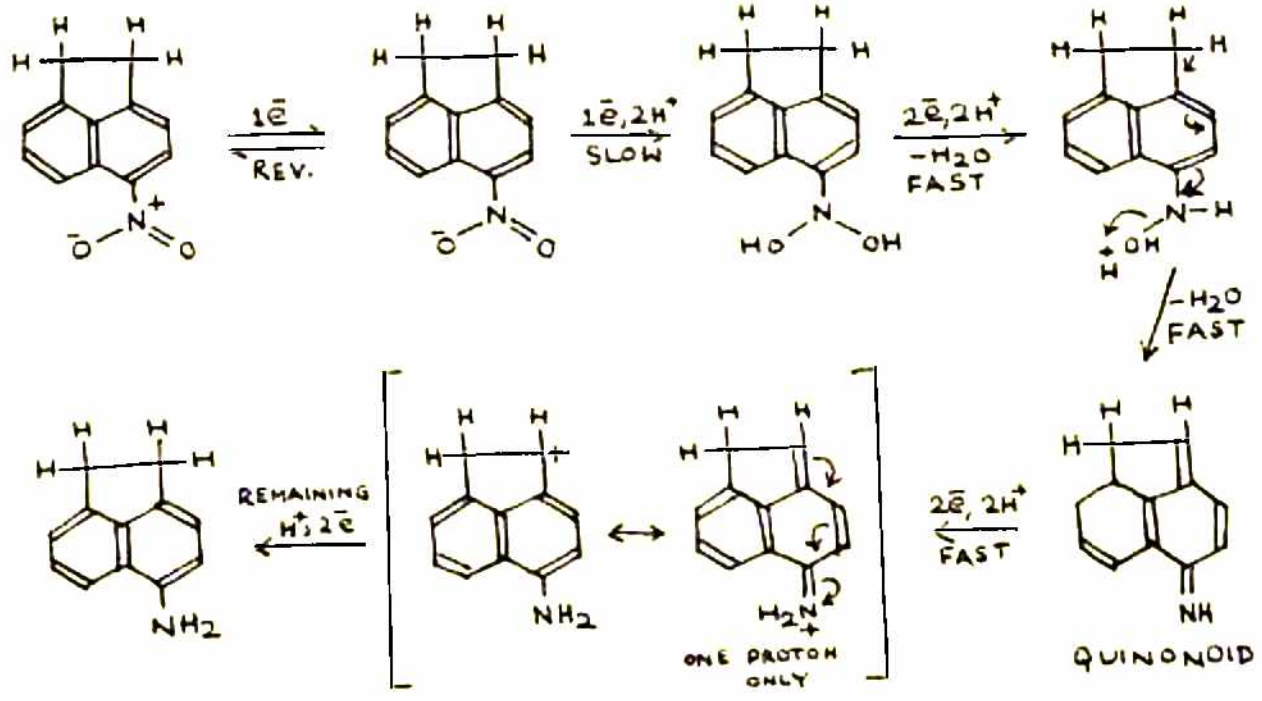
Figure (1) shows that the magnitude of the total current (i_d) is of the same order up to pH 5.7, but with further increase of pH, i_d decreases. This decrease is not due to any change in the number of electrons, but due to the conversion of the normal nitro-compound into polarographically inactive aci-form, the remaining normal nitro-compound undergoing six electron, two-step reduction. Thus at all pH

values (1.7 to 11.35) the reduction of nitro-group involves six electrons. Below pH 3 the reduction is one-step of six electrons, and above pH 3, the hydroxylamine stage (four electrons) becomes more and more stable, with further reduction to amine (two electrons) in the second step. The kinetics of the conversion of the normal nitro-compound into aci-form has been studied polarographically by us and found to be second order; details are given in Chapter V.

Taking $D = 5.53 \times 10^{-6}$ $cm^2/sec.$ and using Koutecky's method, values of kinetic parameters (αn_a and $-\log k^o$) were evaluated from the data for the polarographic waves at various pH values. The -log k vs. E plot for single steps (pH less than 3) and the same plot for the first step (pH greater than 3) yielded straight lines (Fig. 2), thus showing that there is only one slow process that determines the rate of the reduction. These results are given in Table I. Values of αn_a showed a regular decrease between pH 4.8 and 11.35. Plots of $-\log k^o$ and $E_{0.5}$ for the first step as well as the plot of $E_{0.5}$ for the second step against pH showed similar results (Fig. 3). These values of $-\log k^o$ and $E_{0.5}$ first increased up to a certain pH and then decreased with further increase of pH. The decrease beyond a certain pH may be due to the fact that at higher pH values the amount of active depolarizer left is much less (more of the normal nitro-compound converted into the aci-form) and the concentration effect on $E_{0.5}$ as

well as on -log k^o overcomes the influence of pH on these quantities.

The probable mechanism (below pH 3) when single step six electron reduction is taking place, may well be



Above pH 3, where the hydroxylamine stage becomes more and more stable with pH increase, the reduction may well be

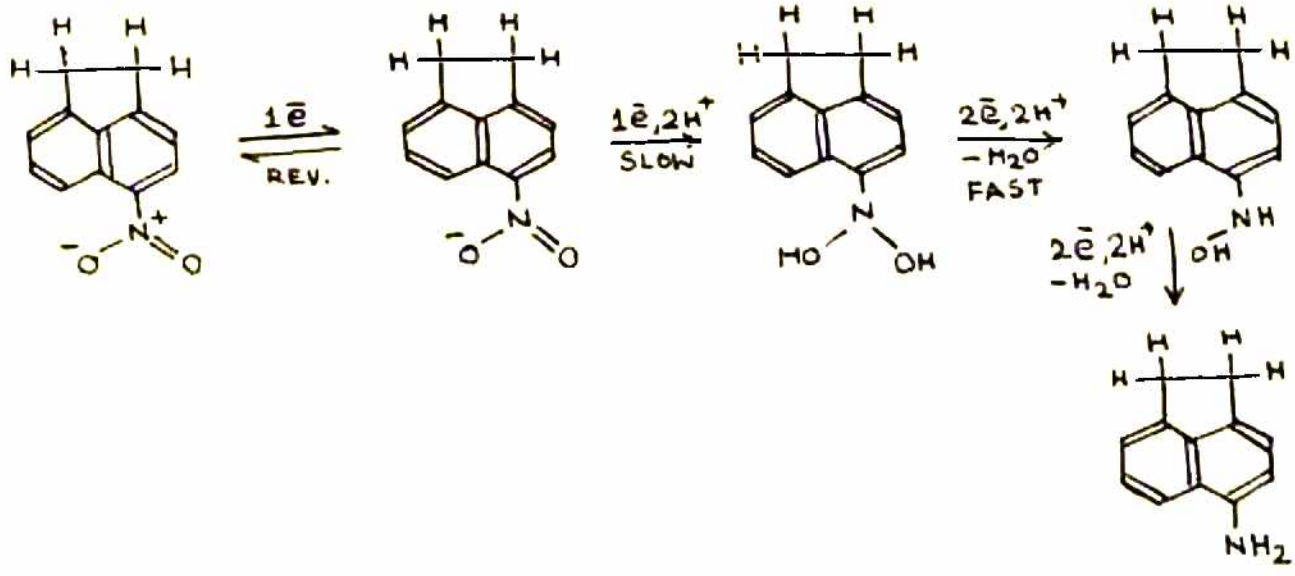


Table I

Kinetic parameters at different pH values

Concentration of depolarizer = 1.04 millimole

Ionic strength μ = 0.27 M; Ethyl alcohol = 40%; Temp. = 33°C

Height h = 40 cms.

Sl. No.	pH	i_{d_1} μ.a.	i_{d_2} μ.a.	i_d μ.a.	-log k^o N.H.E.	$E^1_{0.5}$ volt (S.C.E.)	$E^2_{0.5}$ volt (S.C.E.)	αn_a
1.	1.7	21.2	-	21.2*	3.661	0.385	-	0.333
2.	2.95	20.8	-	20.8*	4.213	0.490	-	0.330
3.	3.9	15.0	5.6	20.6	4.573	0.500	0.865	0.399
4.	4.8	14.8	5.8	20.6	5.077	0.560	1.00	0.437
5.	5.7	14.0	6.4	20.4	5.356	0.600	1.180	0.418
6.	7.15	13.4	6.0	19.4	6.239	0.710	1.40	0.4131
7.	8.25	13.2	3.2	16.4	6.488	0.820	1.527	0.383
8.	9.55	12.6	3.2	15.8	6.936	0.880	1.440	0.380
9.	10.4	12.5	2.9	15.4	6.780	0.880	1.440	0.370
10.	10.95	9.2	4.8	14.0	6.406	0.820	1.43	0.364
11.	11.35	2.4	1.9	4.3	5.646	0.730	1.20	0.333

* Single step reduction.

Legend of the Figures

Fig. 1: Current-voltage curves of 5-nitro-ace-naphthene (1.04 millimole) at various pH values, after allowing the solutions to attain equilibrium.

Curve A at pH 1.7

Curve B at pH 2.95

Curve C at pH 3.9

Curve D at pH 5.7

Curve E at pH 8.25

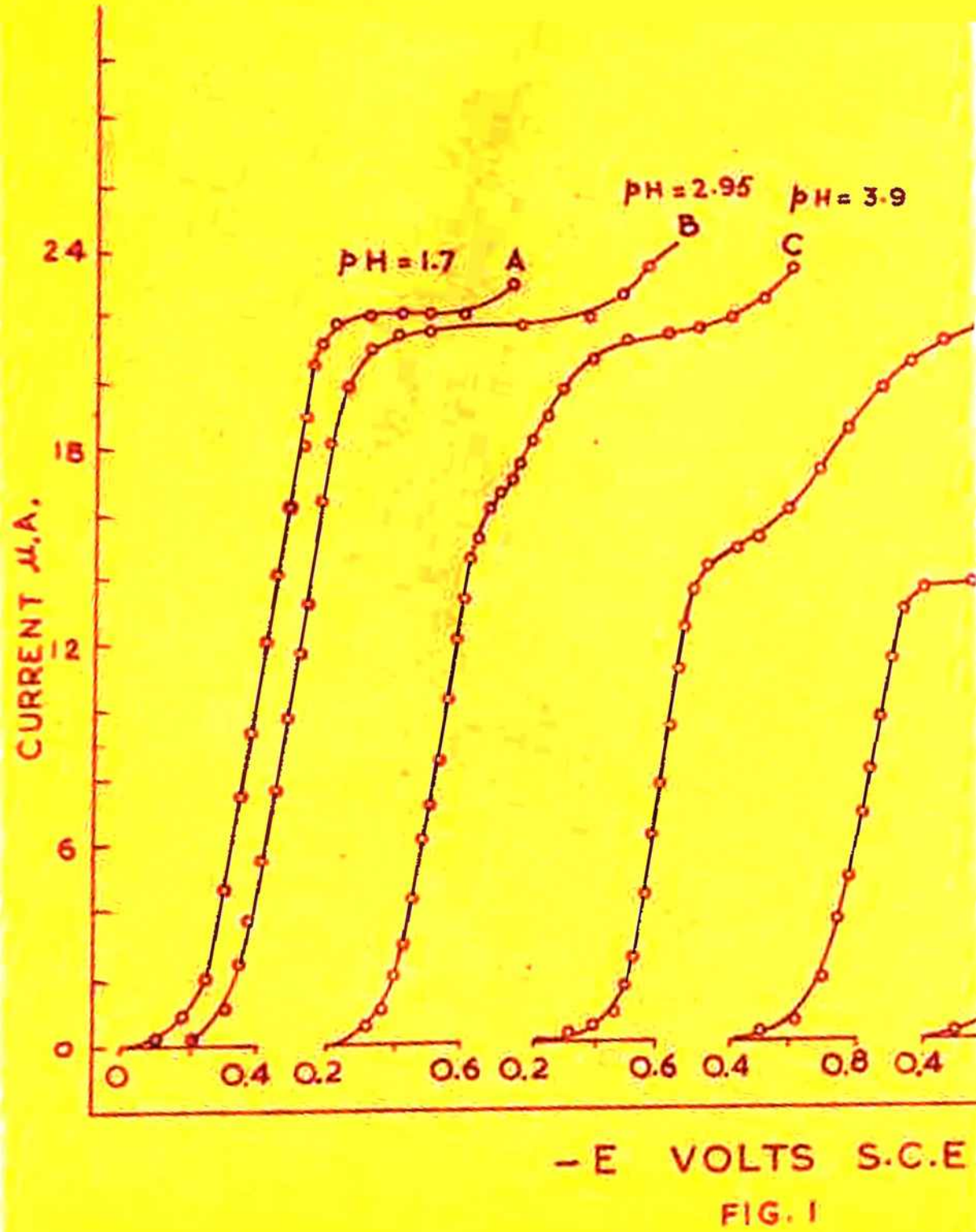
Curve F at pH 10.95

Curve G at pH 11.35

Fig. 2: Plot of -log k vs. E at various pH values Curves A, B, C, D, E, F, G, H, I, J and K at 1.7, 2.95, 3.9, 4.8, 5.7, 7.15, 8.25, 9.55, 10.4, 10.95 and 11.35, respectively.

Fig. 3: Plots of -log k^{o} and $E^{1}_{0.5}$ for the first step and the plot of $E^{2}_{0.5}$ for second step against pH.

-x-


pH = 1.7
A
pH = 2.95
B
pH = 3.9
C
24
18
12
6
0
CURRENT μ.A.
0
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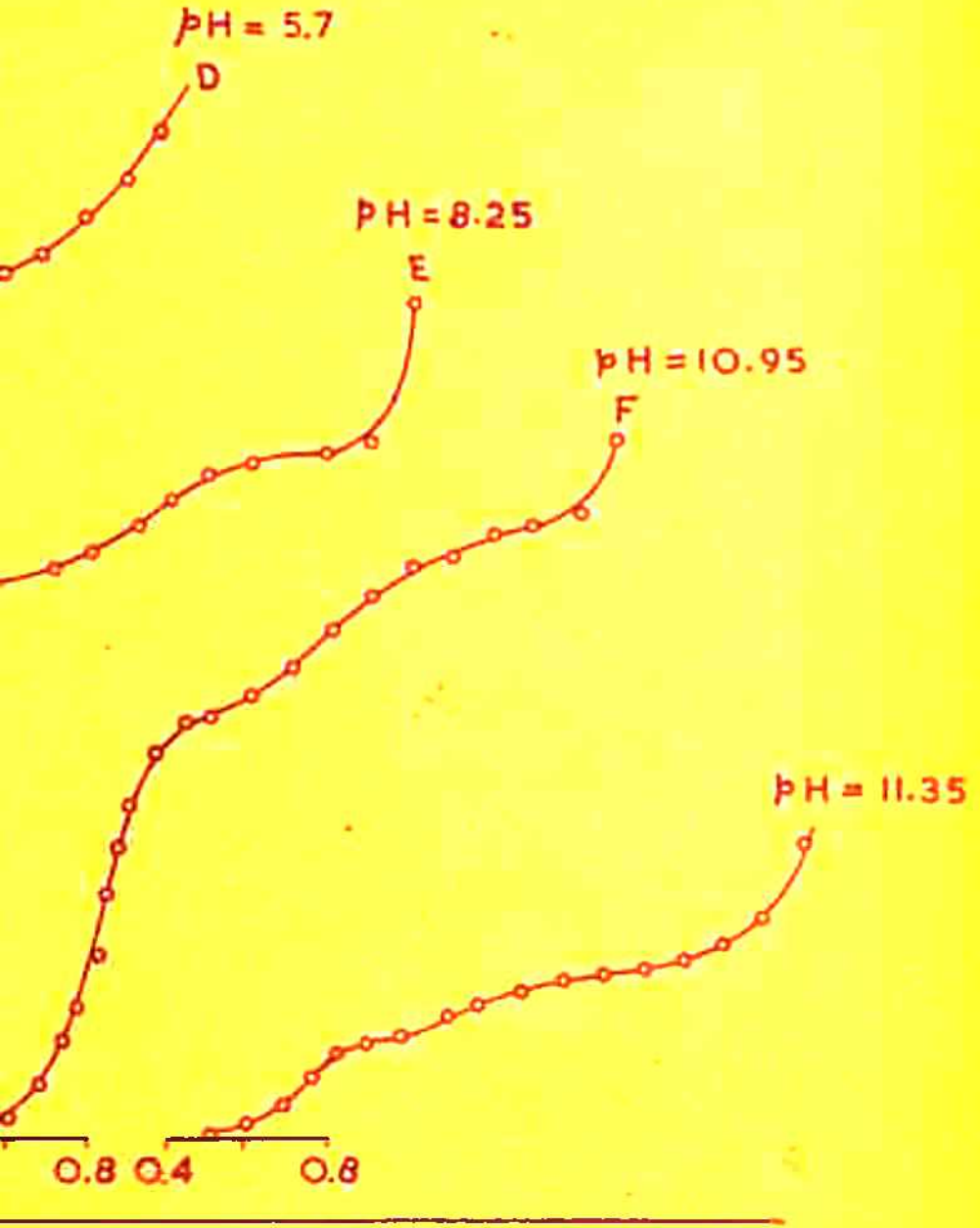
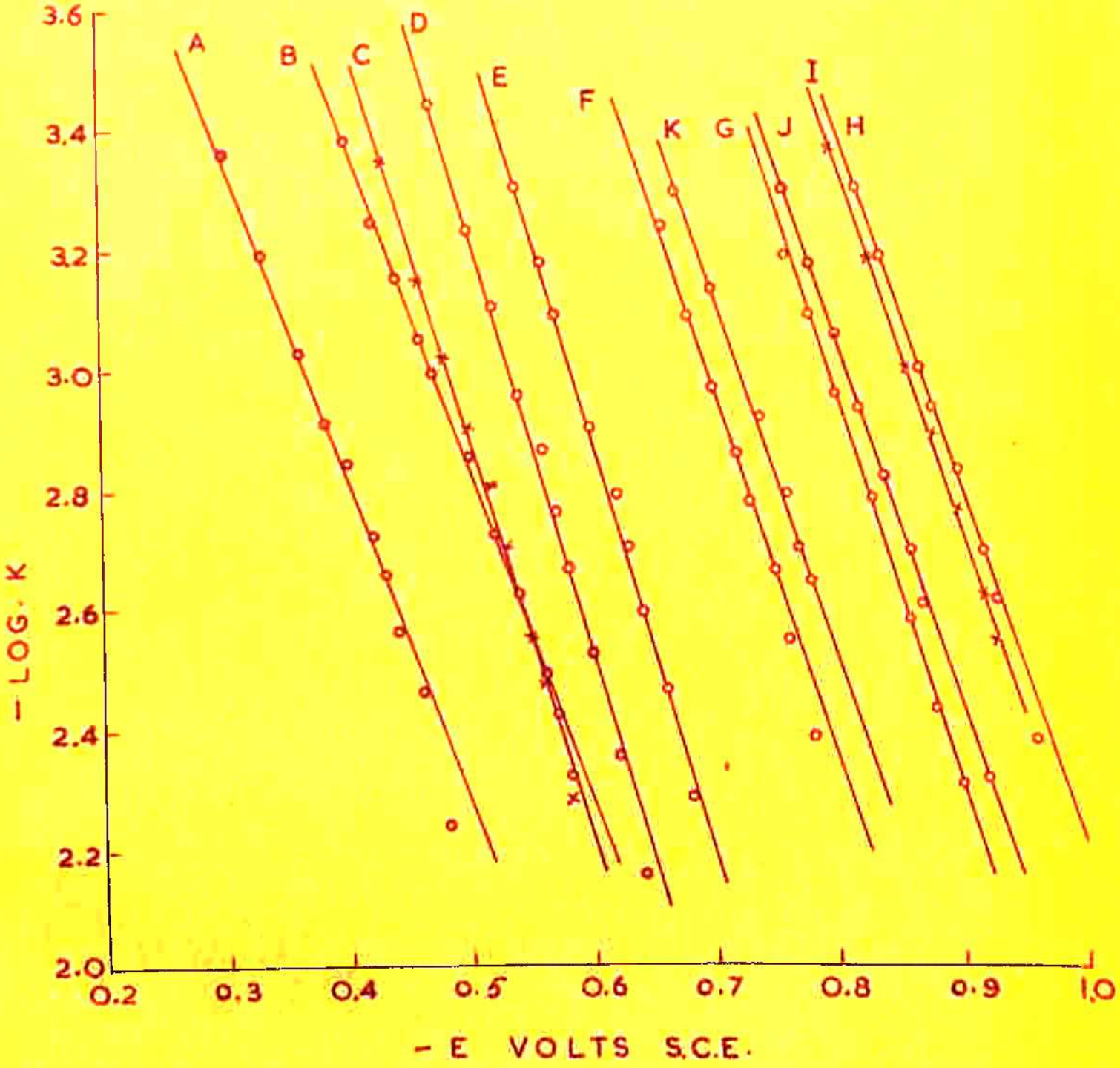
0.2
0.6
0.2
0.6
0.4
0.8
0.4
-E VOLTS S.C.E

FIG. 1


pH = 5.7
D
pH = 8.25
E
pH = 10.95
F
pH = 11.35
0.8
0.4
0.8


3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
- LOG. K
A
B
C
D
E
F
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I
H
0.2
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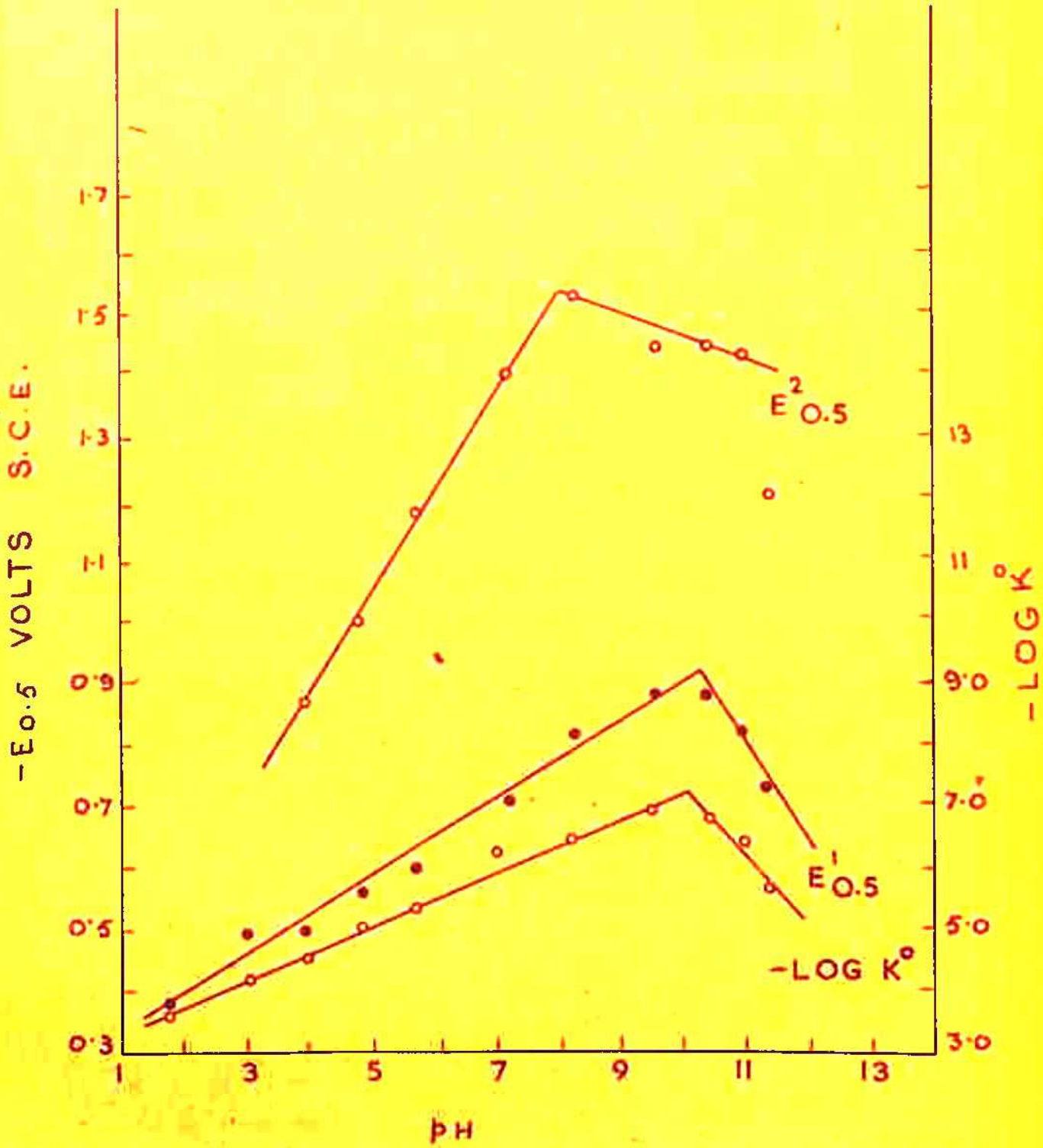
0.8
0.9
1.0
- E VOLTS S.C.E.

FIG. 2


-Eo.5 VOLTS S.C.E.
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1·3
1·1
0·9
0·7
0·5
0·3
1
3
5
7
9
11
13
pH
E²0.5
E¹0.5
-LOG K°
13
11
9·0
7·0
5·0
3·0
-LOG K°

FIG. 3

II. Polarography of 5-nitro-orotic acid:

Kapoor and Jain[21] during the polarographic studies of some nitro-pyrimidines have reported that 5-nitro-orotic acid undergoes a single step ($6\bar{e}$) reduction between pH 7 and 9 in Britton-Robinson buffers and above pH 9, the reduction process splits into two waves, one corresponding to $4\bar{e}$ followed by another wave of $2\bar{e}$. They explained it to be due to the retardation of the reduction of 5-nitro-orotic acid possibly owing to the negative charge of the ionised carboxyl group.

The author while studying the effect of surface-active-substances on the reduction of nitro-group in certain aromatic nitro-compounds observed two well defined steps for the reduction of 5-nitro-orotic acid at pH 8, in the absence of s.a.s. This led us to repeat the polarographic study of 5-nitro-orotic acid which gave some interesting results and the same have been incorporated in the present work.

Experimental

Stock solution of 5-nitro-orotic acid (potassium salt, anhydrous) - Sigma Chemicals Co., U.S.A., was prepared in redistilled air free water. AnalaR reagents were used to prepare the following HCl/KCl, Na_2HPO_4/citric acid, boric acid/

NaOH and Na_2HPO_4/NaOH buffer systems of constant ionic strength (μ = 0.54 M), adjusted by KCl. Triton X-100 (0.0004 to 0.001%) was used as maximum suppressor. The capillary used for dme had m = 2.931 mg/sec., t = 3.05 sec./drop in 0.54 M-KCl (open circuit) at h = 40.0 cms(uncorrected for back pressure).

Results and Discussion

Current/voltage curves at various pH values:

5-nitro-orotic acid gave two steps cathodic wave between pH 1 and 9. Above pH 9 the reduction wave split into three steps, Fig. (1). The half-wave potential ($E_{0.5}$) for both the steps shifted to more negative values with increased pH from 1 to 9. In order to know the nature of these reduction steps, effect of concentration of the depolarizer and the height of the mercury column (Fig. 2, 3a, 3b) on these reduction steps were examined at pH 1, 9 and 10. Studies at pH 1.0 showed that i_d/c and $i_d/\sqrt{h}$ were constant for both steps, whereas at pH 9, these quantities were constant for first step only and for the second step i_d/c showed a decrease and i_d/h was constant (rather than $i_d/\sqrt{h}$). At pH 10.0, i_d/c and $i_d/\sqrt{h}$ were constant for the first step only and for the second and the third step i_d/c showed a decrease, while i_d/h were constant. These observations indicated that the first step

(pH 1 to 10) was purely diffusion controlled. The second step too was diffusion controlled in highly acidic medium, but exhibited adsorption characteristics in alkaline medium. Also the third step at pH 10.0 had adsorption characteristics.

Effect of concentration of depolarizer and that of height of mercury column on $E_{0.5}$, as well as, the slopes of the linear plots of $\log(i/i_d-i)$ vs. E at pH 1, 9 and 10 showed that it was irreversible reduction.

Number of electrons involved in the electrode process, at various pH values, was determined by comparing the limiting current values of 5-nitro-orotic acid with those of the known wave ($4\bar{e}$) of nitrobenzene under identical experimental conditions. These were further supported by determining the values of diffusion coefficient (D) at pH 1, 9 and 10 with the help of McBain-Dowson's cell, using King-Cathard equation.

Table I

Number of electrons from McBain-Dowson's cell

pH	D $cm^2/sec.$	step	Number of electrons for diffusion controlled step
1.0	10.2×10^{-6}	1st	$6.24 \simeq 6$
		2nd	$3.93 \simeq 4$
9.0	9.315×10^{-6}	1st	$5.6 \simeq 6$
10.0	10.15×10^{-6}	1st	$4.15 \simeq 4$

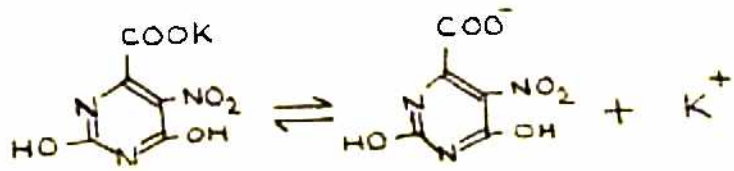
From these observations it was concluded that 5-nitro-orotic acid was reduced in two steps up to pH 9; first step corresponding to a $6\bar{e}$ and the second one to a $4\bar{e}$ process. However, above pH 9, the first and the second steps were $4\bar{e}$ each and third step a $2\bar{e}$ reduction process.

Values of kinetic parameters (αn_a and $-\log k^o$) were determined by using Koutecky's method, for the diffusion controlled first step at pH 1 to 10. Results are tabulated in Table II. The plots of $-\log k^o$ vs. pH and $E^1_{0.5}$ vs. pH (pH 1 to 9) resulted in identical S-shaped curves, whereas, the $E^2_{0.5}$ vs. pH (pH 1 to 9) was a linear plot (Fig. 4).

The -log k vs. E plot for the first step (pH 1 to 10) and the same plot for the second step (pH 1.0) yielded straight lines (Fig. 5); thus showing that there was only one slow process which determined the rate of the reduction. Values of αn_a showed no regularity, but $-\log k^o$ increased with pH, indicating electrode process becoming more irreversible with increase in pH. This may be due to the increased difficulty of available H^+ ions which play an important role in the reduction process.

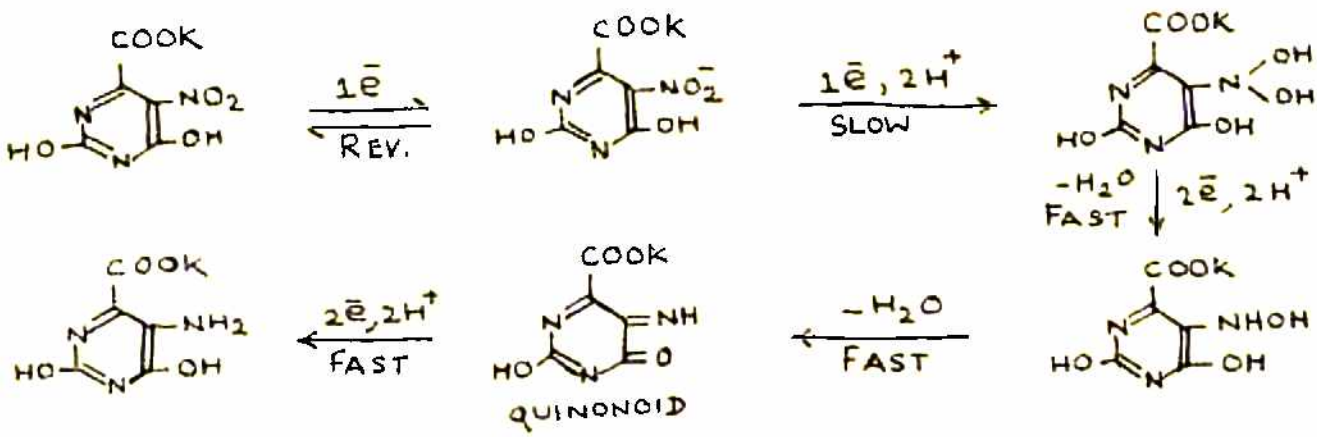
Effect of concentration of depolarizer and the height of mercury column on αn_a and $-\log k^o$ have been shown for the diffusion controlled first step, at pH 1, 9 and 10 and also for the second step at pH 1.0. The results are given in Table IIIa and IIIb.

The probable reduction mechanism of the 5-nitro-orotic acid below pH 9, where two steps ($6\bar{e}$, $4\bar{e}$) are obtained - may be as follows. The equilibrium, given below, may exist below pH 9, involving neutral and singly charged species.

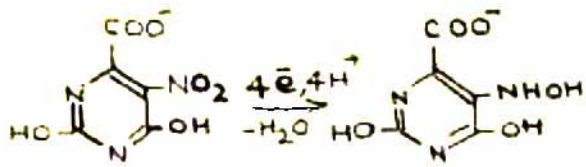


The neutral molecule is reduced at dme in single step, $6\bar{e}$, through quinonoid form and the singly charged undergoing, $4\bar{e}$, single step reduction.

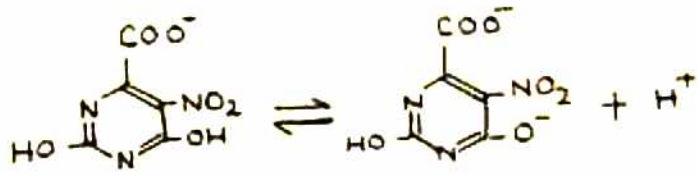
First step, $6\bar{e}$:



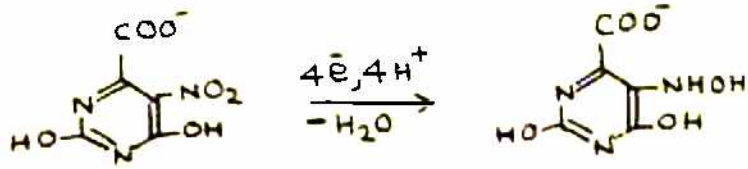
Second step, $4\bar{e}$:



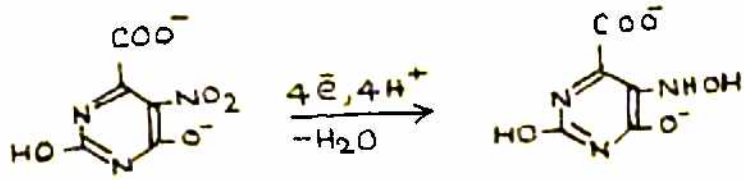
However, above pH 9, the species present in equilibrium may be singly and doubly charged as mentioned below:



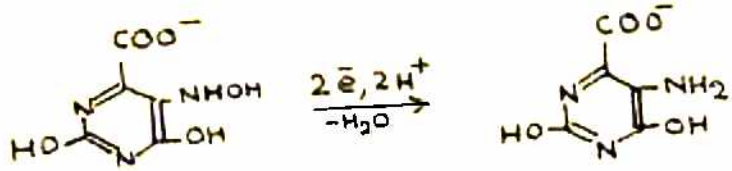
Here the singly and doubly charged species undergo $4\bar{e}$ reduction leading to corresponding hydroxylamines, through first and second steps respectively. The third step corresponds to the further reduction of singly charged hydroxylamine to the amine stage.



1st. step.



2nd. step.



3rd. step.

It can be seen from Table II that the half-wave potentials of the first and the second waves shift, regularly, to more cathodic value with increase in pH from 1 to 9. However, at pH 10, this sequence breaks and the half-wave potentials for the first and the second waves are much positive as compared to the values of half-wave potentials at pH 9, This fact shows that the reduction mechanisms at pH 9 and 10 are different and involve different species.

Tueci[52] et al. studied the relative stability of the complexes of certain 5-substituted orotic acid derivatives and have given the order $5\text{-}NH_2 > 5\text{-}I > 5\text{-}Br > 5\text{-}NO_2$. This order suggests that the complex forming capacity of 5-nitro-orotic acid is the least and that of its 5-amino-orotic acid is the greatest. Thus, the adsorption character of the second wave at pH 9 and second and third waves at pH 10 may be due to the formation of a complex between the reduced form of the depolarizer and the mercury.

Table II

Values of αn_a and $-\log k^o$ at various pH

0.4 mM of depolarizer; Temp. = 30°C; Height = 40.0 cms.

Ionic strength of buffer μ = 0.54 M.

Sl. No.	pH	i_d μ.a.	$-E_{0.5}$ volts S.C.E.	αn_a	$-\log k^o$ N.H.E.	Remarks
						Triton X-100
1.	1.0	10.45[a]	0.250	0.3413	2.954	0.001%
		7.50[b]	0.928	-	-	
2.	2.0	10.25[a]	0.328	0.420	3.485	0.001%
		6.60[b]	1.052	-	-	
3.	3.0	9.40[a]	0.395	0.353	3.7585	Nil
		6.80[b]	1.130	-	-	
4.	4.0	9.2[a]	0.450	0.2943	3.945	Nil
		6.60[b]	1.250	-	-	
5.	5.8	8.3[a]	0.700	0.2775	5.037	0.0004%
		6.25[b]	1.530	-	-	
6.	7.1	7.7[a]	0.880	0.374	6.8943	0.0004%
		5.6[b]	1.60	-	-	
7.	7.95	10.0[a]	1.010	0.3812	7.732	Nil
		3.4[b]	1.73	-	-	
8.	9.00	8.6[a]	1.080	0.3458	7.721	0.001%
		3.85[b]	1.745	-	-	
9.	10.00	6.0[a]	1.065	0.4165	8.582	0.001%
		4.4[b]	1.560	-	-	
		2.1[c]	1.90	-	-	

a ... 1st step; b ... 2nd step; c ... 3rd step.

Table IIIa

Concentration effect on αn_a and $-\log k^o$

Temp. = 35°C; Height = 40.0 cms, Triton X-100 = 0.001%

pH	Concentration ml*	$-\log k^o$ N.H.E.	αn_a	$-E_{0.5}$ volts S.C.E.
		For 1st step		
1.0	0.20	2.52813	0.5625	0.230
	0.40	2.8266	0.4613	0.250
	0.70	3.0740	0.2815	0.308
	1.00	3.1432	0.2359	0.348
		For 2nd step		
	0.2	10.4553	0.747	0.860
	0.4	9.953	0.624	0.945
	0.7	8.695	0.432	1.048
	1.0	8.4492	0.35994	1.180
		For 1st step		
9.0	0.3	7.3285	0.333	1.080
	0.4	7.1161	0.312	1.090
	0.7	6.6090	0.262	1.125
	1.0	6.2260	0.223	1.170
		For 1st step		
10.0	0.20	7.726	0.3820	1.065
	0.30	7.493	0.3525	1.080
	0.40	7.2611	0.3262	1.090
	0.70	6.8076	0.28284	1.140

* 0.1 ml = 0.08 mM depolarizer.

Table IIIb

Height effect on αn_a and $\log k^o$

Temp. = 35°C; 0.32 mM of depolarizer; Triton X-100=0.001%

pH	Height cms.	$-\log k^o$ N.H.E.	αn_a	$-E_{0.5}$ volts S.C.E.
		For 1st step		
1.0	40.0	2.8266	0.4613	0.250
	50.0	2.93013	0.3915	0.270
	60.0	2.9753	0.3712	0.275
		For 2nd step		
	40.0	9.952	0.624	0.945
	50.0	10.254	0.604	0.986
	60.0	11.94734	0.5807	1.000
		For 1st step		
9.0	40.0	7.1161	0.312	1.130
	50.0	7.9164	0.3557	1.130
	60.0	8.568	0.336	1.130
		For 1st step		
10.0	30.0	7.554	0.36162	1.065
	40.0	7.726	0.3820	1.065
	50.0	8.024	0.4080	1.065

Legend of the Figures

Fig. 1: Current-voltage curves for 0.4 mM. depolarizer at various pH values.

Fig. 2: Current-voltage curves for various concentrations of depolarizer, at pH 9.0 and pH 10.0.

Fig.3a: Effect of height on the current-potential curve at pH = 9.0.

Fig.3b: Effect of height on the current-potential curve at pH = 10.0.

Fig. 4: Plot of $-\log k^{\circ}$, $E^{1}_{0.5}$ and $E^{2}_{0.5}$ against pH.

Fig. 5: $-\log k$ vs. E plot at various pH values.

-x-

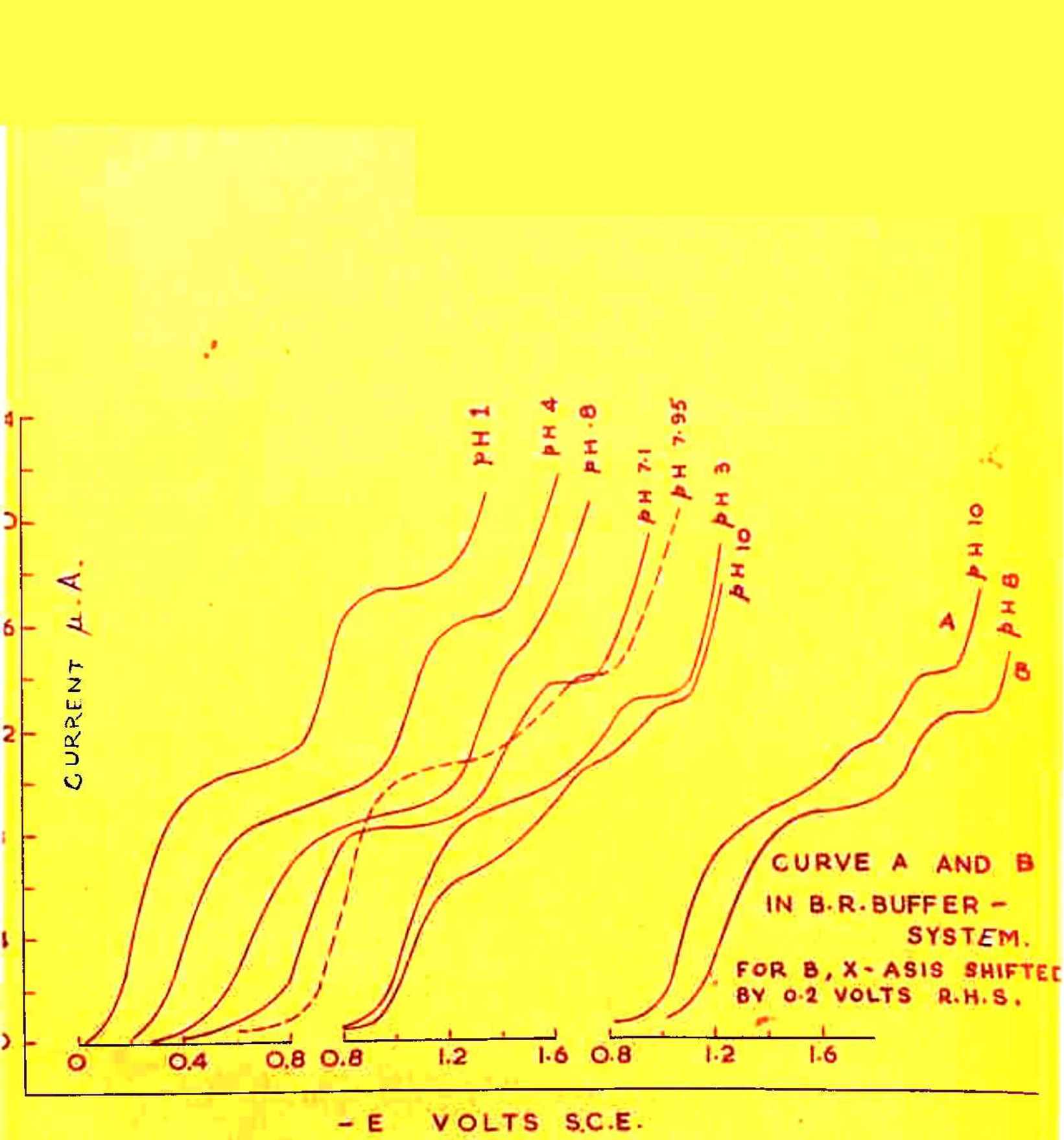

CURRENT μ.A.
pH 1
pH 4
pH 8
pH 7.1
pH 7.95
pH 3
pH 10
A
pH 10
pH 8
B
CURVE A AND B
IN B.R. BUFFER -
SYSTEM.
FOR B, X-ASIS SHIFTED
BY 0.2 VOLTS R.H.S.
0
0.4
0.8
0.8
1.2
1.6
0.8
1.2
1.6
-E VOLTS S.C.E.

FIG. 1

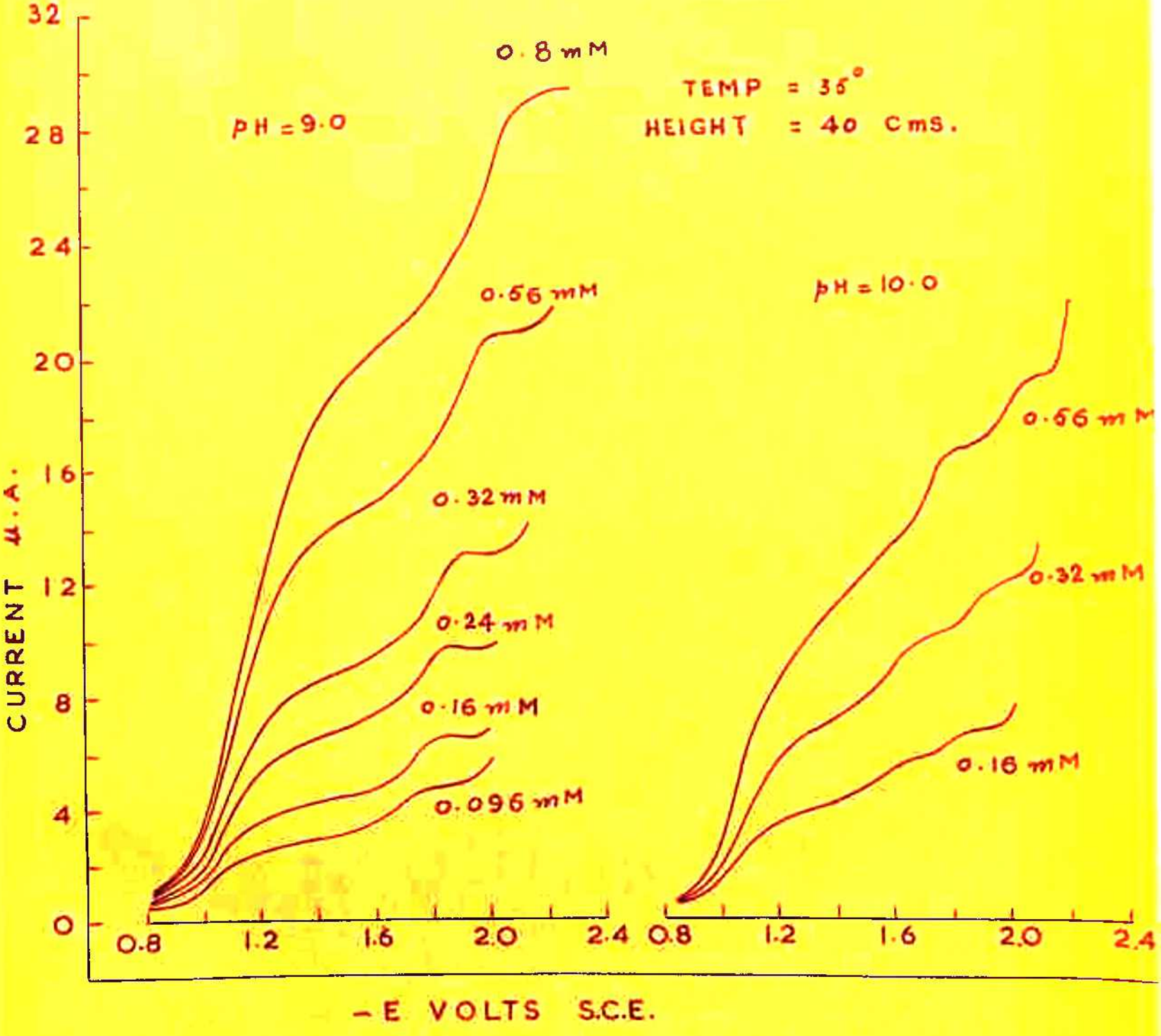

32
28
24
20
16
12
8
4
0
CURRENT μ.A.
0.8 mM
TEMP = 35°
HEIGHT = 40 Cms.
pH = 9.0
0.56 mM
0.32 mM
0.24 mM
0.16 mM
0.096 mM
pH = 10.0
0.56 mM
0.32 mM
0.16 mM
0.8
1.2
1.6
2.0
2.4
0.8
1.2
1.6
2.0
2.4
-E VOLTS S.C.E.

