A.C. POLAROGRAPHY IN AQUEOUS AND NONAQUEOUS MEDIA

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SUPERVISOR'S CERTIFICATE

Certified that the research work described in the thesis entitled "A.C. POLAROGRAPHY IN AQUEOUS AND NONAQUEOUS MEDIA" was carried out by Sri Malay Kumar Chatterjee, M.Sc., under my guidance and supervision during the period January, 1963 to June, 1967.

(S.L. GUPTA)

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C O N T E N T S

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P A R T I

GENERAL INTRODUCTION

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The polarographic method first discovered by Heyrovsky in 1922 consists in recording current vs. voltage curves using a dropping mercury electrode. Alternating current polarography refers to the technique in which a small sinusoidal alternating potential is superimposed on to the direct potential under polarographic conditions and the resulting alternating current is measured. The term a.c. polarography is used in connection with the studies of electron transfer reactions. The same experimental technique can also be used to study the behaviour of surface active substances, which produce capacity changes at the interface even in the absence of electron transfer. The study of surfactants by this method has been termed tensammetry.

Alternating current polarography began in 1938 with Müller et al.[1] who were the first to apply a small sinusoidal alternating voltage under polarographic conditions with the aim to develop a more rapid method of polarographic analysis. Although the authors envisaged a possible application of their method to quantitative analysis and inspite of the fact that their expectations seemed to be borne out in practice it is now known that their theoretical considerations were in error. Kivalo[2] has recently given a new theoretical analysis of the method of Müller et al.

The method of Müller et al. was modified by Boeke and van Suchtelen[3]. They found that a much more accurate indication of the half-step potential could be obtained from phase shift measurements. They used an alternating voltage of 50 to 300 mV which is large by present day standards. However, the method was found to be laborious and not suitable for routine analysis.

The work of Muller et al. and of Boeke and van Suchtelen was aimed solely at improving the polarographic method for analytical purposes. A real insight into the actual processes occurring at the dropping mercury electrode in the presence of an alternating field was first shown by Grahame[4]. He measured the resistance and capacity of the cell with an impedence bridge using an alternating voltage of 1 mV or less at a frequency of 1000 c.p.s. He was also the first to carry out the measurements at an accurately timed instant in the life cycle of the mercury drop, thus avoiding some of the bridge balancing difficulties encountered by the previous investigators. He found that steep rise in capacity occurred within certain regions of the applied direct potential and that these abrupt rises were always accompanied by a large increase of the direct current through the cell. He also realised that these capacity changes occurred only with reversible electrode processes such as the discharge of Cd^{+2} in a supporting electrolyte of sodium chloride. In countradistinction irreversible processes such as the reduction of oxygen or of hydrogen ion, etc., did not give rise to any noticeable increase in capacity. This method could also be used as an analytical technique[5]. However, the

difficulties in balancing the bridge made the method impracticable for routine work.

The first practicable instrument suitable for a.c. polargraphic analysis was described by MacAleavy[6,7] in Belgian and French patents of 1941 and 1942. Independently Breyer and Gutman[8] devised a similar instrument which was a subject of a patent by the firm of George H. Sample[9]. Starting in 1944 Breyer and his coworkers began a systematic investigation of the new field which they termed a.c. polarography. It was found that in simple cases such as the discharge of many inorganic ions the summit potential coincided with d.c. polarographic half-step potential and that the magnitude of the alternating current was a linear function of the concentration of depolarizer. Moreover, Grahame's findings that only reversible reactions gave rise to pseudo-capacity was substantiated. It soon became evident that a.c. polarography offers a number of advantages over the d.c. technique in analytical work. At the same time it provides more information about the mechanism of polarographic processes and has also been used to measure electron transfer rates.

An important development has been the application, particularly since 1953 by Breyer and his coworkers[10] of a.c. polarography to the study of organic depolarizers. Almost invariably adsorption processes were found to play a decisive role in the electro-chemical reactions, and their influence could be detected in the base current changes, in the shape of a.c. wave, and in the dependence on concentration and temperature of the faradaic

alternating current as well as in the phase shift associated with the process. The main characteristics generally found can be summarized as follows:-

(1) Organic depolarizers frequently give rise to alternating currents at very low concentrations.

(2) The summit potential (E_s) and the half-step potential ($E_{1/2}$) generally do not coincide.

(3) The alternating current-concentration curves are frequently non-linear and show the form of an adsorption isotherm in contrast to the linear d.c. calibration curves.

(4) Unlike simple inorganic ions organic depolarisers give rise to a.c. waves even when the underlying polarographic process is irreversible.