FIG. 2

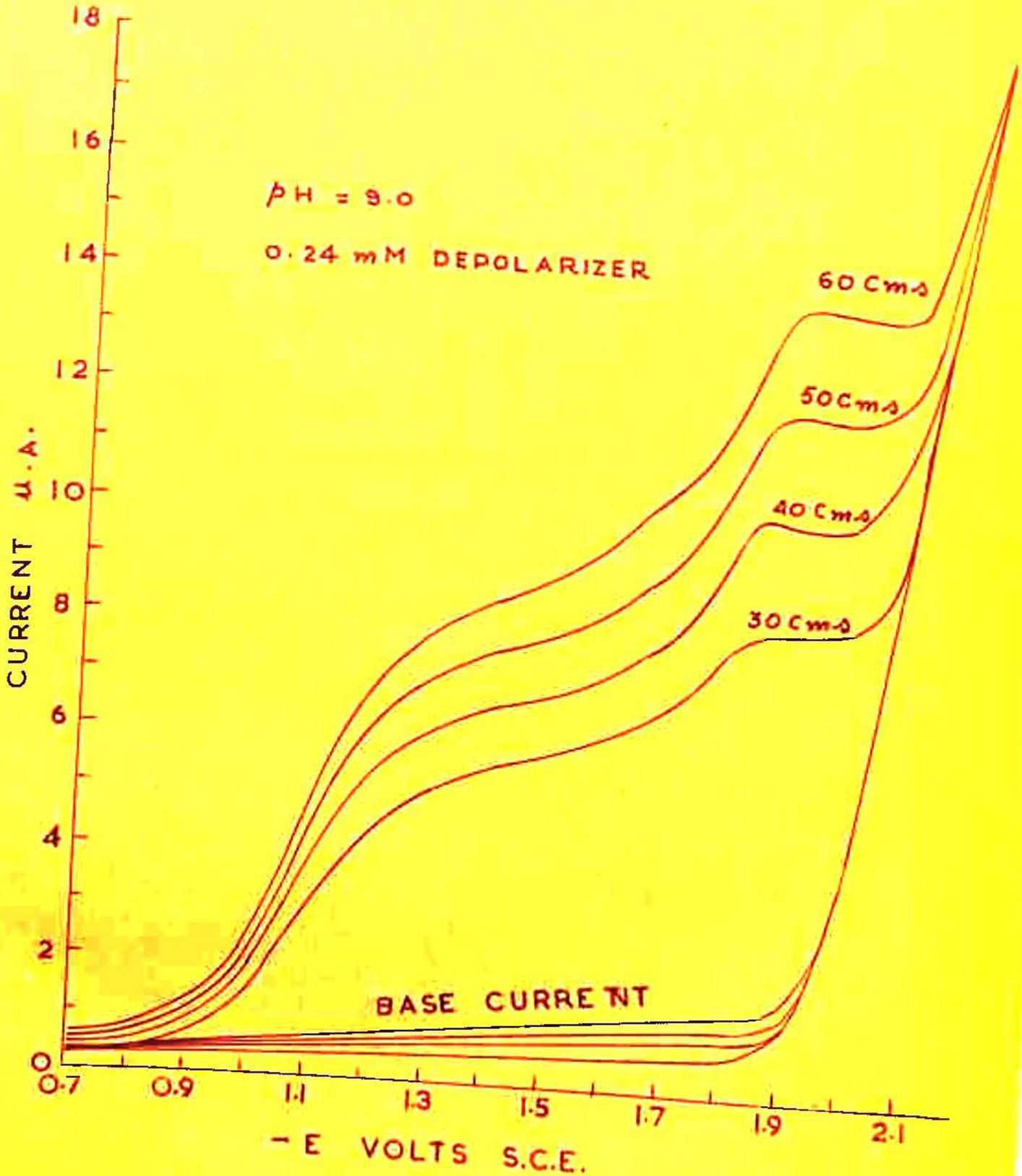

18
16
14
12
10
8
6
4
2
0
CURRENT μ.A.
PH = 9.0
0.24 mM DEPOLARIZER
60 Cms
50 Cms
40 Cms
30 Cms
BASE CURRENT
0.7
0.9
1.1
1.3
1.5
1.7
1.9
2.1
- E VOLTS S.C.E.

FIG. 3 (α)

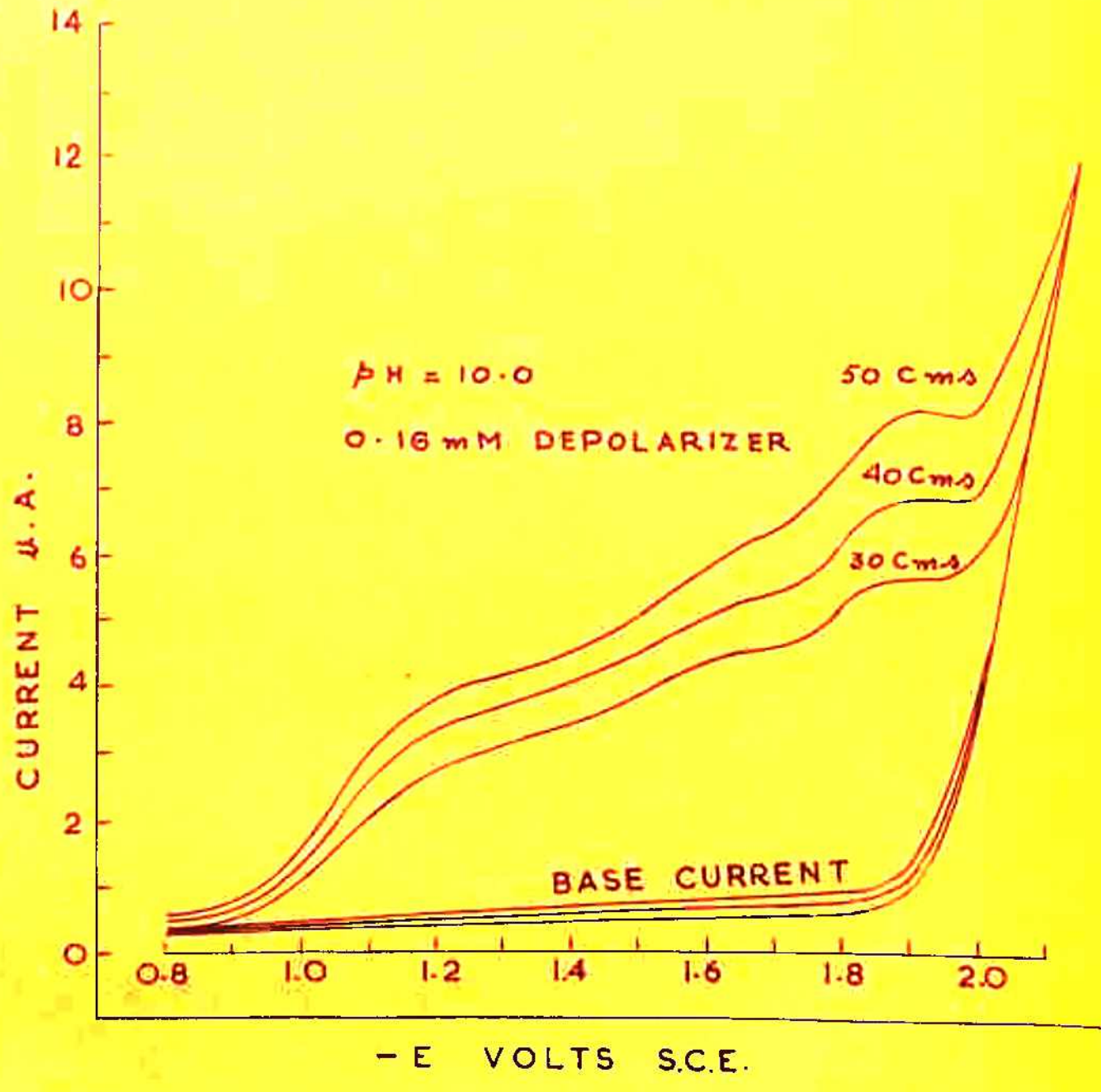

14
12
10
8
6
4
2
0
CURRENT μ.A.
pH = 10·0
0·16 mM DEPOLARIZER
50 Cms
40Cms
30 Cms
BASE CURRENT
0·8
1·0
1·2
1·4
1·6
1·8
2·0
– E VOLTS S.C.E.

FIG. 3 (b)

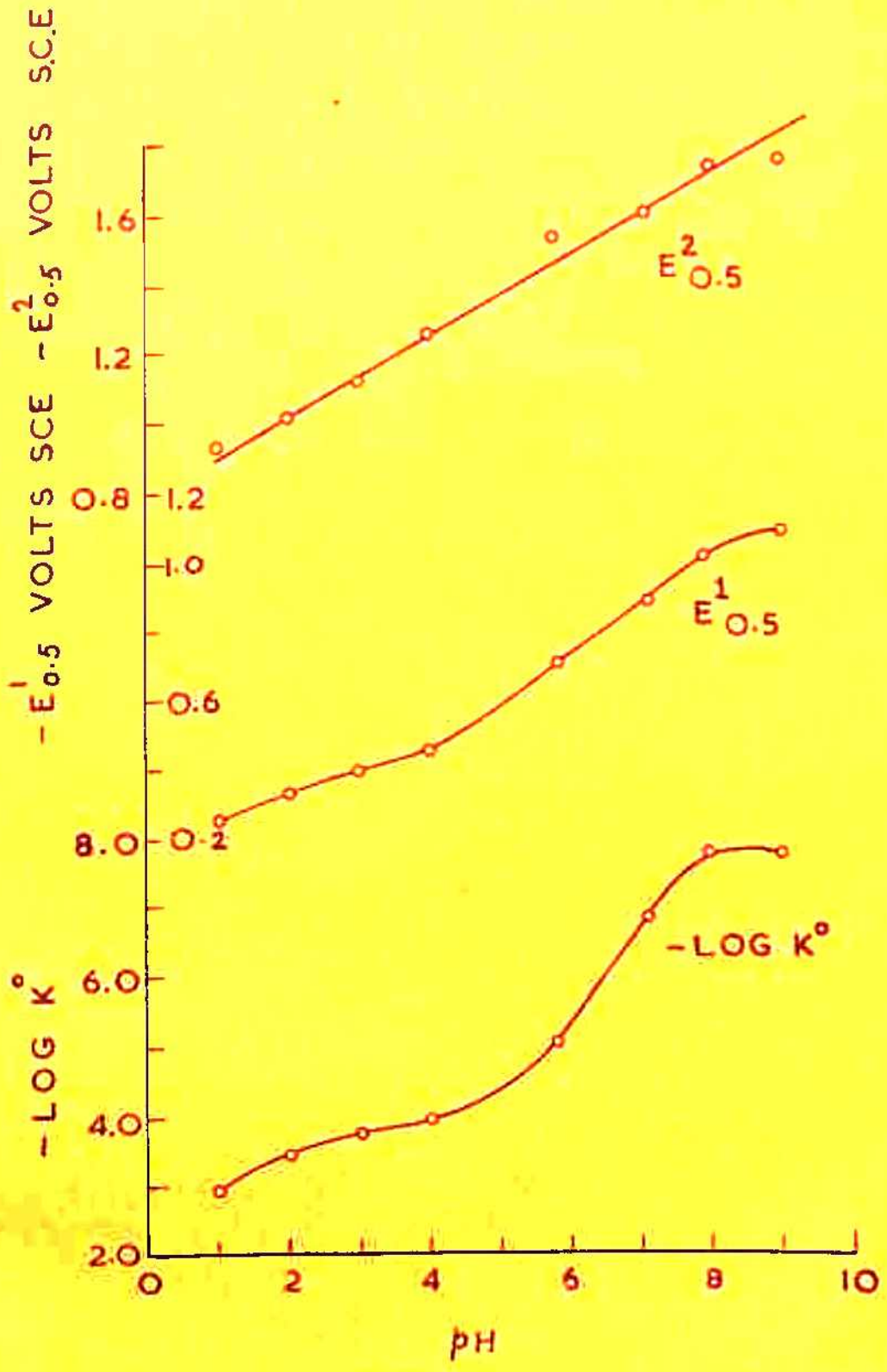

-LOG K°
8.0
6.0
4.0
2.0
-E¹0.5 VOLTS SCE
1.2
1.0
0.6
0.2
-E²0.5 VOLTS S.C.E
1.6
1.2
0.8
E²0.5
E¹0.5
-LOG K°
0
2
4
6
8
10
pH

FIG. 4

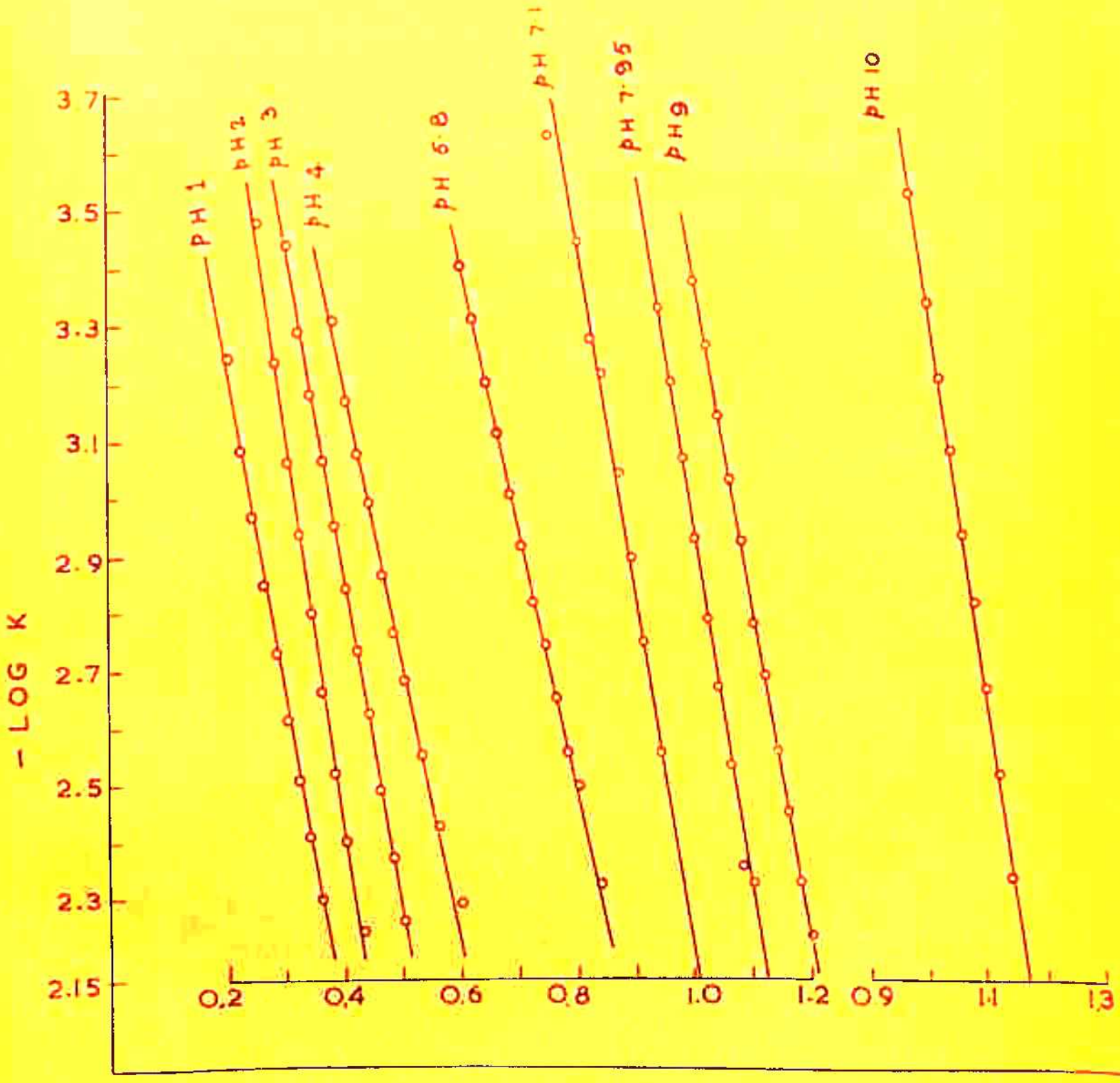

pH 1
pH 2
pH 3
pH 4
pH 6·8
pH 7·1
pH 7·95
pH 9
pH 10
3.7
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.15
- LOG K
0.2
0.4
0.6
0.8
1.0
1.2
0.9
1.1
1.3
- E VOLTS S.C.E.

FIG. 5

III. Polarography of ortho and para nitrocinnamic acid in aqueous-methanolic medium:

Polarographic behaviour of cinnamic acid and its derivatives has been studied by several workers[52-58]. The more recent studies were made by M.J.D. Brand[59] et al. and H. Lund[60]. They have studied the polarographic behaviour of cis- and trans-cinnamic acids and substituted cinnamic acids in 50% ethyl alcohol using acetate buffer, which showed a $2\bar{e}$ reduction wave between pH 4 and 8.

A review of the literature indicated that no polarographic study has been made on the nitro-derivatives of cinnamic acid. In the present investigation the polarographic reduction of ortho and para- nitrocinnamic acids (transforms) has been carried out with the aim to record the reduction wave (S) for the nitro-group and for the saturation of the -C=C- double bond.

Experimental

Methyl alcohol (B.D.H., A.R.) used for stock solutions was redistilled at 54.5°C in all-glass fractionating column and the middle one-third of the distillate was used for experiments. Ortho-nitrocinnamic acid was L. Light and Co. product and para-nitrocinnamic acid of B.D.H. (L.R.) grade. Other chemicals for buffer systems and supporting electrolyte were of analytical reagent grade. HCl/KCl, ammonium acetate/NaOH

and NaOH buffer systems (μ = 0.58 M) were used for various pH values. All experiments were carried out at a temperature of 32°C. The capillary used for dme had m = 2.586 mg/sec. and t = 2.96 sec./drop in 0.58 M KCl (open circuit) at h = 65.0 cms (uncorrected for back pressure).

Results and Discussion

It was observed that in highly acidic medium the nitro-group gave the usual two waves, first being a $4\bar{e}$ reduction resulting with the formation of hydroxylamine which further showed a $2\bar{e}$ reduction giving amine. This view was supported by the comparison of the magnitudes of the first wave for the reduction of ortho-nitrocinnamic acid and that of the first wave ($4\bar{e}$) of nitrobenzene reduced under identical conditions. No wave could be recorded for the saturation of the double bond (-C=C-) due to the hydrogen discharge.

In weakly acidic, neutral and alkaline media only nitro-group gave one step reduction up to hydroxylamine stage, whereas, in highly alkaline medium (0.1 M - NaOH, 80% methyl alcohol, pH = 11.5) the nitro-group gave the usual $4\bar{e}$ single step reduction and another wave at quite a far cathodic potential which was due to the saturation of the double bond (-C=C-) involving $2\bar{e}$ as reported[59,60]. That the reduction of nitro-group of the acid in highly alkaline

medium (0.1 M - NaOH, 80% methyl alcohol, pH = 11.5) involved $4\bar{e}$ was supported by the fact that the magnitudes of this wave height and that of the nitrobenzene (at pH = 11.5) under identical conditions were again similar. This was further confirmed from the value of diffusion coefficient "D" determined by McBain-Dowson cell using King-Cathard equation. The value of "D" thus obtained was 10.08×10^{-6} $cm^2/sec.$ from which the value of "n" for the reduction of nitro-group of the acid came to be $3.86 \simeq 4$. Separation of the second wave (for the saturation) was better defined in the case of ortho derivative than the para derivative as shown in Fig. 1. The use of maximum suppressor was eliminated because no maximum appeared at any pH values.

The plots of i_d vs. $\sqrt{h}_{corrected}$ for both the waves at pH 11.5 were linear indicating that the currents were diffusion controlled. Plots of log $i/(i_d-i)$ vs. E were linear for the nitro-group reduction wave but their slopes were much higher than the expected theoretical value. Also the same plots for the second wave deviated from linearity (Fig. 2), indicating that the electrode processes were irreversible. Further the half-wave potential of both the waves shifted to more cathodic potentials with increase in height of the mercury reservoir, which also supported the fact that processes were irreversible.

The plots of i_d vs. C (concentration of the depolarizer)

for both waves were linear within the range of 0.4 to 1.0 mM. During the study of the effect of the concentration of the depolarizer on i_d, it was observed that the $E_{0.5}$ of these two waves shifted towards more cathodic potential with the increase of the concentration of the depolarizer and thus at higher concentration (1.0 mM.) the separation of the second wave from the wave due to the discharge of the supporting electrolyte cation became less sharp particularly in the case of the para derivative.

The kinetic parameters were calculated by Koutecky's method for irreversible processes. The plots of -log k vs. E for nitro-group reduction up to hydroxylamine stage yielded straight lines at all pH values and for the second wave at pH 11.5 the same plot gave a linear curve (Fig. 3), indicating that these processes were controlled by a single rate determining step. From the slope of these plots the values of αn_a were computed and the value of rate constant at zero potential (k^o) were also found out. The results are summarised in Table I.

The reduction of the nitro-group can be explained as suggested by L. Holleck[20]. Brand and Fleet suggested that above pH 8 the cinnamic acid is reduced without preprotonation and below this pH the acid is reduced in the form of mono-protonated anion. Thus we can conclude that under the

above experimental conditions there is no pre-protonation of the acid and that the two electron addition be a single slow process controlling the rate of the electrode reaction

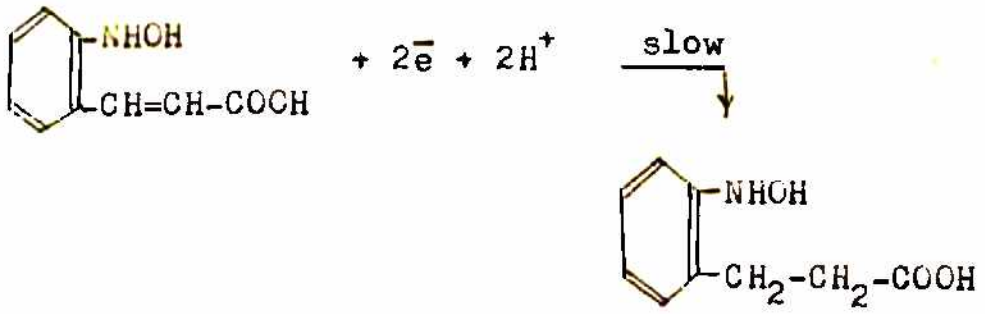


Table I

Values of kinetic parameters for the reduction of ortho and para derivatives of cinnamic acid.

u = 0.58 M; Temp. = 32°C; H = 65.0 cms; 80% methyl alcohol

pH	$i d_{NO_2}$ μ.a.	$-E_{0.5}$ volt S.C.E.	αn_a	-log k^o N.H.E.
	Ortho-nitro-cinnamic acid			
1.8	10.8	0.290	0.385	1.975
	3.6[a]	0.850	-	-
4.75	9.3	0.530	0.286	3.690
5.5	9.2	0.585	0.281	4.019
6.3	8.8	0.630	0.326	4.489
6.9	8.8	0.688	0.311	4.635
8.5	9.7	0.892	0.165	4.895
9.25	8.9	0.920	0.190	4.904
11.5	8.9	0.948	0.282	5.421
11.5	3.2[b]	1.900	0.529	18.070
	Para-nitro-cinnamic acid:			
1.8	10.8	0.240	0.375	2.451
	5.2[a]	0.815	-	-
4.75	9.8	0.445	0.318	4.245
5.5	9.75	0.525	0.371	4.834
6.3	9.50	0.598	0.387	4.975
6.9	9.50	0.668	0.364	5.244
8.5	9.30	0.890	0.210	5.424
9.25	9.60	0.930	0.345	6.600
11.5	9.50	0.960	0.420	7.630
11.5	2.8[b]	1.960	0.541	17.825

a) The 2nd wave for NO_2 group in acidic medium.

b) Wave for the hydrogenation of -C=C- bond in 0.1 M - NaOH, 80% methyl alcohol.

Legend of the Figures

Fig. 1: Current-voltage curves for ortho and para nitro-cinnamic acids in 80% methyl alcohol, at various pH values. Concentration of depolarizer 0.6 mM.

Fig. 2: Plots of $\log \frac{i}{i_d - i}$ vs. -E V. S.C.E., for $-NO_2$ group and for the saturation of double bond (C=C) in ortho and para nitro-cinnamic acids in 0.1 M - NaOH, 80% methyl alcohol (pH = 11.5).

Fig. 3: Plots of -log k vs. -E in 0.1 M - NaOH, 80% methyl alcohol (pH = 11.5).

Curve A for saturation of -C=C- bond in ortho-derivative.

Curve B for saturation of -C=C- bond in para-derivative.

Curves C and D for para and ortho nitro-derivatives, respectively.

-x-

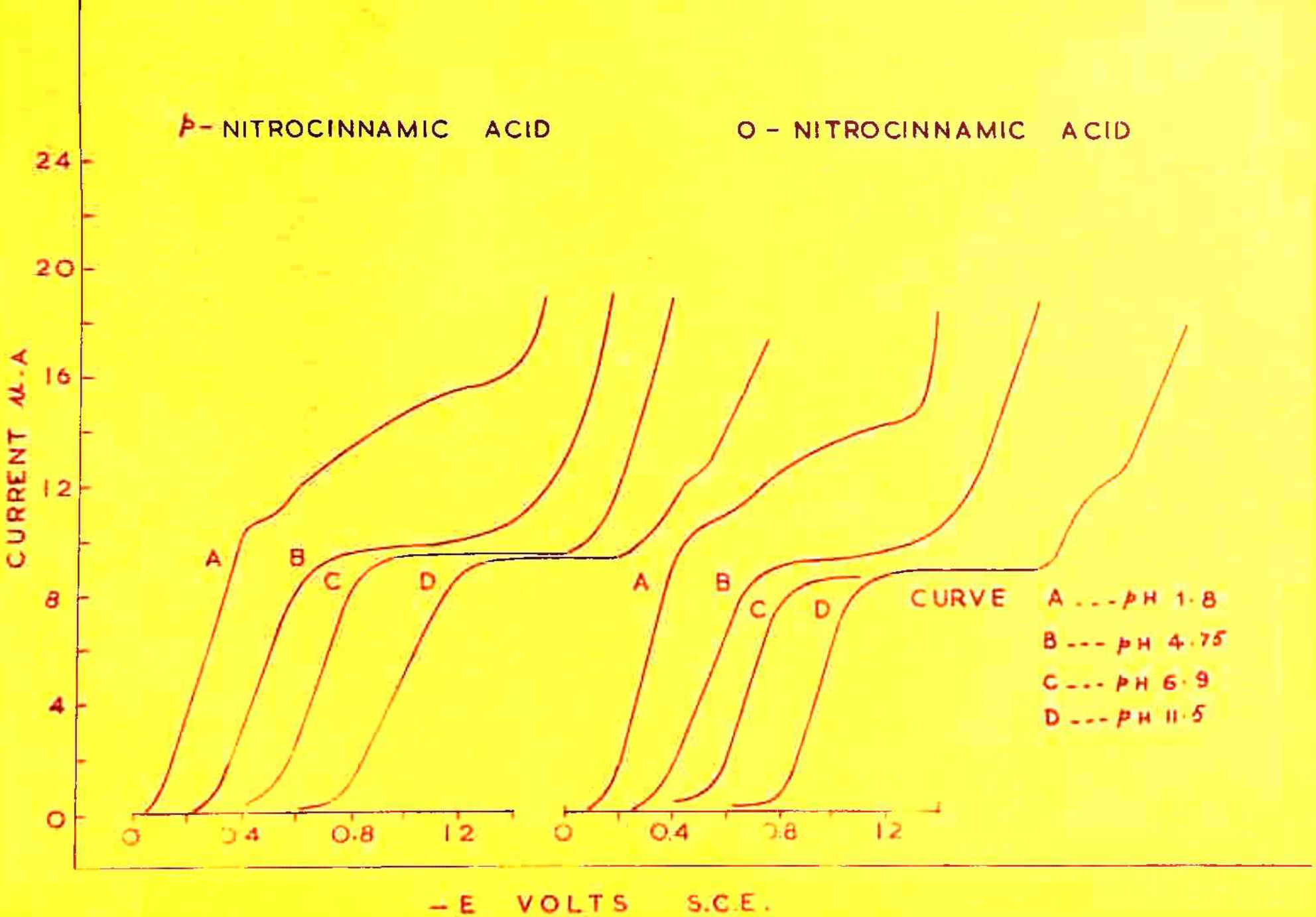

p- NITROCINNAMIC ACID
O - NITROCINNAMIC ACID
CURRENT M.A
24
20
16
12
8
4
0
A
B
C
D
0
0.4
0.8
1.2
CURVE A ... pH 1.8
B --- pH 4.75
C --- pH 6.9
D --- pH 11.5
-E VOLTS S.C.E.

FIG. 1

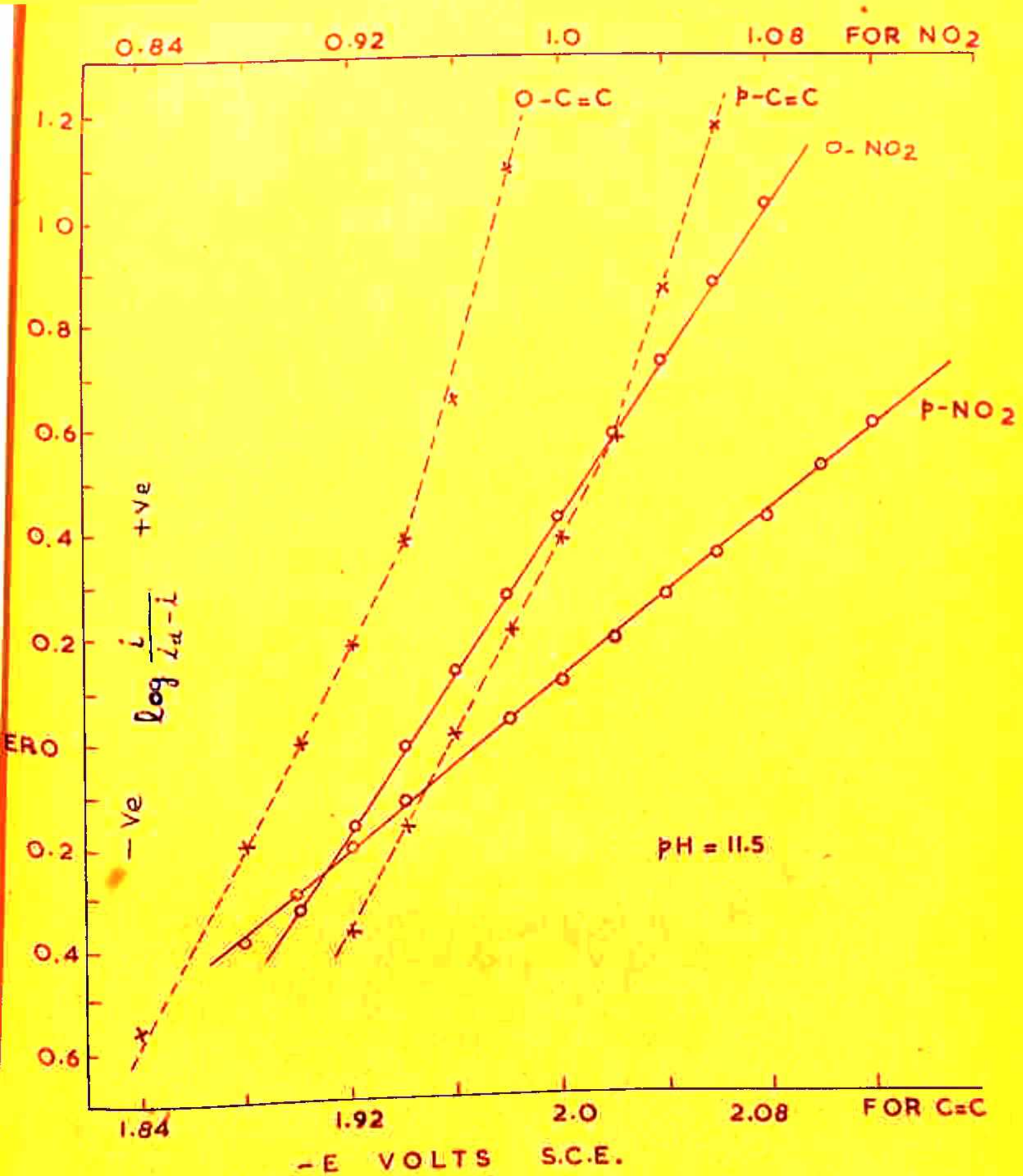

0.84
0.92
1.0
1.08
FOR NO2
O-C=C
P-C=C
O-NO2
P-NO2
1.2
1.0
0.8
0.6
0.4
0.2
ERO
0.2
0.4
0.6
+Ve
Log i/(iL-i)
-Ve
pH = 11.5
1.84
1.92
2.0
2.08
FOR C=C
-E VOLTS S.C.E.

FIG. 2

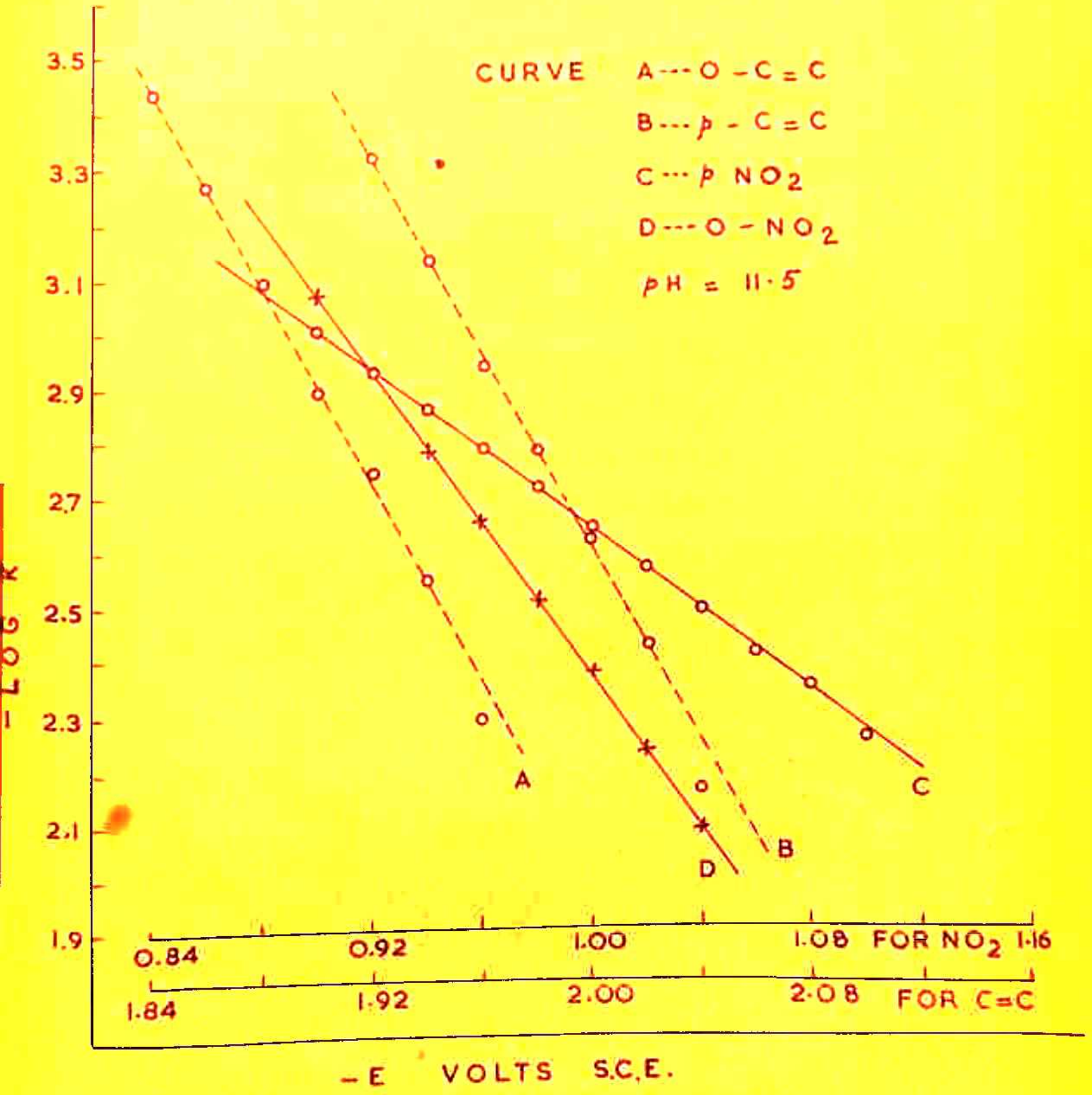

CURVE
A --- O - C = C
B --- p - C = C
C --- p NO2
D --- O - NO2
pH = 11·5
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
A
B
C
D
0.84
0.92
1.00
1.08 FOR NO2 1.16
1.84
1.92
2.00
2.08 FOR C=C
-E VOLTS S.C.E.

FIG. 3

IV. Polarography of 2-[N-methyl-N-(5-nitro-2-pyridyl)-amino]-ethanol in different supporting electrolytes:

As no polarography studies have been reported on this compound, it was taken up to study its behaviour at the dme at various pH and also to investigate the effect of the nature of supporting electrolyte on its kinetic parameters (αn_a and $-\log k^o$).

Experimental

Stock solution of 2-[N-methyl-N-(5-nitro-2-pyridyl)-amino]-ethanol was made in double distilled ethyl alcohol. Other chemicals used for buffer systems and supporting electrolytes were analytical reagent grade. HCl/KCl, Na_2HPO_4/ citric acid, boric acid /NaOH and NaOH buffer systems of constant ionic strength (μ = 0.54 M), adjusted by KCl, were used. Triton X-100 (0.001%) was used as the maximum suppressor. The capillary used for dme had m = 2.931 mg/sec., t = 3·05 sec/drop in 0.54 M KCl (open circuit) at h = 40.0 cms (uncorrected for back pressure.

Results and Discussion

The current-voltage curves recorded at various pH values showed that the nitro-group gave the usual reduction pattern, i.e., in highly acidic pH (pH $<$ 4), the reduction was two

steps ($4\bar{e}$, $2\bar{e}$) respectively. Whereas, in weakly acidic, neutral and alkaline pH the reduction stopped at hydroxylamine ($4\bar{e}$) stage because of its increased stability. Fig. 1 gives the current-voltage curves recorded at 33°C. In the acidic range (pH 1 to 5) the height of the first step was fairly constant, but increased with further increase in pH.

Koutecky's method of the slow electrode reaction was applied for the analysis of the first reduction wave which was found to be diffusion controlled irreversible process and involved single rate determining step as the -log k vs. E plot of this step yielded a straight line at all pH values. Results are given in Table I. αn_a did not show any regularity. $E_{0.5}$ and -log k^o increased with pH, thus electrode process became more irreversible with increase of pH because of the increased difficulty of the availability of the H^+ ions which are involved in the reduction process.

The effect of the nature of the supporting electrolyte on αn_a, $E_{0.5}$ and -log k^o was studied by taking Li^+, Na^+, K^+ as monovalent, Mg^{+2}, Ca^{+2} and Ba^{+2} as divalent and La^{+3} as trivalent cations and Cl^-, Br^-, I^- as monovalent anions. The experiments were carried out at constant pH.

Table II gives the effect of halide ions on the kinetic parameters. From the observations it was seen that $E_{0.5}$ as well as αn_a did not change appreciably with KI, KBr and KCl

as indifferent electrolytes. But -log k^{o} decreased in the order $I^{-} > Br^{-} > Cl^{-}$.

Table III gives the results on the influence of supporting electrolyte cations on the kinetic parameters. $E_{0.5}$ and αn_a did not show any regularity with LiCl, NaCl and KCl as indifferent electrolytes. But -log k^{o} increased in the order $K^{+} > Na^{+} > Li^{+}$, i.e., with the increase of the atomic weight of the cation the electrode process became more irreversible. Similar observations were noticed in divalent cation systems, i.e., -log k^{o} increased in the order $Ba^{+2} > Ca^{+2} > Mg^{+2}$. αn_a did not alter much, whereas, $E_{0.5}$ shifted to more cathodic side from Ba^{+2} to Mg^{+2}. These results are tabulated in Table IV.

Table V gives the effect of mono, di and trivalent cations on the kinetic parameters. αn_a and $E_{0.5}$ showed no appreciable variation. However, the value of -log k^{o} showed a slight increase with increasing atomic weight and valence of the cations.

Further, the values of $E_{0.5}$, αn_a and -log k^{o} decreased with increase in ionic strength (μ) of the supporting electrolyte vide Table VI. Similar observations were also made by Holleck for m-chloro-nitrobenzene[20].

From these observations it is, therefore, concluded that,

(a) Wave-height is practically independent of the nature of cation or anion and ionic strength of the supporting electrolyte.

(b) The value of -log k^o decreases in the order $I^- > Br^- > Cl^-$. The tendency of halide ions to increase the apparent reversibility is in conformity with their absorbabilities[61-64] on the mercury drop surface. The accelerating effect on the electrode reaction may be attributed to the change of electrode surface by the adsorption of the halide ions. This accelerating effect on the electrode process with increase in adsorbability may be due to some sort of activated complex formed at the electrode surface which results in the decrease of the activation energy of the electrode. The same effect of halide ions on the kinetic parameters was also observed at different concentration (0.6 mM) of the depolarizer.

(c) The value of -log k^o increases with increase in the atomic weight of the cations. This may be due to the increase of the radius of the cations with increase in their atomic weight. The thickness of the electrical double layer is thus enhanced and thereby increasing the value of zeta potential and thus retarding the electrode process by offering a greater potential barrier.

The -log k^o increases only to a small extent in solutions of mono, di and tri- valent cations (Table V) as compared to

the values in solutions of indifferent electrolytes having cations of the same valence but increasing atomic weight (Table III, IV). This small variation of -log k^o in solutions of mono, di and trivalent cations may be due to the accelerating effect of increased valence of the cations on the electrode processes, thereby, counteracting the retarding effect of increasing atomic weight of these cations.

(d) The values of $E_{0.5}$, αn_a and -log k^o decrease with the increase in ionic strength of the supporting electrolyte. This is again due to the lowering of the thickness of the electrical double layer, thereby, reducing the zeta potential and accelerating the electrode processes.

Table I

Kinetic parameters (αn_a and -log k^o) at various pH's.

Concentration of depolarizer = 0.4 mM; μ = 0.54 M (Buffers)

Height = 40.0 cms.; Temp. = 33°C.

pH	i_{d_1} μ.a.	i_{d_2} μ.a.	$-E^1_{0.5}$ volts S.C.E.	$-E^2_{0.5}$ volts S.C.E.	-log k^o_1	αn_a
1.0	8.45	2.8	0.135	0.620	1.901	0.469
2.0	8.4	3.0	0.145	0.960	2.788	0.559
2.9	8.1	3.2	0.341	1.090	3.779	0.619
4.0	8.4	not well defined	0.430	-	4.64	0.600
4.8	8.55	no wave	0.490	-	4.813	0.503
6.0	9.55	-	0.604	-	5.056	0.408
7.2	9.35	-	0.685	-	5.521	0.381
8.0	10.25	-	0.740	-	5.833	0.379
9.0	10.75	-	0.804	-	5.894	0.333
10.0	10.95	-	0.850	-	6.017	0.334
11.0	11.0	-	0.865	-	6.294	0.439

$E^2_{0.5}$ and i_{d_2} for 2nd step.

Table II

Kinetic parameters (αn_a and -log k^o) in KI, KBr, and KCl as indifferent electrolytes.

Temp. = 33°C; Height = 40.0 cms.; pH = 6.25.

Supporting Electrolyte	i_d μ.a.	$-E_{0.5}$ volt S.C.E.	αn_a	-log k^o N.H.E.
	Concentration of depolarizer = 0.4 mM			
0.2 M-KI	11.3	0.854	0.2969	5.6225
0.2 M-KBr	11.2	0.847	0.3093	5.6945
0.2 M-KCl	11.2	0.847	0.3150	5.7590
	Concentration of depolarizer = 0.6 mM			
0.2 M-KI	16.4	0.905	0.2272	5.123
0.2 M-KBr	16.4	0.900	0.2293	5.134
0.2 M-KCl	16.2	0.900	0.2330	5.166

Table III

Effect of Li^+, Na^+, K^+ on αn_a and -log k^o.

Temp.= 33°C, Height = 40.0 cms., pH = 6.25.

Concentration of depolarizer = 0.4 mM.

Supporting Electrolyte	i_d μ.a.	$-E_{0.5}$ volt S.C.E.	αn_a	-log k^o N.H.E.
0.2 M-LiCl	11.0	0.840	0.3607	5.167
0.2 M-NaCl	10.9	0.833	0.2947	5.499
0.2 M-KCl	11.2	0.847	0.3150	5.759

Table IV

Effect of Mg^{++}, Ca^{+2} and Ba^{+2} on αn_a and $-\log k^o$.

Temp. = 33°C; Height = 40.0 cms., pH = 5.90

Supporting Electrolyte	i_d μ.a.	$-E_{0.5}$ volt S.C.E.	αn_a	$-\log k^o$ N.H.E.
	0.4 mM. depolarizer			
0.2 M-$MgCl_2$	10.75	0.800	0.3125	5.528
0.2 M-$CaCl_2$	11.1	0.810	0.3334	5.733
0.2 M-$BaCl_2$	11.25	0.820	0.3314	5.810
	0.6 mM. depolarizer			
0.2 M-$MgCl_2$	15.8	0.848	0.2477	5.148
0.2 M-$CaCl_2$	16.6	0.867	0.2558	5.273
0.2 M-$BaCl_2$	16.6	0.875	0.2562	5.347

Table V

Effect of Na^{+}, Ca^{+2}, and La^{+3} on αn_a and $-\log k^{o}$.

pH = 2.0; Temp. 33°C; Height = 40.0 cms.