It was mentioned earlier that the technique used in a.c. polarography can also be used with advantage in the study of surface active but non-reducible substances, a field of investigation known as tensammetry. The first detailed study of the effect of surface active substances on the capacity of mercury aqueous interface was made by Frumkin and coworkers[11-14]. They mostly worked with stationary mercury surface and used a sensitive impedence bridge for measurement of the capacity. Their experiments showed the existence of two maxima with a capacity-potential curve of sodium sulphate saturated with octyl alcohol. Grahame and coworkers[15-18] studied the phenomenon using a dropping mercury electrode and an impedence

bridge with a special arrangement for measuring the capacity and resistance at a particular moment in the life of the mercury drop. Heyrovsky[19] investigated the phenomenon by use of an oscillograph by observing the current voltage curves, which showed halts at certain stages indicating large changes in capacity. Breyer and coworkers[20-26] and Doss and coworkers[27-43] carried out extensive investigations making use of a simple technique of imposing a constant a.c. ripple of low amplitude and d.c. voltage and measuring the a.c. part of the current produced. Breyer and Hacobian named it "Tensammetry". Recently Gupta and Sharma[44-55] have utilized and successfully used this technique with advantage in the study of surface active substances at the dropping mercury electrode in pulsating field. Loveland and Elving[56-60] studied the same by employing an ingenious circuit for getting a straight picture on the oscillograph of differential capacities at the various imposed d.c. potentials.

The general results obtained are that at the electrocapillary maximum the surface active substances get strongly adsorbed, and depress the differential capacity. The potential-differential capacity curve therefore exhibits a minimum in the neighbourhood of electro-capillary maximum. At potential sufficiently cathodic or anodic to the electro-capillary maximum, desorption of the surface active substance takes place due to the preferential adsorption of the solvent molecules caused by the highly charged mercury surface. This desorption appears to take place mostly in an abrupt manner at a fairly well

bridge with a special arrangement for measuring the capacity and resistance at a particular moment in the life of the mercury drop. Heyrovsky[19] investigated the phenomenon by use of an oscillograph by observing the current voltage curves, which showed halts at certain stages indicating large changes in capacity. Breyer and coworkers[20-26] and Doss and coworkers[27-43] carried out extensive investigations making use of a simple technique of imposing a constant a.c. ripple of low amplitude and d.c. voltage and measuring the a.c. part of the current produced. Breyer and Hacobian named it "Tensammetry". Recently Gupta and Sharma[44-55] have utilized and successfully used this technique with advantage in the study of surface active substances at the dropping mercury electrode in pulsating field. Loveland and Elving[56-60] studied the same by employing an ingenious circuit for getting a straight picture on the oscillograph of differential capacities at the various imposed d.c. potentials.

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defined potential leading to the exhibition of a dynamic capacitance and peak in the a.c.-current d.c. voltage curves which are referred to as the "desorption peak" or "tensammetric peak". Sometimes the desorption takes place over a long range of potentials and instead of peak, a hump is observed.

Lot of work has been done on a.c. polarography of inorganic as well as organic depolarizers in aqueous medium. However, the results obtained in a.c. polarography of organic compounds are rather complex and much further work remains to be done. Suzuki[61] has studied the current time curves obtained with a number of carbonyl compounds under superposition of a square wave voltage. Given and Peover[62] reported that benzophenone in dimethylformamide produced a reversibly reduced a.c. polarographic wave. Breyer and Bauer[63-64] studied the effect of different factors like pH, temperature, and concentration of the depolarizer on the chloranilic acid wave. They said that even at as low a concentration as 10^{-7}M a small a.c. wave was obtained. Their studies with perinaphthenone showed that the reduction was less reversible in alkaline solution. Randles and Somerton[65], Breyer and Bauer[63,64] studied the reduction of benzoquinone at various pH values. Julliard[66] showed that hydroquinone gave an a.c. wave at platinum electrode and the height of the wave was a linear function of concentration in the range of 10^{-4} to 3×10^{-3}M. Berg et al.[67] have reported their studies on other substituted quinones in borate phosphate buffer solution. The a.c. polarographic studies