Supporting Electrolyte	i_d μ.a.	$-E_{0.5}$ volt S.C.E.	αn_a	$-\log k^{o}$ N.H.E.
		0.4 mM. depolarizer		
0.2 M-NaCl	8.5	0.218	0.5095	2.522
0.2 M-$CaCl_2$	8.3	0.225	0.5416	2.576
0.2 M-$LaCl_3$	8.2	0.230	0.5153	2.598
		0.6 mM. depolarizer		
0.2 M-NaCl	12.0	0.252	0.426	2.811
0.2 M-$CaCl_2$	12.0	0.260	0.4372	2.867
0.2 M-$LaCl_3$	11.9	0.260	0.420	2.875

Table VI

Effect of ionic strength (μ) on αn_a and $-\log k^o$.

Height = 40.0 cms., Temp. 33°C;

Ionic strength (μ)	i_d μ.a.	$-E_{0.5}$ volt, S.C.E.	αn_a	$-\log k^o$ N.H.E.
		0.4 mM. depolarizer		
0.1 M-KCl+0.03M-NaOH	10.9	0.887	0.459	7.542
0.5M-KCl+0.03M-NaOH	11.05	0.872	0.445	7.250
1.0M-KCl+0.03M-NaOH	11.0	0.862	0.413	6.803
		0.6 mM. depolarizer		
0.1M-KCl+0.03M-NaOH	15.95	0.930	0.308	6.188
0.5M-KCl+0.03M-NaOH	16.30	0.915	0.297	5.992
1.0M-KCl+0.03M-NaOH	16.05	0.910	0.293	5.914

Legend of the Figures

Fig. 1: Current-voltage curves at various pH values (0.4 mM. depolarizer).

Fig. 2: -log k vs. -E plot at various pH values.

-x-

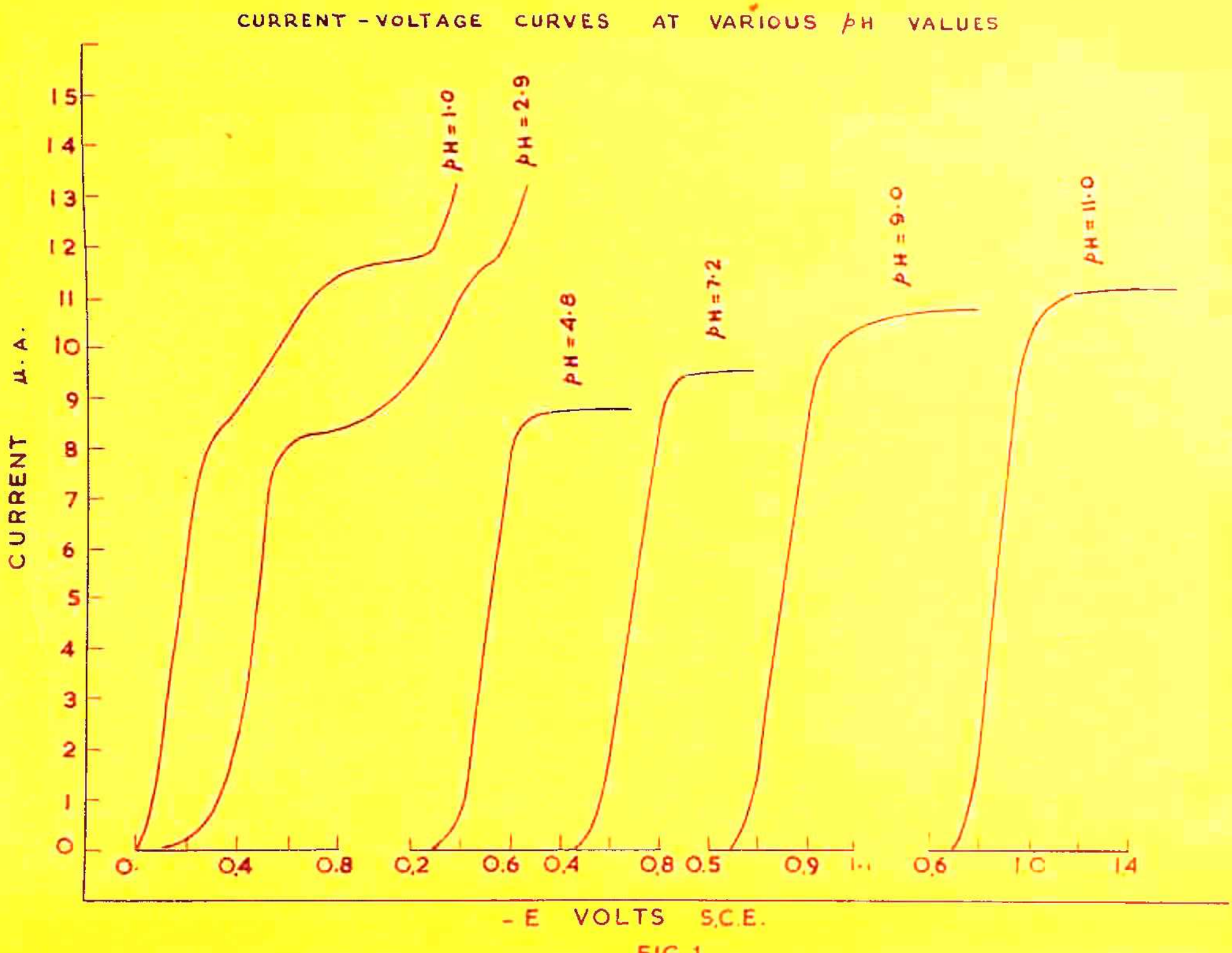

CURRENT - VOLTAGE CURVES AT VARIOUS pH VALUES
CURRENT μ.A.
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
pH = 1·0
pH = 2·9
pH = 4·8
pH = 7·2
pH = 9·0
pH = 11·0
0·
0.4
0.8
0.2
0.6
0.4
0.8
0.5
0.9
1·
0.6
1·0
1.4
- E VOLTS S.C.E.

FIG. 1

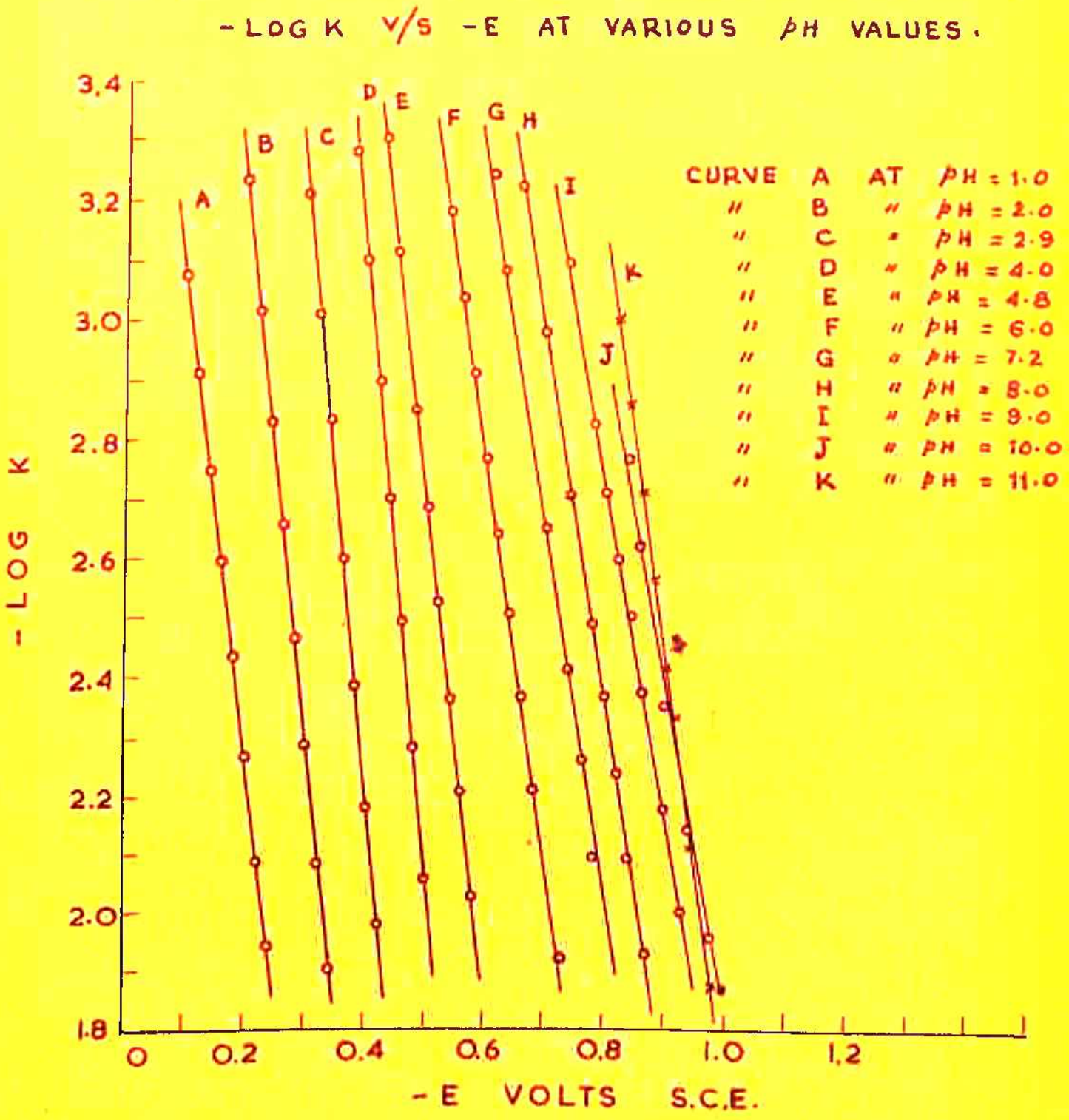

-LOG K V/S -E AT VARIOUS pH VALUES.
CURVE A AT pH = 1.0
" B " pH = 2.0
" C " pH = 2.9
" D " pH = 4.0
" E " pH = 4.8
" F " pH = 6.0
" G " pH = 7.2
" H " pH = 8.0
" I " pH = 9.0
" J " pH = 10.0
" K " pH = 11.0
-LOG K
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
0
0.2
0.4
0.6
0.8
1.0
1.2
-E VOLTS S.C.E.

FIG. 2

V. Polarographic studies of the effect of various physical factors on the kinetic parameters of the reduction of nitrobenzene at dme:

Although considerable work has been done on the reduction of nitrobenzene in aqueous and aqueous-organic solvent mixtures but no attention has been paid to the effect of the experimental conditions on the kinetic parameters (αn_a and -log k^o). The present investigation deals with the detailed study of the variation of these parameters by the alteration of various physical factors, such as, drop-time, concentration of depolarizer, temperature, concentration of solvent, nature of solvent and pH.

Experimental

Nitrobenzene (B.D.H., A.R.) was redistilled at 209°C in an all-glass fractionating column and the middle one-third of the distillate was used for experiments. For non-aqueous study, methanol and all other organic solvents used were of B.D.H. quality and were fractionally distilled before use. Formic acid and glacial acetic acid (B.D.H.)were used as such without further purification. Other chemicals used for buffer systems and supporting electrolytes were analytical reagent grade. In aqueous medium HCl/KCl, Na_2HPO_4/citric acid,glycine/NaOH and NaOH buffer systems were used. Ionic strength (μ = 0.58 M) was brought to a definite value by adjusting the

amount of supporting electrolyte. SCE was used as reference electrode. In case of formic acid and glacial acetic acid mercury pool was used and the potentials converted with respect to SCE. "iR" correction was made in the study of non-aqueous media. Triton X-100 was used as maximum suppressor. The capillary used for dme had m = 2.586 mg/sec. and t = 2.96 sec./drop in 0.58 M.KCl (open circuit) at h=65.0 cms. (uncorrected for back pressure).

A recording polarograph LP60 was used for these investigations. The potentials were varied manually and the maximum currents recorded. Some of the observations were also taken using a manual set-up and average currents were recorded in this case.

Results and Discussion

Koutecky's theory of the slow electrode reaction was used for the analysis of the 1st polarographic reduction wave which is considered to be a completely irreversible process and consumes $4\bar{e}$ per molecule resulting with the formation of phenylhydroxylamine.

(1) Effect of m and t on kinetic parameters

It is seen from Table I that the values of αn_a and $-\log k^o$ were independent of drop-time, whereas, $E_{0.5}$ shifted towards more negative values with increase of height. If k is

not a function of t, this shift in $E_{0.5}$ with height is given by the relation,

$$\Delta E_{0.5} = \frac{RT}{\alpha n_a F} \ln \frac{t_1}{t_2} .$$

Using the $E_{0.5}$ values at h = 45.0 cms. and 65.0 cms. the measured values of $\Delta E_{0.5}$ was found to be 7mV, whereas the corresponding calculated values using above equation was 6.5 mV. Also the plot of i/i_{30} vs. $\sqrt{h/h_{30}}$ (Fig. 1) showed the expected behaviour of an irreversible process[65].

(2) Effect of concentration of the depolarizer on the kinetic parameters:

Values of αn_a and $-\log k^o$ did not change with concentration of electro-active species for a given amount of alcohol content and pH (Table II).

(3) Effect of temperature on kinetic parameters

With increase of temperature (both in aqueous and methanolic media) $i_{d_{max.}}$ showed a regular increase. αn_a decreased and $-\log k^o$ values showed that system was less irreversible with increase in temperature. $E_{0.5}$ values did not show any appreciable change in both cases (Table III).

(4) Effect of ethyl alcohol concentration on kinetic parameters

With increase in concentration of ethyl alcohol, αn_a decreased and $-\log k^o$ increased. $E_{0.5}$ shifted to more

negative potentials and i_d first decreased up to about 40% ethyl alcohol and then again increased with increase in percentage of alcohol (Table IV).

The fact that i_d first decreased and then increased with increase in percentage of ethyl alcohol might be due to the change in the viscosity of aqueous-alcoholic system, which showed gradual increase in the viscosity of the system up to about 50% ethyl alcohol and then decreased regularly with further increase in percentage of alcohol[66]. Similar variation of i_d with increase in concentration of ethyl alcohol was observed in case of p-nitroaniline[67]. Recently R.S. Subrahmanya[68] et al. have also reported similar observations during the study of nitrobenzene in ethanol.

That the change in the magnitude of the current by change in the percentage of alcohol in aqueous solution was due to the change in the viscosity of the system and not due to the variation in the number of electrons involved in the reduction process was further confirmed by comparing the value of diffusion coefficient of nitrobenzene calculated from Ilkovic equation (n=4) to that of iodobenzene reported in literature[69], under similar conditions.

The shift in the $E_{0.5}$ with increase in ethyl alcohol concentration to more cathodic potentials might be due to adsorption of alcohol on dme and thus requiring more activation energy for the reduction processes to take place. The

adsorption of ethyl alcohol at dme could be confirmed from the shape of electro-capillary curves (Fig. 2). The changes of αn_a and -log k^o with ethyl alcohol concentration might be due to the changes in the structure of the electrical double layer by the adsorbed film.

(5) Effect of the nature of the solvent on kinetic parameters

There can be no obvious trend in the $E_{0.5}$, -log k^o and αn_a of ions in different solvents since these quantities are a complicated function of various physical properties of the solvent. However, some encouraging results were obtained particularly considering the calculated values of rate constants at $E_{0.5}$ as it is known that at $E_{0.5}$, the current is controlled both by diffusion and the rate of the reaction[70].

The solvents used were methyl alcohol, ethyl alcohol, normal propyl alcohol, iso-propyl alcohol, gl- acetic acid and formic acid which are protic and dimethyl formamide, acetone, methyl-ethyl-ketone, acetonitrile and pyridine which are aprotic in nature.

Nitrobenzene gave one wave ($4\bar{e}$) in methyl, ethyl, iso-propyl, and n-propyl alcohols. Plot of -log k vs. E resulted in straight line (Fig. 3) thus showing single rate determining process in all these alcohols. Table V gives the various parameters in alcohols using lithium chloride as supporting electrolyte at a fixed pH 5.6 (unbuffered). Current decreased

from methyl alcohol to n-propyl alcohol, whereas $-\log k_{0.5}$ increased, i.e., reduction of $-NO_2$ gr. became more difficult as solvent was changed from methyl to n-propyl alcohol. $E_{0.5}$, αn_a and $-\log k^o$ did not give any regular variation.

Experiments in these four alcohols were repeated using LiCl (0.25 M) and sodium perchlorate (0.25 M) as supporting electrolytes without any pH adjustment. It was observed that in both the cases of the supporting electrolytes used, the change in $E_{0.5}$, $-\log k_{0.5}$ and i_d was similar. αn_a and $-\log k^o$ did not show any regularity in LiCl as supporting electrolyte, whereas they were increased in sodium perchlorate as supporting electrolyte. These results are given in Table VI.

In gl. acetic acid[71] and formic acid using 1.0M-Amm. acetate as supporting electrolyte, $-NO_2$ group reduced in one step and the rate of reaction was controlled by one slow process as the plot of -log k vs. E yielded straight lines (Fig. 4) in both acids. Table VII gives the values of αn_a, and $-\log k^o$ in these two acids. Reduction was easier in formic acid as already observed for inorganic cations[72].

In aprotic media, 0.25 M-sodium perchlorate was used as supporting electrolyte. In acetone, acetonitrile[73], methyl ethyl ketone and pyridine single step reduction($4\bar{e}$) took place whereas in dimethyl formamide[74-77] two steps ($1\bar{e}$, $3\bar{e}$) were involved. The magnitude of i_d increased in order acetone > acetonitrile > methyl ethyl ketone > dimethyl formamide >

pyridine. The variation of i_d with nature of the aprotic solvent might be due to the difference in physical properties of these solvents. Plots of -log k vs. E in case of acetone, acetonitrile, methyl-ethyl-ketone and the same plot for the 2nd wave in dimethyl formamide showed single inflection (Fig. 5), suggesting, thereby, that there were more than one slow processes which determined the rate of reduction. However, in case of pyridine, reduction was more complicated as -log k vs. E plot is S-shaped.

(6) Effect of pH on kinetic parameters:

The dependence of αn_a, -log k^o and $E_{0.5}$ on pH are summarised in Table VIII. Plots of -log k vs. E for pH 5 to 11 yielded straight lines, but in more acidic medium (pH 1 to 3), this plot showed a break (Fig. 6) indicating that more than one rate determining steps were involved. Plot of $E_{0.5}$ vs. pH and -log k^o vs. pH (Fig. 7) resulted in identical S-shaped curves as expected[78]. It was seen that $E_{0.5}$ and -log k^o increased regularly with increase in pH, whereas αn_a was gradually decreased with increase in pH from 5 to 11.0. It may be noted from Tables V and IX that the values of i_d, $E_{0.5}$, and -log k^o at pH 5.6 were higher in unbuffered methanolic medium than the corresponding values in buffered ones. However, αn_a was independent of buffer capacity.

Table IX gives the results obtained in the study of the effect of pH on kinetic parameters in methamolic buffered medium.

Plot of -log k vs. E in weakly acidic medium and neutral medium gave straight lines but in highly acidic medium this plot showed a break (Fig. 8) as observed in aqueous medium, indicating that more than one rate determining steps were involved. It was seen here that the values of $i_{d_{max.}}$, $E_{0.5}$, $-\log k^{o}$ and αn_a increased with increase in pH, whereas, there was no regularity in $i_{d_{max.}}$ observed in aqueous medium. Also αn_a decreased in aqueous medium with increase in pH.

Recently R.S. Subrahmanya[68] et al. have also observed that -log k vs. E plot deviates from linearity in highly acidic side. They explained this departure from linearity as due to potential dependence of α[79].

It appears that in weakly acidic, neutral, and alkaline aqueous and alcoholic media the reduction of nitrobenzene involves only one rate determining step as proposed by Holleck[20] and given below:-

$$C_6H_5NO_2 + 1\bar{e} \underset{\text{Rev}}{\rightleftharpoons} C_6H_5NO_2^- \xrightarrow[2H^+]{1\bar{e}} C_6H_5N\begin{matrix}OH\\OH\end{matrix} \xrightarrow[-H_2O]{\text{Fast}} C_6H_5NHOH \quad (2\bar{e}, 2H^+)$$

(slow)

However, in highly acidic medium (both aqueous and alcoholic) where the rate determining step involves two consecutive reactions, the result may be interpreted as due to two

consecutive $1\bar{e}$ and $2\bar{e}$ transfer processes as given below:

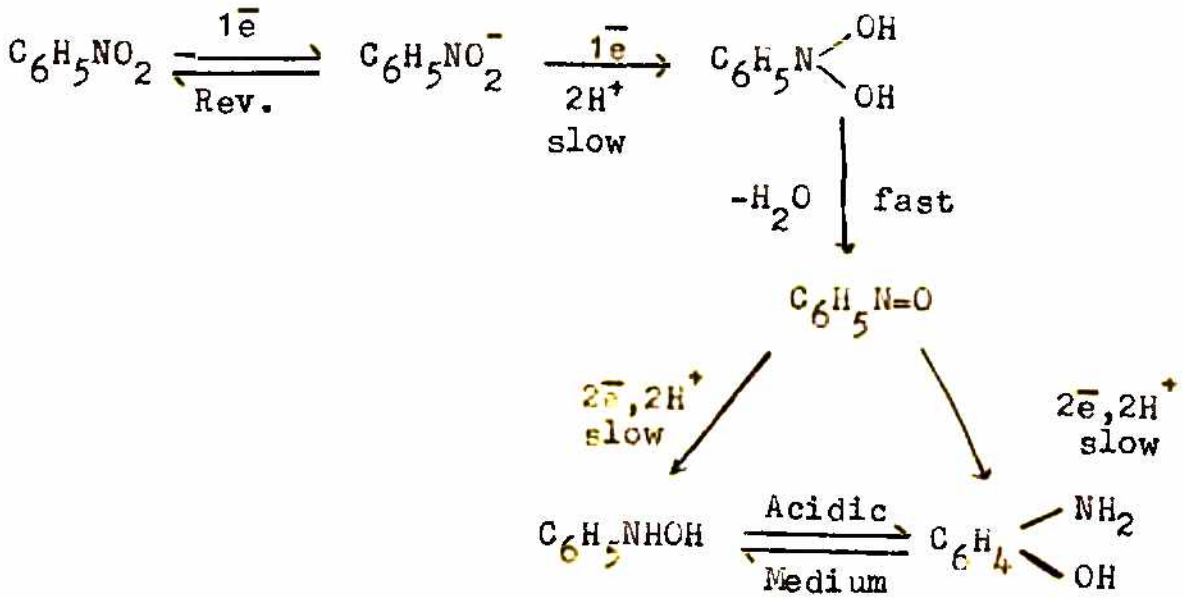


Table I: Effect of m and t on kinetic parameters.

pH = 11.0 buffered; Temp. = 35°C; 10% ethyl alcohol;

μ = 0.58 M; Concn. = 5.0 x 10^{-4}M (nitrobenzene).

Height cms.	$i_{d_{max.}}$ μ.a.	t sec.	-log k^o (N.H.E.)	αn_a	$-E_{0.5}$ volt (S.C.E.)
65.0	6.4	2.96	9.01	0.782	0.700
55.0	6.0	3.49	9.00	0.786	0.697
45.0	5.4	4.35	8.995	0.784	0.693

Table II: Effect of concentration of the depolarizer on the kinetic parameters.

Temp. = 35°C; 10% ethyl alcohol; μ = 0.58 M; Height=65.0 cms.

Concn. of nitrobenzene in millimoles	$i_{d_{max.}}$ μ.a.	-log k^o (N.H.E.)	αn_a	$-E_{0.5}$volt (S.C.E.)
	pH = 11.0 buffered			
0.30	3.55	8.97	0.788	0.694
0.50	6.40	9.01	0.782	0.700
0.70	7.35	8.95	0.789	0.689
0.90	9.60	8.94	0.778	0.694
	pH = 7.2 buffered			
0.50	5.70	6.015	0.861	0.444
0.90	10.80	6.050	0.859	0.449

Table III: Effect of temperature on kinetic parameters both in aqueous and methanolic media.

Ethyl alcohol = 0.5%; Concn. = 0.5 x 10^{-3}M Nitrobenzene, pH = 7.6 buffered; Height = 65.0 cms.; μ = 0.58 M

Temp.	$i_{d_{max.}}$ μ.a.	D x 10^{-6} cm^2/Sec.	-log k^o (N.H.E.)	αn_a	$-E_{0.5}$ volt (S.C.E.)
10°C	6.7	4.55	7.74	0.991	0.505
23°C	7.4	5.38	7.28	0.944	0.508
30°C	8.0	6.30	7.13	0.922	0.510

Methyl alcohol = 100%; Concn. = 0.48 x 10^{-3}M Nitrobenzene, pH = 5.7 buffered; Height = 65.0 cms.; μ = 0.40 M.

10°C	9.00	11.25	7.859	0.756	0.617
20°C	10.65	15.75	7.302	0.712	0.615
30°C	11.75	19.17	7.016	0.693	0.612

Table IV: Effect of ethyl alcohol concentration on kinetic parameters.

Temp. = 20°C; Height = 65.0 cms.; μ = 0.250 M lithium chloride; Concn. = 0.6×10^{-3} M. nitrobenzene.

% ethyl alcohol	$i_{d_{ave}}$ μ.a.	$-\log k^{o}$ (N.H.E.)	αn_a	$-E_{0.5}$ volt (S.C.E.)
10	7.77	4.074	0.31	0.495
30	6.95	4.638	0.298	0.790
50	7.20	4.765	0.269	0.880
70	8.15	5.514	0.228	0.947
100	10.90	6.640	0.192	0.958

Table V: Various parameters in alcohols using lithium chloride as supporting electrolyte at a fixed pH 5.6 (unbuffered).

Temp. = 30.5°C; Concn. = 0.48×10^{-3} M nitrobenzene; Height = 65.0 cms., pH = 5.6 unbuffered; μ = 0.25 M.

Alcohol	$i_{d_{max.}}$ μ.a.	$-\log k^{o}$ (N.H.E.)	αn_a	$-E_{0.5}$ volt (S.C.E.)	$-\log k_{0.5}$ (S.C.E.)
Methyl alcohol	12.45	8.194	0.6677	0.750	2.690
Ethyl alcohol	11.55	8.755	0.7645	0.720	2.835
Iso-propyl alcohol	8.75	6.472	0.3280	0.898	2.975
n-propyl alcohol	8.25	5.038	0.3485	0.800	3.020

Table VI: Various parameters in alcohols using lithium chloride and sodium perchlorate as supporting electrolytes.

Temp. = 30.5°C; Concn. = 0.48 x 10^{-3}M Nitrobenzene;

Height = 65.0 cms.

Alcohol	$i_{d_{max.}}$ μ.a.	-log k^{o} (N.H.E.)	αn_a	$-E_{0.5}$ volt (S.C.E.)	-log $k_{0.5}$ (S.C.E.)
0.25 M - lithium chloride as supporting electrolyte					
Methyl alcohol	13.4	8.399	0.566	0.863	2.708
Ethyl alcohol	10.7	7.391	0.420	0.907	2.832
Iso-propyl alcohol	8.45	7.842	0.436	0.931	2.970
n-propyl alcohol	8.10	7.405	0.410	0.900	3.030
0.25 M - sodium perchlorate as supporting electrolyte					
Methyl alcohol	11.80*	5.636	0.2368	0.970	2.84
Ethyl alcohol	9.50*	5.945	0.2494	1.006	2.88
Iso-propyl alcohol	8.425*	6.664	0.2907	1.035	2.925
n-propyl alcohol	8.15*	6.883	0.3166	0.999	2.99

* Average currents.

Table VII: Various parameters in formic acid and gl. acetic acid using 1.0 M-Amm.acetate as supporting electrolyte.

Temp. = 30.5°C; Concn. = 0.48 x 10^{-3}M; Nitrobenzene;

Height = 65.0 cms., 1.0 M Ammonium acetate(supporting electrolyte).

Solvent	$i_{d_{ave}}$ μ.a.	$-E_{0.5}$ volt (S.C.E.)	αn_a	$-\log k^o$ (N.H.E.)
Formic acid	7.40	0.090	0.4193	1.850
Gl.acetic acid	6.95	0.465	0.378	4.164

Table VIII: Effect of pH on kinetic parameters in aqueous medium.

Temp. = 35°C; Concn. = 0.5x10^{-3}M; nitrobenzene; Height=65.0 cms.

Ethyl alcohol = 10%; μ = 0.58 M.

pH Buffered	$i_{d_{max.}}$ μ.a.	$-\log k^o$ (N.H.E.)	αn_a	$-E_{0.5}$volt (S.C.E.)	Potential of inflection point vs. S.C.E.
1[a]	6.50	2.00	0.798	0.160	-0.171
2[a]	6.60	2.90	0.980	0.240	-0.240
3[a]	6.35	3.56	0.875	0.275	-0.287
5	6.50	5.29	0.878	0.4025	b
7.2	5.70	6.015	0.861	0.444	b
9.1	7.10	8.115	0.856	0.6025	b
11.0	6.4	9.01	0.782	0.700	b

a - αn_a and $-\log k^o$ for these rusn have been evaluated from the lower segment of the straight line in Fig.6, these values are doubtful for the reasons Koutkey's method does not hold good when more than one rate determining step is involved.

b - No band.

Table IX: Effect of pH on kinetic parameters in methanolic medium.

Temp. = 30.5°C; Concn. = 0.48 x 10^{-3} M nitrobenzene;

Height = 65.0 cms., μ = 0.25 M.

pH Buffered	$i_{d_{max.}}$ μ.a.	-log k^o (N.H.E.)	αn_a	$-E_{0.5}$ volt (S.C.E.)	Potential of inflection point Vs. S.C.E.
2.9[a]	7.00	2.99	1.2	0.1025	-0.1215
3.6[a]	10.95	4.97	0.5405	0.4925	-0.52
4.7	11.2	5.779	0.6430	0.5320	b
5.6	11.75	6.167	0.6679	0.558	b
7.9	13.1	9.022	0.6882	0.810	b

a - αn_a and -log k^o are doubtful as pointed earlier in Table VIII.

b - No band.

Legend of the Figures

Fig. 1: Dependence of curve on drop-time (mercury height) at various potentials for solution of 10% ethyl alcohol, pH = 11.0 and μ = 0.58 M.

Fig. 2: Electrocapillary curves for various ethyl alcohol concentrations, based on variation of the drop-time at the dme with potential. Percentage ethyl alcohol A = 20%; B = 30% and C = 40%. Time to expressed in seconds for 50 drops.

Fig. 3: Plots of -log k vs. -E (S.C.E.) using sodium perchlorate (0.25 M) as supporting electrolyte.

Curve A in Methyl alcohol
Curve B in Ethyl alcohol
Curve C in Iso-propyl alcohol
Curve D in n-propyl alcohol.

Fig. 4: Plot of -log k vs. -E (Hg.pool), using 1.0 M - ammonium acetate as supporting electrolyte.

Curve A in Formic acid.
Curve B in gl. acetic acid.

Fig. 5: Plot of -log k vs. -E (S.C.E.), using 0.25 M - sodium perchlorate as supporting electrolyte.

Curve A in Acetone

Curve B in Acetonitrile

Curve C in Methyl ethyl ketone

Curve D in Dimethyl formamide (In case of D x-axis shifted by 0.2 V to L.H.S.)

Curve E in Pyridine.

Fig. 6: Plot of -log k vs. -E (S.C.E.) in aq. medium.

Curve A at pH = 1.0

Curve B at pH = 2.0

Curve C at pH = 3.0

Curve D at pH = 5.0

Curve E at pH = 7.2

Curve F at pH = 9.1

Curve G at pH =11.0

Fig. 7: Variation of $E_{0.5}$ and -log k^{o} with pH in aq. medium.

Fig. 8: Plot of -log k vs. -E (S.C.E.) in methyl alcohol.

Curve A at pH=2.9

Curve B at pH = 3.6

Curve C at pH = 4.7

Curve D at pH = 5.6

Curve E at pH = 7.9

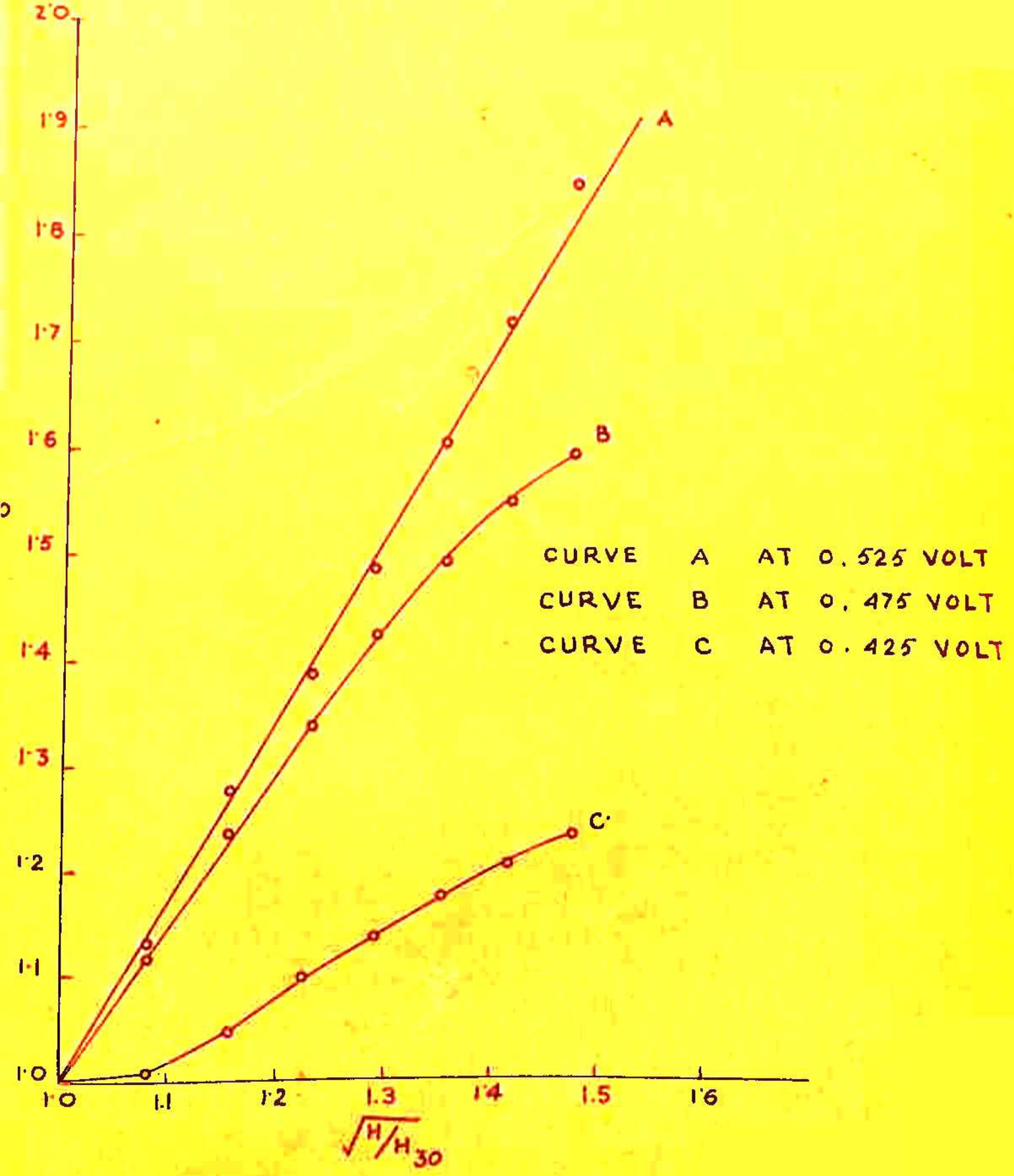

2·0
1·9
1·8
1·7
1·6
1·5
1·4
1·3
1·2
1·1
1·0
1·0
1·1
1·2
1·3
1·4
1·5
1·6
A
B
C
CURVE A AT 0.525 VOLT
CURVE B AT 0.475 VOLT
CURVE C AT 0.425 VOLT
$\sqrt{H/H_{30}}$

FIG. 1

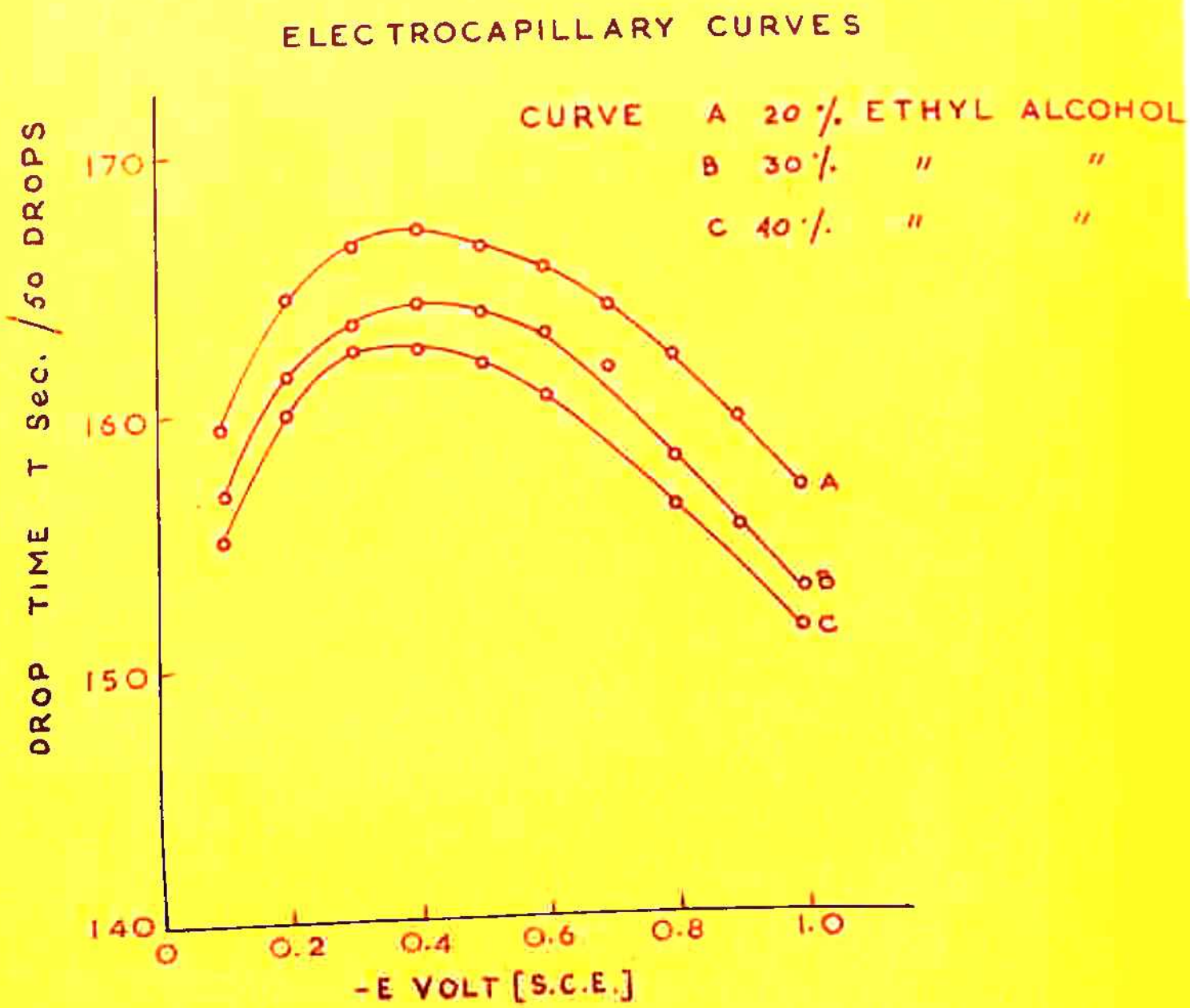

ELECTROCAPILLARY CURVES
CURVE A 20 % ETHYL ALCOHOL
B 30 % " "
C 40 % " "
DROP TIME T Sec. /50 DROPS
170
160
150
140
0
0.2
0.4
0.6
0.8
1.0
-E VOLT [S.C.E.]
A
B
C

FIG. 2

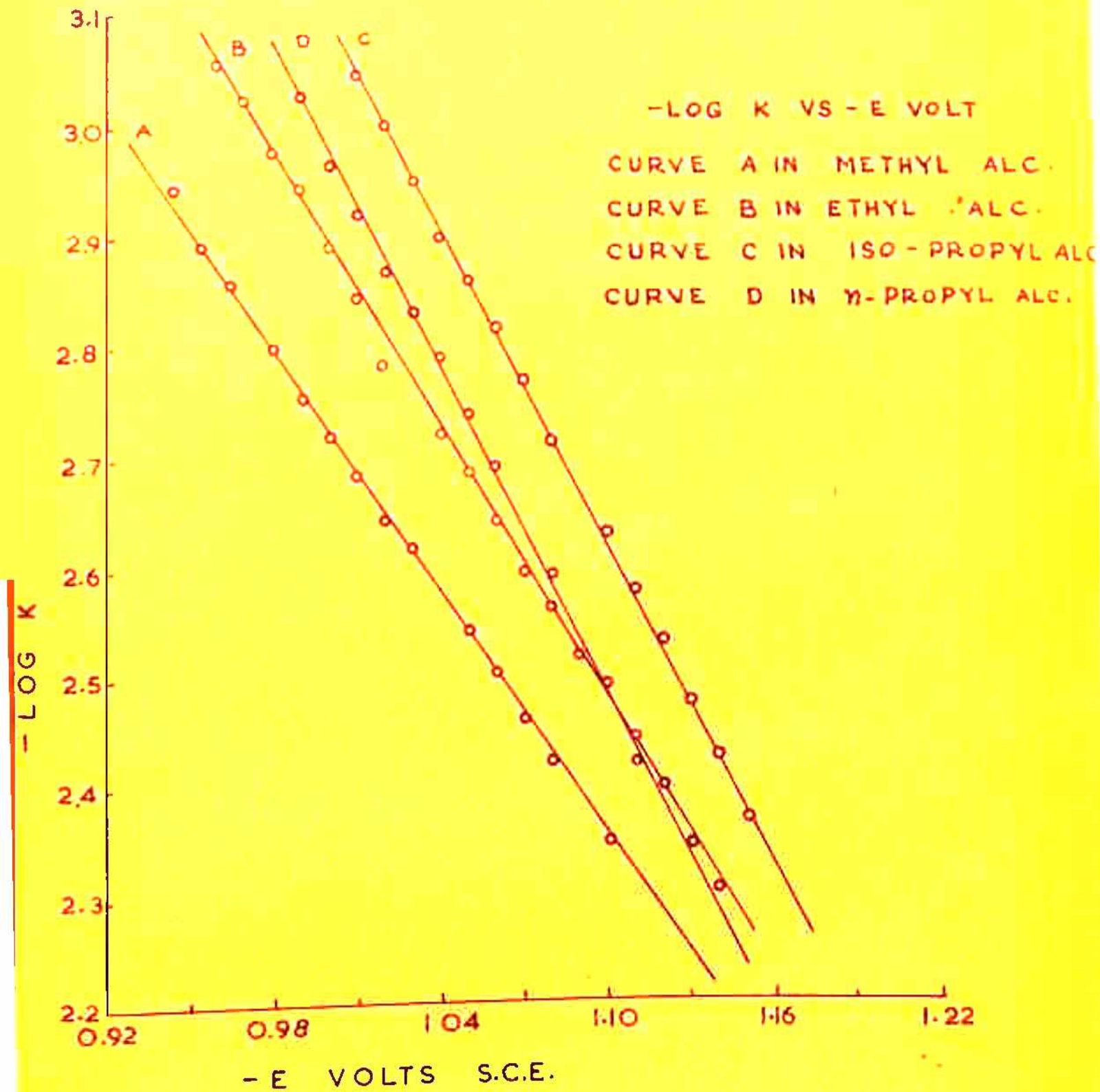

-LOG K VS - E VOLT
CURVE A IN METHYL ALC.
CURVE B IN ETHYL ALC.
CURVE C IN ISO - PROPYL ALC
CURVE D IN n-PROPYL ALC.
A
B
D
C
3.1
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
- LOG K
0.92
0.98
1.04
1.10
1.16
1.22
- E VOLTS S.C.E.

FIG. 3

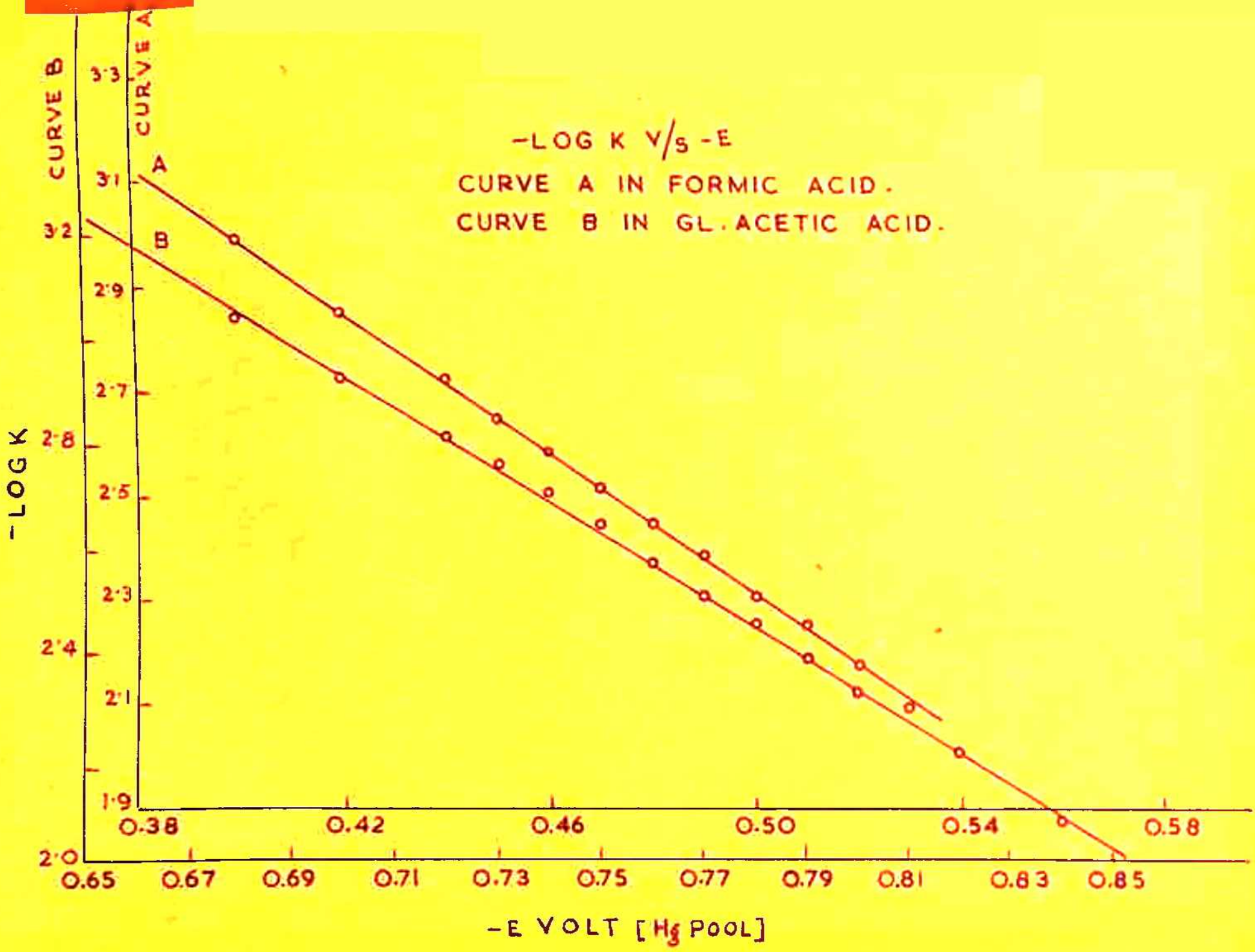

-LOG K V/S -E
CURVE A IN FORMIC ACID.
CURVE B IN GL. ACETIC ACID.
CURVE B
CURVE A
A
B
-LOG K
3·3
3·1
3·2
2·9
2·7
2·8
2·5
2·3
2·4
2·1
1·9
2·0
0.38
0.42
0.46
0.50
0.54
0.58
0.65
0.67
0.69
0.71
0.73
0.75
0.77
0.79
0.81
0.83
0.85
-E VOLT [Hg POOL]

FIG. 4

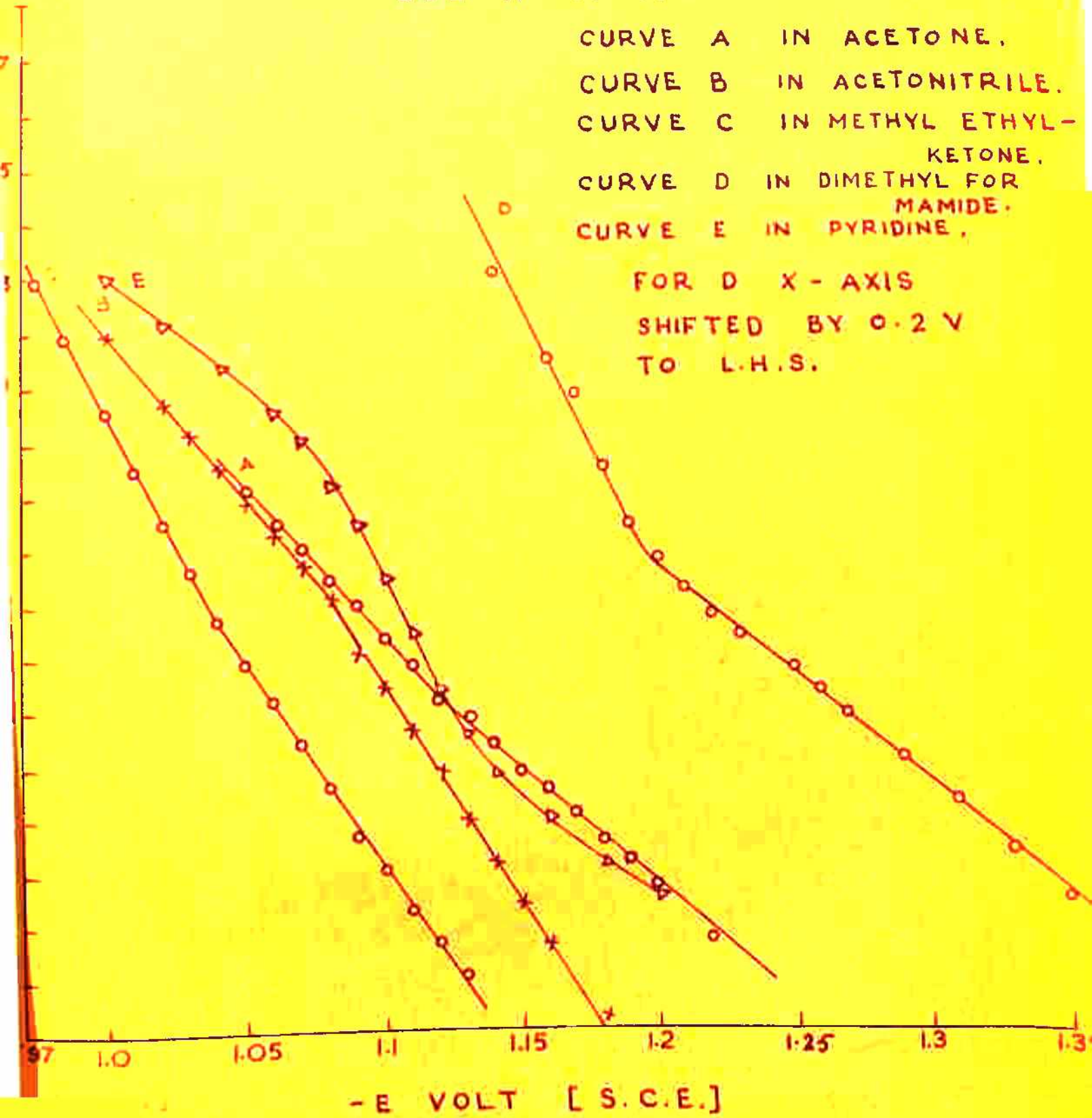

-LOG K VS -E.
CURVE A IN ACETONE.
CURVE B IN ACETONITRILE.
CURVE C IN METHYL ETHYL-KETONE.
CURVE D IN DIMETHYL FORMAMIDE.
CURVE E IN PYRIDINE.
FOR D X-AXIS SHIFTED BY 0·2 V TO L.H.S.
A
B
C
D
E
.97
1.0
1.05
1.1
1.15
1.2
1.25
1.3
1.3
-E VOLT [S.C.E.]

FIG. 5

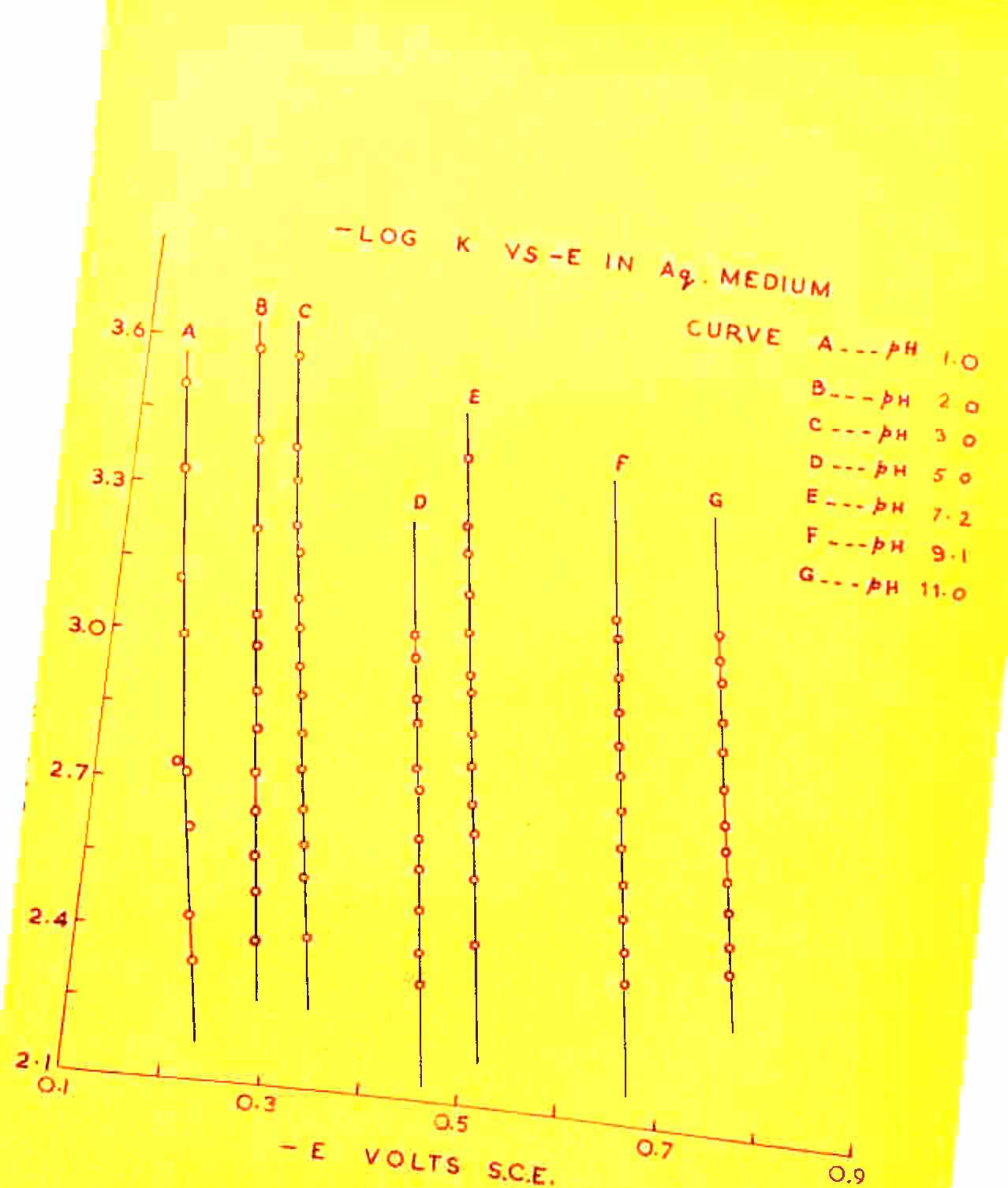

-LOG K VS -E IN Aq. MEDIUM
CURVE
A --- pH 1.0
B --- pH 2.0
C --- pH 3.0
D --- pH 5.0
E --- pH 7.2
F --- pH 9.1
G --- pH 11.0
3.6
3.3
3.0
2.7
2.4
2.1
A
B
C
D
E
F
G
0.1
0.3
0.5
0.7
0.9
- E VOLTS S.C.E.

FIG. 6

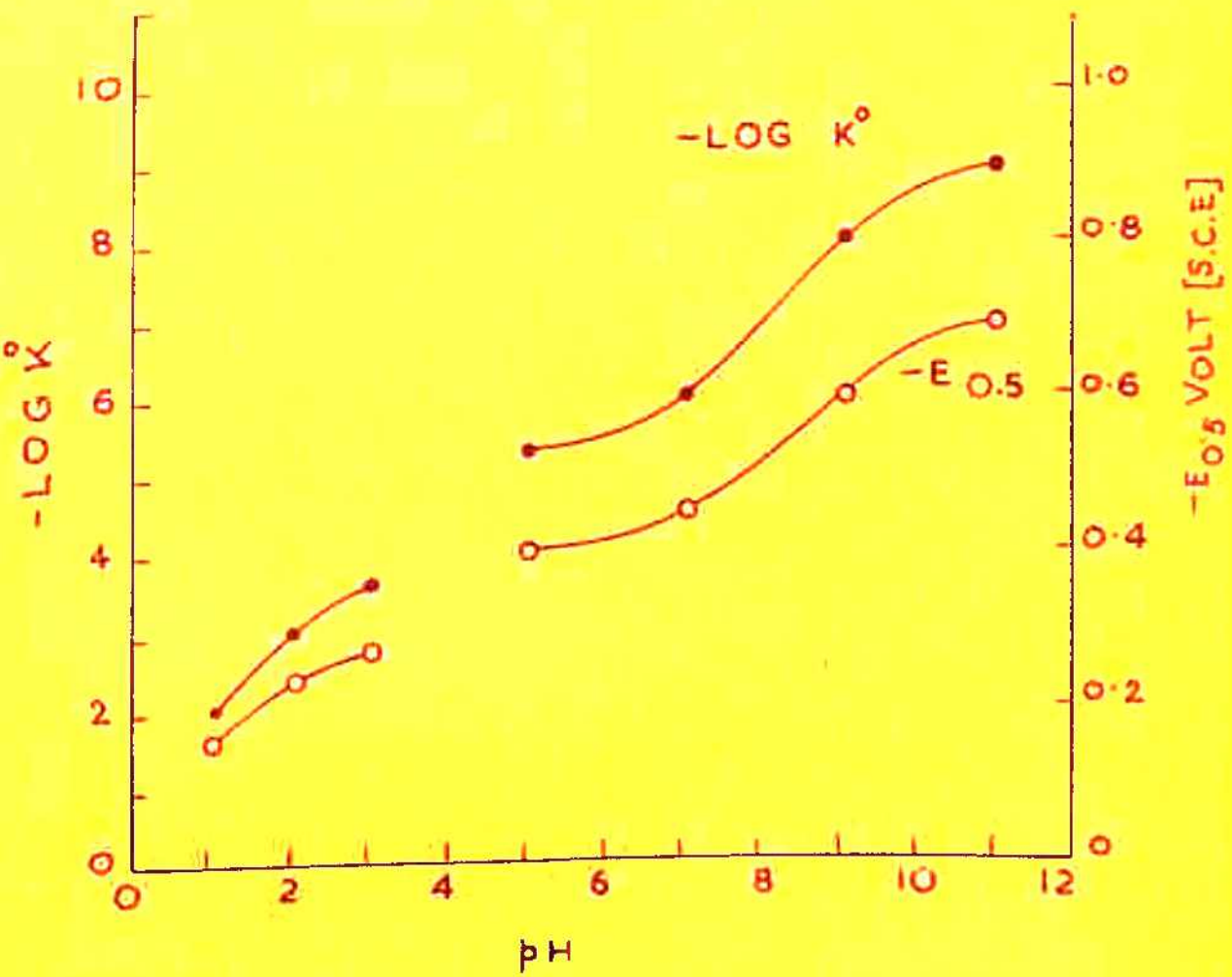


FIG. 7

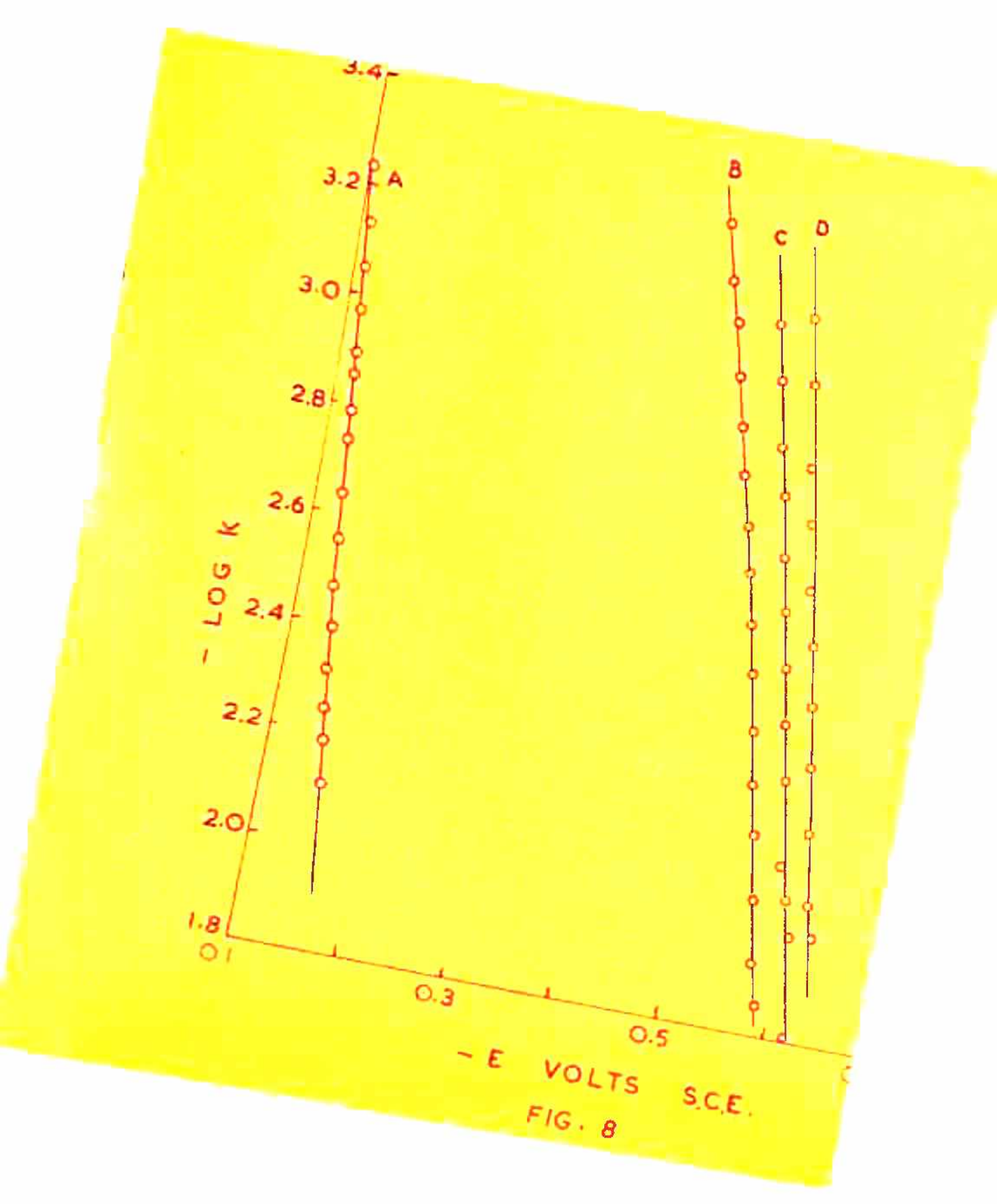


FIG. 8

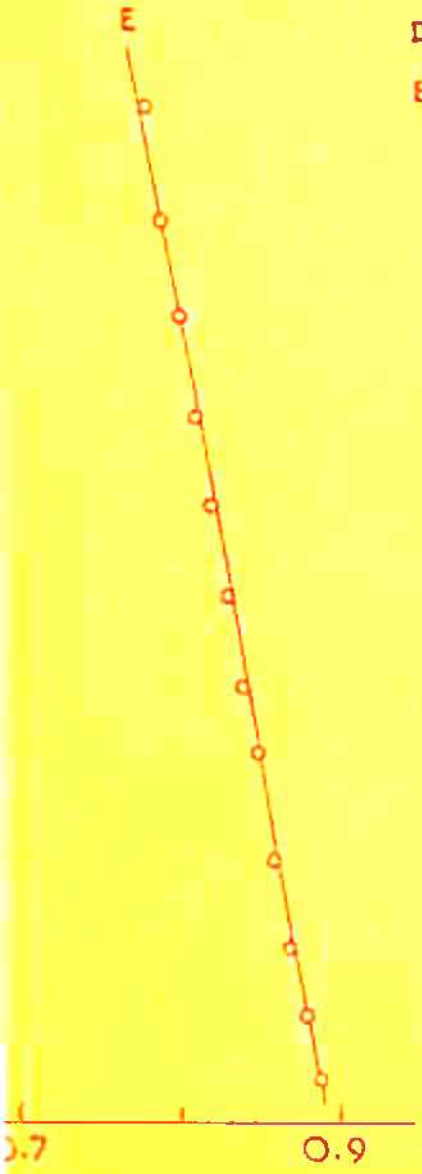
CURVE A --- pH 2.9

B --- pH 3.6

C --- pH 4 7

D --- pH 5·6

E --- pH 7·9



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-x-

C H A P T E R IV

INFLUENCE OF SUBSTITUENTS ON THE POLAROGRAPHIC REDUCTION OF AROMATIC NITRO-COMPOUNDS

INTRODUCTION

One of the recent trends in the field of chemistry is to acquire the knowledge regarding the factors affecting and controlling the reactivity of substances. In this connection the influence of structural modifications of a molecule on its reactivity has been extensively investigated by taking the rate (k) and equilibrium (K) parameters as a measure of reactivity. For example, kinetic studies of a series of compounds undergoing similar reaction but with difference in structure, can be utilized to examine as to how the change in structure affects the rate of reaction. Similarly in the reactions which involve equilibrium, equilibrium constants[1] are utilized for structure-reactivity correlationships. These studies are of immense value from the point of view of reaction mechanism[2]. At the same time, the applications of such investigations for elucidation of the structure of the reacting molecule, have also been made and the usefulness of such investigations is widely recognised[3].

The introduction of a substituent in the molecule can affect its reactivity in a number of ways. In other words, the overall substitution effect may be one or the combination of more than one of the following effects, such as, polar, resonance and steric[4], which have been well described by Taft Jr.[5].

For a long time chemists have tried to correlate reactivities of organic compounds by devising some form of empirical relationship. The reasons for the usefulness of the rate and equilibrium constants as a measure of reactivity are very fundamental in nature. From the principles of thermodynamics we know that change in free energy plays a major role in the occurrence of a reaction. Equilibrium and rate constant are related to change in free energy. The former is related to standard free energy change and the latter to the free energy of activation.

$$-\Delta F = RT\ln K$$

$$-\Delta F^{*} = RT\ln k + RT\ln \frac{kT}{h}$$

The above observations indicate that any quantity characteristic of a reaction which is related to free energy change could be made use of as the basis of structural correlations.

In the early 1930's, Hammett[6] at Columbia and Burkhardt[7] at Manchester, discovered linear relationship involving log k or log K for a number of systems. This work led to the formulation of the Hammett equation (1937)[8,9]. This equation describes the influence of polar meta- or para- substituents on the side-chain reactions of benzene derivatives. It does not apply to the influence of ortho-substituents, which may exert steric effects. The Hammett equation takes the forms;

$$\log (k/k_o) = \sigma\rho$$

$$\log (K/K_o) = \sigma\rho$$

where k or K is the rate or equilibrium constant, respectively, for a side-chain reaction of a meta- or para-substituted benzene system, and k_o or K_o is the constant for the "parent" compound. The substituent constant, σ, is a measure of the polar effect of the substituent (relative to hydrogen), and is, in principle, independent of the nature of the reaction. The reaction constant "ρ" depends on the nature of the reaction, also depends on reaction conditions, but is independent of the kind and position of the substituents.

Extensive work on the application of this rule to rate and equilibrium processes involving meta- and para- substituents in aromatic nucleus, has been carried out[10] and this led to valuable information regarding molecular structure and reaction mechanism.

The first application of this rule to polarographic data on compounds with similar structure led a few workers[11-17] to examine the possibility of investigating the influence of substituents on polarographic reduction taking halfwave potential as the basic characteristic of the compounds undergoing reduction. Zuman correlated the halfwave potentials of a series of compounds for substitution function (σ) and found

the Hammett's equation to polarographic reduction, taking $E_{0.5}$ as the basis of correlation ($\Delta E_{0.5} = \sigma\rho$), to be fairly successful specially in the case of reversible systems. In the case of irreversible systems it is the free energy of activation (ΔF^*) which governs the occurrences of the process. ΔF^* is related to rate constant rather than $E_{0.5}$ and, therefore, the consideration of the values of rate constants for structural correlations in irreversible systems appears more reasonable.

As no data are available in literature relating rate constants obtained polarographically with the structure of the reducible substances, the present investigation gives the results obtained in the study of the influence of substituents on rate constants of the reduction of aromatic nitrocompounds by conventional polarography.

EXPERIMENTAL

Nitrobenzene and meta-nitrotoluene were redistilled in all glass fractionating column and the middle one-third of the distillate was used for experiments. Solid compounds which were of either B.D.H. or E. Merck's quality, were recrystallised before use. Other chemicals used for buffer systems and supporting electrolyte were analytical reagent grade. Disodium hydrogen phosphate/citric acid and boric acid/sodium hydroxide buffers of constant ionic strength

(0.58 M) were used. 0.001% Triton x 100 was used as maximum suppressor throughout the studies. Experiments were carried out at 25°C. Capillary used for dme had m=2.586 mg./sec. and t = 2.96 sec./drop in 0.58 M KCl (open circuit) at h = 65.0 cms. (uncorrected for back pressure).

RESULTS AND DISCUSSION

The necessary condition for a discussion of structural effect can be as follows[18]:-

(1) The number of electrons transferred in the reaction, as indicated by the wave-height, is the same.

(2) The courses of plots of $E_{0.5}$ v/s pH and $i_{lim.}$ v/s pH are analogous for all substances studied; the slope of $E_{0.5}$ v/s pH graph remains practically constant in the entire reaction series.

(3) The character of all the compared limiting currents is the same (i.e., in all cases the limiting currents are diffusion-controlled; when kinetic currents are involved a correction of the measured values of the $E_{0.5}$ is necessary).

(4) The degree of irreversibility of all compared systems is the same, i.e., either all the systems involved are reversible, or for irreversible systems the slopes of the wave determined, for

example, from a logarithmic analysis and expressed in terms of the transfer coefficient does not vary substantially for the substances in question.

(5) When the composition of the supporting electrolyte (in particular, the presence of non-aqueous solvents and the type and concentration of cations or anions) or the presence of surface-active-substances has a pronounced effect on the polarographic behaviour of any of the substances, it has the same effect on all members of that particular reaction series.

The mechanism is assumed to be identical for the entire reaction series if the above conditions are fulfilled. For such compounds, and only for such compounds, can the structural effects on shifts of the $E_{0.5}$ (or on rate constant k) be treated quantitatively.

Dennis[19] et al. observed that the substituents, nitro, carboxyl, chloro, methyl, make the reduction of nitrobenzene increasingly difficult in that order. Nitro and carboxyl group in ortho and para position show a greater effect than in the meta position. Two methyl substituents, as in 1:4 dimethyl-2-nitrobenzene and 1:2 dimethyl-3-nitrobenzene, have little effect on the ease of reduction of the nitro-group, but methyl groups substituted in a way that inhibits sterically the resonance of the nitro-group in nitro-mesitylene and

nitrodurene make the nitro-group more difficult to reduce[20].

In order to examine the influence of substituents on polarographic irreversible reductions of substituted nitrobenzenes in this investigation, the rate constants at E_{zero}, $E_{0.25}$, $E_{0.5}$ and $E_{0.75}$ have been compared. The use of the values of rate constant at $E_{0.5}$ has also been suggested by Tanaka[21] et al. as it is known that at $E_{0.5}$, the current is controlled both by diffusion and the rate of reaction. It may be noticed that in this reaction series, the values of $dE_{0.5}/dpH$ are constant (Table I) indicating that the halfwave potentials of all compounds compared were no longer pH dependent.

Table II gives the values of rate constants at zero potential at pH 6.8. From the magnitudes of the rate constants at zero potential, it is noticed that the reduction of nitro-group becomes more difficult in para position with the substituents in the order -

$$-NO_2 > CHO > COOH > Cl > CH_3 > OCH_3$$

which agrees fairly well, except for halogen derivative, with the order reported in literature taking $E_{0.5}$ as the basic quantity. The deviation found for halogen derivatives may be due to the changes in the values of the transfer coefficient. Halogen atoms are deformable and in some electrode reactions they are assumed to act as electron bridges. Hence for halogen derivatives the orientation in the transition state differs

from the orientation in other members of the reaction series.

Fig. I and II give the comparative study of the plots of $E_{0.25}$, $E_{0.5}$ and $E_{0.75}$ v/s σ (substitution constant) and -log $k_{0.25}$, -log $k_{0.5}$ and -log $k_{0.75}$ against σ, respectively. The slopes of these plots (Table III) corresponded to the reaction constant "ρ" which were found to be in good agreement with each other. However, the plot of -log k^{o} v/s σ did not give satisfactory results. (The failure of the values of -log k_{o} v/s σ was because, at zero potential the rate constant "k" is pure kinetically controlled, whereas on the rising part of the c/v curve it is both diffusion and kinetic controlled.) It can, therefore, be concluded that the Hammett's equation can also be applied to the values of rate constants at $E_{0.25}$, $E_{0.5}$ and $E_{0.75}$, respectively.

It is generally observed that the points of para and meta acids deviate from the straight line plot. These deviations may be explained due to the influence of unit charge on the orientation of the molecule at the moment of impact or by the effect of the strong coulombic field of the ionized grouping on the transition state[22].

From the fairly satisfactory values of "ρ" obtained from the plots, it can be concluded that the mechanisam of electrode reaction postulated

$$R\text{-}NO_2 + 1\bar{e} \underset{\text{Rev.}}{\rightleftharpoons} R\text{-}NO_2^- \xrightarrow[\text{slow}]{1\bar{e},2H^+} R\text{-}N(OH)(OH) \xrightarrow{2\bar{e},2H^+} R\text{-}NHOH$$

with a single rate determining step (under-given conditions - log k v/s E plot yielded straight line) is valid. Secondly that the polarographic rate constants at $E_{0.25}$, $E_{0.5}$ and $E_{0.75}$ can also be made use of as the basis of understanding the influence of the substituents on polarographic reduction.

-x-

Table I

Values of $\frac{dE_{0.5}}{d\ pH}$ for substituted Nitro-benzene series.

$E_{0.5}$ measurements were done at pH 10.3 and 4.4.

Substitution	$dE_{0.5}/d\ pH$
H	0.054
p-Cl	0.057
p-OCH_3	0.0575
p-CH_3	0.058
m-CH_3	0.0562
p-CHO	0.063
m-CHO	0.047
p-COOH	0.061
m-COOH	0.064

Table II

Values of $-\log k^{o}$ for different substituted nitrobenzenes.

pH = 6.8 buffered; μ = 0.58 M; Temp. = 25°C

S.No.	Substitution	$-\log k^{o}$ N.H.E.
1.	p-OCH_3	8.068
2.	p-CH_3	7.042
3.	m-CH_3	6.852
4.	H	6.066
5.	p-Cl	6.049
6.	m-COOH	5.950
7.	p-COOH	5.586
8.	m-CHO	5.463
9.	p-CHO	4.519
10.	m-NO_2	4.392
11.	p-NO_2	4.007

Table III

Values of reaction constants (ρ) obtained by plotting $E_{0.25}$, $E_{0.50}$, $E_{0.75}$ and $-\log k_{0.25}$, $-\log k_{0.50}$, $-\log k_{0.75}$ against (σ_x) substitution constant.

Plot	Reaction constant (ρ)
$-E_{0.25}$ vs. σ_x	0.195
$-\log k_{0.25}$ vs. σ_x	0.220
$-E_{0.5}$ vs. σ_x	0.215
$-\log k_{0.5}$ vs. σ_x	0.180
$-E_{0.75}$ vs. σ_x	0.258
$-\log k_{0.75}$ vs. σ_x	0.224

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Legend of the Figures

Fig. 1: Plots of E_x vs. σ_x (substitution constant) at pH 6.8.

Curve A for $E_{0.25}$ vs. σ_x

Curve B for $E_{0.5}$ vs. σ_x

Curve C for $E_{0.75}$ vs. σ_x

Fig. 2: Plots of $-\log k_x$ vs σ_x at pH 6.8.

Curve A for $-\log k_{0.25}$ vs. σ_x

Curve B for $-\log k_{0.5}$ vs. σ_x

Curve C for $-\log k_{0.75}$ vs. σ_x.

-x-

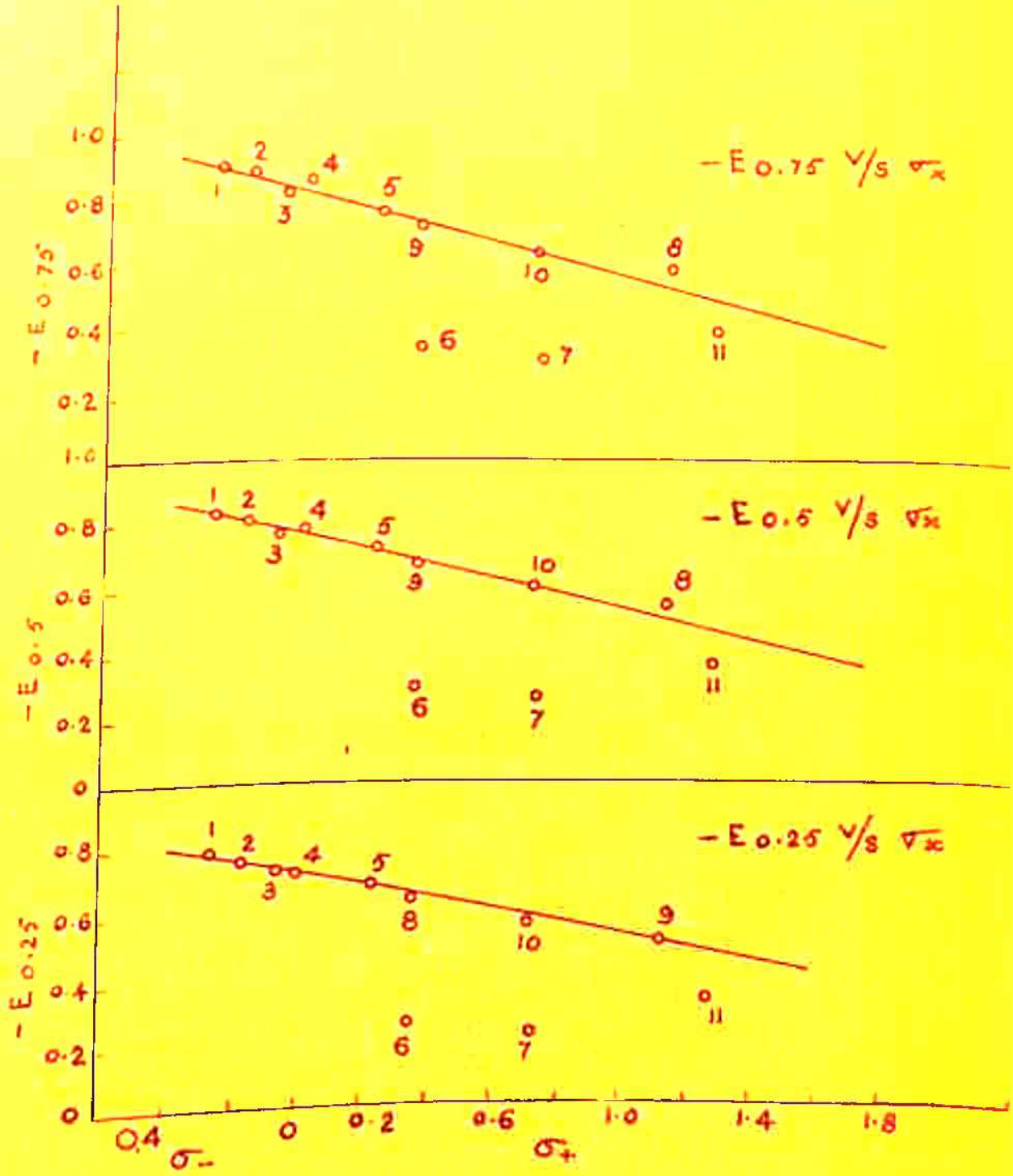


FIG · 1

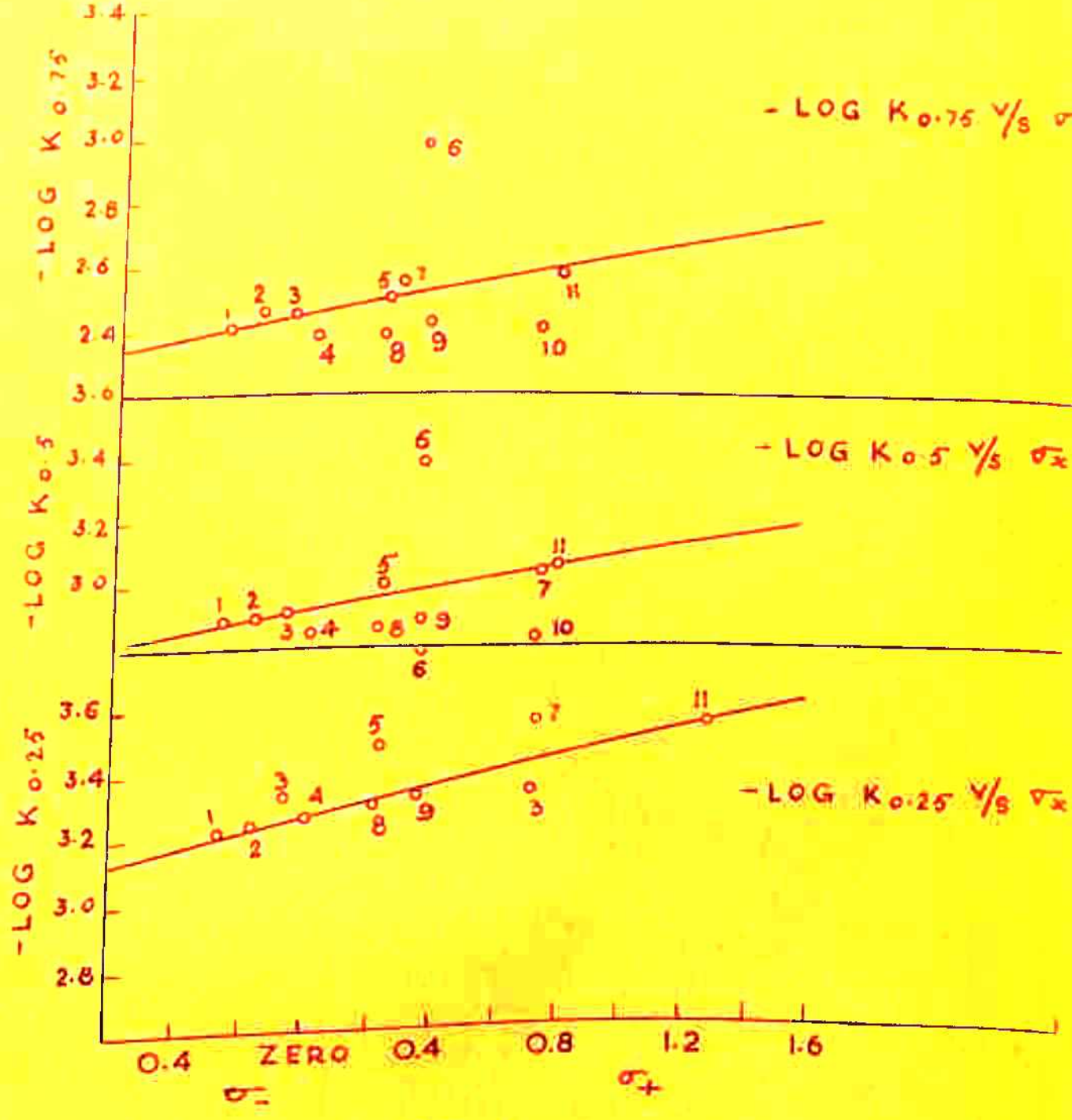

- LOG K 0.75 V/S σ
- LOG K 0.5 V/S σx
- LOG K 0.25 V/S σx
- LOG K 0.75
- LOG K 0.5
- LOG K 0.25
3.4
3.2
3.0
2.8
2.6
2.4
3.6
3.4
3.2
3.0
2.8
1 2 3 4 5 6 7 8 9 10 11
0.4 ZERO 0.4 0.8 1.2 1.6
σ−
σ+

FIG. 2

C H A P T E R V

POLAROGRAPHIC STUDIES ON THE KINETICS OF THE REACTIONS IN SOLUTIONS

INTRODUCTION

Use of polarographic analysis in the field of reaction kinetics has been reviewed by G. Semerano[1]. The applicability of the method depends on the direct or induced polarographic activity of one or more of the organic substances taking part in the reaction. The technique has been employed in the kinetic measurements during decomposition reactions[2,3], addition reactions[4], oxidation-reduction reactions[5,6], hydrolytic reactions[7], dihydrochlorination reactions[8], auto-oxidations[9], polymerisation reactions[10], diazotisation reactions[11], electrolytic dissociation equilibrium of weak acids[12] and tautomeric changes[13,14].

The use of polarographic technique in the study of reaction kinetics in solution of a system undergoing tautomeric change will, however, be taken in detail as the studies in this chapter are related with this aspect.

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

$$R - CH_2NO_2 + OH^- \longrightarrow R - CHNO_2^- + H_2O \qquad (I)$$

This neutralization is a relatively slow process and the rates of neutralization by different bases have been investigated

by Maron[15] et al. and more recently by Pearson[16]. In both the investigations the reaction rate was followed conductometerically.

D. Turnbull[17] et al. represented the tautomeric equilibrium between the normal nitro-paraffin and its aci-nitro-form as follows:

$$R - CH_2.NO_2 \rightleftharpoons R - \bar{C}HNO_2 \rightleftharpoons R - CH = NO_2^- \rightleftharpoons R - CH = NO_2H$$

(The latter three molecules are collectively called "aci-nitro-paraffin".) The equilibrium is slow enough that the aci-nitro-component can be estimated by titration with bromine[17-19], in much the same way as enols can be determined in the presence of their keto tautomers. The equilibrium ratio

$$K_i = \frac{(R - CH = NO_2H)}{(R - CH_2NO_2)}$$

increases by successive alkyl substitution and also the accumulation of nitro-groups on the same carbon atom further increases the proportion of the aci-nitro-form.

P.J. Elving[19] et al. applied high frequency technique to follow the tautomeric interconversion of nitro-paraffins in presence of hydroxyl ions. The values of rate constants obtained by these different methods[17-24] are in the order nitromethane > nitroethane > 1-nitropropane > 2-nitropropane.

Use of polarographic technique as a tool to evaluate the rate of tautomeric interconversion depends on the fact that the aci-form is not reduced polarographically even at the most negative potentials available for ordinary aqueous solutions. M.J. Astle[13] et al. studied the kinetics of the conversion of normal nitro-paraffins into polarographically inactive aci-form between pH range 6 to 11.0 and rates were found to decrease in the same order as mentioned above. During the polarographic study of hydroxy-tertiary-nitrobutanes, Elving[25] et al., reported that the decrease in polarographic wave height in alkaline media was due to the cleavage of the tertiary nitro-group. H. Sayo[26] et al. observed a decrease in the height with α-nitro-iso-butyric acid derivatives but no evidence was obtained on the fission of the nitro-group. They further extended the studies on ethyl α-nitro-iso-butyrate, α-nitro-iso-butyramide, t-nitro-butane and tris-(hydroxy-methyl)-nitromethane and found that the decrease in polarographic wave height of these aliphatic tertiary nitro-compounds, in moderately alkaline media, was not due to the cleavage of the nitro-group but to other reactions of other substituents leading to the formation of the aci-ion of secondary nitro-compounds[27]. Phenyl-nitromethane and nitro-cyclohexane also undergo aci-conversion and kinetics of this have been taken up by D. Jannakoudakis[28].

This chapter gives the results obtained in the polaro-graphic study of the reduction of -

I 1-chloro-1-nitro-propane.

II β-nitropropionic acid.

III 5-nitro-ace-naphthene.

and the kinetics of their conversion into polarographically inactive aci-form on which no data were available in literature.

I POLAROGRAPHY OF 1-CHLORO-1-NITROPROPANE

The present investigation gives the results obtained in the polarographic study on the reduction of 1-chloro-1-nitropropane and of the kinetics of its conversion into aci-form in solution, on which no data are available in literature.

Experimental

1-chloro-1-nitropropane (Fluka) was redistilled in an all-glass fractionating column and its stock solution (0.10 M) was made in redistilled ethyl alcohol. Other chemicals used for buffer systems and supporting electrolyte were analytical reagent grade. HCl/KCl, Na_2HPO_4/citric acid, boric acid/NaOH and NaOH buffers were used. Ionic strength (μ = 0.54 M) was brought to a definite value by adjusting the amount of supporting electrolyte. Maximum suppressor was not needed as no maximum appeared over the whole pH range. Temperature was maintained at 25°C. Capillary used for dme had m = 2.931 mg/sec. and t = 3.05 sec./drop in 0.54 M KCl (open circuit) at h = 40.0 cms (uncorrected for back pressure).

The current-voltage curves were recorded, after allowing the test solution to stand for 24 hours. This was necessary as the current values were changing with time even at pH = 1.0. The kinetic studies were made between pH 1 to 9.05. The conversion into aci-form above pH 8.05 was too fast to record

current values accurately with time. The potential at which the currents were measured at regular intervals of time, corresponded to the potential at the plateau of the second step in the reduction of the depolarizer.

Results and Discussion

(a) Reduction of 1-chloro-1-nitropropane

The test solution after attaining the equilibrium gave the current-voltage curves as shown in Fig. (1). The total height (i_{d_1} and i_{d_2}) of the two steps decreased gradually with the increase of pH and no wave could be recorded beyond pH 8. The height (i_{d_1}) of the first step showed a regular decrease with increase in pH, whereas, no regularity was observed for (i_{d_2}), height of the second step. Similarly $E^1_{0.5}$ for first step showed a positive shift with increase of pH and no regularity was observed in $E^2_{0.5}$ for the second step (Table I).

During the study of nitro-paraffins[13,29-31] it was observed that these undergo single step ($4\bar{e}$) reduction in buffered solutions of wide pH range and the appreciable decrease in the wave height was observed only above pH 5 and $E_{0.5}$ first shifted to cathodic side up to a certain pH value and then showed constancy. However, in case of 1-chloro-1-nitropropane it was observed that the current decreased with time even in acidic medium (pH = 1.0). The aci-conversion of 1-chloro-1-

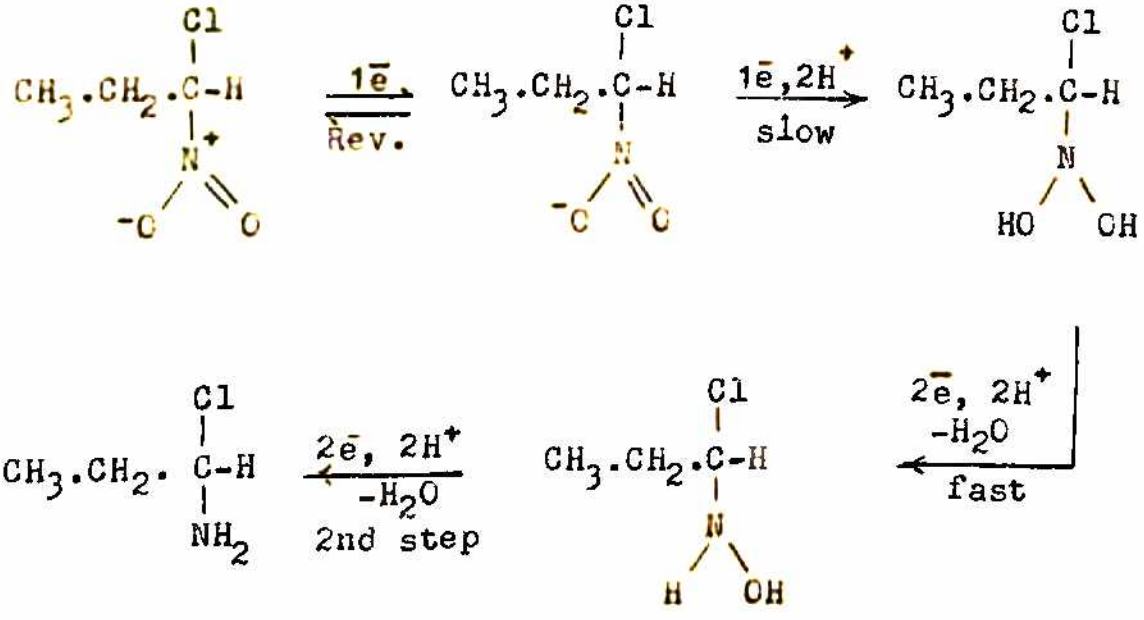
nitropropane even in strongly acidic medium may be due to the presence of chlorine atom in the molecule. Further, it was observed that with the decrease of the concentration of the depolarizer (solutions analysed after attaining the equilibrium), the $E^{1}_{0.5}$ showed a positive shift (Table II). Thus the positive shift of the $E^{1}_{0.5}$ at all pH values may be for the reasons:

(i) either half-wave potential is independent of pH and the positive shift is due to the decrease in the concentration of the depolarizer (as more of it is converted into polarographic inactive aci-form and remaining normal nitro-compound undergoing two steps $4\bar{e}$ and $2\bar{e}$ reduction at dme);

(ii) the concentration effect on half-wave potential predominates the pH effect and thus results in a positive shift.