on nitro compounds were carried out by Suzuki[61] with oscillographic polarography. Nitrophenols were reversibly reduced in alkaline pH rather than in acidic pH values. Holleck and Kastening[68,69] studied the effects of surfactants on the reduction of nitro compounds at the d.m.e. by a.c. polarography. Takahasi and Shirai[70] studied the reduction of nitrophenols in alkaline and acidic pH values. Breyer and Bauer[71] found that nitrobenzene either gave two different waves or a single wave with increased wave height where a maximum is present in d.c. polarographic studies. A.C. polarographic studies of the effect of inhibitors on the reduction of nitrophenols have been reported by Cheah and Hacobian[72]. Breyer and Biegler[73] reported that cystine gave two waves the first one is tensammetric in nature. Barnes[74] studied by a.c. polarography of some of the dye stuffs and pigments like basic fuchsin, crystal violet and methylene blue. Gupta and Agarwal[75] reported their studies on methylene blue and methyl violet by a.c. polarography. Some more work on the dye stuffs were done by Suzuki[61] on phenolphthalein, Kalousek and Ralek[76] on phenosafranin, Randles and Somerton[65] on pyocyanine. The unsaturated hydrocarbons were studied at the d.m.e. by a.c. polarography by Aten et al.[77-78]. Some studies of cetyl pyridinium bromide and cerfak were reported by Gupta and Agarwal[75]. Breyer and Hayes[79] have studied the a.c. polarographic behaviour of oxine.

Further, no data are available on a.c. polarographic studies of organic compounds in non-aqueous medium, although some work is being carried out by Schwabe and Berg[80].

Peover[62,81] has also reported the a.c. polarographic studies of benzophenone and its derivatives and nitrobenzene and its derivatives in dimethylformamide and acetonitrile media using a univector polarograph. Recently Gupta et al.[82] have shown the advantages of a.c. polarography of organic compounds in non-aqueous media over aqueous medium.

Proposed work by the candidate

Although considerable work has been done on the a.c. polarographic studies of inorganic and organic depolarizers and on the effect of surface active substances on the dropping mercury electrode capacity with several applications of the technique, there are still many aspects of the problem which need detailed and systematic investigation. This thesis, therefore, contains the results obtained in a systematic and detailed study of the following investigations on which very little or no data are available in literature.

(1) A.C. polarographic studies of nitrobenzene in aqueous and non-aqueous media..

This includes the results obtained in the study of the effect of various physical factors on the magnitude of the peak and peak potential observed with nitrobenzene at the dropping mercury electrode.

The effect of concentration on the peak potentials of a large number of organic nitro compounds has also been investigated.

(2) A.C. polarographic studies on electrode processes in presence of adsorbed films.

This gives the results obtained in the a.c. polarographic studies of the mixturesof reducible organic compounds, mixtures of organic reducible species and surface active substances as well as the mixtures of inorganic and organic reducible species.

(3) A.C. polarographic studies on the structural influence on the peak potentials of a series of nitro compounds.

This consists of the effect of different substituent groups, in the benzene nucleus, on the potential of the peak observed with nitrobenzene in aqueous and non-aqueous media.

(4) Application of the technique to the study of the solubility of the sparingly soluble salts and complex metal ions.

A.C. polarographic technique has been successfully applied with advantage to study the solubility of the sparingly soluble salts as well as the composition and stability constant of a number of metal complexes.

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P A R T II

TECHNIQUE AND RESULTS

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Technique

The technique of a.c. polarography consists in studying the variation of the alternating current with the applied direct potential when a small sinusoidal alternating voltage is imposed on the electrode under polarographic conditions. The circuit used, therefore, consists of a conventional circuit for polarographic work together with a source of alternating voltage and a means for measuring the alternating current in the circuit. The aim in such work is to measure the alternating current that flows as a result of oxidation-reduction or adsorption - desorption processes. Many methods are available for this. The bridge method adopted by Grahame[1] is undoubtedly the most precise but it is very laborious. On the other hand, the a.c. polarographic technique developed by Breyer and Gutman[2] and modified by Doss and Kalyansumdaram[3] as well as Doss and Gupta[4] is shown to be very convenient for such investigations. The only further modification introduced was that the series resistance was made as small as possible. This was achieved by introducing suitable resistance in the a.c. ripple circuit and minimising the resistance across which the a.c. ripple is obtained.

This technique essentially consists in applying to a

dropping mercury electrode (d.m.e.) an a.c. ripple of low amplitude over the d.c. potentials and measuring the a.c. component of the resulting pulsating current by measuring the a.c. voltage drop across the resistor put in series with the d.m.e. This is done by feeding the voltage to an amplifier (Brüel and Kjaer, vacuum tube voltmeter, type 2407, Copenhagen, least count 0.2 mV and maximum amplification 60 db), and applying the amplified and rectified current into a galvanometer. The voltage drop resistor consists of a resistance box, the magnitude of the resistance necessary for producing a particular voltage drop being measured for calculating the current passing. This has rendered the measuring system independent of the frequency of the ripple[3].