The kinetic parameters ($-\log k^{o}$ and αn_a) for its reduction at various pH values were calculated by analysing the first step, using Koutecky's method[32]. The value of diffusion-coefficient needed for rate constant calculation was taken as 1.383×10^{-5} $cm^2/sec.$, reported in literature for compounds with similar structure[13]. The value of diffusion coefficient could not be found experimentally because of its conversion into aci-form even in strongly acidic medium.

-log k vs. E plot for first step yielded a straight line (Fig.2), thus showing single rate determining step at all pH values. These results are given in Table I. Values of αn_a showed no regularity, whereas, the values of -log k^o and $E^1_{0.5}$ showed a regular decrease with increase in pH, which may be due to reasons as mentioned above. The reduction mechanism can be as follows:



(b) Kinetics of conversion of 1-chloro-1-nitropropane into aci-form

It is clear from the equation (I) that the conversion of normal nitro-compound into aci-form will depend on (a) concentration of the depolarizer and (b) concentration of (OH^-) ions. The buffer solution ensures the constantcy of (OH^-) and hence the rate of transformation will depend on the

concentration of depolarizer only. Fig. 3 gives the variation in the magnitude of the current with time. Excellent constant values of rate constants were obtained using a first order equation (Table III). 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 i_{t_1}/i_{t_2} vs. (t_2-t_1)), which yielded a straight line (Fig.3 Curve A').

Thus the rate of reaction may be given by

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

where "a" is the original concentration,
"x" is the fraction of depolarizer converted into aci-form in time t.

Or $$k = \frac{2.3}{t} \log\left(\frac{a}{a-x}\right)$$

$$k = \frac{2.3}{t_2-t_1} \log\left(\frac{a-x_1}{a-x_2}\right).$$

In terms of current it can be shown that the above equation takes the form

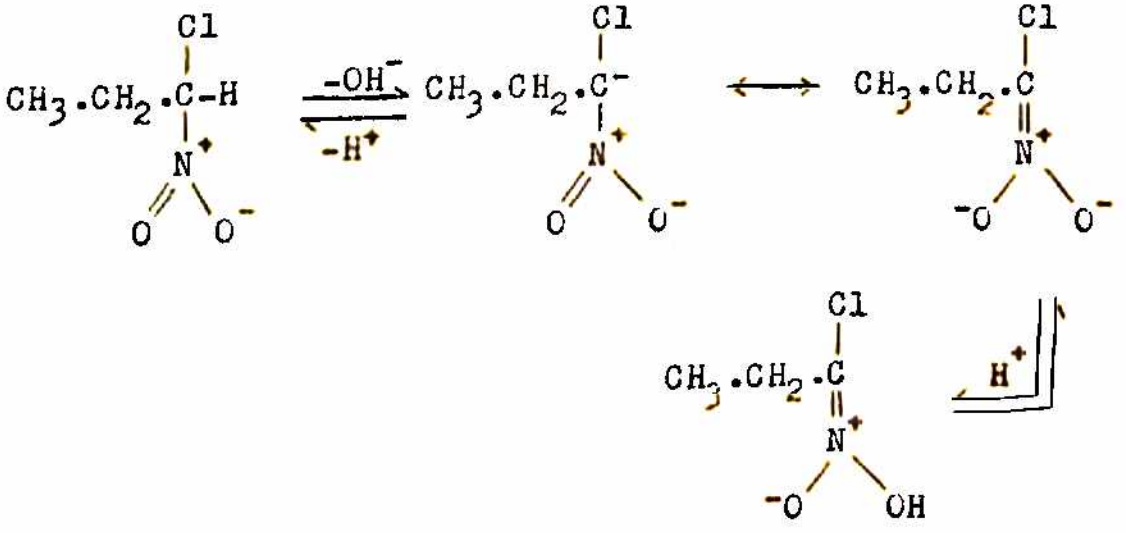
$$k = \frac{2.3}{t_2-t_1} \log\ (i_{t_1}/i_{t_2}) \qquad \text{(II)}$$

where i_{t_1} and i_{t_2} are currents corresponding to concentration of normal nitro-compound at time intervals t_1 and t_2.

Values of rate constant for the transformation, at various pH values, obtained by using above equation (II), are tabulated in Table IV.

Although the rate of transformation increased with pH, there was no direct relation between the rate of conversion and OH^- ions in the solution. This might arise from the fact that OH^- 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 as reported in previous studies[13].

The equilibrium between normal nitro-compound and its aci-form can be represented as follows:



Aci-form

Table I

Values of currents, $E_{0.5}$'s and rate constant (k) at various pH values.

Temp. = 25°C; Concentration of depolarizer = 1.0 mM.

μ = 0.54M; Height = 40.0 cms.

Sl. No.	pH	i_{d_1}* μ.a.	$-E^{1*}_{0.5}$ Volt S.C.E.	-log k^{o*} N.H.E.	αn_a*	i_{d_2}** μ.a.	$-E^{2}_{0.5}$** Volt S.C.E.
1	1.0	8.4	0.290	3.048	0.419	1.2	0.770
2	1.9	8.0	0.290	3.048	0.419	1.2	0.840
3	2.95	7.65	0.282	3.0374	0.4663	0.7	0.80
4	4.0	6.4	0.270	2.9112	0.4534	1.05	0.780
5	5.0	6.0	0.255	2.815	0.4714	0.90	0.860
6	6.0	5.45	0.245	2.7709	0.4657	1.10	0.900
7	7.15	3.2	0.200	2.7363	0.538	0.80	0.900
8	8.05	1.30	0.190	-	-	1.10	0.880
9	9.05	No wave could be recorded.					

* For first step. ** For second step.

Table II

Effect of concentration of depolarizer on $E^{1}_{0.5}$

Temp. = 25°C; μ = 0.54 ; Height = 40.0 cms.

pH	Concentration mM	i μ.a. Total	$E^{1}_{0.5}$ Volts S.C.E.
2.95	2.00	13.25	0.320
	1.00	8.30	0.282
	0.60	5.50	0.270
4.00	2.00	12.40	0.315
	1.00	7.40	0.270
	0.60	5.10	0.260

Table III

Rate constant (k) for the transformation of 1-chloro-1-nitro-propane into aci-form.

Temp. = 25°C; 1.0 mM depolarizer pH = 1.90

μ = 0.54 M

Time Minutes	$k \times 10^3$ Min^{-1}.
7	3.22
12	3.642
17	3.788
22	3.806
27	3.820
32	3.850
37	3.870
43	4.000
	$k_{ave.} = 3.84 \times 10^{-3}$ Min^{-1}.

Table IV

Values of rate constant (k) of the transformation of normal nitro-compound into aci-form, at various pH values.

Temp. = 25°C; 1.0 mM. depolarizer, μ = 0.54 M.

pH	$k \times 10^3$ Min^{-1}.
1.9	3.84
4.0	4.393
6.0	4.816
7.15	13.400
8.05	52.400

Legend of the Figures

Fig. 1: Current-voltage curves at various pH values after allowing the test solutions to attain equilibrium.

Curves: A, B, C, D, E and F at pH 1.0, 2.95, 4.0, 5.0, 6.0 and 7.15, respectively.

Fig. 2: Plot of -log k vs. E at various pH values.

Curve A pH 1.0 and 1.9

B pH 2.95

C pH 4.0

D pH 5.0

E pH 6.0

F pH 7.15

Fig. 3: Variation of current with time at

pH 1.0 - Curve A

pH 4.0 - Curve B

pH 8.05 - Curve C

Curve A', plot of log $\frac{i_{t_1}}{i_{t_2}}$ vs. (t_2-t_1).

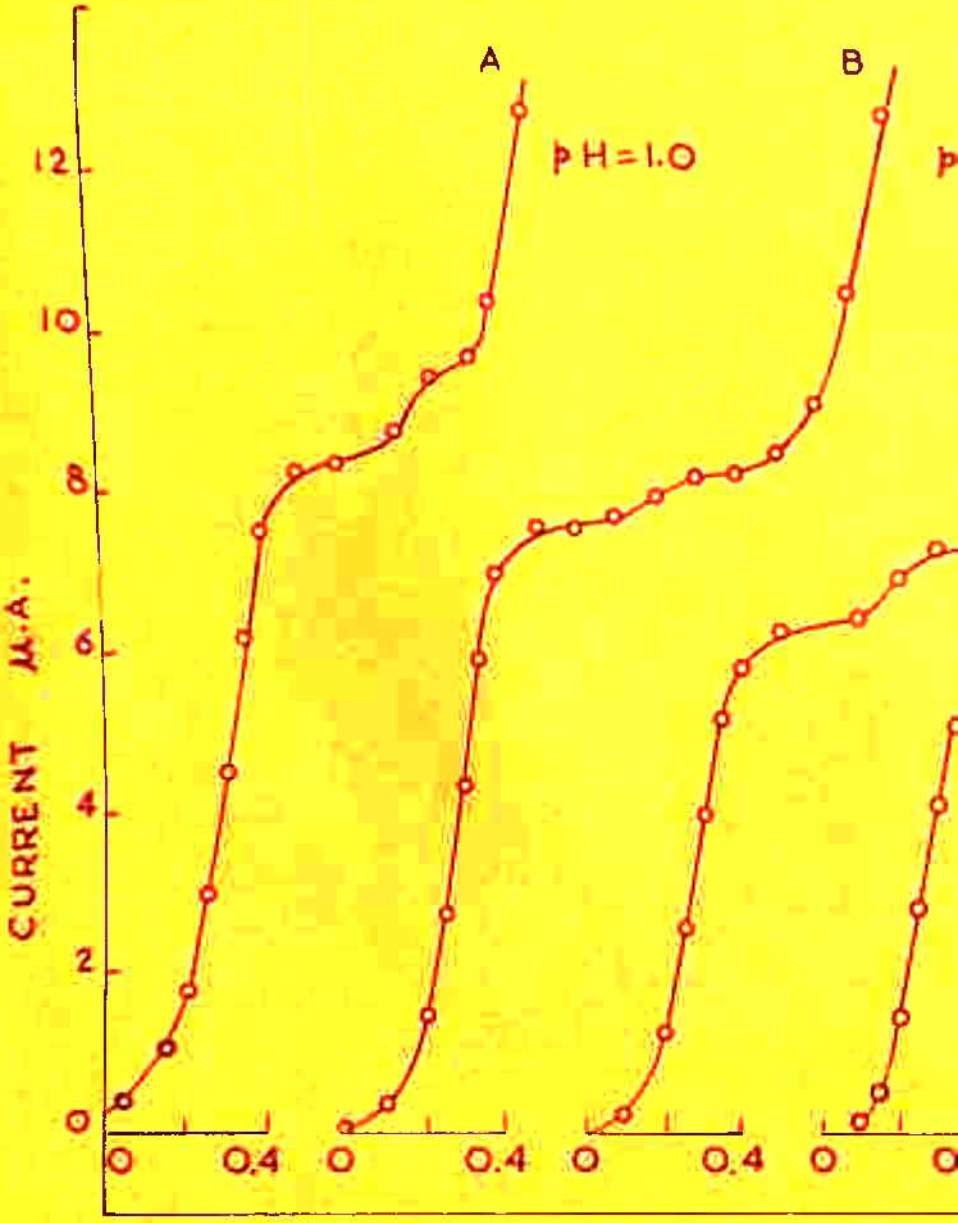
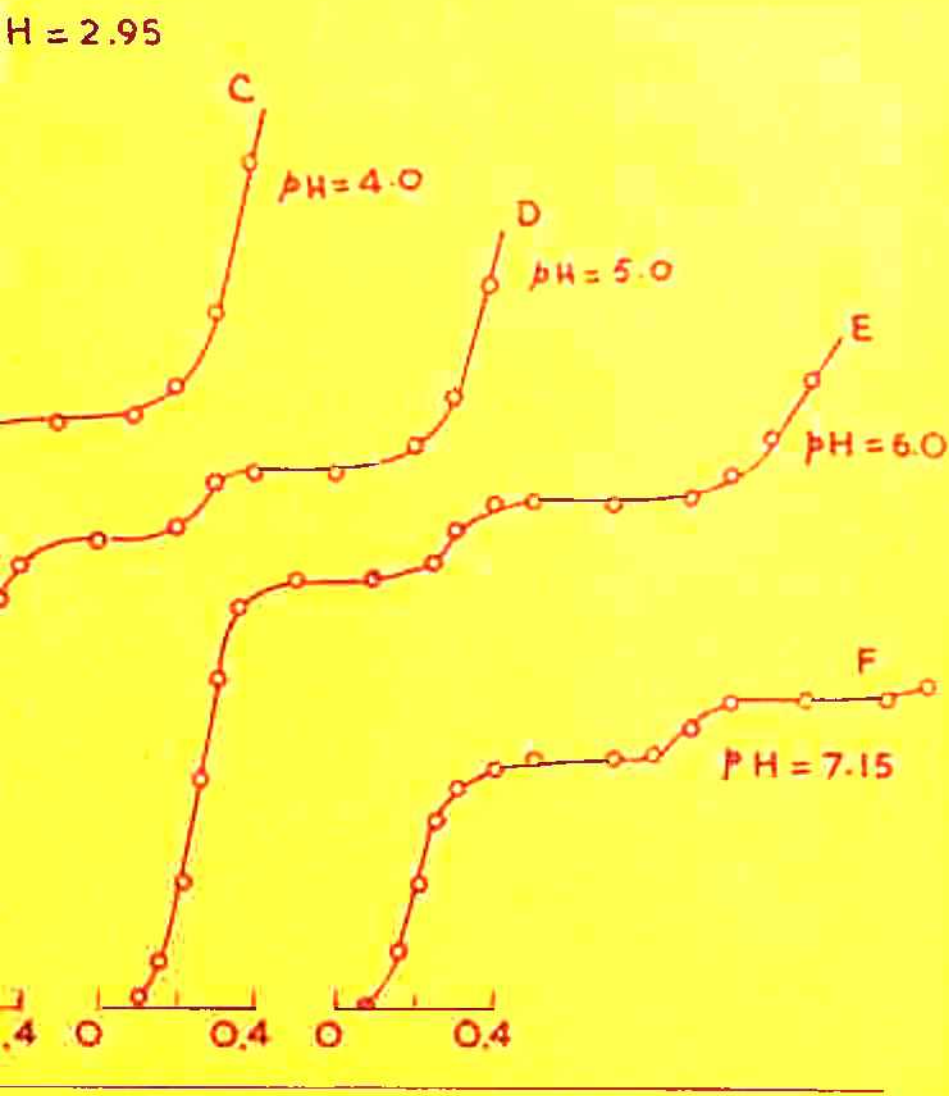


FIG. 1


H = 2.95
C
pH = 4.0
D
pH = 5.0
E
pH = 6.0
F
pH = 7.15
.4
0
0.4
0
0.4
S.C.E.

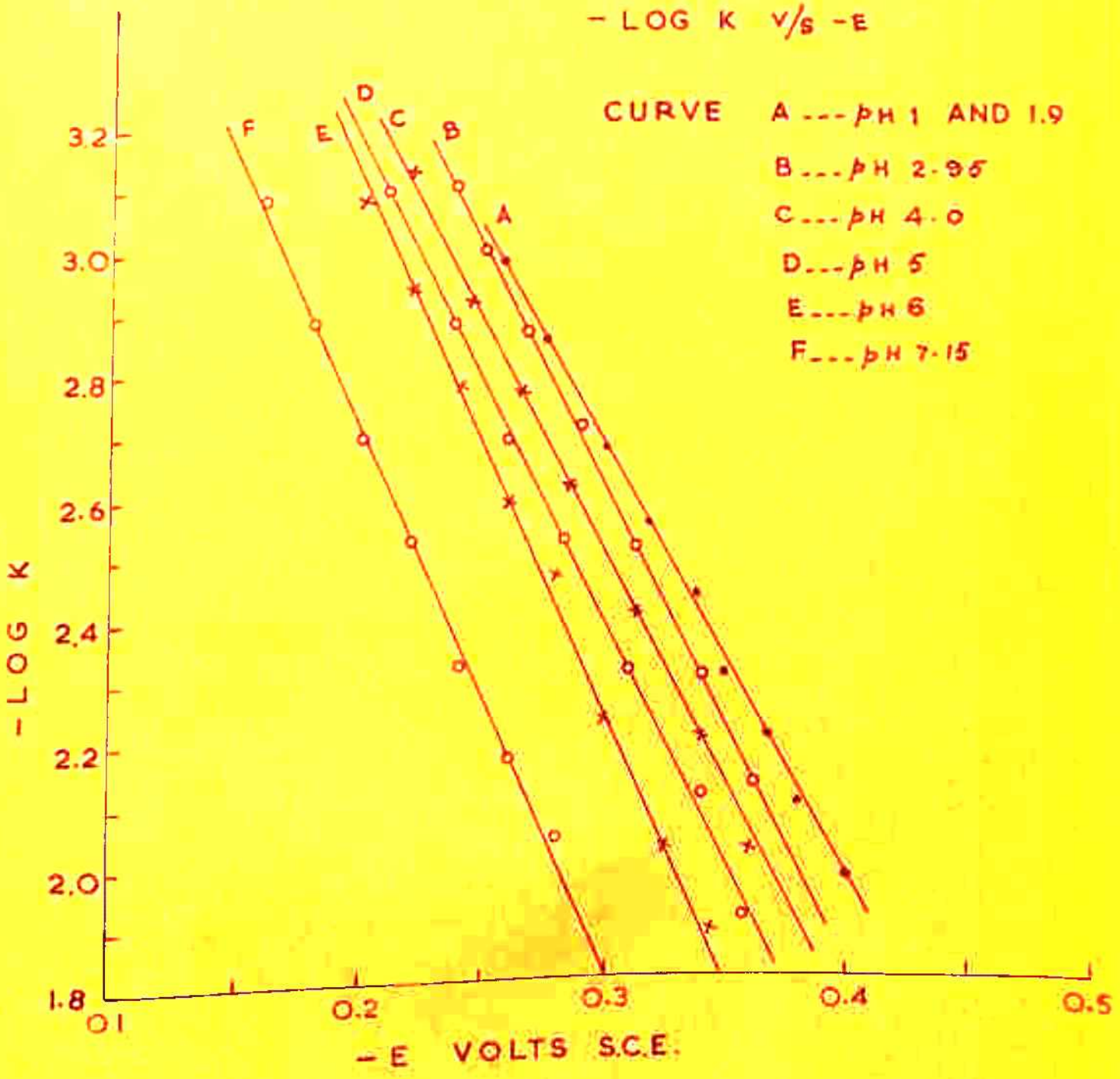

- LOG K V/S -E
CURVE A --- pH 1 AND 1.9
B --- pH 2.95
C --- pH 4.0
D --- pH 5
E --- pH 6
F --- pH 7.15
A
B
C
D
E
F
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
- LOG K
0.1
0.2
0.3
0.4
0.5
- E VOLTS S.C.E.

FIG. 2

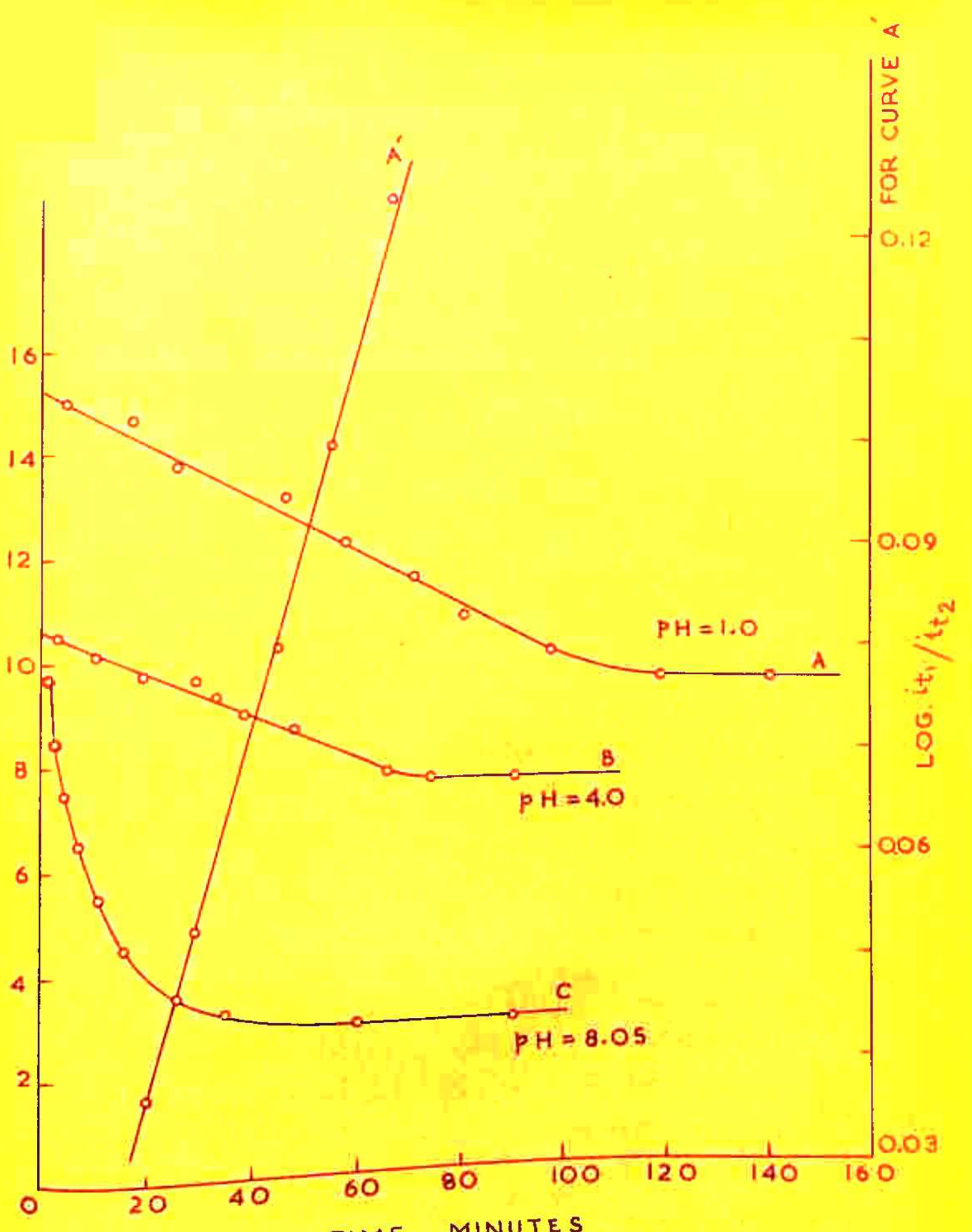

A'
A
B
C
pH = 1.0
pH = 4.0
pH = 8.05
16
14
12
10
8
6
4
2
0
20
40
60
80
100
120
140
160
0.12
0.09
0.06
0.03
TIME MINUTES
LOG. i_{t_1}/i_{t_2} FOR CURVE A'

FIG. 3

II POLAROGRAPHY OF β-NITROPROPIONIC ACID

The present investigation gives the results obtained in the polarographic study of the reduction of β-nitropropionic acid and the kinetics of its conversion into aci-form in solution, on which no data are available in literature.

Experimental

Stock solution of β-nitropropionic acid (Aldrich Chemical Co., U.S.A., mp 63°C) was made in double distilled water. Other chemicals used for buffer systems and supporting electrolyte were analytical reagent grade. HCl/KCl, Na_2HPO_4/ citric acid, boric acid/NaOH and NaOH buffers were used. Ionic strength (μ = 0.54 M) was brought to a definite value by adjusting the amount of supporting electrolyte. Maximum suppressor was not needed as no maximum appeared over the whole pH range. Temperature was maintained at 35°C. Capillary used for dme had m = 2.931 mg/sec. and t = 3.05 sec./drop in 0.54 M KCl (open circuit) at h = 40.0 cms (uncorrected for back pressure).

Reproducible current-voltage curves were recorded, after allowing the test solution to stand for 24 hours. This was necessary as the current values were changing with time beyond pH 6. The kinetic studies were done between pH 8 and 9 as below pH 8, the conversion into aci-form was too slow and

above pH 9, it was too fast to record current values accurately with time. The potential at which the currents were measured at regular intervals of time, corresponded to the potential at the plateau of the reduction step of the depolarizer.

Results and Discussion

(a) Reduction of β-nitropropionic acid:

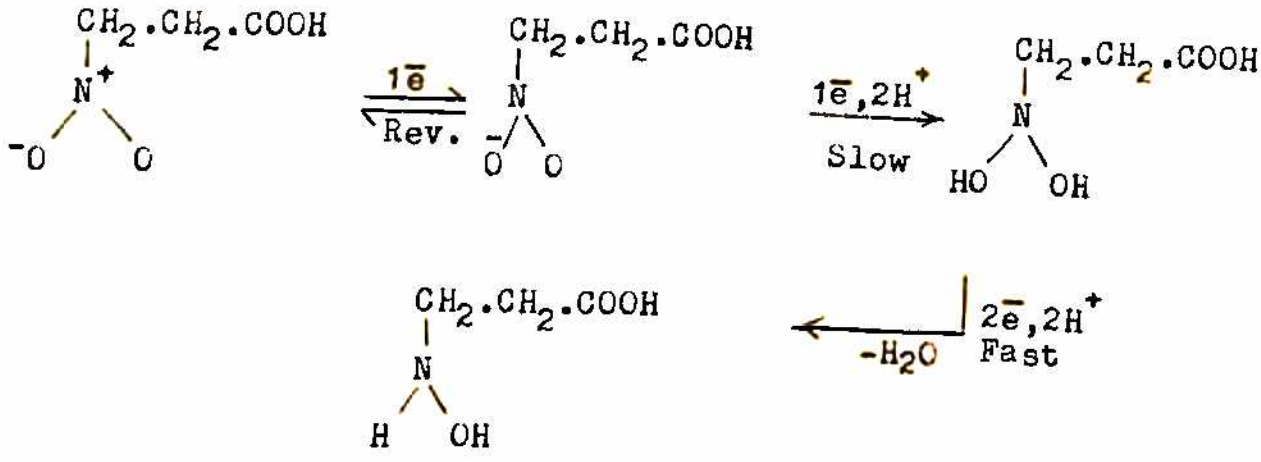
The test solution after attaining the equilibrium gave the single step reduction wave (as shown in Fig. 1) over the whole pH range. No appreciable change in the value of diffusion current was observed up to pH 6, but further increase of pH was accompanied by a regular decrease in the wave height and no wave could be recorded beyond pH 10. Half-wave potential shifted towards more cathodic side up to pH 8.5. Beyond this pH, $E_{0.5}$ showed a positive shift. Values of the i_d/c within concentration range 1.0×10^{-4} to 1.6×10^{-3} M, $i_d/\sqrt{h}$, cathodic shift of $E_{0.5}$ with the concentration of the depolarizer and the plots of $\log \frac{i}{i_d - i}$ vs. E (all at pH 2.1) showed that it was diffusion controlled irreversible reduction.

The diffusion coefficient "D" (1.383×10^{-5} $cm^2/sec.$) of the depolarizer was obtained by McBain-Dowson cell using King-Cathard equation[33]. This value of "D" agrees fairly well with the value of "D" reported for similar structure compound

viz. 1-nitropropane (1.285×10^{-5} $cm^2/sec.$)[13]. Using the above value of "D" in Ilkovic Equation the number of electrons involved in the reduction was $3.77 \simeq 4$, at all pH values and the decrease in the magnitude of i_d with increase in pH (beyond pH 6) was not due to any change in the number of electrons, but due to the conversion of the normal nitro-compound into polarographic inactive aci-form and the remaining normal nitro-compound undergoing $4\bar{e}$ reduction at dme.

Taking the value of $D = 1.383 \times 10^{-5}$ $cm^2/sec.$ and using Koutecky's method, the values of kinetic parameters (αn_a and $-\log k^o$) were evaluated from the data for the polarographic wave at various pH values. -log k vs. E plot (Fig. 2) for each step yielded a straight line, thus showing single rate determining step at all pH values. These results are given in Table I. Values of αn_a showed no regularity, whereas, the values of $-\log k^o$ and $E_{0.5}$'s first increased up to pH 8.5 and then decreased with further increase in pH. The decrease in the values of $-\log k^o$ and $E_{0.5}$ beyond a certain pH may be due to the fact that at higher pH values the amount of active depolarizer left is much less (more of normal nitro-compound converted into aci-form) and the concentration effect on $E_{0.5}$ as well as on $-\log k^o$ predominates the influence of pH on these quantities.

The probable reduction mechanism may be as follows:



(b) Kinetics of the conversion of β-nitropropionic acid into aci-form

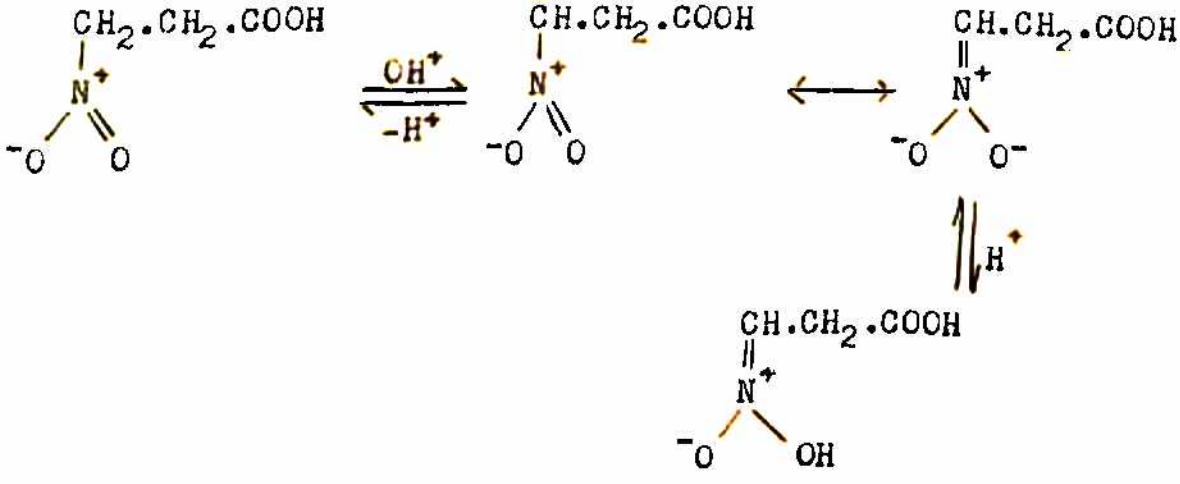
Fig.(3), curve "A", gives the variation in the magnitude of the current with time at various pH values. Excellent constant values (Table II) of rate constants were obtained using a first order equation (II), (As derived earlier for 1-chloro-1-nitropropane). This is further confirmed from the plot of $\log(\frac{a-x_1}{a-x_2})$ vs. (t_2-t_1), (in terms of current, $\log \frac{i_{t_1}}{i_{t_2}}$ vs. (t_2-t_1)), which yields a straight line (Fig. 3, curve B).

Values of rate constant for the transformation at various pH values, obtained by using the first order equation, are tabulated in Table III. The extent of conversion of normal nitro-compound into aci-form at a specific pH was found to be independent of initial concentration of the depolarizer.

In this case also the rate of transformation increased with pH, as explained earlier (Chapter V, Part I).

Thermodynamic parameters, i.e., increase in free energy (ΔG), increase of heat content (ΔH) and increase of entropy (ΔS) for the activated complex formed during this transformation process have been calculated from the values of rate constants (2.532×10^{-3} and 6.053×10^{-3} Min^{-1}. at 23°C and 35°C, respectively) using Eyring theory[34,35]. The values of ΔG, ΔH and ΔS are 21.28 k.cal/mole, 1.33 k.cal/mole, and -64.79 cal./deg. mole, respectively, at 35°C.

The equilibrium between normal nitro-compound and its aci-form can be represented as follows:-



Aci-form.

Table I

Kinetic parameters -log k^{o}, αn_a and $E_{0.5}$ at various pH values.

Temp. = 35°C, Height = 40.0 cms, μ = 0.54 M

Conc. of depolarizer = 1.0 mM.

Sl. No.	pH	i_d μ.a	$-E_{0.5}$ volts S.C.E.	αn_a	-log k^{o} N.H.E.
1	1.0	22.3	0.695	0.213	4.380
2	2.1	21.0	0.725	0.225	4.523
3	3.1	20.6	0.740	0.211	4.548
4	4.0	19.4	0.800	0.252	5.131
5	5.0	19.5	0.900	0.246	5.825
6	6.0	19.7	0.970	0.2596	5.900
7	7.0	17.0	1.010	0.2954	6.476
8	8.5	15.8	1.140	0.210	6.938
9	9.0	11.8	1.040	0.2437	6.686
10	10.0	4.10	1.000	0.210	6.241

Table II

Rate constant (k) for the transformation of β-nitropropionic acid into aci-form.

Temp. = 23°C; 1.0 mM depolarizer, pH = 8.5; μ = 0.54 M

Time	k x 10^{3} Min^{-1}.
3	2.452
8	2.616
13	2.76
18	2.593
23	2.580
28	2.595
33	2.537
38	2.487
48	2.441
58	2.428
68	2.371

$k_{ave.}$ = 2.532 x 10^{-3} Min^{-1}.

Table III

Value of rate constant (k) for the transformation of normal nitro-compound into aci-form.

Temp. = 35°C; μ = 0.54 M; 1.0 mM. depolarizer.

S.No.	pH	k Min^{-1}.
1	8.0	1.963 x 10^{-3}
2	8.5	6.053 x 10^{-3}
3	9.0	1.925 x 10^{-2}

Legend of the Figures

Fig. 1: Current-voltage curves at various pH values, after allowing the solutions to attain equilibrium.

Curves A, B, C, D, E and F at pH value 1.0, 4.0, 6.0, 8.5, 9.0 and 10.0, respectively.

Fig. 2: -log k vs. E plot at various pH values.

Curves A, B, C, D, E, F, G, H and I at pH, 1, 2.1, 3.1, 4, 5, 6, 7, 8, and 9, respectively.

Fig. 3: Curve A, variation of current with time at pH = 8, 8.5, 9.0, 10 and 11, respectively.

Curve B, plot of $\log \frac{i_{t_1}}{i_{t_2}}$ vs. (t_2-t_1) at pH 8.5.

-x-

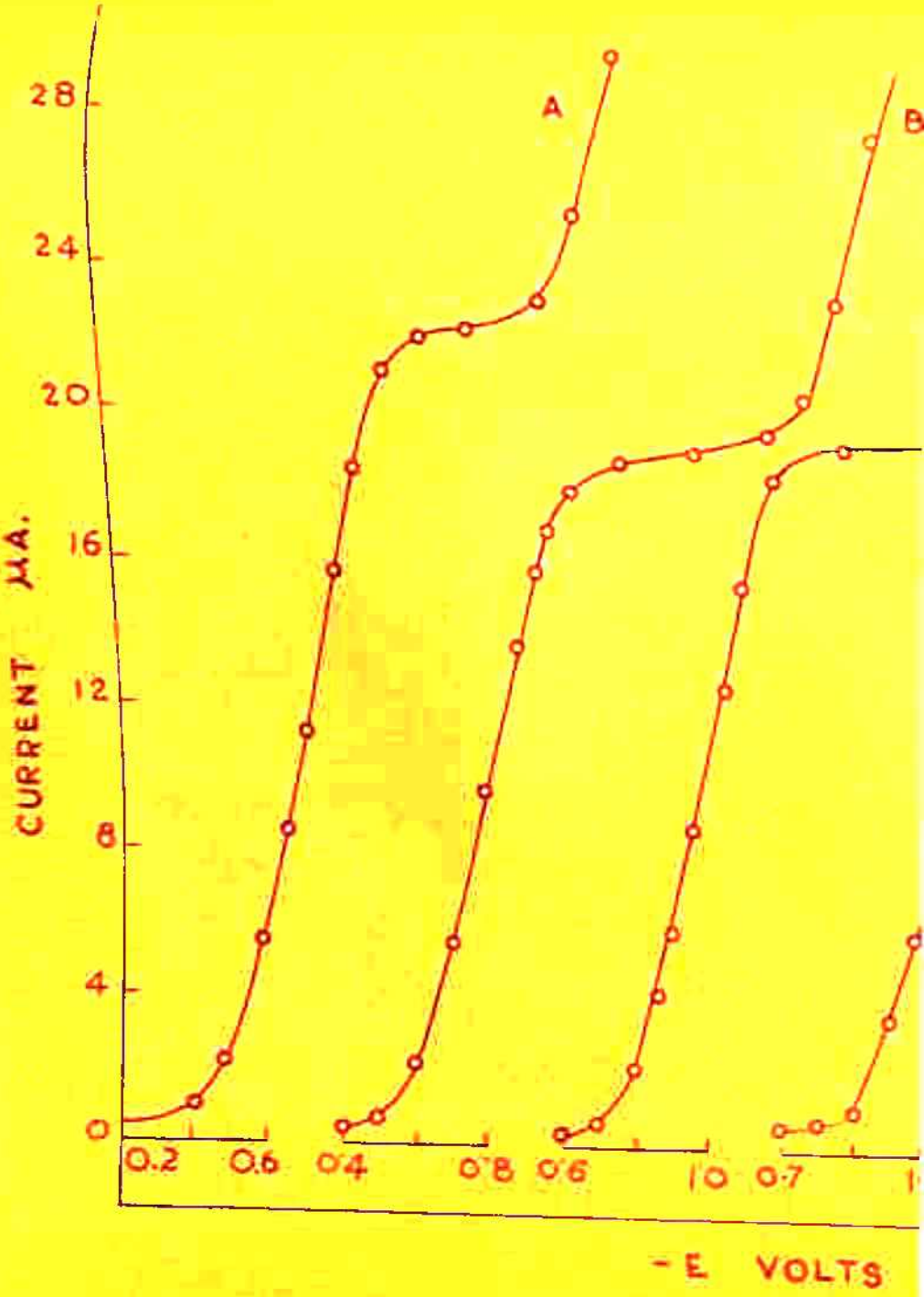
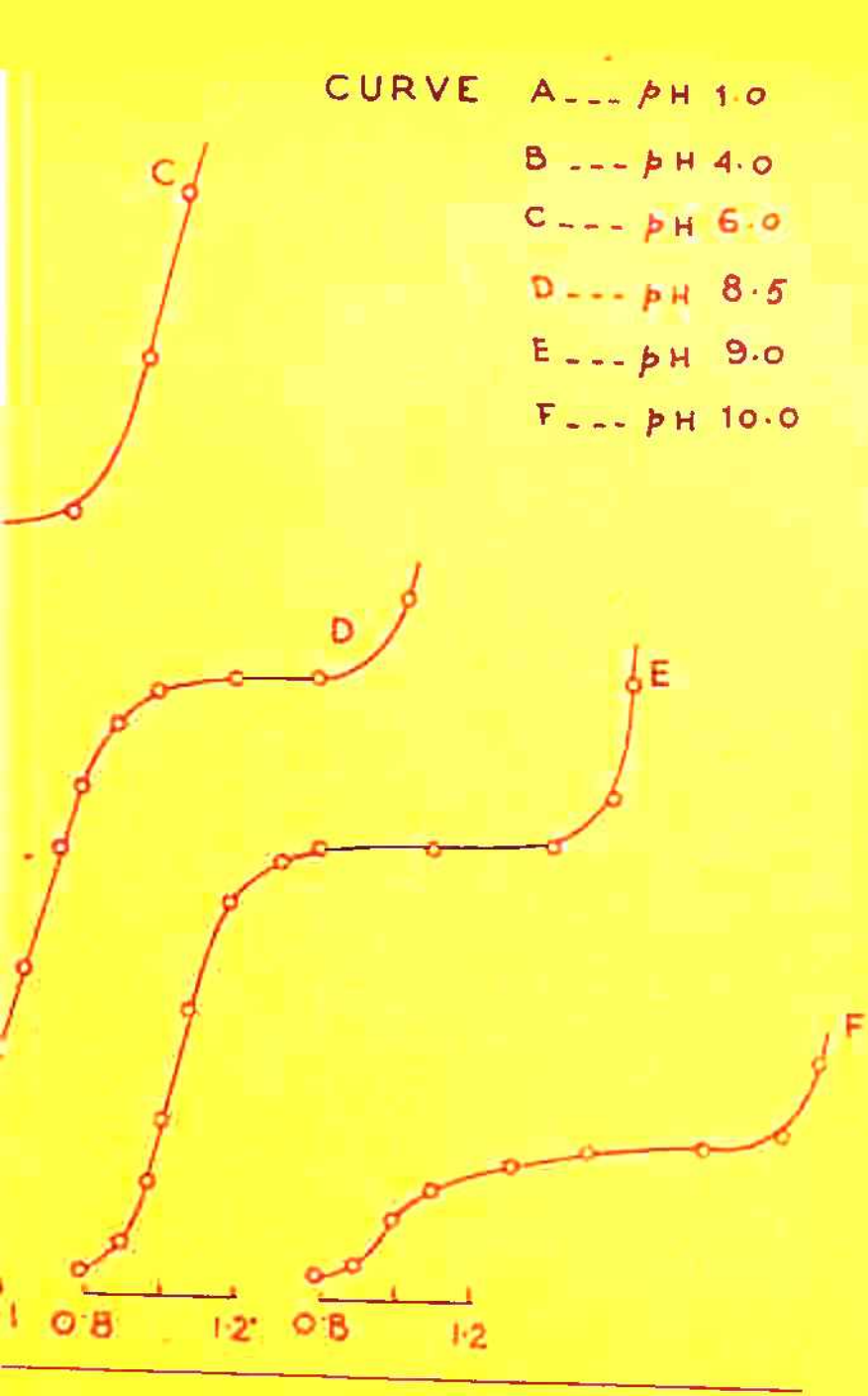


FIG. 1


CURVE A --- pH 1.0
B --- pH 4.0
C --- pH 6.0
D --- pH 8.5
E --- pH 9.0
F --- pH 10.0
C
D
E
F
0·8
1·2
0·8
1·2
S.C.E.

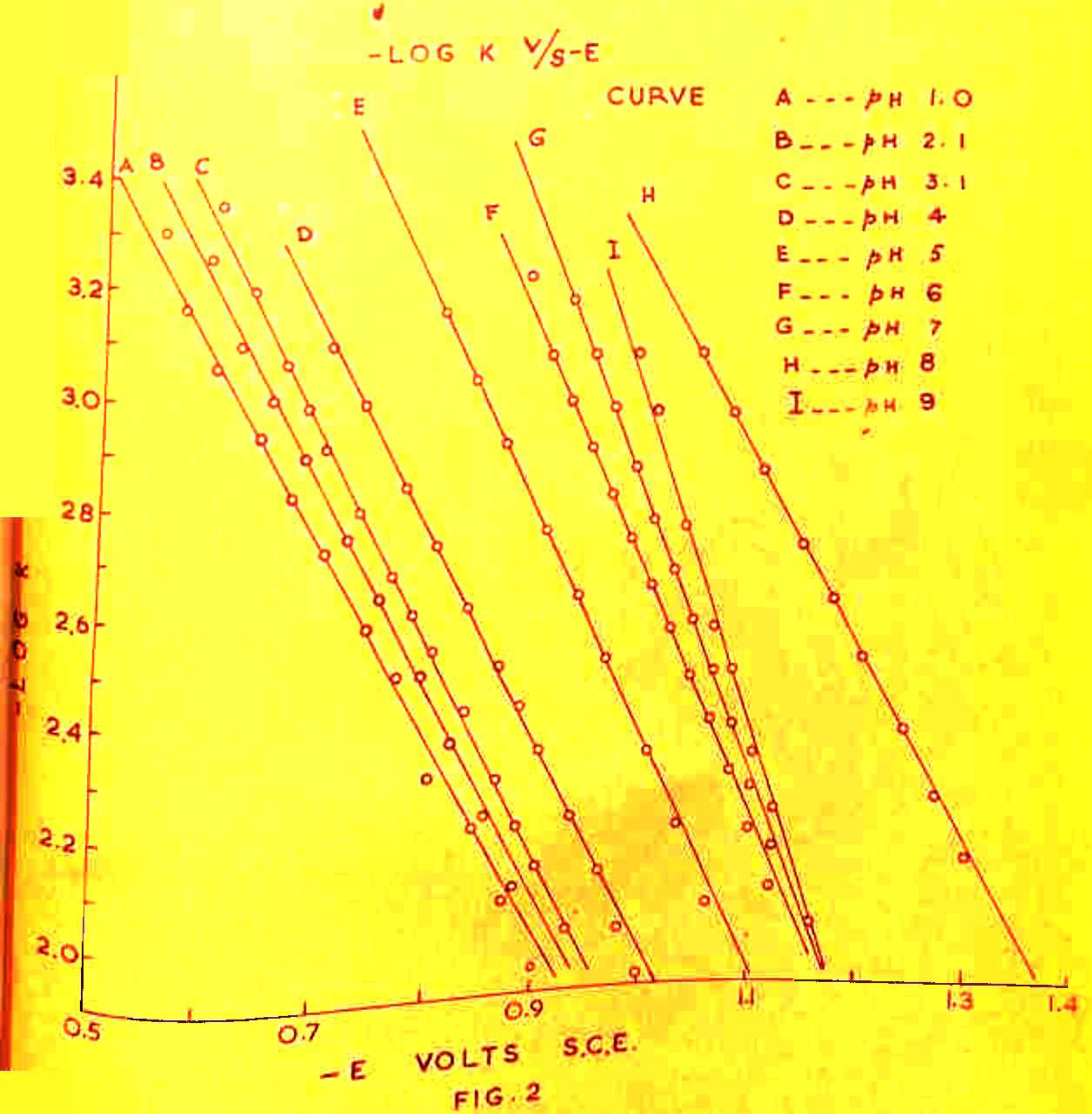

-LOG K V/S-E
CURVE
A --- pH 1.0
B --- pH 2.1
C --- pH 3.1
D --- pH 4
E --- pH 5
F --- pH 6
G --- pH 7
H --- pH 8
I --- pH 9
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
0.5
0.7
0.9
1.1
1.3
1.4
-E VOLTS S.C.E.

FIG. 2

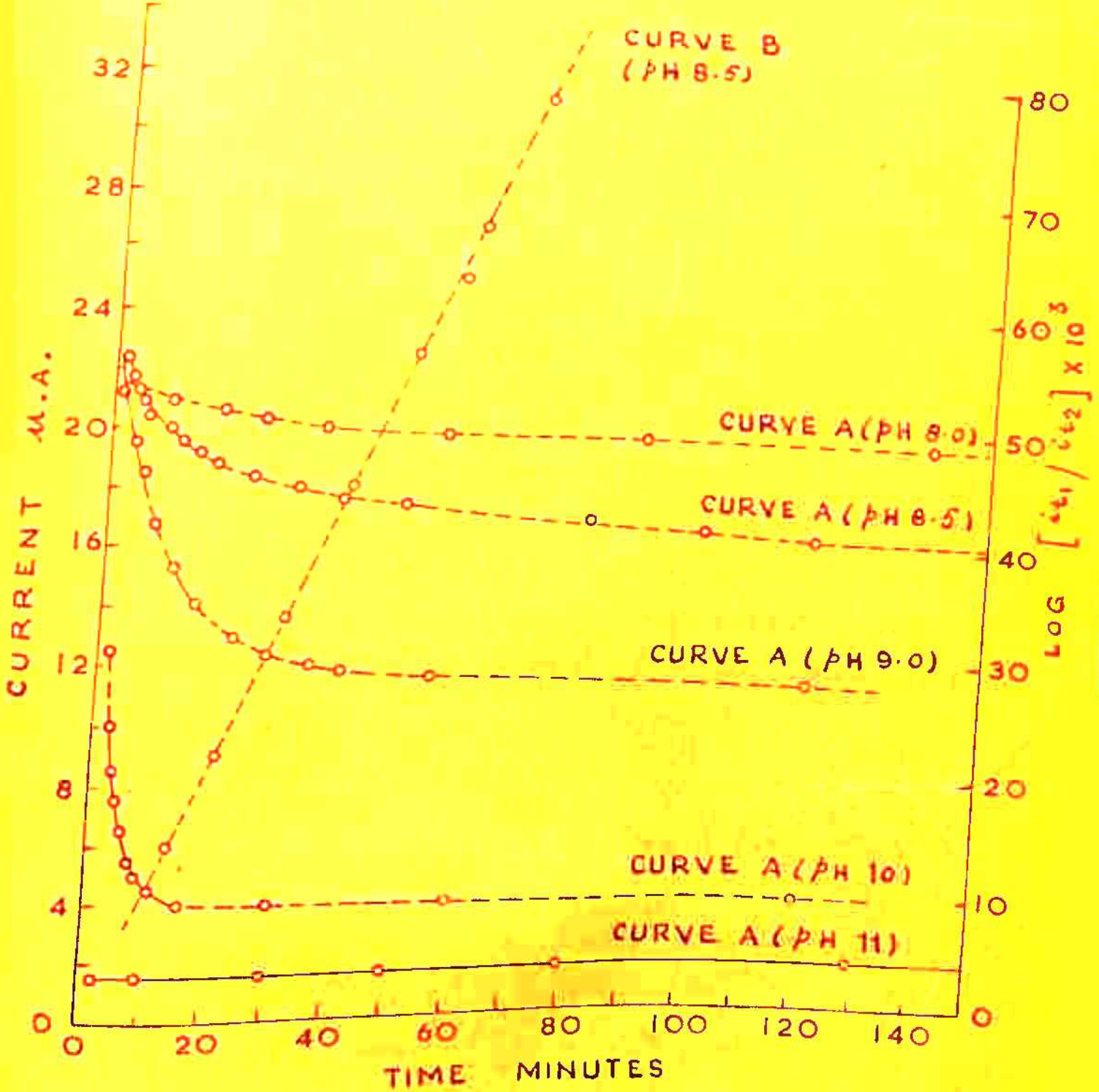

CURVE B
(PH 8.5)
CURVE A (PH 8.0)
CURVE A (PH 8.5)
CURVE A (PH 9.0)
CURVE A (PH 10)
CURVE A (PH 11)
CURRENT M.A.
LOG [i_{d_1} / $C_{Cd^{++}}$] X 10^3
TIME MINUTES
0
4
8
12
16
20
24
28
32
0
10
20
30
40
50
60
70
80
0
20
40
60
80
100
120
140

FIG. 3

III KINETICS OF THE CONVERSION OF 5-NITRO-ACE-NAPHTHENE INTO THE ACI-FORM

The present investigation is a polarographic study of the kinetics of conversion of 5-nitro-ace-naphthene into the aci-form in solution, on which no data are available in literature.

Experimental

A stock solution of 5-nitro-ace-naphthene (Aldrich Chemical Comp., U.S.A., mp 102°C) was prepared in redistilled absolute alcohol. Other chemicals used were analytical reagent grade. Triton X-100 (0.001%) was used as maximum suppressor. Temperature maintained throughout the experiments was 33°C. The capillary used for the dme gave m = 2.91 mg/sec., t = 3.05 sec./drop in 0.54 M-KCl (open circuit) at h = 40.0 cms (uncorrected for back pressure).

Kinetic studies were made in highly alkaline solutions since the rate of conversion was slow at pH < 11. The potential at which current was measured at regular intervals of time was that of the plateau of the second step in the reduction of 5-nitro-ace-naphthene (Chapter III, Part I).

Results and Discussion

From (I), the conversion of normal nitro-compound into

aci-form will depend on (a) concentration of the depolarizer and (b) concentration of OH^-. If OH^- is present in excess, the transformation will depend only upon the concentration of depolarizer. Fig. 1, Curve A, shows the variation of current with time in presence of excess of OH^- ions. Fairly constant values of rate constants were obtained using a second order equation (Table I). This is further confirmed from the plot of t vs. $1/(a-x)$ (in terms of current, t vs. $1/\sqrt{i_t}$) which yielded a straight line (Fig. 1, Curve B). The slope of this plot gave the value of k which agrees fairly well with the value of k obtained using a second order equation (as given below). These results are tabulated in Table II.

Thus the rate of the reaction follows the equation

$$2A \longrightarrow \text{Products},$$

with

$$\frac{dx}{dt} \propto (a-x)^2 \propto i_t,$$

where 'a' is the initial concentration of depolarizer and 'x' is the concentration converted into aci-form in time t.

This on integration gives

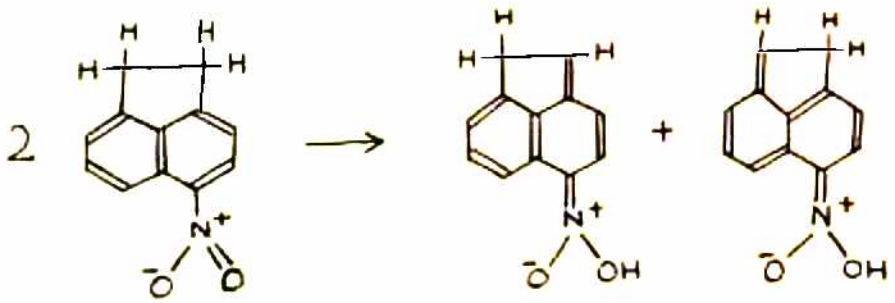
$$k = \frac{1}{t_2-t_1}\left[\frac{(a-x_1)-(a-x_2)}{(a-x_1)(a-x_2)}\right]$$

in terms of current it can be shown that

$$k = \frac{1}{t_2 - t_1}\left[\frac{\sqrt{i_{t_1}} - \sqrt{i_{t_2}}}{\sqrt{i_{t_1} i_{t_2}}}\right]$$

where i_{t_1} is current corresponding to normal nitro-compound at time t_1 and i_{t_2} is the current corresponding to normal nitro-compound at time t_2.

The reaction can probably be represented as follows:



Although the rate of transformation increased with increase of OH^-, there was no direct relationship between rate of conversion and the concentration of OH^-. Similar observations have been reported in case of nitro-paraffins[13].

The alcoholic solution of the parent compound was allowed to attain equilibrium in aqueous alkali. The product was chromatographed on a silica gel thin layer plate, whereby two distinct spots other than the parent compound were detected. R_f values of the parent compound and the two aci-forms were 0.87, 0.43 and 0.20, respectively, using chloroform as the eluant solvent. This also supports that

two different compounds are formed by the action of alkali.

Thermodynamic parameters, i.e., increase of free energy (ΔG), increase of heat content (ΔH) and increase of entropy (ΔS) for the activated complex, formed during this transformation process, have been calculated from the values of rate constants (7.68×10^{-4} and 3.63×10^{-3} concn.$^{-1}$ Min^{-1}. at 14°C and 33°C, respectively) using Eyring theory[34,35]. The values of ΔG, ΔH and ΔS are 21.44 k.cal/mole, 14.28 k.cal/mole and -23.45 cal./deg. mole, respectively at 33°C.

-x-

Table I

Rate constant (k) for the transformation of 5-nitro-acenaphthene into aci-form.

Temp. = 33°C; 0.25 M-NaOH, 1.25 mM depolarizer.

Time (Min.)	k x 10^{+3} ($conc^{-1}.min^{-1}$.)
3	3.869
5	3.911
8	3.695
10	3.849
13	3.835
15	3.656
18	3.701
20	3.616
25	3.35
27	3.383
30	3.36
35	3.35

$k_{ave.} = 3.63 \times 10^{-3}$ $conc^{-1}.min^{-1}$.

Table II

Rate constant (k) for transformation. 1.25 mM depolarizer,
Temp. = 33°C; Ionic strength (adjusted with KCl) = 0.25 M

Concn. of NaOH M	$k_{ave.}$ $conc^{-1}.min^{-1}$ from equation	k $conc^{-1}.min^{-1}$. from slope
0.10	2.58×10^{-3}	2.13×10^{-3}
0.15	2.86×10^{-3}	2.34×10^{-3}
0.25	3.63×10^{-3}	2.94×10^{-3}

Legend of the Figure

Fig. 1: Curve A, variation of current with time in 0.25 M - NaOH.

Curve B, plot of $1/\sqrt{i_t}$ vs. t (0.25 M - NaOH)

-x-

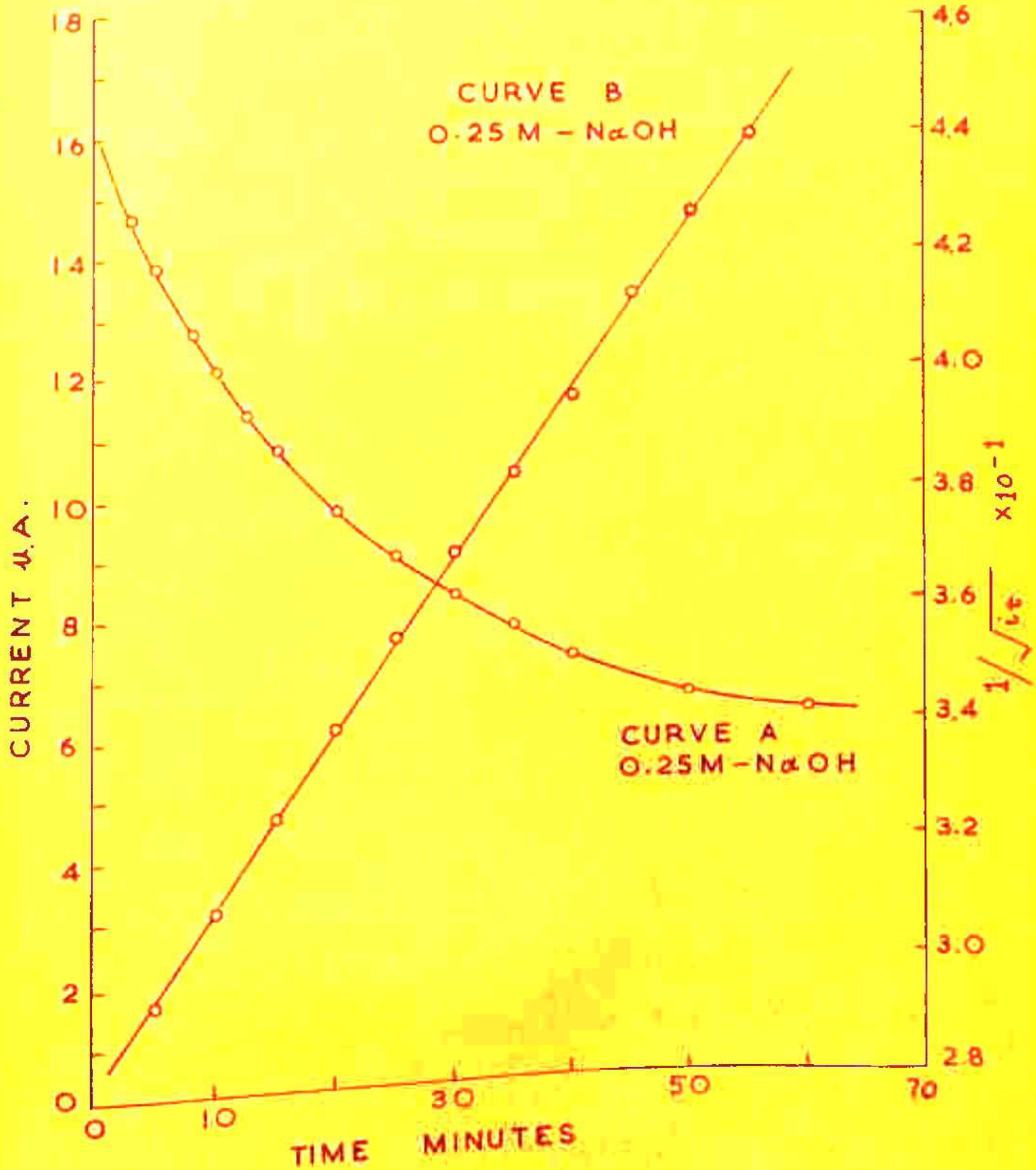

CURVE B
0·25 M – NaOH
CURVE A
0·25M – NaOH
CURRENT μA.
TIME MINUTES
0
10
30
50
70
0
2
4
6
8
10
12
14
16
18
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
4.4
4.6
X10⁻¹
1/√t

FIG. 1

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-x-

C H A P T E R VI

STUDIES ON THE INFLUENCE OF SURFACE ACTIVE SUBSTANCES ON ELECTRODE PROCESSES

Introduction

The influence of surface active substance (s.a.s.) has been a frequent subject of study. The presence of a s.a.s., even in traces has the following effects on the polarographic curves of a depolarizer; a decrease in the limiting current or even the elimination of the wave, a shift of a reduction wave towards negative and of a oxidation wave towards positive potentials, often accompanied by a depression of the limiting current, a splitting of a single wave into two waves and a minimum in the limiting current. These effects are classified as inhibitions of the electrode process. On the other hand, adsorbed substances may, sometimes, accelerate the electrode process. Under this heading fall the effects shown by a series of compounds that lower the hydrogen over potential and the effects observed during the reduction of week organic acid anions and of other reducible anions[1].

Following are the two different mechanisms for influencing the depolarization process, depending on the type of adsorbate. In the presence of an uncharged s.a.s. it is mostly a steric effect, but with charged adsorbable substances there is an additional electric effect (change of ψ potential) reinforcing the steric inhibitor when the charges on the depolarizer and on the adsorbed ion have the same sign and opposing it when the signs are different.

less attention has been paid to the influence of s.a.s. on organic depolarizers. Their presence here can affect the number and the shape of the waves, the half-wave potentials and the reduction mechanism of reversible and especially of irreversible processes. The inhibitory effect of eosin on the polarographic reversible behaviour of some quinones has already been described by K. Wiesner[2]. It depresses limiting current of the reversible cathodic wave for the quinone without affecting the $E_{0.5}$. Additional more negative wave can be observed, which corresponds to the inhibited reduction at the covered surface. In irreversible reductions, both steric inhibition by the film and electric effects due to a change in the ζ-potential of the electric double layer (for ionic s.a.s.) can operate. These facts have been pointed out by a number of authors[3-11].

Remarkable results were obtained in an investigation of surface-active-substance on the reduction of nitro-compounds. L. Holleck[12] et al. studied the polarographic reduction of p-nitro-aniline in solutions of different pH with varying concentration of tylose, gelatin and agar. These agents do not only suppress maximum but also alter the mechanism of the process. This is demonstrated by the formation of definite steps in the polarographic curve, the relative height of which depends on the kind of s.a.s. used. Studies were also made of the effect of tylose on the reduction of m-nitrobenzoic

acid and para and meta nitrobenzaldehyde at different pH. The effects varied, depending on the nature and configuration of the reacting materials.

Effect of gelatin on the polarographic waves of para- and ortho- nitroanilines was taken by N.Tanaka[13] et al. At pH 8.8 the addition of more than 0.01% gelatin to a solution containing para or ortho nitroaniline causes the wave to split into two waves separated by 0.3 to 0.4 volt. With increasing concentration the ratio of the height of the new second wave to that of the 1st wave increases, at any particular gelation concentration this ratio is larger for para compound. This permits a simultaneous determination (to ± 10%) of the two compounds in their mixtures.

L. Holleck[14] et al. studied the effect of camphor on the reduction of p-nitroaniline and observed that the addition of increasing amounts of camphor to para-nitroaniline solutions at pH of 2.8, 7 and 11, tends to a limiting value for the height of the 1st plateau of the polarogram. This height decreases with increasing pH. At pH 11, the height of the 1st stage is about 1/6 of the total height.

L. Holleck[15,16] reported that the deformation of the polarographic current-voltage curves, resulting from the addition of materials active in lowering surface tension to solutions of aromatic nitro-compounds, leads to the conclusion on

the nature of the intermediate radicals arising during cathodic reduction. These are weak acids which exist in equilibrium with the corresponding acid anion

$$R - NO_2H \rightleftharpoons R - NO_2^- + H^+.$$

L.Holleck[17] et al. has suggested that inhibitors (camphor) in the reduction of nitro-compounds act by slowing up the penetration reaction, based on examination of the current-time curves of the polarographic single drop. The cessation of inhibition at certain potentials depends not only on the potential dependence of the adsorption equilibrium but also on a delayed equilibrium.

During the studies of s.a.s. on para-nitrochlorobenzene, Holleck[17] et al. reported that cyclopentanone oxime, belzaldoxime, valeronitrile, benzonitrile, para-tolunitrile, dibenzylsulfoxide, diphenyl sulfoxide and dibenzyl sulfide (listed in increasing activity) acted as inhibitors on the polarographic reduction of para-nitrochlorobenzene, causing its wave to split into two waves, the $E_{0.5}$ of this 2nd wave was

$$E_{0.5} = \text{const.} - \frac{x}{\alpha \log C_{inh.}},$$

where $C_{inh.}$ is the concentration of inhibitor and x and α are specific constants; x = space required by depolarizer particle/space required by an inhibitor particle.

Inhibiting action of s.a.s. on the polarographic behaviour of nitronaphthols was taken up by L. Holleck and D. Jannakoudakis[18]. The addition of 0.1% triphenylphosphime oxide has no effect at pH 4, but decreases the wave height at pH 7 to 10, giving no wave at pH 12. The addition of camphor and tylose has no effect at pH 4, but depresses the diffusion current at pH 7 to 9. Naphthol has no effect on $E_{0.5}$ or diffusion current.

B. Jakuszewski[19] took 1-(4-phenyl-3-sulfophenyl)-3-heptadencyl-5-pyrazolone as anionic-active and (stearamido ethyl) tri-methyl ammonium methyl sulfate as the cation-active agent. Separation of polarographic waves of nitrobenzene in alkaline solutions took place only in the presence of anion-active substances or of compounds containing negative groups.

S. Hacobian[20] et al. have taken up the effects of pH and inhibitors on d.c. and sine wave polarographic studies of ortho, meta and para- nitrophenols. Pietrzyk and Rogers[5] have used dedecyltrimethylammonium chloride as s.a.s. to study its effect on the polarographic reduction of nitrobenzene, para-chloronitrobenzene, ortho and para-nitroanisole, o-nitrophenol, methyl-p-nitrobenzoate and p-nitrobenzaldehyde. In acidic solution, the two waves for each compound were shifted in a more cathodic direction, the 2nd being shifted 600 mV. or more. In basic solutions, large shifts towards less cathodic potentials were found in the 2nd wave for several nitro-compounds.

These anodic and cathodic shifts gave an application to analyses of mixtures.

From this available literature on effect of s.a.s. on the reduction of nitro-group, it is evident that in the reduction of aromatic nitro-compounds in alkaline solution, the first electron reduction step, associated with the uptake of the electron, is not inhibited by surface active substance. In the presence of s.a.s. (camphor), only the subsequent electrode process involving three or five electrons (with aniline) is inhibited; this reduction corresponds with the formation of a substituted hydroxylamine or amine. The inhibition causes a splitting of the original single wave into two waves. The first electron wave appears at the original potential whilst the second wave is displaced to more negative potentials. The shift depends on the kind and on the concentration of the s.a.s. It is remarkable that this effect can be achieved by certain s.a.s. (diphenyl-sulphoxide and tri-phenyl-phosphine) even in anhydrous methanol[21].

In acidic media, in which the group is protonated, the s.a.s. hinders the uptake of even the first electron and the whole wave for nitroaniline, for example, is shifted to more negative potentials. The initial one electron reduction of the unprotonated molecule produces an anionic radical

$$R - NO_2 + 1\bar{e} \rightleftharpoons R\text{-}NO_2^- \qquad (I)$$

which appears to be stabilized by the presence of the s.a.s. This process is reversible with a half-wave potential between -0.6 to -0.9 volt (vs. S.C.E.), depending upon the substituent in the benzene nucleus. This radical can reduce chemically certain inorganic anions, such as periodate, the electrode reduction of which is completely hindered in the presence of s.a.s.[22]. A typical catalytic current results, in which the periodate is consumed through the reduction of the $R\text{-}NO_2$, $R\text{-}NO_2^-$ couple, leading to a current many times larger than the diffusion current for reaction (I).

This chapter gives the results obtained in the study of the behaviour of non-ionic, cationic and anionic s.a.s. on the reduction of

I 2-[N-methyl-N-(5-nitro-2-pyridyl)-amino]-ethanol

II 5-nitro-ace-naphthene

III 5-nitro-orotic acid.

at dme using conventional polarographic technique on which no data are available in literature.

Experimental

The following s.a.s. were employed in these studies:

(A) Non-ionic s.a.s.

(1) Gelatiφn (0.20%, aqueous)

(2) Triton X-100, Tx100, (0.50%, aqueous)

(3) Polyoxy ethylene (20) sorbiton monolaurate, Tween 20, (0.5%, aqueous)

(4) Polyoxy ethylene (20) sorbiton monopalmiate, Tween 40, (0.5%, aqueous)

(5) Polyoxy ethylene (20) sorbiton monooleate, Tween 80, (0.5%, aqueous)

(6) Camphor, (0.5%, ethyl alcohol).

(B) Cationic sa.s.

(1) Cetyl pyridinium bromide, C.P.B. (0.50%, aqueous)

(2) Methylene blue, M.B., (0.5%, aqueous)

(C) Anionic s.a.s.

(1) Bromo cresol purple, B.C.P., (0.4%, ethyl alcohol)

(2) Sodium lauryl sulphate, S.L.S., (0.5%, aqueous)

(3) Aerosol O.T., AOT, (0.5%, aqueous).

The capillary used for dme had the following characteristics, m = 2.931 mg/sec. (in 0.54 M-KCl, open circuit), t = 3.05 sec./drop at h = 40.0 cms (uncorrected for back pressure).

Koutecky's method was used to calculated the kinetic parameters (αn_a and $-\log k^o$) for the electrode processes.

Results and Discussion

I Effect of s.a.s. on

2-[N-methyl-N (5-nitro-2-pyridyl)-amino]-ethanol.

During the polarographic studies of this compound, it was observed that it gave the usual two steps ($4\bar{e}$, $2\bar{e}$) reduction in acidic pH and a single step ($4\bar{e}$) in weakly acidic, neutral and alkaline media. Acid pH 1.85 (HCl/KCl buffer) and alkaline (0.05 M-NaOH+0.2 M-KCl) were selected for the experimental work. At pH 1.85, 0.4 mM. of depolarizer was used (except for methylene blue, 1.0 mM. of depolarizer) to record the current-voltage curves at 35°C, whereas, the current-voltage curves in alkaline pH were recorded for 0.6 mM of depolarizer, at 33°C.

(A) Studies in acidic medium (pH 1.85)

Gelatiøn (0.002 to 0.02%) - the current-voltage curves of the depolarizer at different concentration of gelatiøn are given in Fig. 1. At 0.002% of gelation two well defined steps were recorded but with further increased concentration of gelatiøn, both the steps shifted to more cathodic potentials. At concentration of sas > 0.008% only first step remained. Half-wave potential of this shifted to more cathodic side and its height decreased with further increased concentration of s.a.s. Kinetic parameters (αn_a and $-\log k^o$) were calculated for the first step. αn_a decreased, while $-\log k^o$

increased with the increased concentration of s.a.s., showing increased irreversibility of the electrode process. Table I gives the values of αn_a and $-\log k^o$ at various concentration of gelation.

Triton X-100 (0.001 to 0.012%) - the current-voltage curves at varied concentration of Tx100 are given in Fig. 2. Along with the cathodic shift of both the steps and finally removal of the 2nd step at higher concentration (> 0.003%), an interesting point observed was that the first step showed a inflection in its lower portion, the height of which decreased with increase in concentration of the s.a.s. It was probably due to the increased stability of the product resulting from the consumption of $1\bar{e}$ by the protonated nitro-group ($R\text{-}NO_2H^+ + 1\bar{e} \rightleftharpoons R\,NO_2^- + H^+$). However, this effect which has been noted for the first time in acidic medium is different from the normal behaviour, where the whole wave shifts to more cathodic potential with increase in concentration of the s.a.s., showing thereby that the first electron addition to the protonated nitro-group is also hindered by s.a.s.[23]. The values of αn_a and $-\log k^o$ in the absence of Tx100 and in presence of 0.001% Tx100 were 0.520, 0.501 and 2.30, 2.3325, respectively, indicating that the electrode process became more irreversible in presence of s.a.s.

Camphor (0.002 to 0.026%) - the current-voltage curves at various concentration of camphor are given in Fig. 3. The

wave height of the first step, although decreased with increased concentration of s.a.s., its $E_{0.5}$ remained unchanged. The second step exhibited a marked cathodic shift and disappeared at concentration of s.a.s. > 0.018%.

Cetyl-pyridinium-bromide (0.002 to 0.018%), Fig. 4 gives the current-voltage curves for varied concentration of C.P.B. Both the steps shifted to more negative potentials, the height of the first step decreased with the increase of concentration of s.a.s. and second step disappeared at concentration >0.004%. Values of αn_a and $-\log k^o$ showed that the electrode process became more irreversible with concentration of sas (Table II).

Methylene blue (0.002 to 0.04%); Fig. 5 gives the current-voltage curves at various concentrations of M.B. A pre-wave of adsorption characteristics was noticed at all concentrations of M.B. It was due to the adsorption of the reduced form of M.B.[24,25] at dme. Along with this pre-wave, removal of the second step, the decrease in the wave height of the first step and its cathodic shift with increase in concentration of s.a.s. were observed. Kinetic parameters (αn_a and $-\log k^o$) indicated the increased irreversibility of the electrode process with increase in s.a.s. concentration (Table III).

Aerosol OT (0.002% to 0.015%) - the current-voltage

curves at varied concentration of AOT are given in Fig. 6. Behaviour of AOT was similar to that of Tx100, i.e., removal of second step and splitting of the first step into $1\bar{e}$ and $3\bar{e}$ process. Kinetic parameters (αn_a and $-\log k^o$) were 0.442 and 2.5363, respectively, at 0.002% of AOT.

Further, Figures 7 and 8 give the -log k vs. E plots for various concentrations of different s.a.s., which are linear and show single rate determining steps.

(B) Studies in alkaline medium (0.05 M-NaOH+0.2 M-KCl)

Gelatin (0.002 to 0.025%) - current-voltage curves recorded at various concentrations of gelatin are given in Fig. 9. At all concentrations of the gelatin the well defined single step appeared. This step suffered a decrease in its magnitude and its $E_{0.5}$ shifted to more negative potentials with increase in concentration of s.a.s. Kinetic parameters were calculated at 0.008%, 0.012% and 0.018% of gelatin (Table IV). The -log k vs. E plot at 0.008% yielded a straight line, whereas at the other two concentrations it showed a break indicating that the electrode process involved more than one slow step at higher concentration of gelatin.

The remaining non-ionic sas (Tx100, camphor, Tween 20, Tween 40 and Tween 80) split the single step into two (Figures 10 to 14); the wave height of the first step is 1/4th of the

total current and corresponds to the ($R\text{-}NO_2^-$) anion radical formation. Thus in alkaline pH, the first electron reduction step, associated with the uptake of one electron is not inhibited by these s.a.s. Only the subsequent electrode process involving $3\bar{e}$ is inhibited. This inhibition is the cause of splitting of the single wave into two. Kinetic parameters were calculated for 0.001% Tx100, Tween 20, Tween 40 and Tween 80 and 0.008% of camphor (Table V). The -log k vs. E plot for Tx100 showed a break, indicating that more than one rate determining step were involved. In case of the remaining s.a.s. the same plot yielded a straight line, showing single slow process which controls the rate of electrode reaction.

In presence of Aerosol OT (0.001 to 0.01%) and bromo-cresol-purple (0.002 to 0.015%), the well defined single step was recorded along with a pre-wave of adsorption characteristics (Fig. 15), which was due to the adsorption of the s.a.s. at dme. The height of the main step decreased and its $E_{0.5}$ shifted to more negative potentials with increase of s.a.s. concentration. Kinetic parameters (αn_a and -log k^o) were calculated for the reduction process in presence of 0.002, 0.004, 0.007 and 0.01% AOT. The -log k vs. E plot (for concentration of s.a.s. $>$ 0.004%) showed a break, thus at higher concentration of s.a.s. the electrode process is controlled by more than one slow step. The same plot for B.C.P. gave straight line even up to 0.01% of s.a.s. At 0.004% of AOT

and B.C.P., αn_a were 0.354 and 0.3013 and -log k^o 6.70 and 6.153, respectively.

Cetyl-pyridinium bromide (0.002 to 0.015%) distorted the wave in the upper part at concentration > 0.004%. Methylene blue (0.002 to 0.008%) gave the usual pre-wave of adsorption characteristics (Fig. 16). At higher concentration of M.B. (> 0.002%) the main wave split into two for the same reasons as observed in case of Tx100, etc., i.e., uptake of $1\bar{e}$ forming ($R\text{-}NO_2^-$) radical anion not affected but further $3\bar{e}$ addition phenomenon is inhibited by M.B. The -log k vs. E plot for C.P.B. (concentration $\leq$ 0.004%) yielded a straight line (at 0.004%, αn_a = 0.368 and -log k^o = 6.737). The same plot for M.B. even at 0.002% of s.a.s. gave a break.

Figures 17 to 20 record the plot of -log k vs. E for various s.a.s. at different concentrations.

Table I

Kinetic parameters (αn_a and -log k^o) in presence of gelatin. pH = 1.85; Temp. = 35°C; height = 40.0 cms., concentration of depolarizer = 0.4 mM.

% Gelatin	i_d μ.a.	$-E_{0.5}$ volt S.C.E.	-log k^o N.H.E.	αn_a
0.002	9.00	0.200	2.3363	0.465
0.008	8.60	0.250	2.8130	0.396
0.020	8.20	0.330	3.2926	0.370

Table II

Kinetic parameters (αn_a and -log k^o) in presence of cetyl-pyridinium bromide.

pH = 1.85; Temp. = 35°C; Height = 40.0 cms.,

Concentration of depolarizer = 0.4 mM.

% C.P.B.	i_d μ.a.	$-E_{0.5}$ Volt S.C.E.	-log k^o N.H.E.	αn_a
0.002	8.90	0.220	2.5482	0.4579
0.008	8.30	0.330	3.2460	0.3120
0.018	8.00	0.410	3.6550	0.3312

Table III

Kinetic parameters (αn_a and -log k^o) in presence of methylene blue.

pH = 1.85, Temp. = 35°C; Height = 40.0 cms., 1.0 mM depolarizer.

% M.B.	i_d μ.a.	$-E_{0.5}$ volt S.C.E.	-log k^o N.H.E.	αn_a	$i_{ads.}$* μ.a.
0.002	17.8	0.340	2.7756	0.308	0.60
0.012	17.2	0.405	3.6800	0.303	2.60
0.040	16.0	0.460	4.0567	0.322	6.00

* $i_{ads.}$ ... adsorption current.

Table IV

Kinetic parameters (αn_a and -log k^o) in presence of gelatin. (0.05 M-NaOH+0.2 M-KCl).

Temp. 33°C; Height = 40.0 cms., 0.6 mM depolarizer.

% Gelatin	i_d μ.a.	$-E_{0.5}$ volt S.C.E.	-log k^o N.H.E.	αn_a
0.008	15.4	0.920	6.163	0.3137
0.012	14.8	0.930	-log k vs. E plot	
0.018	14.5	0.960	gave a break.	
0.025	14.15	0.975		

Table V

Kinetic parameters (αn_a and -log k^o) in presence of s.a.s. (0.05M-NaOH+0.2M-KCl).

Temp. = 33°C; Height = 40.0 cms., 0.6 mM. depolarizer.

% S.A.S.	i_d μ.a.	$-E_{0.5}$ volt S.C.E.	-log k^o N.H.E.	αn_a
0.008 % Camphor	15.6	0.920	6.690	0.360
0.001 % Tween 20	15.7	0.920	6.728	0.3813
0.001 % Tween 40	15.7	0.920	6.751	0.3652
0.001 % Tween 80	15.7	0.920	6.761	0.3681

CURRENT - VOLTAGE CURVES IN ACIDIC pH

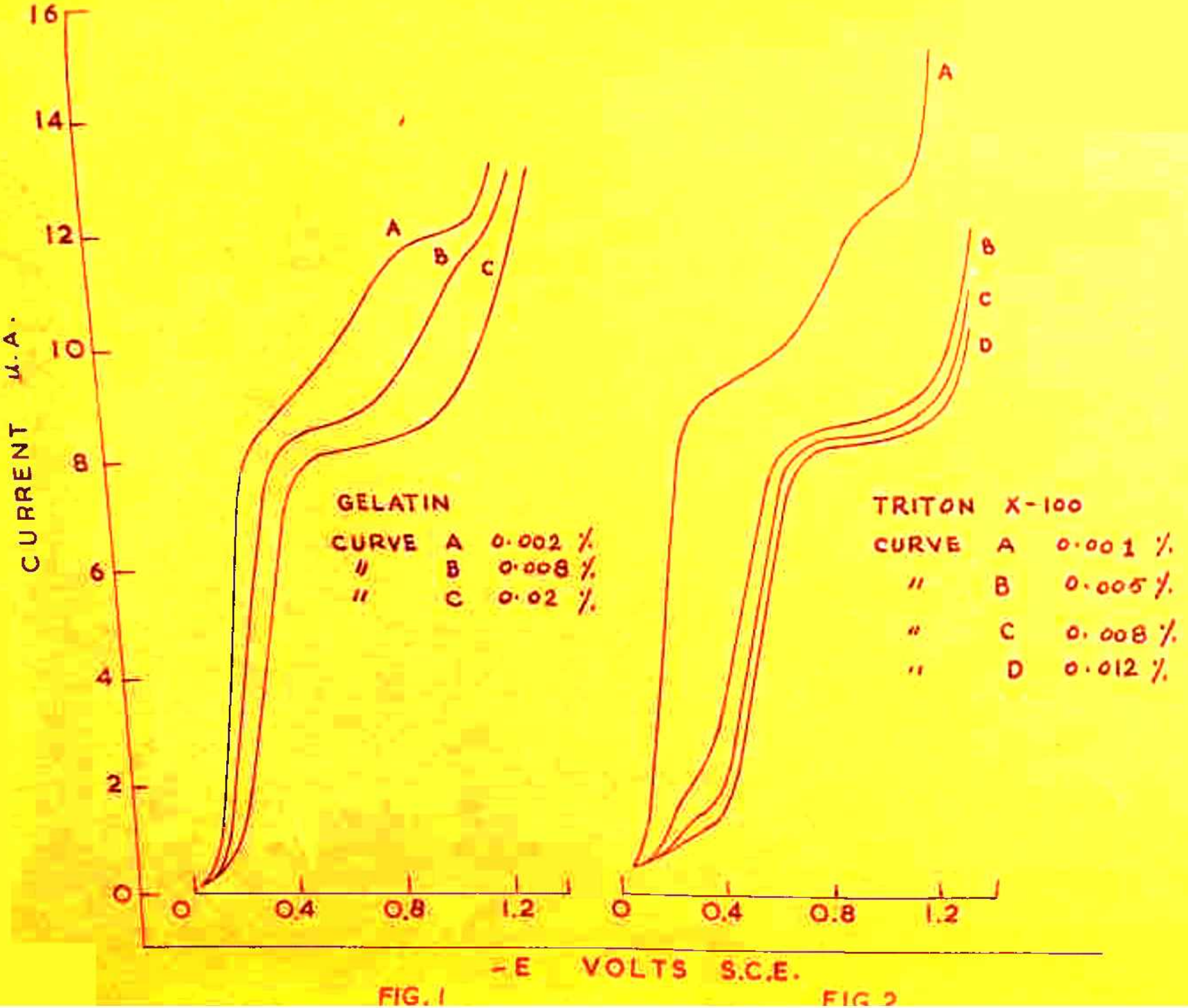


FIG. 1

FIG. 2

CURRENT - VOLTAGE CURVES IN ACIDIC pH

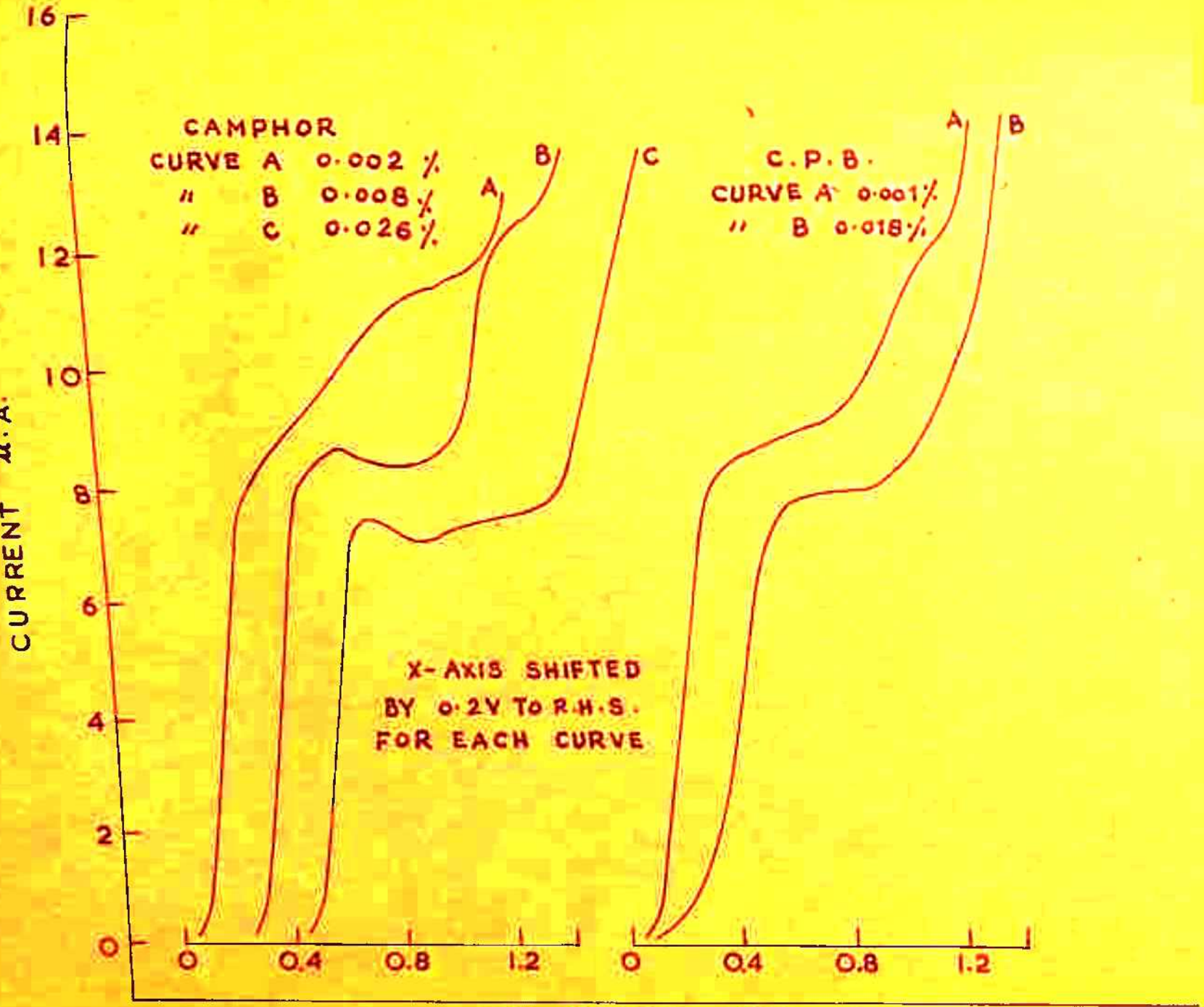


FIG. 3

FIG. 4

CURRENT - VOLTAGE CURVES IN ACIDIC PH

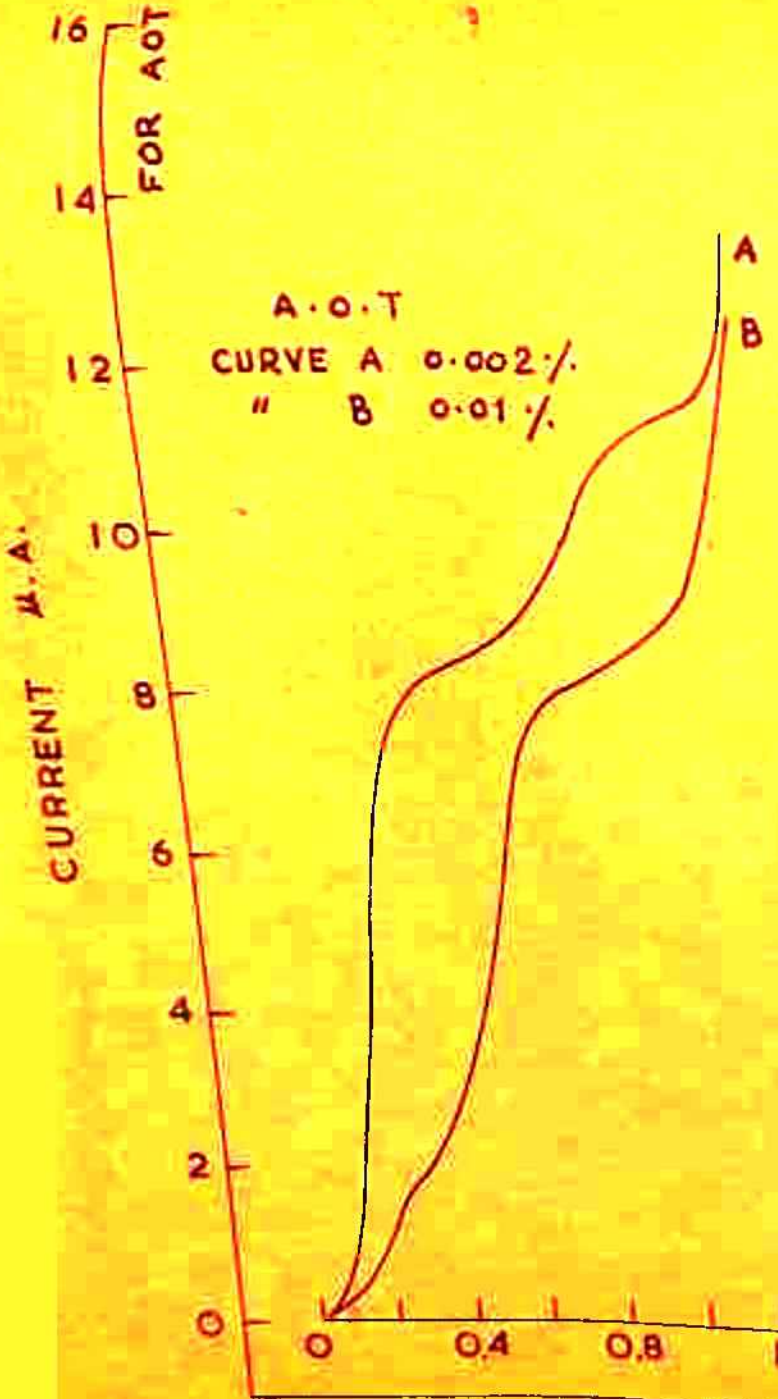


FIG. 6

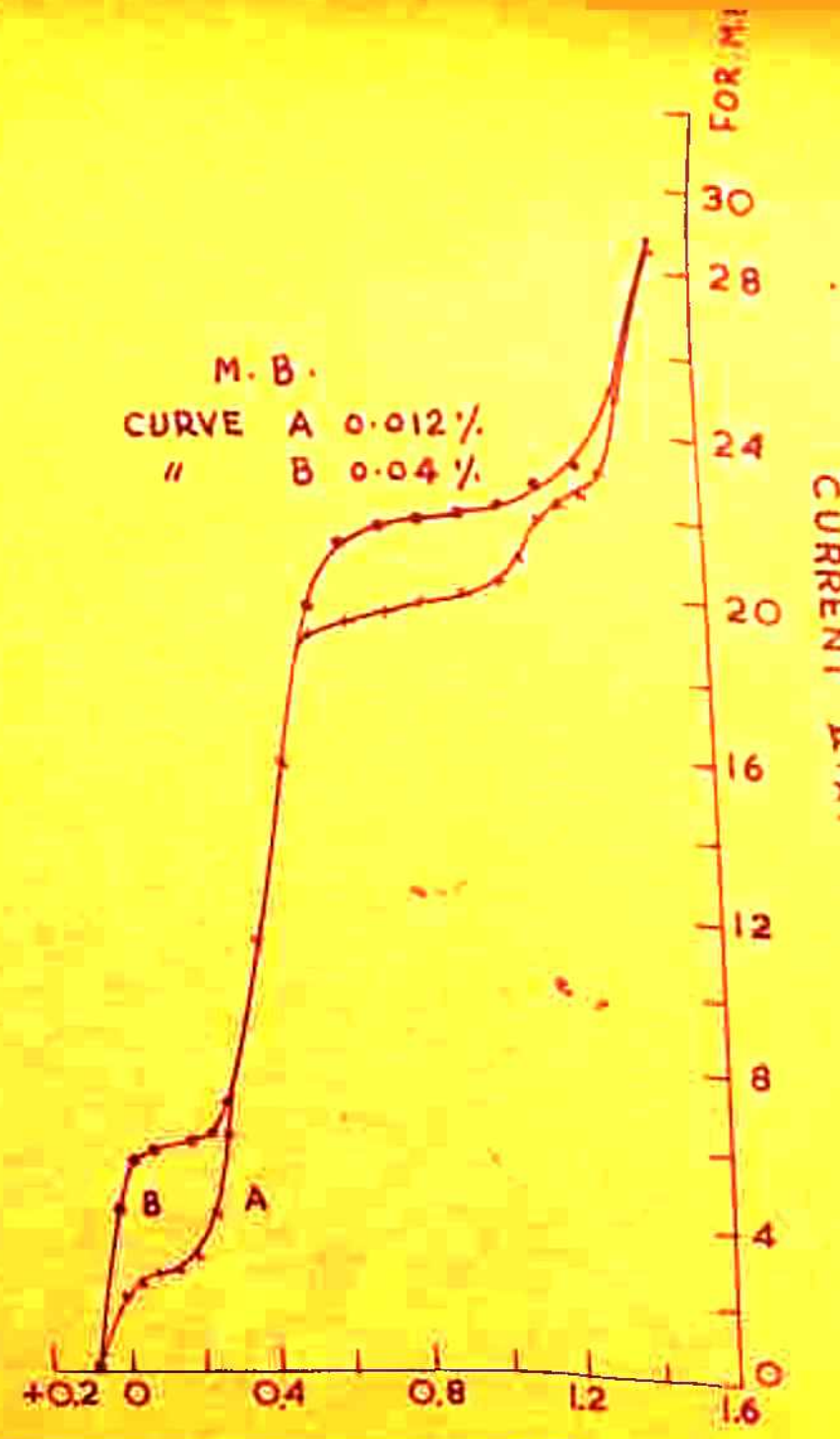


FIG. 5

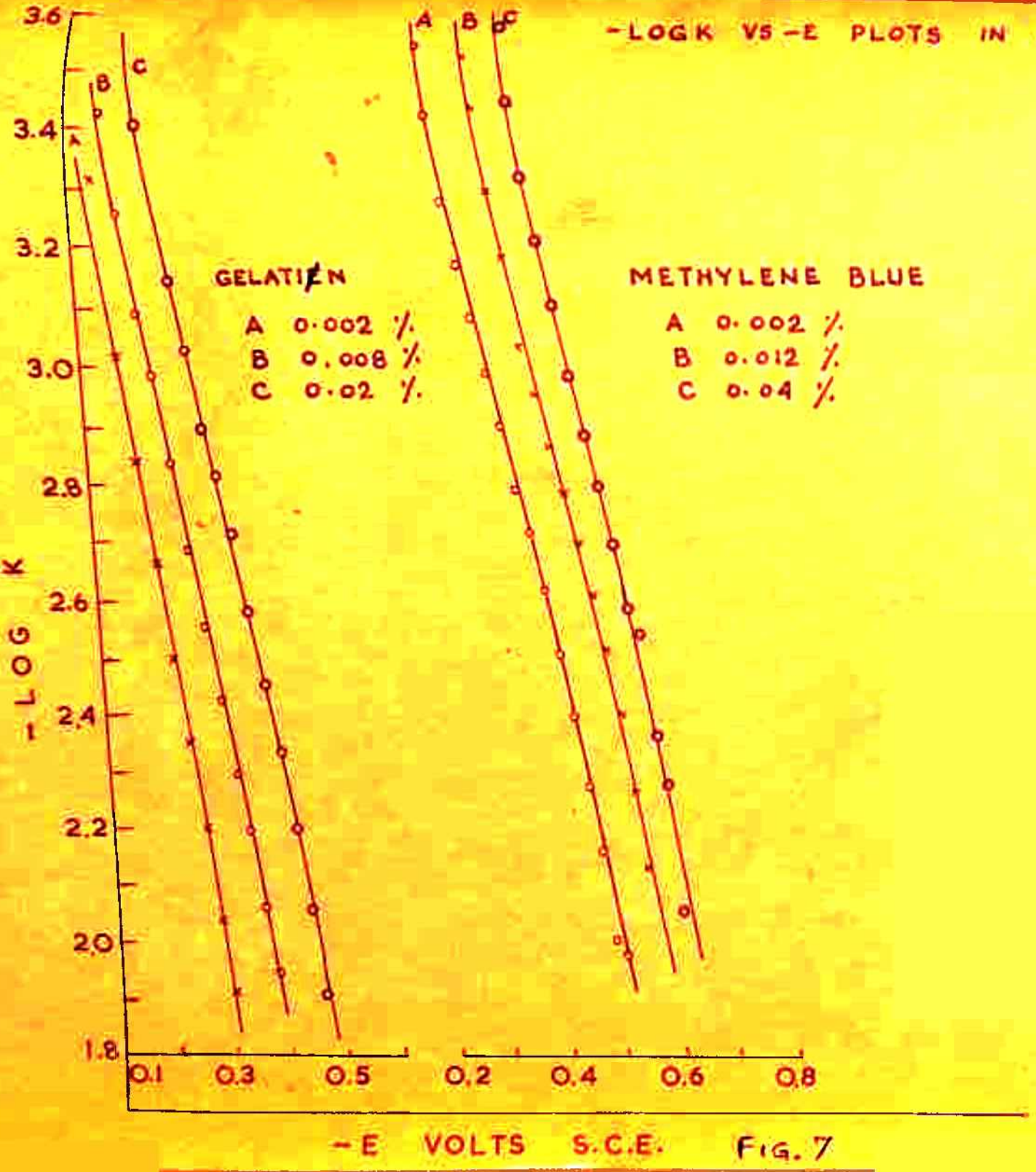

-LOG K VS -E PLOTS IN ACIDIC pH
GELATIEN
A 0·002 %.
B 0.008 %.
C 0·02 %.
METHYLENE BLUE
A 0·002 %.
B 0·012 %.
C 0·04 %.
-LOG K
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
0.1
0.3
0.5
0.2
0.4
0.6
0.8
-E VOLTS S.C.E.