Results

1. A.C. polarographic studies of nitrobenzene in aqueous and non-aqueous media.

This work deals with a detailed and systematic studies of the effect of various factors such as (i) effect of pH (ii) effect of change of indifferent electrolyte (iii) effect of change of temperature and frequency of the a.c. ripple, etc., on the magnitude and peak potentials of the reduction peaks observed with nitrobenzene in aqueous and non-aqueous media. The effect of change of concentration of the depolarizer on the peak potentials of reduction peaks observed with nitrobenzene and its derivatives in aqueous medium have also been investi-

gated. The following are the main results obtained as a result of these studies:-

In buffered solution, the shift of peak potential of nitrobenzene to more negative values with increase in pH is linear. There is only one peak up to a pH of 10, but another small peak is obtained at -0.15 Volt vs. s.c.e. at pH $\geqslant$ 11.0 which has been confirmed to be due to the dissolved oxygen. The increase of the magnitude of the nitrobenzene peak with decrease in the amplitude of the a.c. ripple is also linear. The calibration curve of nitrobenzene is more sensitive in alkaline than in acidic medium. The magnitude of the peak depends on the nature of the anions and the concentration of the supporting electrolyte. Increase of the frequency of the a.c. ripple decreases the magnitude of the nitrobenzene peak and shows that the electrode process responsible for the reduction of nitrobenzene peak is faster than the electrode process corresponding to the oxygen peak at pH = 11.6. The causes of these variations have been discussed.

The tensammetric peak of bromothymol blue completely disappears and the reduction peak of nitrobenzene becomes enhanced when the medium is changed from aqueous to methanolic one. This is of particular importance in eliminating the nature of the a.c. peaks observed with organic compounds at the dropping mercury electrode which is not possible in aqueous supporting electrolytes. The advantages of these studies in methanolic medium as compared to those in aqueous medium have been stated.

Further, it has been observed that the effect of pH and concentration of the supporting electrolyte on the magnitude of the peak and peak potential of nitrobenzene in non-aqueous medium is practically the same as that in aqueous medium, but the magnitude and peak potential remain practically unaffected with increase in temperature of the solution. This is unlike the behaviour of nitrobenzene in aqueous medium in which with increase of temperature the peak magnitude increases although the peak potential remains practically constant. The effects of various organic hydroxylic and non-hydroxylic solvents on the magnitude and peak potential of nitrobenzene have also been studied. In general the magnitude of the peak increases and the peak potential shifts to more negative values as we change the medium from aqueous to non-aqueous. In non-aqueous buffered systems the magnitude of the peak usually decreases and the peak potential becomes less cathodic than those in unbuffered solutions. In a buffered solution of homologous series of primary alcohols the magnitude of the nitrobenzene peak progressively decreases and the peak potential becomes more negative with increasing number of CH_2 groups in the solvent molecule. In non-hydroxylic solvents the peak potential is generally more cathodic than those in hydroxylic solvents. The causes of these effects have been discussed.

In course of our studies with some of the organic nitro-compounds at the dropping mercury electrode which give reduction peaks, we have observed that in certain cases the peak potential changes to more cathodic values by increasing the concentration

of the solute whereas in other cases there is no shift in the peak potential with change in the concentration of the solute. Nitrobenzene, ortho and meta nitro benzoic acids and para nitrophenol peaks do not shift with concentration at alkaline pH value (pH = 11.3), whereas the peak potentials of ortho and meta nitrophenols, di and tri nitrophenols, ortho and meta nitrotoluenes and meta and para nitroanilines progressively shift to more cathodic values with increase of their concentrations. In acidic pH values (pH = 3.5) the peak potentials of all the nitro compounds tried shift to more cathodic values with increase in concentration of the solute. This shift of peak potentials with increase in concentration of the solute may be related to the greater tendency of the irreversible nature of the electrode process. The causes of these effects have been discussed.

2. A.C. polarographic studies on electrode processes in presence of adsorbed films.

This work deals with detailed and systematic studies on -

(a) A.C. polarographic studies of the mixtures of reducible organic compounds.

(b) A.C. polarographic studies of the mixtures of organic reducible species and surface-active substances.

(c) A.C. polarographic studies of the mixtures of inorganic and organic reducible species.