FIG. 7

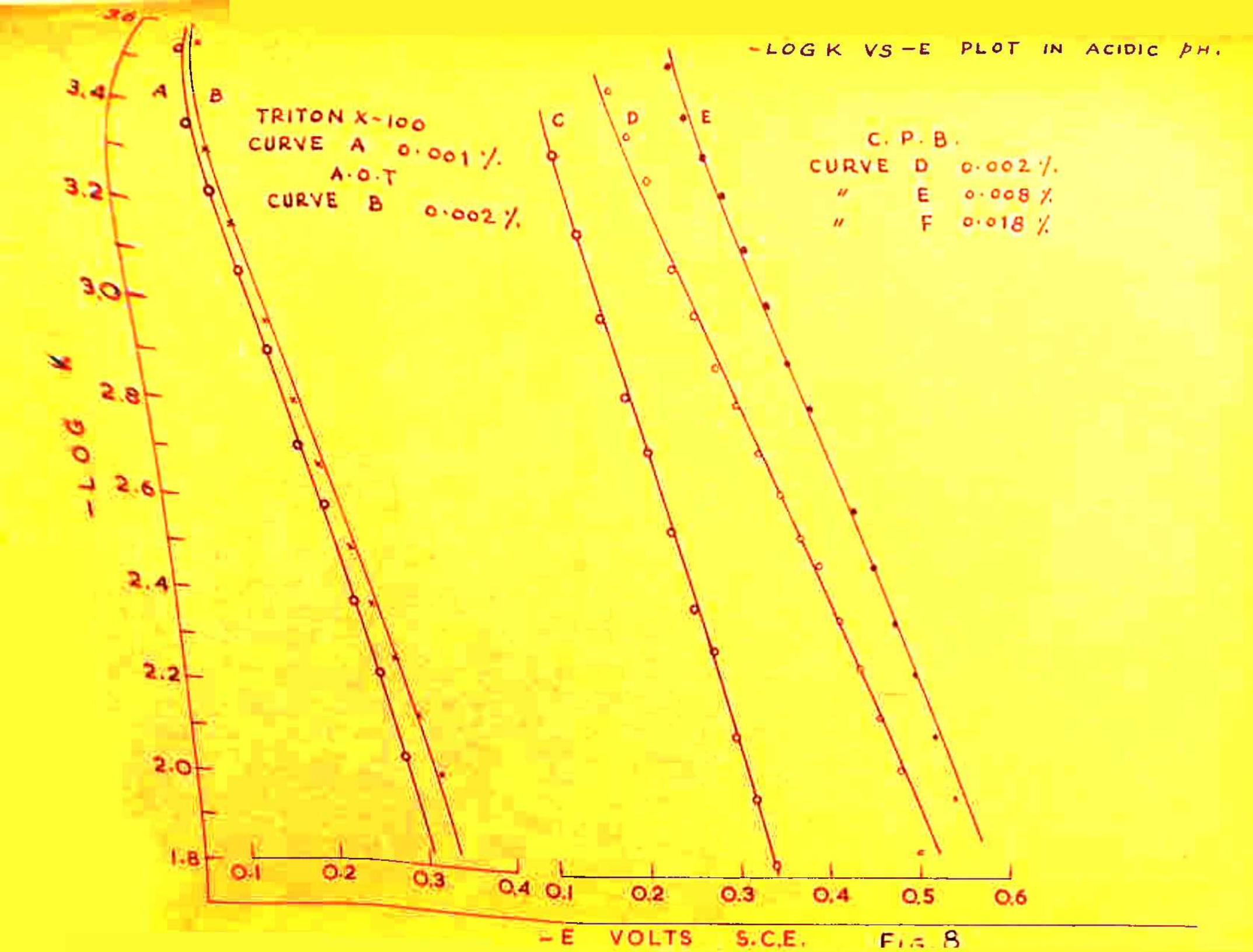

-LOG K VS -E PLOT IN ACIDIC pH.
TRITON X-100
CURVE A 0·001 %.
A·O·T
CURVE B 0·002 %.
C. P. B.
CURVE D 0·002 %.
" E 0·008 %
" F 0·018 %
A
B
C
D
E
-LOG K
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
0.1
0.2
0.3
0.4
0.1
0.2
0.3
0.4
0.5
0.6
-E VOLTS S.C.E.

Fig. 8

CURRENT - VOLTAGE CURVES IN ALKALINE pH

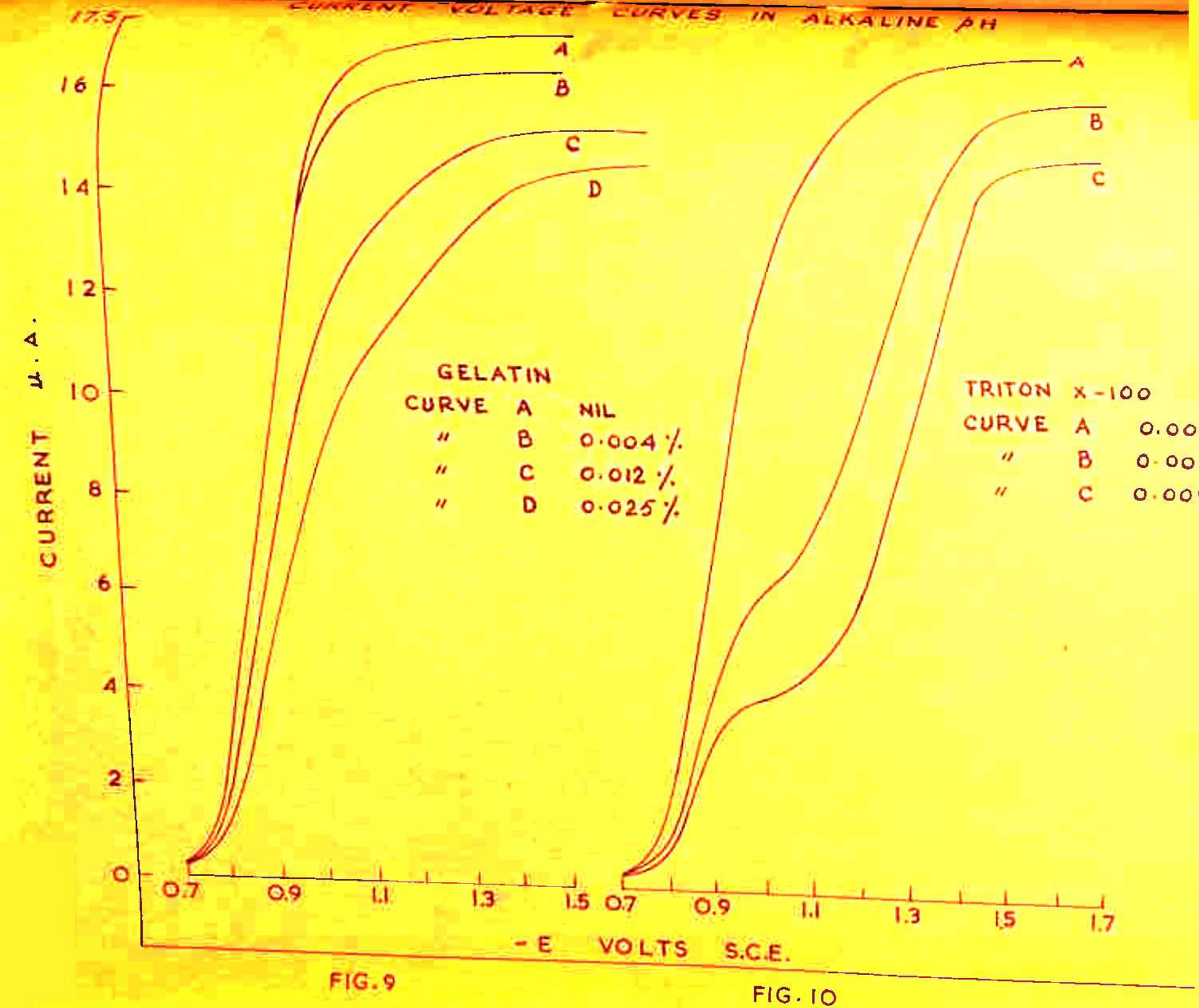
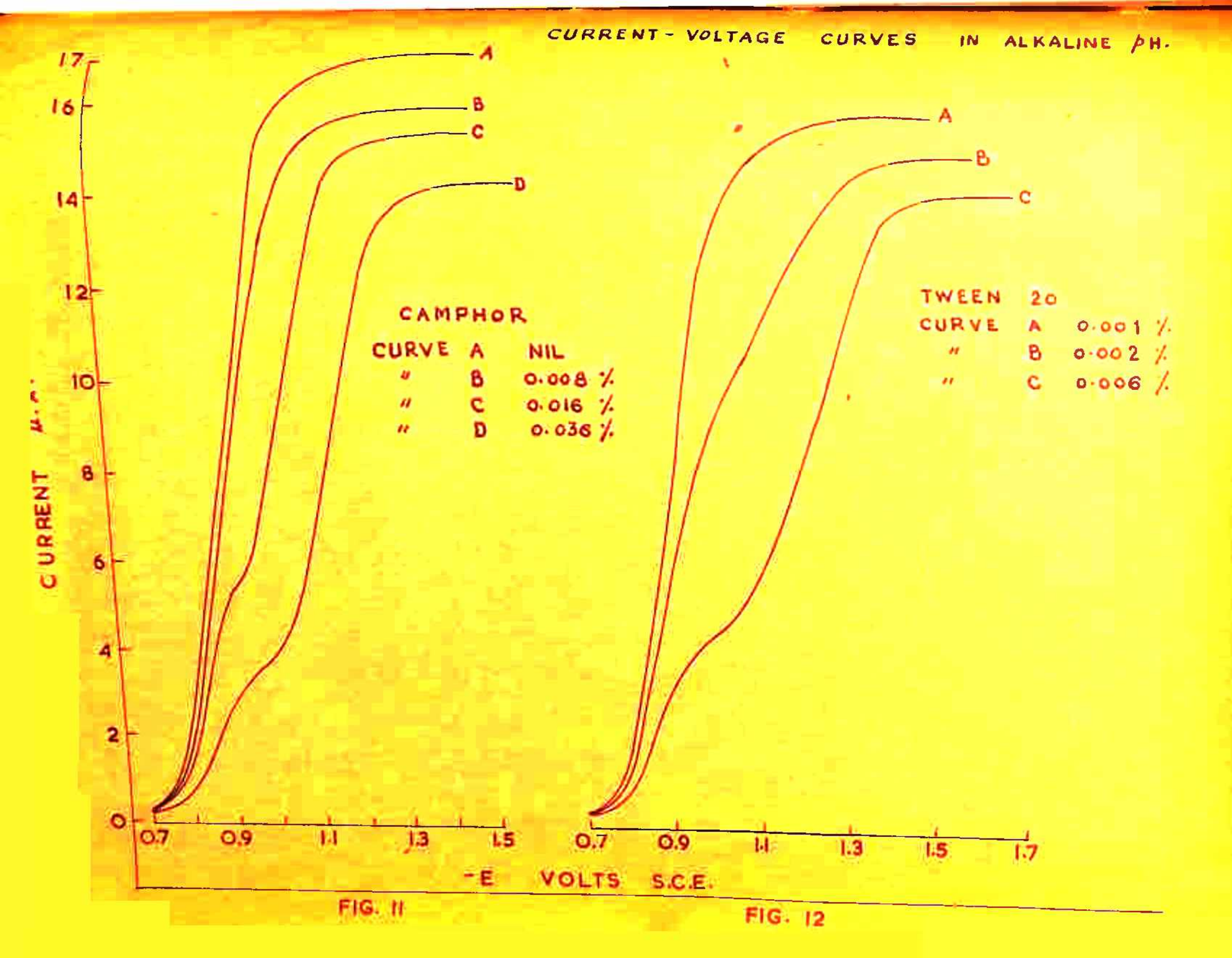


FIG. 9

FIG. 10


CURRENT - VOLTAGE CURVES IN ALKALINE pH.
CURRENT μ.a.
17
16
14
12
10
8
6
4
2
0
A
B
C
D
CAMPHOR
CURVE A NIL
" B 0.008 %
" C 0.016 %
" D 0.036 %
0.7
0.9
1.1
1.3
1.5
-E VOLTS S.C.E.
FIG. 11
A
B
C
TWEEN 20
CURVE A 0.001 %
" B 0.002 %
" C 0.006 %
0.7
0.9
1.1
1.3
1.5
1.7
FIG. 12

CURRENT - VOLTAGE CURVES IN ALKALINE PH.

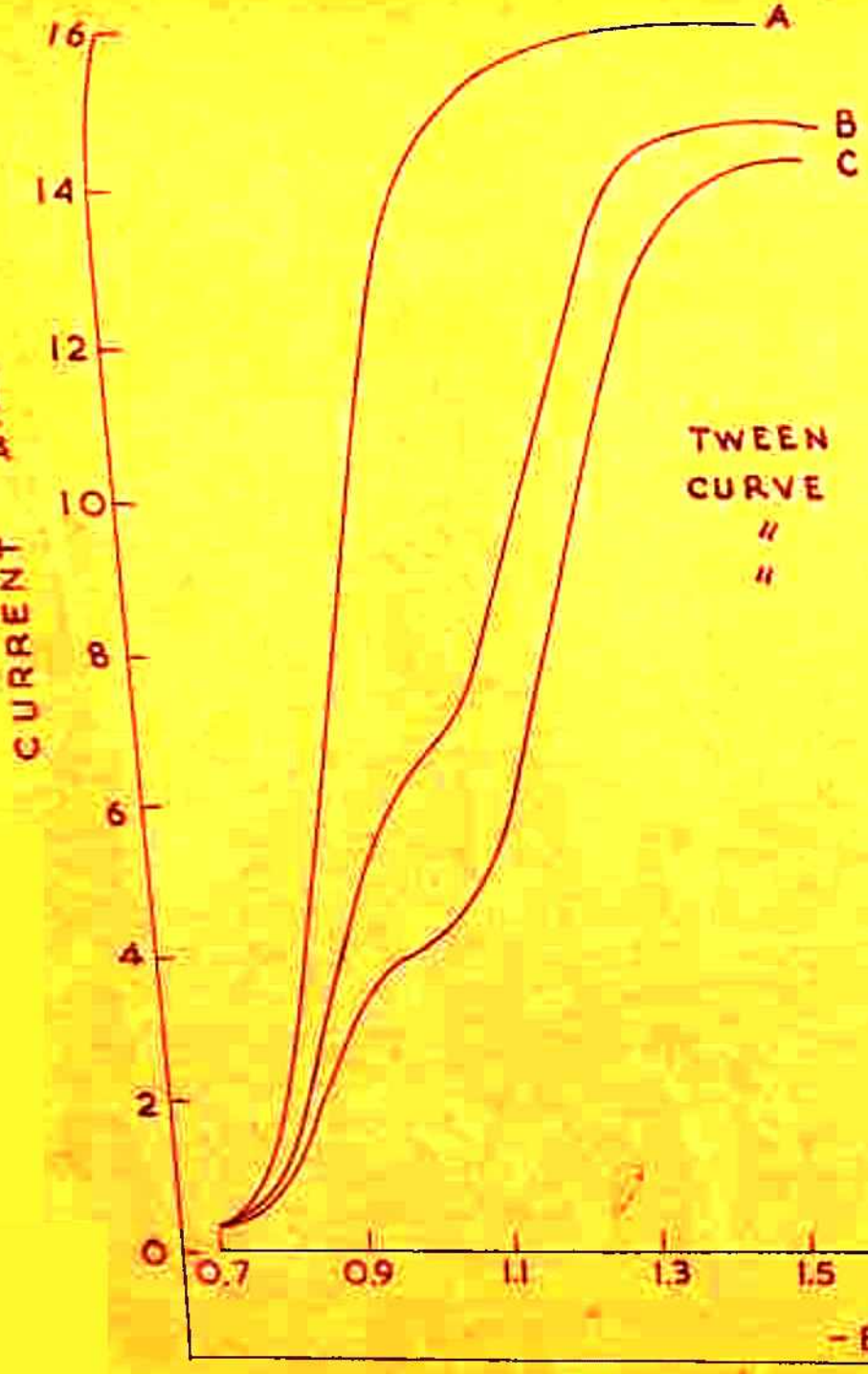


FIG. 13

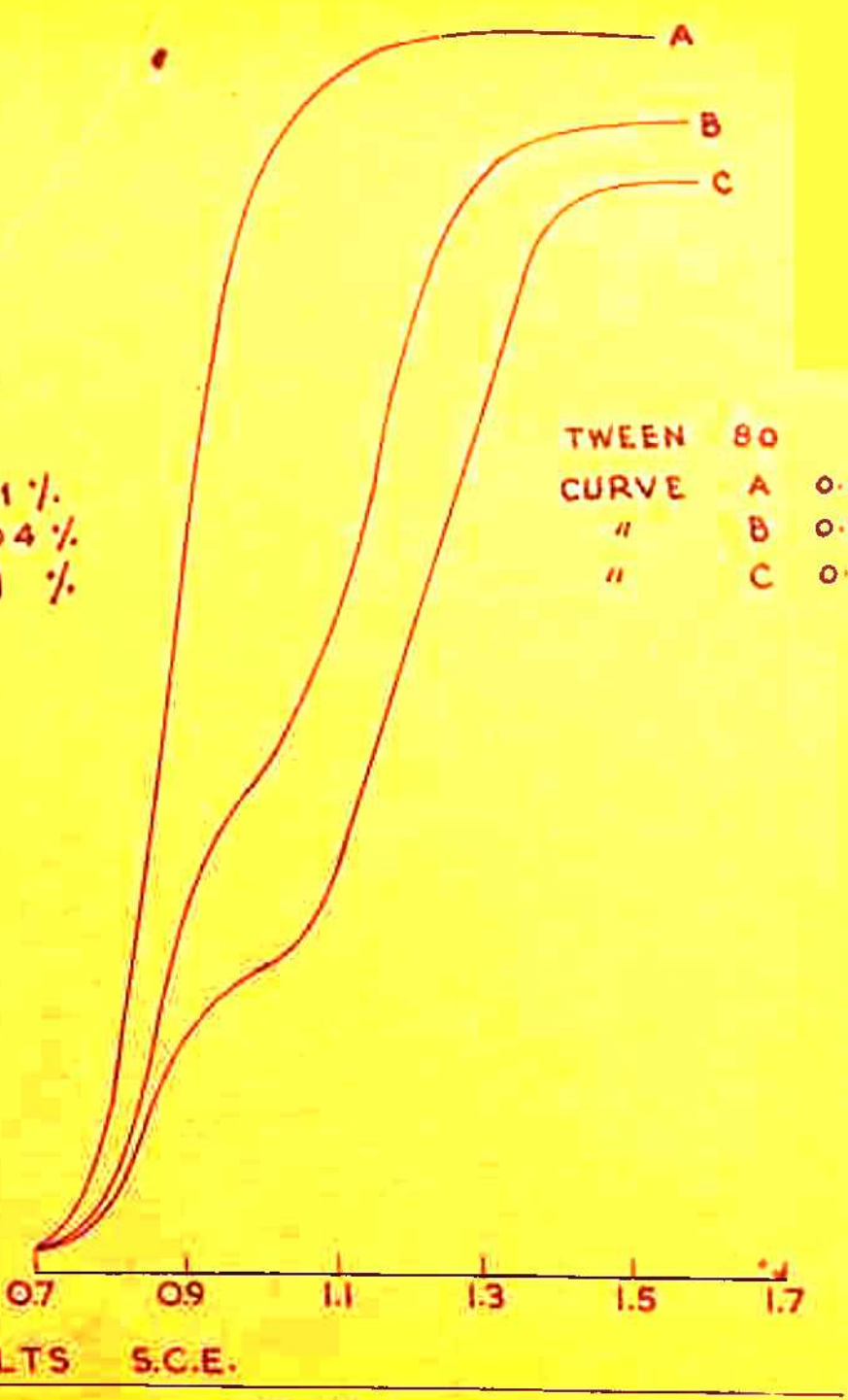
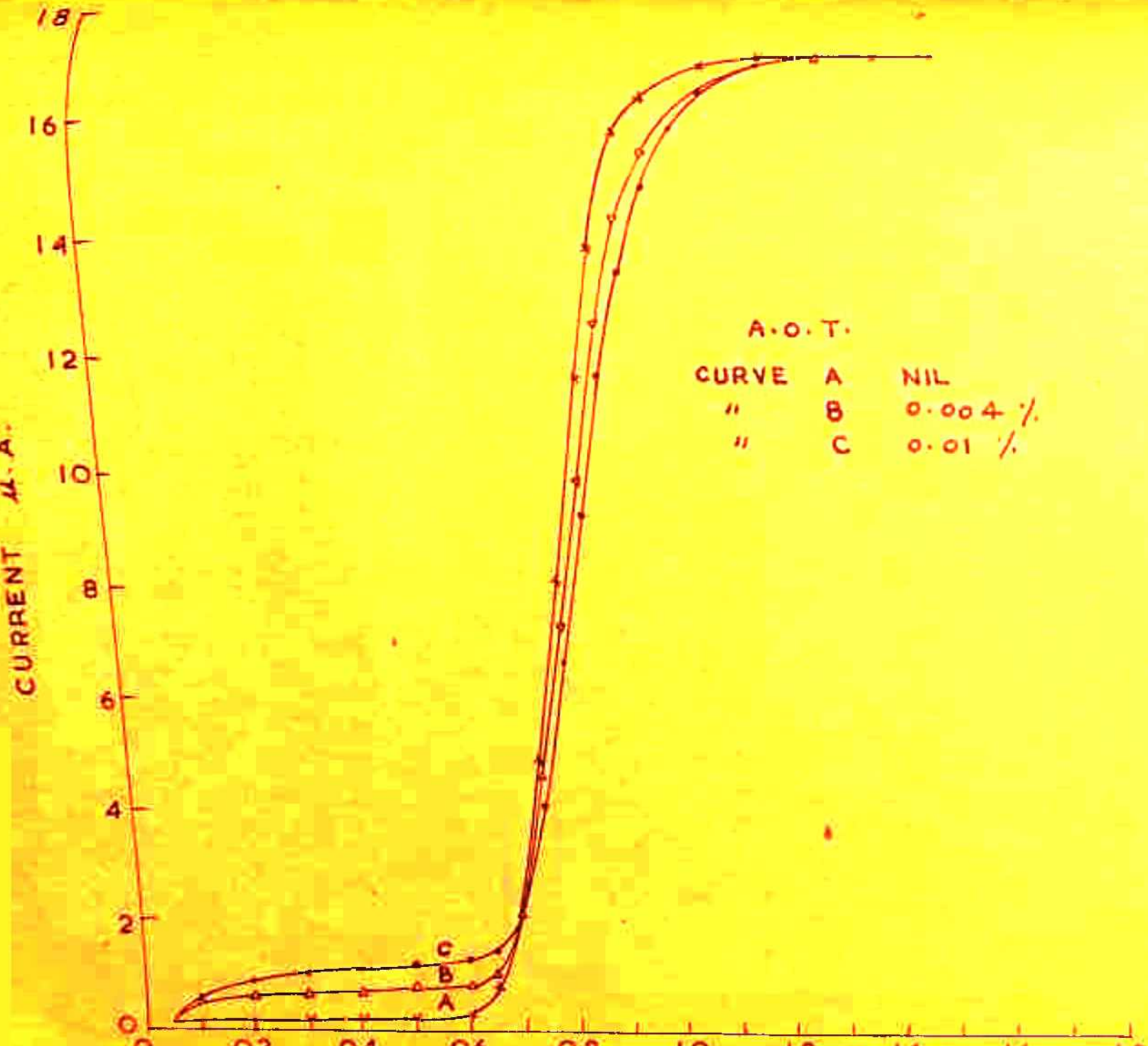


FIG. 14

CURRENT - VOLTAGE CURVES IN ALKALINE PH.



A.O.T.

CURVE A NIL

" B 0.004 %

" C 0.01 %

FIG. 15

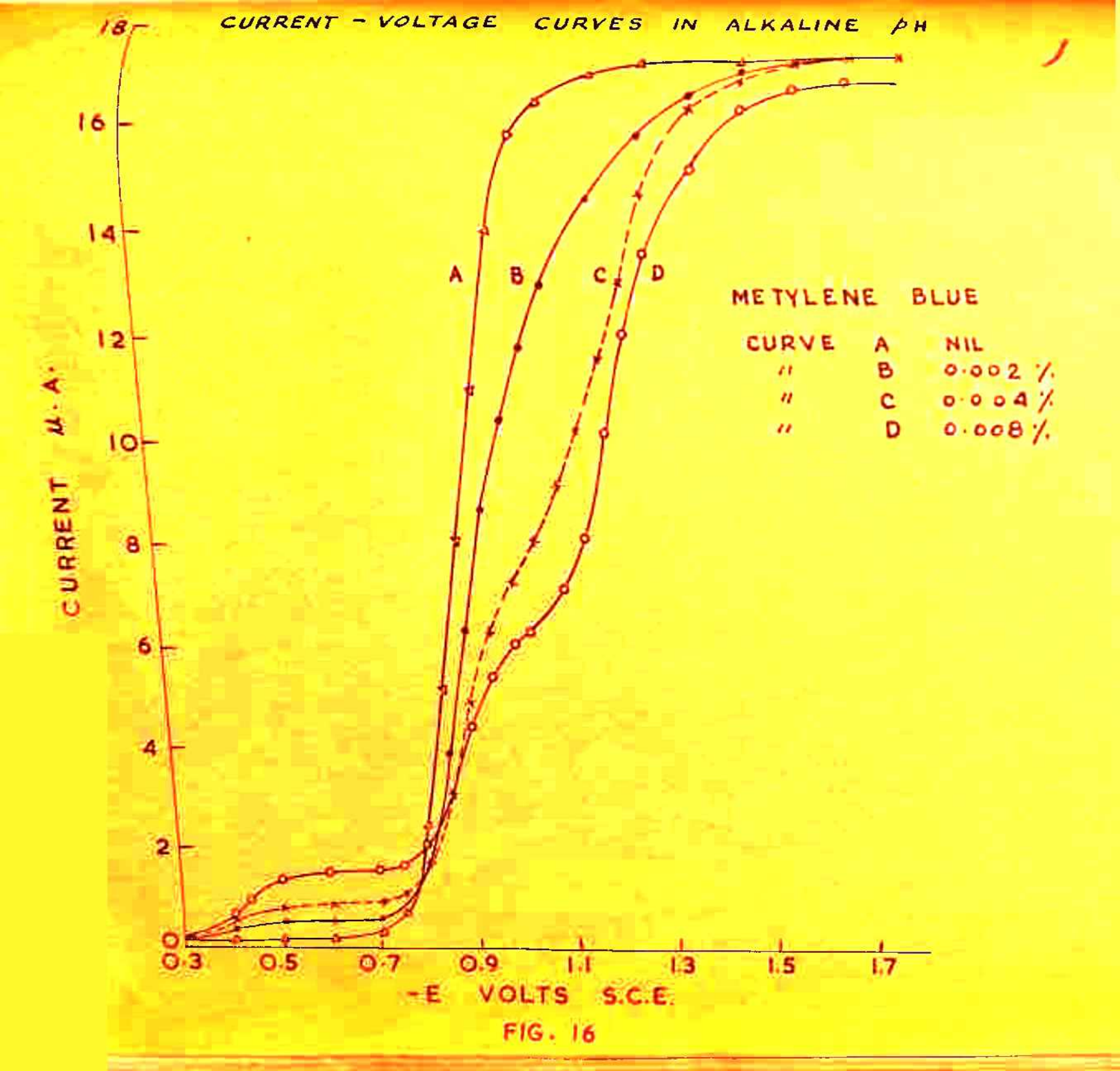
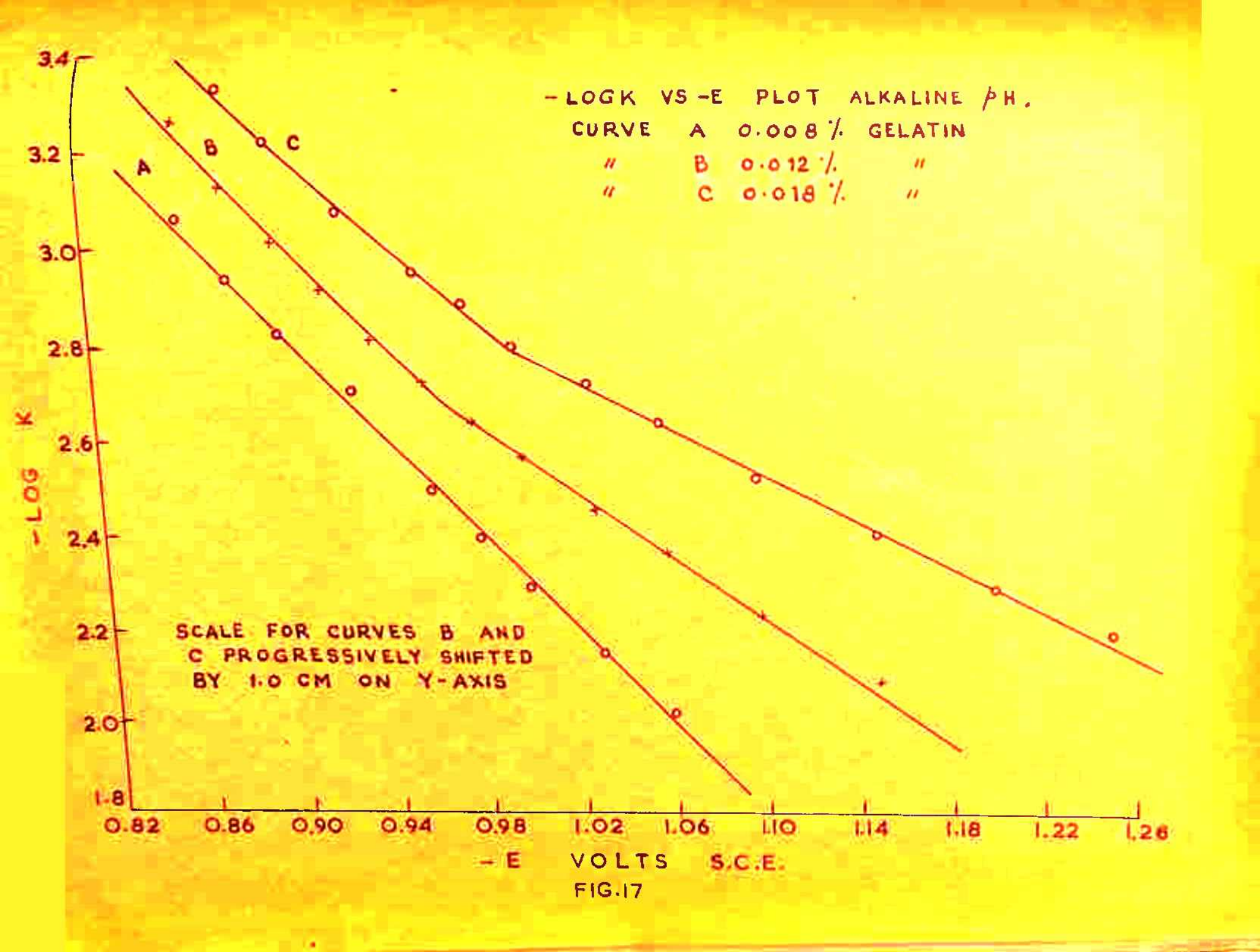

CURRENT - VOLTAGE CURVES IN ALKALINE pH
CURRENT μ.A.
18
16
14
12
10
8
6
4
2
0
0.3
0.5
0.7
0.9
1.1
1.3
1.5
1.7
-E VOLTS S.C.E.
A
B
C
D
METYLENE BLUE
CURVE A NIL
" B 0·002 %
" C 0·004 %
" D 0·008 %

FIG. 16


-LOGK VS -E PLOT ALKALINE PH.
CURVE A 0.008 % GELATIN
" B 0.012 % "
" C 0.018 % "
A
B
C
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
-LOG K
SCALE FOR CURVES B AND C PROGRESSIVELY SHIFTED BY 1.0 CM ON Y-AXIS
0.82
0.86
0.90
0.94
0.98
1.02
1.06
1.10
1.14
1.18
1.22
1.26
-E VOLTS S.C.E.
FIG.17

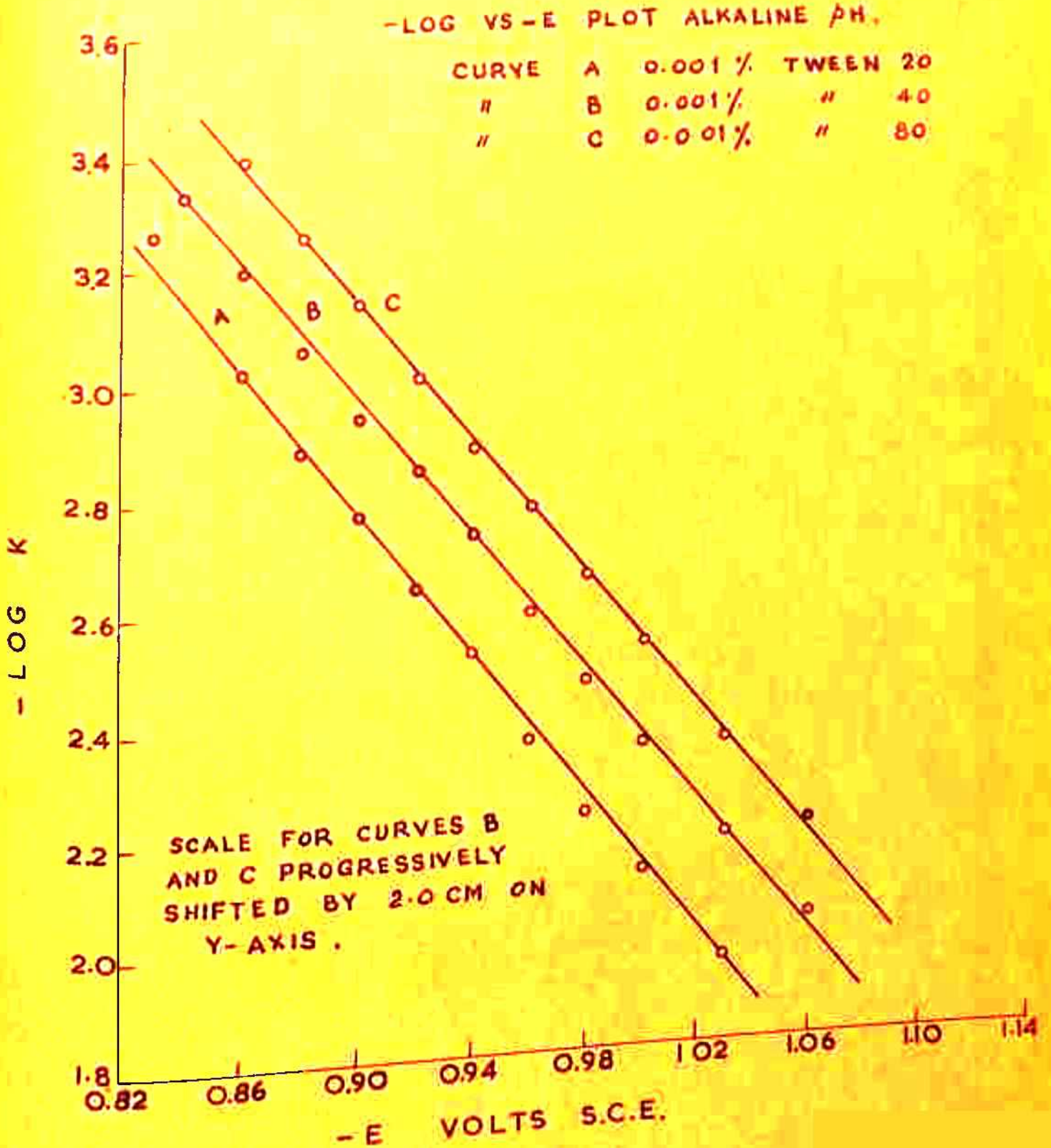

-LOG VS -E PLOT ALKALINE PH.
CURVE A 0.001 % TWEEN 20
" B 0.001 % " 40
" C 0.001 % " 80
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
A
B
C
SCALE FOR CURVES B AND C PROGRESSIVELY SHIFTED BY 2.0 CM ON Y-AXIS.
- LOG K
0.82
0.86
0.90
0.94
0.98
1.02
1.06
1.10
1.14
- E VOLTS S.C.E.

FIG. 18

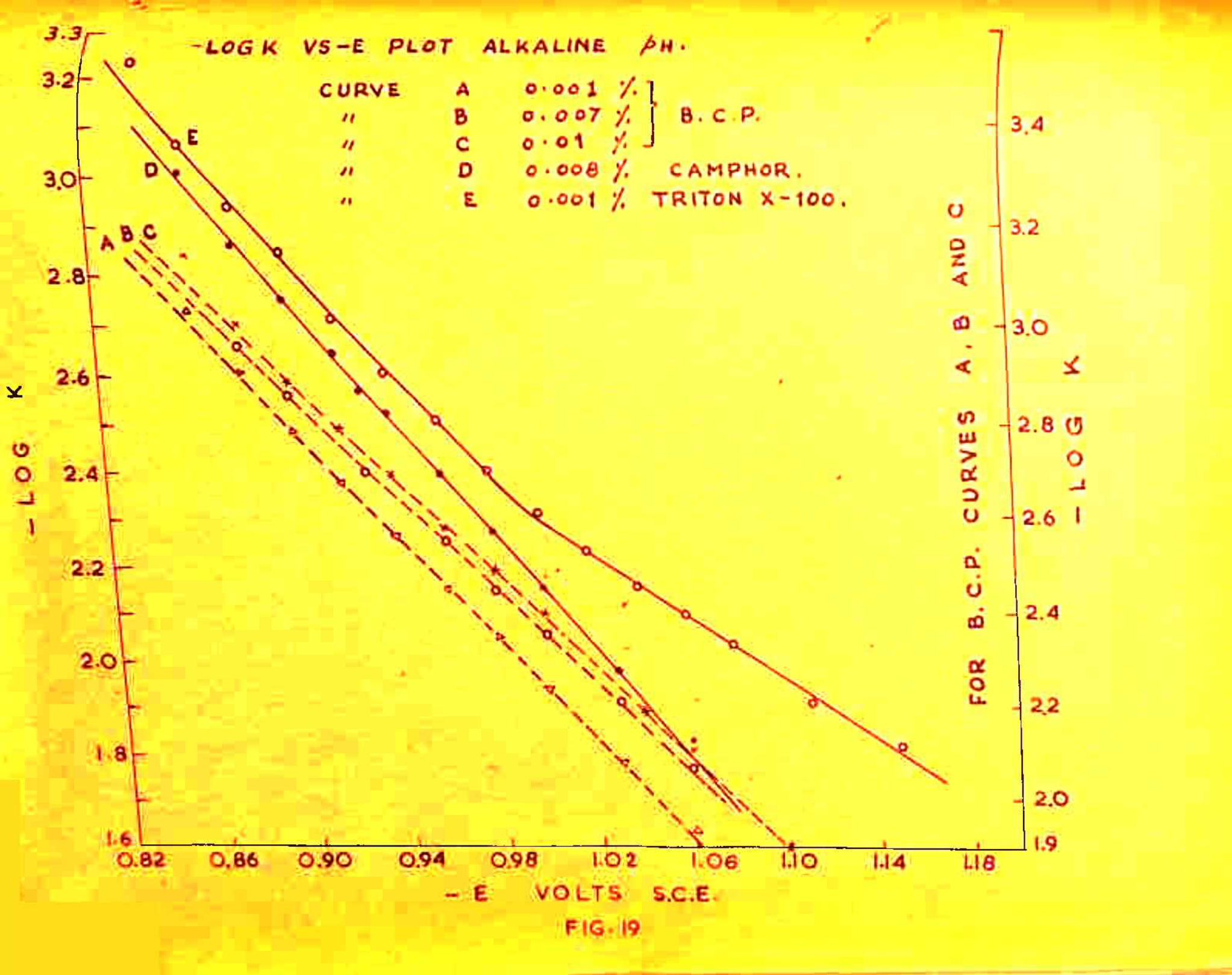

-LOG K VS-E PLOT ALKALINE pH.
CURVE A 0·001 %. B.C.P.
" B 0·007 %.
" C 0·01 %.
" D 0·008 % CAMPHOR.
" E 0·001 % TRITON X-100.
A B C D E
3.3
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
- LOG K
0.82 0.86 0.90 0.94 0.98 1.02 1.06 1.10 1.14 1.18
- E VOLTS S.C.E.
FOR B.C.P. CURVES A, B AND C
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.9
- LOG K

FIG. 19

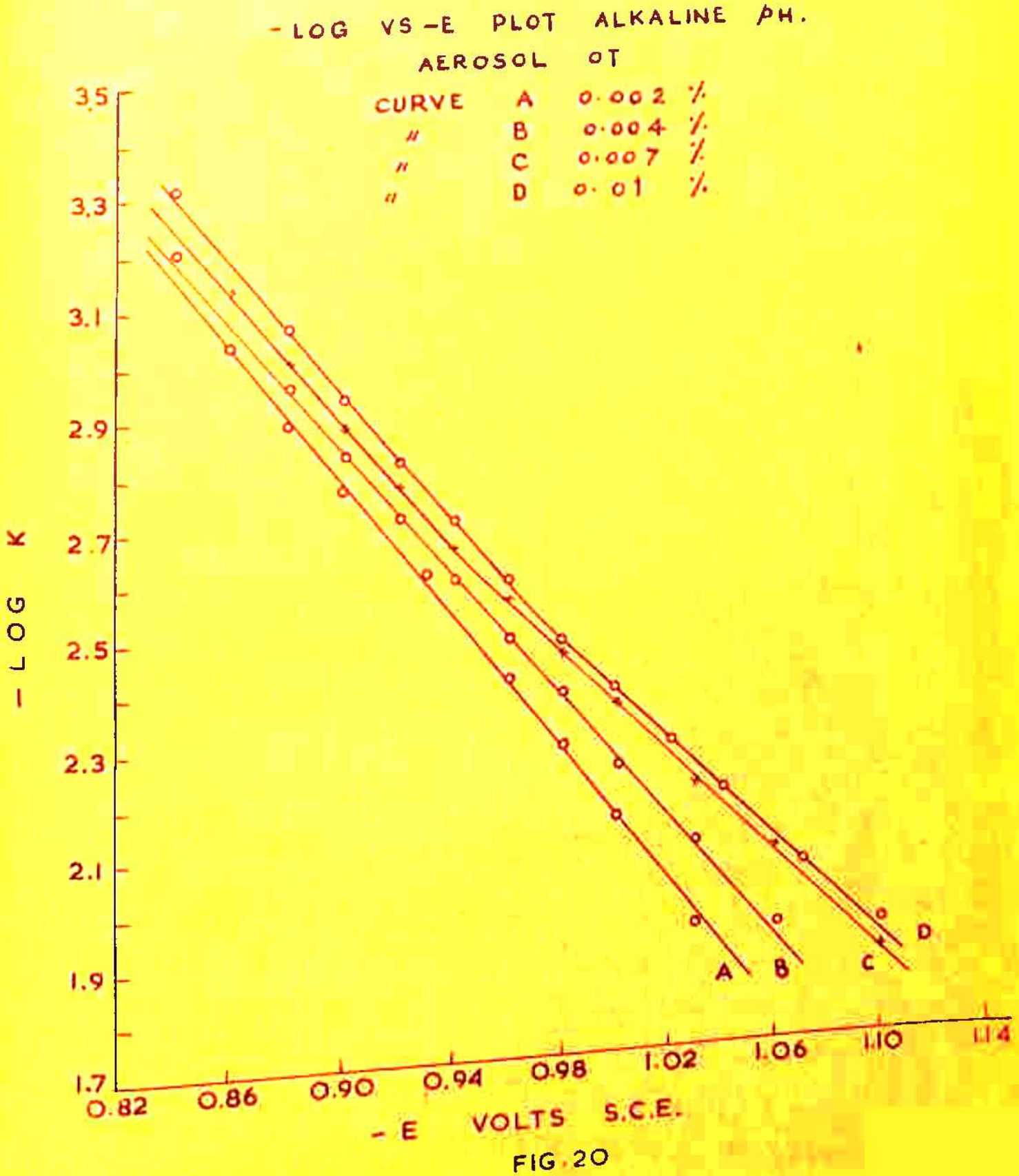

- LOG VS -E PLOT ALKALINE PH.
AEROSOL OT
CURVE A 0.002 %
" B 0.004 %
" C 0.007 %
" D 0.01 %
- LOG K
3.5
3.3
3.1
2.9
2.7
2.5
2.3
2.1
1.9
1.7
0.82
0.86
0.90
0.94
0.98
1.02
1.06
1.10
1.14
- E VOLTS S.C.E.
A
B
C
D

FIG. 20

II Effect of S.A.S. on 5-nitro-ace-naphthene

During the polarographic studies of 5-nitro-ace-naphthene it was observed that it gave single step ($6\bar{e}$) reduction below pH 3 and two steps ($4\bar{e}$, $2\bar{e}$) above pH 3. No appreciable change in the total wave height was observed up to 5.7, beyond which the lowering of the current was attributed to the conversion of the normal nitro-compound into polarographic inactive aci-form. The kinetics of this conversion has already been discussed (Chapter V, Part III). Current-voltage curves were therefore, recorded at constant temperature of 35°C using 1.0 millimole (at pH 1.85) and 0.5 millimole (at pH 5.7) of the depolarizer.

(A) Studies at pH 1.85

Camphor could not be used successfully even up to 0.12% to suppress the maximum, whereas, 0.012% of gelatin suppressed the polarographic maximum. With Triton X-100 (0.002 to 0.4%), Tween 20, Tween 40 and Tween 80 (each 0.004 to 0.04%), single step ($6\bar{e}$) was exhibited at all concentrations of these s.a.s. The height of this step decreased with increased concentration of s.a.s. Half-wave potential of the step remained constant in case of Tx100, whereas, in case of Tween 20, Tween 40 and Tween 80, it shifted to more cathodic side with increased concentration of s.a.s. Kinetic parameters (αn_a and $-\log k^o$) were calculated for the reduction of the depolarizer at various

concentrations of s.a.s. The -log k vs. E plot yielded straight line even up to 0.04% of Tx100. The irreversibility of the electrode process increased as -log k^{o} increased with concentration of Tx100. The -log k vs E plot in case of Tween 20, Tween 40 and Tween 80, at higher concentration of these s.a.s. showed a break indicating that the rate of electrode process is controlled by more than one slow step. These results are tabulated in Table I. Current-voltage curves in presence of different concentrations of Tx100, Tween 20, and Tween 80 are drawn in Fig. 1. In Fig. 2, the -log k vs. E plot in presence of these s.a.s. at their varied concentrations are given.

Aerosol OT (0.012 to 0.04%), sodium lauryl sulphate (0.012% to 0.04%) and bromo-cresol-purple (0.0024 to 0.0192%) were used as anionic s.a.s. Concentration below 0.012% in case of A.O.T. and S.L.S. could not remove the maximum, whereas, in case of B.C.P. with concentration > 0.0096% a sharp maximum reappeared, whose height increased with further increased concentration of s.a.s. The reappearance of the maximum at higher concentration of B.C.P. may be due to the desorption of the s.a.s. The $E_{0.5}$ of the step is independent of the concentration of these s.a.s., whereas, i_d showed a decrease with increase in s.a.s. concentration. Kinetic parameters of the electrode process were calculated and it was seen that αn_a was constant, while -log k^{o} decreased, i.e., the process

is rendered less irreversible with increased concentration of B.C.P. In case of S.L.S. and AOT, αn_a and -log k^o both increased with concentration of these s.a.s. These results are tabulated in Table II. As the -log k vs. E plots yielded straight lines even up to these concentrations (AOT $\leq$ 0.04%, S.L.S. $\leq$ 0.04% and B.C.P. $\leq$ 0.0096%), single rate determining step was involved in the reduction of the nitro-compound at dme.

In case of cetyl-pyridinum bromide (0.002 to 0.04%) and methylene blue (0.002 to 0.04%), $E_{0.5}$ of the reduction step shifted to more cathodic side and i_d decreased with increasing concentration of s.a.s. The pre-wave of adsorption characteristics in case of M.B. is due to the adsorption of the reduced form of M.B. at the dme[24,25]. αn_a and -log k^o increased with increase in concentration of these s.a.s. (Table III.) The -log k vs. E plots in presence of various concentrations of C.P.B. and M.B. also yielded straight lines.

Figure 3 gives current-voltage curves in presence of varied concentration of s.a.s.

(B) Studied at pH 5.7

Triton X-100 (0.002 to 0.024%) and Tween 80 (0.004 to 0.048%) showed similar behaviour, i.e., 2nd step disappeared at higher concentrations of s.a.s. With increased concentration

of both s.a.s., the $E_{0.5}$ of the first step shifted to more cathodic side, whereas, the wave height remained constant in case of Tween 80 and decreased in case of Tx100. In case of camphor (0.004 to 0.048%) both the steps existed 2nd step at higher concentration of camphor experienced a sudden dip, just before the discharge of the supporting electrolyte cations. Kinetic parameters (αn_a and -log k^o) were calculated for different concentrations of these three s.a.s. (Table IV). Plots of -log k vs. E were straight lines at all concentrations of s.a.s. i_d, αn_a and -log k^o were independent of camphor concentration. Fig. 4 gives current-voltage curves for the reduction of the depolarizer in presence of Tx100, Tween 80 and camphor.

Aerosol OT(0.002 to 0.03%) exhibited two steps. Up to 0.014% of s.a.s. no appreciable change in i_d and $E_{0.5}$ of the two steps was noticed but at 0.03% of A.O.T., the first step, showed an increase in height by 15%, while, the height of the second step was almost doubled (Fig. 5). This considerable increase in height of the second wave is of great interest as it is usually observed that the wave heights normally decrease by increasing the concentration of the s.a.s. In this particular case the wave may be probably due, at least in part, to catalytic hydrogen evolution, and presumably the AOT serves to accelerate the catalytic step. αn_a and -log k^o were 0.681 and 6.0593, respectively, at 0.002% of s.a.s.

Sodium lauryl sulphate (0.002 to 0.037%) did not affect i_d and $E_{0.5}$ of the first step. The $E_{0.5}$ of the second step too remained constant, while, its height decreased with concentration of s.a.s. (Fig. 5). The -log k vs. E plot at varied concentration of S.L.S. gave straight line. αn_a and -log k^o are given in Table V. Bromocresol purple (0.0024 to 0.0384%) showed a peculiar behaviour. At higher concentration of s.a.s. merging of the two steps was observed along with a marked increase in the height of the resulting single step (Fig. 5). Values of αn_a and -log k^o were 0.615 and 5.7588, respectively, at 0.0024% of B.C.P.

In case of cetyl pyridinium bromide (0.002 to 0.03%) diffusion current (i_d) and $E_{0.5}$ were constant for the first step. Second step was completely removed at concentration > 0.002% (Fig. 6). Methylene blue also removed the second step at concentration > 0.006%. The usual pre-wave due to the adsorption of the reduced form of M.B. was noticed at all concentration of s.a.s. (Fig. 6). $E_{0.5}$ for the first step shifted to more cathodic side and suffered a decrease in height with increasing concentration of M.B. Kinetic parameters were computed at various concentrations of these s.a.s. (Table VI). In the case of M.B. αn_a decreased, while, -log k^o increased. In the case of C.P.B. at concentration 0.002%, the -log k vs. E plots yielded a straight line (αn_a = 0.5085 and -log k^o = 5.3424) and at higher concentrations this plot

showed a break indicating that more than one slow step were involved in controlling the rate of electrode process.

The -log k vs. E plots for various s.a.s. at pH 5.7 are given in Fig. 7.

Table I

Effect of nonionic S.A.S. on kinetic parameters (αn_a and -log k^o)

pH = 1.85; Depolarizer = 1.0 mM; Temp. = 35°C; Height = 40.0 cms.

% S.A.S.	i_d μ.a.	$-E^1_{0.5}$ Volt S.C.E.	αn_a	-log k^o N.H.E
Tx100				
0.002	23.6	0.390	0.30792	3.62566
0.012	22.6	0.390	0.3060	3.6335
0.040	21.3	0.390	0.3216	3.7288
Tween 20				
0.004	23.8	0.405	0.2955	3.6859
0.016	22.7	0.420	0.2922	3.7789
0.040	22.4	0.435	-log k vs. E plot gave a break.	
Tween 40				
0.004	23.1	0.400	0.3240	3.732
0.016	23.0	0.425	-log k vs. E plot gave a break.	
0.040	22.35	0.445	-do-	
Tween 80				
0.004	23.7	0.408	0.3140	3.7262
0.016	23.3	0.445	-log k vs. E plot gave a break.	
0.040	22.9	0.460	-do-	

Table II

Effect of anionic S.A.S. on kinetic parameters (αn_a and $-\log k^o$)

pH = 1.85; Depolarizer = 1.0 mM, Temp. = 35°C;

Height = 40.0 cms.

% S.A.S.	i_{d_1} μ.a.	$-E^1_{0.5}$ Volt S.C.E.	αn_a	$-\log k^o$ N.H.E.
S.L.S.				
0.012	23.1	0.390	0.307	3.6356
0.024	22.6	0.390	0.332	3.6777
0.040	22.0	0.390	0.342	3.7135
A.O.T.				
0.006	23.6	0.390	0.2934	3.6545
0.024	22.6	0.390	0.3300	3.7175
0.040	21.8	0.390	0.3420	3.7385
B.C.P.				
0.0024	24.5	0.390	0.307	3.6056
0.0048	24.4	0.390	0.301	3.5901
0.0096	24.2	0.390	0.304	3.5853

Table III

Effect of cationic S.A.S. on kinetic parameters (αn_a and $-\log k^o$)

pH = 1.85; 1.0 Millimole of depolarizer, Height = 40.0 cms

Temp. = 35°C.

% S.A.S.	i_{d_1} μ.a.	$-E^1_{0.5}$ volt S.C.E.	αn_a	$-\log k^o$ N.H.E.	$i_{d(ads.)}$* μ.a.
C.P.B.					
0.002	24.6	0.400	0.302	3.6552	
0.010	23.5	0.400	0.316	3.7214	
0.040	21.3	0.400	0.325	3.8021	
M.B.					
0.002	22.2	0.380	0.309	3.6458	0.50
0.012	21.8	0.385	0.331	3.6775	2.00
0.040	20.7	0.410	0.321	3.8818	5.90

*$i_{d(ads.)}$ ... Adsorption wave.

Table IV

Effect of nonionic S.A.S. on kinetic parameters (αn_a and $-\log k^o$)

pH = 5.7; 0.5 mM; Height = 40.0 cms., Temp. = 35°C.

% S.A.S.	i_{d_1} μ.a.	$-E^1_{0.5}$ volt S.C.E.	αn_a	$-\log k^o$ N.H.E.
Tx100				
0.002	8.10	0.540	0.5565	5.5664
0.006	7.50	0.545	0.5655	5.6871
0.024	7.10	0.560	0.5310	5.9425
Tween 80				
0.004	7.90	0.550	0.2760	4.8130
0.028	7.80	0.625	0.4104	5.5300
0.048	7.80	0.635	0.4110	5.5843
Camphor				
0.004	7.45	0.525	0.636	5.8130
0.012	7.40	0.525	0.621	5.8040
0.028	7.35	0.525	0.6265	5.8000

Table V

Effect of sodium lauryl sulphate on kinetic parameters (αn_a and -log k^o).

pH = 5.7; 0.5 mM; Height = 40.0 cms.; Temp.=35°C

S.L.S.	i_{d_1} μ.a.	$-E^1_{0.5}$ Volt S.C.E.	αn_a	-log k^o (N.H.E.)	i_{d_2} μ.a.	$E^2_{0.5}$ Volt S.C.E.
0.002%	8.0	0.530	0.648	5.954	4.30	1.080
0.014%	8.0	0.530	0.6294	5.834	4.20	1.080
0.030%	8.0	0.530	0.5760	5.638	3.60	1.080

i_{d_2} and $E^2_{0.5}$ are for 2nd reduction step.

Table VI

Effect of cationic S.A.S. on kinetic parameters (αn_a and $-\log k^o$)

0.5 mM of depolarizer; Temp. = 35°C; pH = 5.7

Height = 40.0 cms.

% S.A.S.	i_{d_1} μ.a.	$-E^1_{0.5}$ volt S.C.E.	αn_a	$-\log k^o$ N.H.E.	$i_{d(ads.)}$* μ.a.
C.P.B.					
0.002	8.05	0.530	0.5085	5.3424	
0.013	8.00	0.530	log k vs. E plot gave a bend.		
0.030	8.00	0.530	-do-		
M.B.					
0.002	7.60	0.555	0.588	5.469	1.10
0.014	7.20	0.610	0.576	6.408	3.00
0.030	7.00	0.638	0.546	6.5005	5.00

* $i_{d(ads.)}$ ... adsorption wave.

III Effect of S.A.S. on 5-nitro-orotic acid:

Polarography of 5-nitro-orotic acid was carried out in aqueous buffers of pH 1 to 10. Below pH 9, it gave two steps ($6\bar{e}$ and $4\bar{e}$), first step being diffusion controlled at all pH values and the second too was diffusion controlled in acidic pH, but attained adsorption character in alkaline range. Above pH 9, the compound was reduced in three steps, first being diffusion controlled ($4\bar{e}$), while second ($4\bar{e}$) and third ($2\bar{e}$) were of adsorption character. The detailed study of its reduction at dme has already been discussed in the third chapter of this thesis.

Studies of the effect of s.a.s. on the reduction of this acid (0.32 mM), using Na_2HPO_4/citric acid buffer (pH = 3.0, μ = 0.54 M) and boric acid/NaOH buffer (pH = 90, μ = 0.54 M) were carried out at constant temperature of 30°C.

(A) Studies at pH 3.0

Triton X-100 (0.001 to 0.006%) and Tween 20(0.001 to 0.01%) influenced the reduction of this acid in identical manner. Both the steps were shifted to cathodic side, second one to such an extent that only first step was observed at higher concentration of s.a.s. (Fig. 1). The -log k vs. E plot for the first step at 0.001% Tx100 gave a straight line (αn_a = 0.3825 and -log k^o = 3.6906), whereas, this plot indicated a break in presence of 0.001% of Tween 20.

Bromo cresol purple (0.001 to 0.01%) and Aerosol OT (0.001 to 0.01%) were the anionic sas tried. In the presence of B.C.P. fusion of the two steps into one, along with the appearance of a pre-wave due to the adsorption of B.C.P. was noticed at higher concentration of s.a.s. (Fig. 2). At concentration $\geq$ 0.005% of AOT, no wave could be recorded. The -log k^o vs. E plots (for the first step only) for B.C.P. and AOT (0.001% each) yielded straight lines giving αn_a 0.3555 and 0.3645 and -log k^o 3.7109 and 3.539, respectively.

Cetyl pyridinium bromide (0.001 to 0.01%) and methylene blue (0.001 to 0.01%) were the cationic s.a.s. used. In the case of C.P.B., both the steps shifted to cathodic side and only first step existed at concentration 0.01% (Fig. 3). The -log k vs. E plots (for the first step) yielded straight lines even up to 0.01% of C.P.B. αn_a decreased and -log k^o increased with concentration of s.a.s. (Table I).

Some interesting results were obtained with methylene blue (Fig. 3). In the presence of 0.001% M.B., although the acid gave two steps - the separation of the second step from the hydrogen wave was unsatisfactory and the first step split into two. At higher concentrations of M.B., second step disappeared and the splitting of the first step was well defined and a pre-wave appeared. This pre-wave of adsorption characteristics was due to the adsorption of the reduced form of

M.B.[24,25]. The splitting of the first step could be explained as follows. The total height of the two steps (formed due to the splitting of the first step) was equal to the original first step (8 μ.a., $6\bar{e}$ process) at all concentrations of s.a.s. and the splitting was due to the increased stability of the intermediate hydroxylamine stage at higher concentration of M.B.

(B) Studies at pH 9.0

Again Triton X-100 (0.001 to 0.006%) and Tween 20 (0.001 to 0.01%) influenced the reduction of the acid in an identical manner. At higher concentration of s.a.s. the first step was shifted (cathodic) to the extent that it got fused into the second step and thus a single step resulted whose height was equal to the sum of the two steps and remained constant with further increase of concentration of Tx100, but with Tween 20 showed a slight decrease with increased concentration of s.a.s., as shown in Fig. 4.

In the case of Aerosol OT (0.001 to 0.01%) both the steps were observed at all concentration of s.a.s. Although the height of the first step was constant, its $E_{0.5}$ shifted to more cathodic side with increased concentration of AOT, whereas, the second step did not alter appreciably (Fig. 5). Kinetic parameters (αn_a and -log k^o) were calculated for

the first step only at 0.001, 0.002 and 0.01% of s.a.s. (Table II). The electrode process was fevoured by s.a.s. as the value of -log k^o decreased at 0.002%. However, at 0.01% the -log k vs. E plots indicated a break, showing that the electrode process involved more than one slow process.

Both the reduction steps existed at all the concentrations of bromo-cresol purple (0.001 to 0.01%). At higher concentrations of s.a.s. a pre-wave of adsorption characteristics was also noticed (Fig. 5). The $E_{0.5}$ shifted to cathodic side and i_d decreased for the first step, whereas, for the second step these quantities did not alter appreciably. Kinetic parameters for the first step at various concentrations of s.a.s. are tabulated in Table III. The reduction was hindred by s.a.s. as -log k^o increased with increased concentration of s.a.s.

In the case of cetyl-pyridinium bromide (0.001 to 0.005%) the first step shifted to more cathodic side with no appreciable change in its height. The second step was deformed into peak at higher concentration of C.P.B. (Fig.6). Table IV gives the values of αn_a and -log k^o at 0.001% and 0.002% of s.a.s., showing the increased irreversibility of the electrode process. Both the steps, along with a pre-wave of adsorption nature were recorded at all concentrations of M.B. (0.001 to 0.01%), Fig. 6. Kinetic parameters for

the first step (which showed a cathodic shift with no appreciable alteration in its height with concentration of s.a.s.), were calculated, Table IV. The electrode process was more irreversible at higher concentration of s.a.s.

Fig. 7 gives the -log k vs. E plots for the various s.a.s. (at different concentrations of s.a.s. and pH).

Table I

Effect of cetyl-pyridinium bromide of αn_a and $-\log k^\circ$

pH = 3.0; μ = 0.54 M; Height = 40.0 cms., Temp. = 30°C, 0.32 mM. depolarizer.

S.A.S.	i_{d_1} μ.a.	$-E^1_{0.5}$ volt S.C.E.	αn_a	$-\log k^\circ$ N.H.E.
0.001%	7.2	0.365	0.357	3.610
0.002%	6.7	0.375	0.354	3.700
0.010%	5.5	0.385	0.3375	4.485

Table II

Effect of Aerosol OT on αn_a and $-\log k^\circ$

pH = 9.0; μ = 0.54 M; Height = 40.0 cms; Temp. = 30°C; 0.32 mM. depolarizer.

S.A.S. %	i_{d_1} μ.a.	$-E^1_{0.5}$ volt S.C.E.	αn_a	$-\log k^\circ$ N.H.E.
0.001	7.60	1.040	0.375	7.6236
0.002	7.60	1.070	0.339	7.3910
0.010	7.60	1.265	-log k vs. E plot gave a break.	

Table III

Effect of bromo-cresol purple on αn_a and $-\log k^o$.
pH=9.0; μ = 0.54 M, Height = 40.0 cms., Temp. = 30°C;
0.32 mM. depolarizer.

S.A.S. %	i_{d_1} μ.a.	$-E^1_{0.5}$ volt S.C.E.	αn_a	$-\log k^o$ N.H.E.
0.001	7.5	1.035	0.5119	9.2081
0.005	6.9	1.075	0.516 0	9.9530
0.010	6.7	1.112	0.4985	10.0980

Table IV

Effect of cationic S.A.S. on αn_a and $-\log k^o$.
pH = 9.0; μ = 0.54 M; Height = 40.0 cms.; Temp. = 30°C;
0.32 mM. depolarizer.

S.A.S.	i_{d_1} μ.a.	$-E^1_{0.5}$ volt S.C.E.	αn_a	$-\log k^o$ N.H.E.
C.P.B.				
0.001%	7.5	1.035	0.3315	6.153
0.002%	7.5	1.060	0.2930	6.729
M.B.				
0.005%	8.30	1.415	0.342	9.325
0.010%	8.35	1.460	0.492	12.610

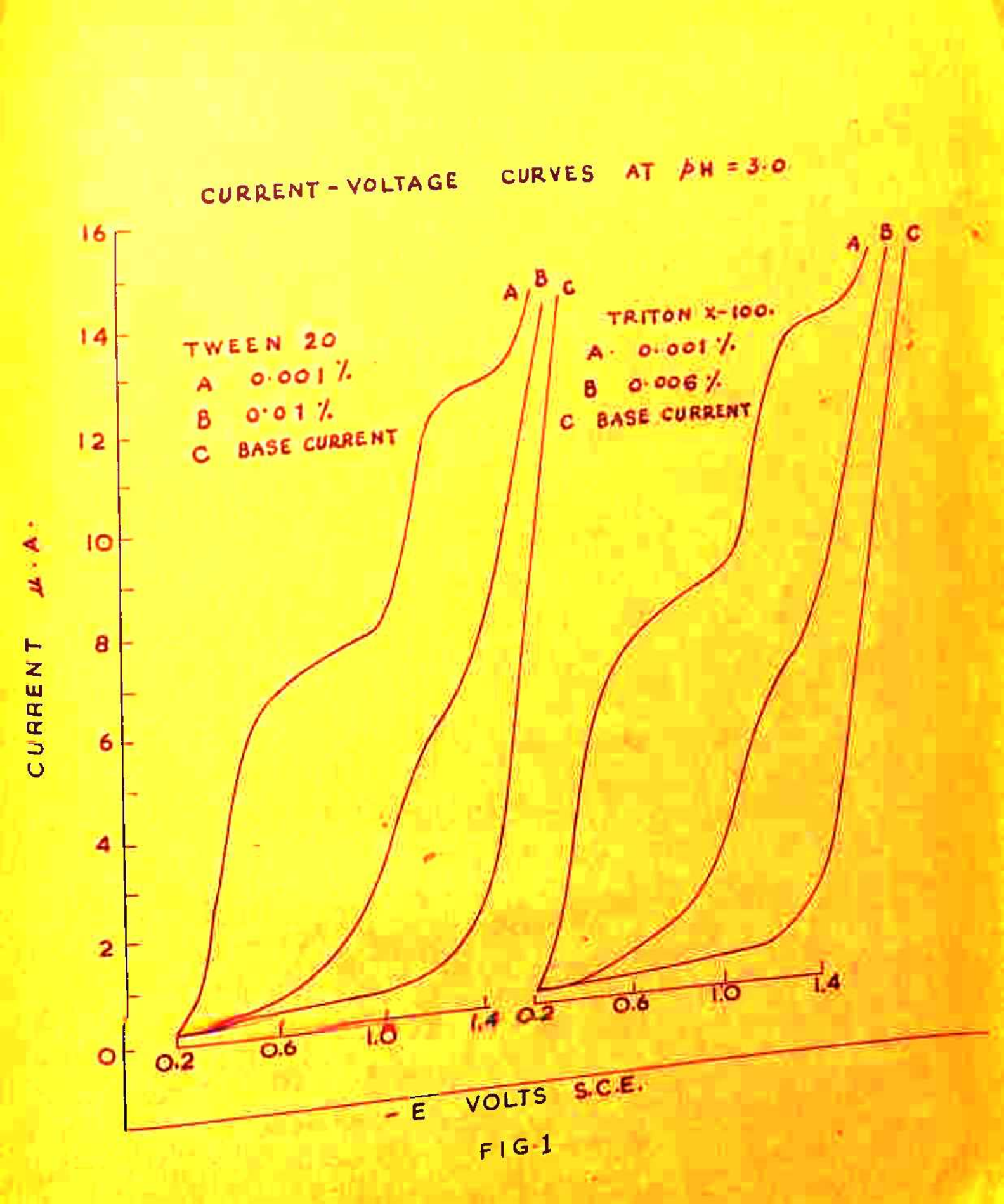

CURRENT - VOLTAGE CURVES AT pH = 3.0
TWEEN 20
A 0.001 %
B 0.01 %
C BASE CURRENT
TRITON X-100.
A 0.001 %
B 0.006 %
C BASE CURRENT
A B C
A B C
CURRENT μ.A.
16
14
12
10
8
6
4
2
0
0.2
0.6
1.0
1.4
0.2
0.6
1.0
1.4
- E VOLTS S.C.E.

FIG-1

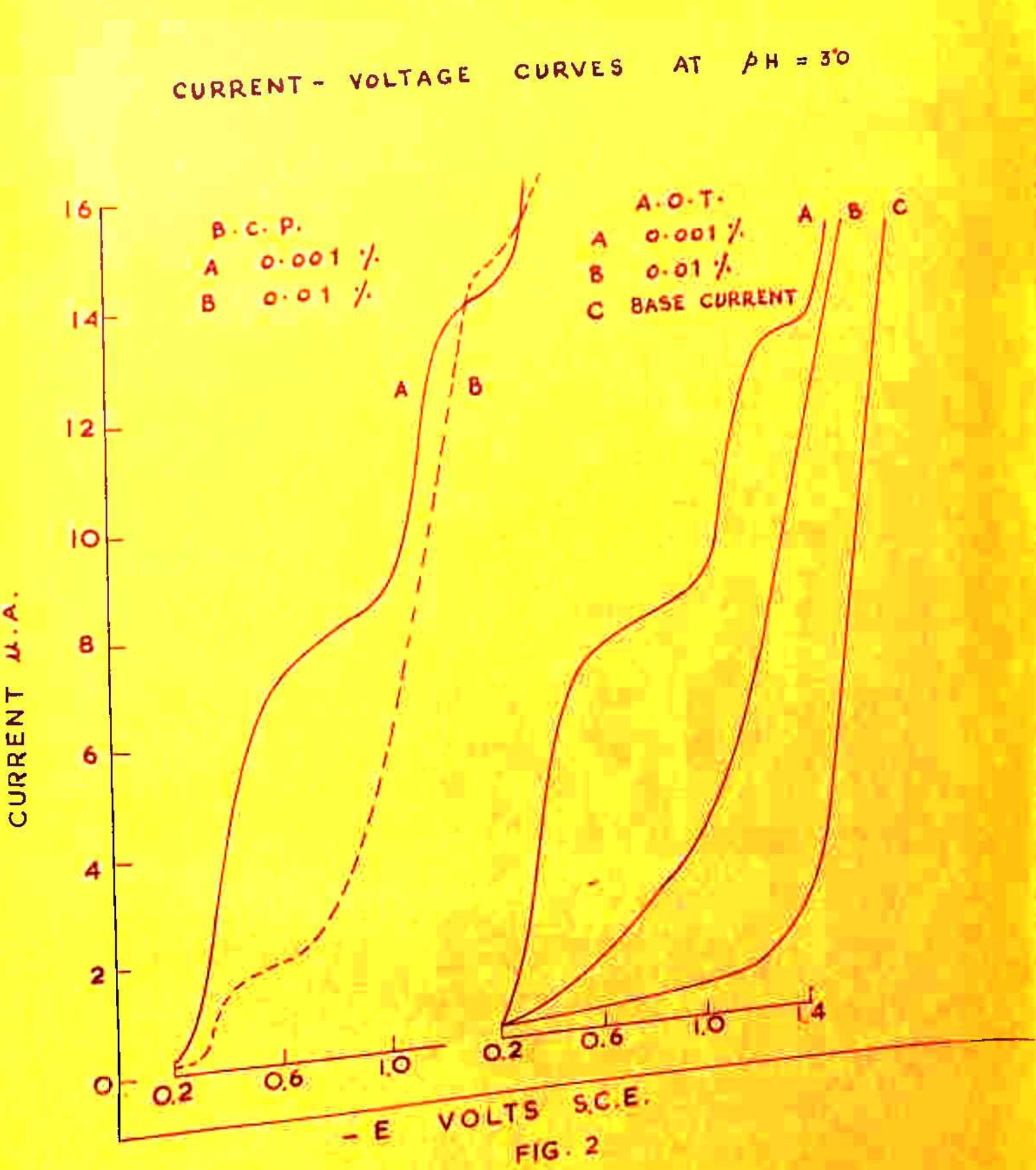

CURRENT - VOLTAGE CURVES AT pH = 3·0
B·C·P.
A 0·001 %
B 0·01 %
A·O·T·
A 0·001 %
B 0·01 %
C BASE CURRENT
A
B
C
16
14
12
10
8
6
4
2
0
CURRENT μ.A.
0.2
0.6
1.0
1.4
- E VOLTS S.C.E.

FIG. 2

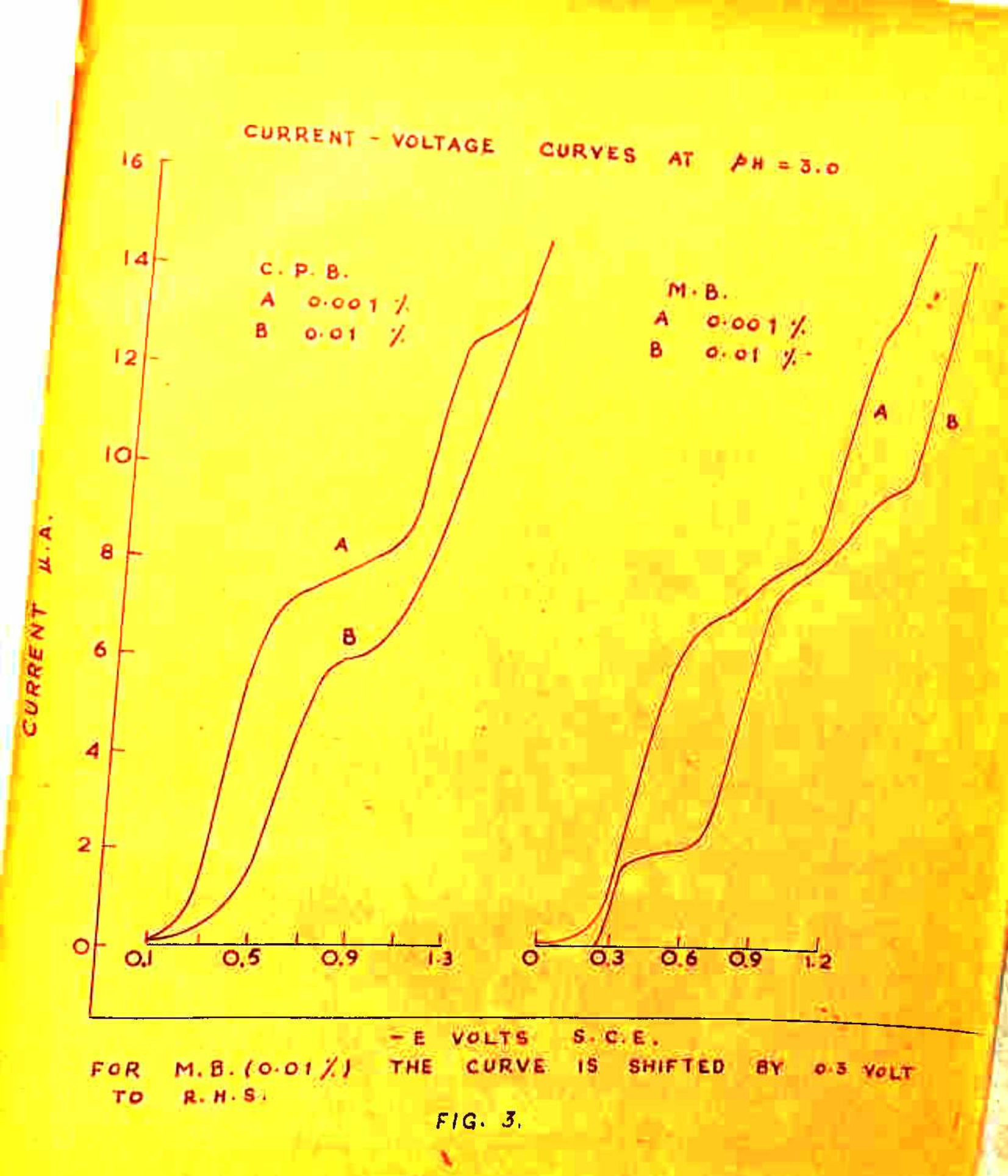

CURRENT - VOLTAGE CURVES AT PH = 3.0
C. P. B.
A 0.001 %
B 0.01 %
M. B.
A 0.001 %
B 0.01 %
A
B
A
B
CURRENT μ.A.
16
14
12
10
8
6
4
2
0
0.1
0.5
0.9
1.3
0
0.3
0.6
0.9
1.2
- E VOLTS S.C.E.
FOR M.B. (0.01 %) THE CURVE IS SHIFTED BY 0.3 VOLT TO R.H.S.

FIG. 3.

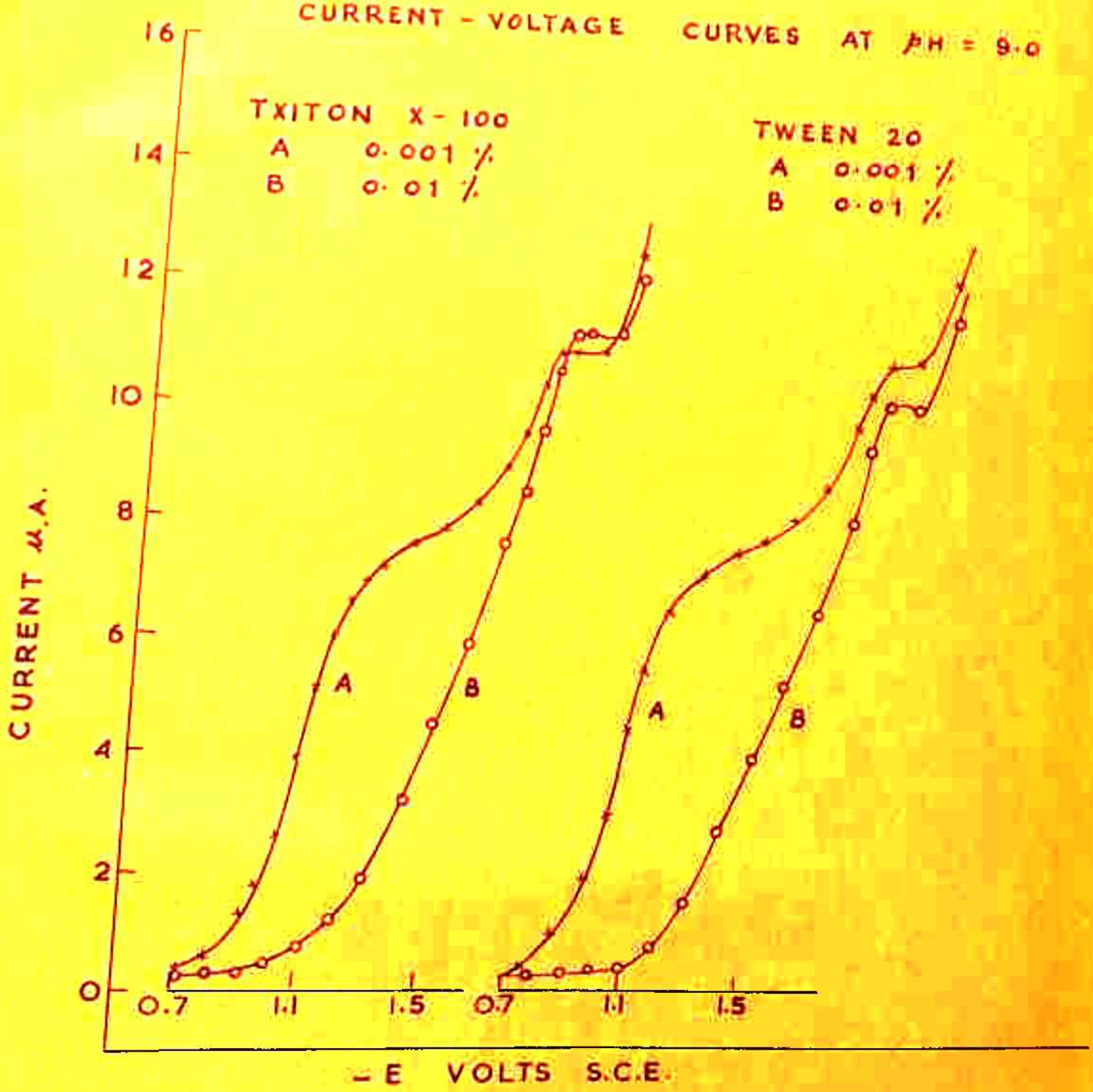

CURRENT - VOLTAGE CURVES AT PH = 9.0
TXITON X - 100
A 0.001 %
B 0.01 %
TWEEN 20
A 0.001 %
B 0.01 %
CURRENT μA.
16
14
12
10
8
6
4
2
0
0.7
1.1
1.5
0.7
1.1
1.5
A
B
A
B
- E VOLTS S.C.E.

FIG. 4

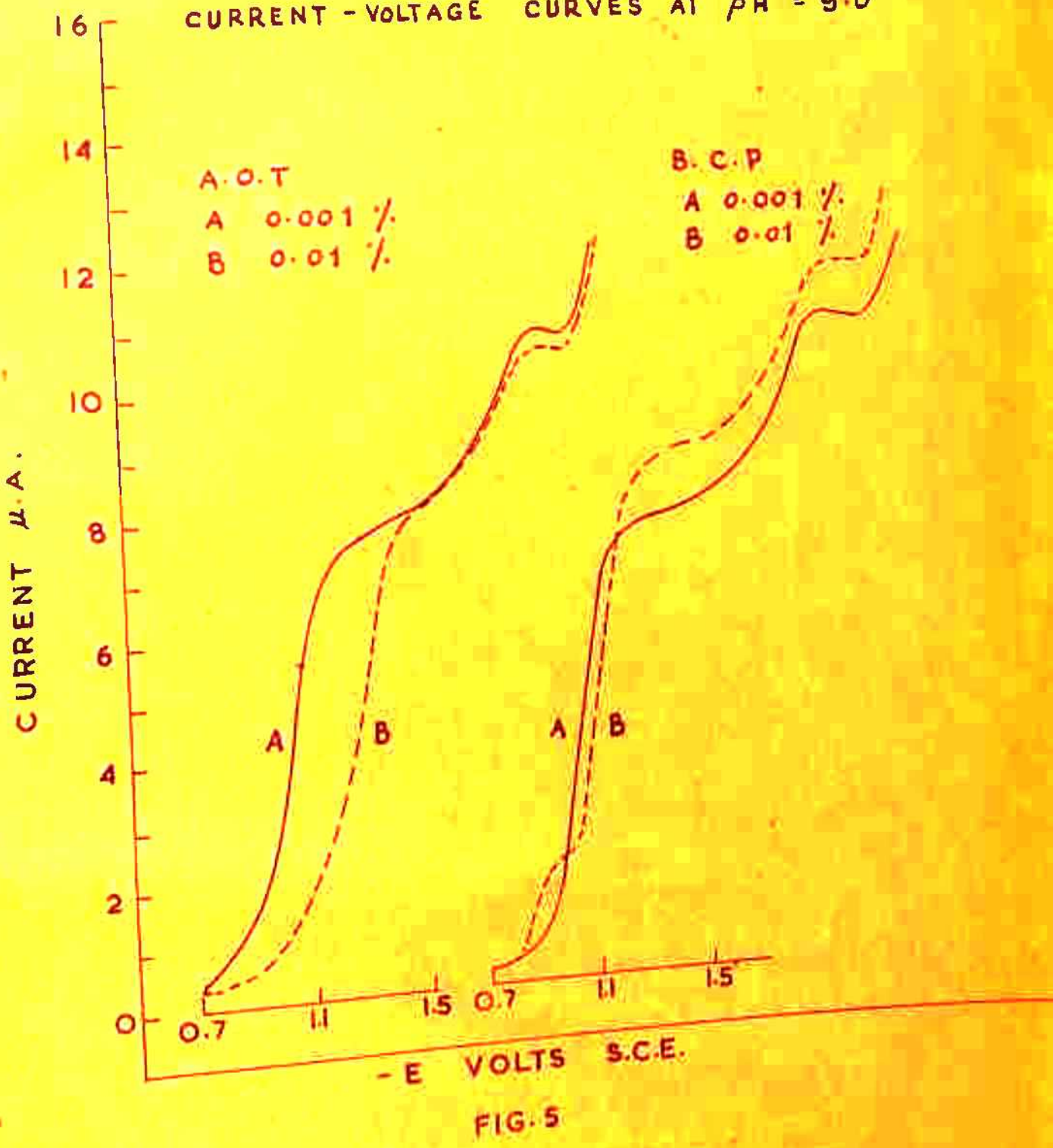

CURRENT - VOLTAGE CURVES AT pH = 9·0
A·O·T
A 0·001 %
B 0·01 %
B·C·P
A 0·001 %
B 0·01 %
CURRENT μ.A.
16
14
12
10
8
6
4
2
0
A
B
A
B
0.7
1.1
1.5
0.7
1.1
1.5
-E VOLTS S.C.E.

FIG. 5

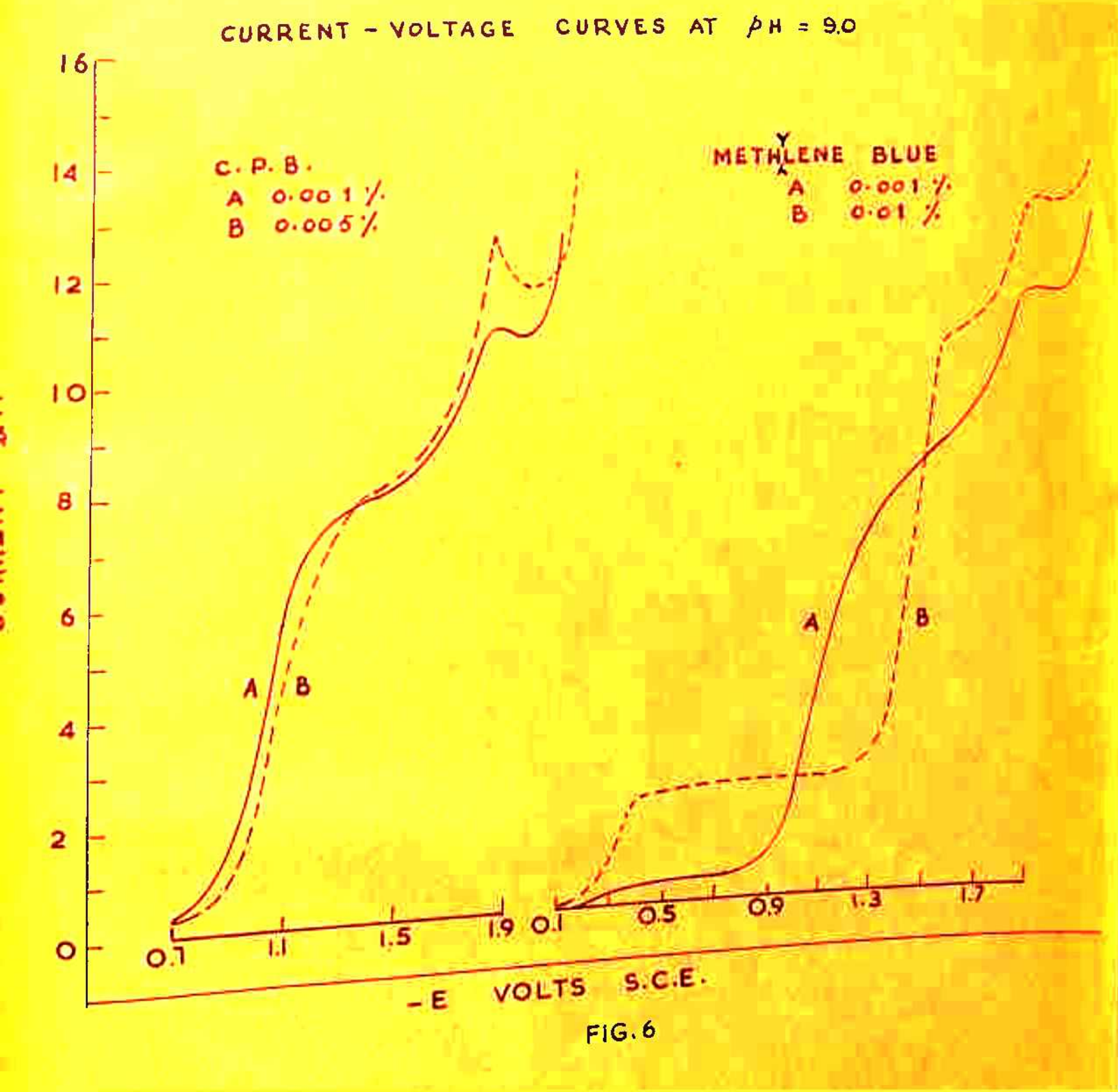

CURRENT - VOLTAGE CURVES AT pH = 9.0
16
14
12
10
8
6
4
2
0
C. P. B.
A 0.001 %
B 0.005 %
METHYLENE BLUE
A 0.001 %
B 0.01 %
A
B
A
B
0.7
1.1
1.5
1.9
0.1
0.5
0.9
1.3
1.7
-E VOLTS S.C.E.

FIG. 6

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