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

The influence of organic reduction waves on one another has been studied by a.c. polarography. p-nitrophenol can be estimated quantitatively from its mixture with nitrobenzene as well as with ortho or meta nitrophenol and vice-versa within specified concentration ranges. The magnitudes of nitrobenzene and p-nitrophenol peaks progressively decrease with increasing concentration of benzaldehyde and p-nitroaniline. Magnitude and peak potentials of benzaldehyde and p-nitroaniline are not influenced by increasing the concentration of nitrobenzene or p-nitrophenol. When nitrobenzene is mixed with ortho or meta nitrophenol, the individual peaks disappear and instead a new peak appears whose peak potential and magnitude differ from the individual peaks. The causes of these effects have been discussed.

The effect of nature and concentration of the surface-active substances (s.a.s.) on the a.c. reduction peaks of nitrobenzene and nitrophenols (ortho, meta and para) and vice-versa has been studied. The magnitude of the reduction peak is not influenced up to a certain concentration of the s.a.s. but with concentrations higher than this the magnitude of the reduction peak of nitrobenzene progressively decreases till it attains a certain minimum value whereas magnitudes of reduction peaks of nitrophenols (ortho, meta and para) diminish progressively till they are completely removed by s.a.s. Magnitude and the peak potential of the tensammetric peaks are not

influenced by organic reducible substances. There is a linear relation between the concentration of the s.a.s. just required to decrease the nitrobenzene peak to its minimum value. Ionic surfactants are more efficient in suppressing the reduction peak than non-ionic ones.

The influence of organic reduction waves on a.c. reduction peaks of inorganic cations and vice-versa, has been studied. p-nitrophenol can be estimated quantitatively from its mixture with Cd^{+2} as well as Tl^{+} (ous) ions and vice-versa, within specified concentration ranges at pH 7.0. Benzaldehyde can be estimated from its mixture with Cd^{+2} at pH 3.8 but their estimations are not possible at pH 7.0. Nitrobenzene can be estimated in presence of Zn^{+2} and Ni^{+2} within specified concentration ranges. Estimations of Cd^{+2} and Pb^{+2} from their mixtures with m-nitroaniline and p-nitrophenol and m-nitrotoluene and p-nitrophenol respectively have also been made.

3. A.C. polarographic studies on the structural influence on the E_{peak} potentials of series of nitro compounds.

This work relates to the a.c. polarographic studies of the influence of various substituent groups on the peak potential of nitrobenzene in aqueous and methanolic media. The results obtained are as follows:-

The different substituent groups tried are NO_2, COOH, CHO, Cl, OH, NH_2 and CH_3. The influence of their substitutions in the parent nitrobenzene molecule have been studied at the para position in aqueous and methanolic media. The effect of these

substituents in different positions of the nitrobenzene molecule has also been observed. Substituents like NO_2, COOH, CHO and Cl shift the peak potential to less cathodic values, whereas groups like OH and NH_2 shift it to more cathodic values as compared to the peak potential of nitrobenzene. In general the reduction of nitrobenzene becomes more difficult in the para position with the substituents in the order $NO_2 > Cl > CHO > COOH > CH_3 > OH > NH_2$. The effect of position isomers has also been studied. The behaviour of different substituents on the nitrobenzene peak potential has been explained by the inductive and tautomeric effects of the substituted groups. Hammett's free energy relationship between the peak potentials of the substituted nitrobenzenes and their substitution constant values has also been established in methanolic medium.

4. Applications of the technique to the study of the solubility of the sparingly soluble salts and complex metal ions.

Solubility of sparingly soluble salts like lead sulfate, lead iodide, cadmium oxalate and thallous bromide have been determined by a.c. polarography at different temperatures. From the solubility of lead hydroxide the composition and stability constant of the complex between lead and sodium hydroxide have been established.

It has been shown that a.c. polarography can be applied with advantage for the determination of the formula and dissociation constant of the complex involving one reduction peak such as cadmium-ammonia, cadmium-thiocyanate, cadmium-iodide, lead-hydroxide, lead-oxalate and cupric-β-resorcylic acid

complexes as well as two reduction peaks such as copper-ammonia complex. Copper forms only one complex with pyridine having composition $\left[Cu^{I}(Py)_2\right]^{+}$ and stability constant 1.376×10^{8} which agrees fairly well with the value of 1.608×10^{8} obtained by conventional polarography.

The technique has also been used to study the systems of complexes such as cadmium-oxalate and zinc-thiocyanate in step equilibrium. It is shown that cadmium forms three complexes with oxalate whereas zinc gives four complexes with thiocyanate. The stability constants of various complexes have been determined and they agree fairly well with the values given in the literature. The advantages of the method over conventional polarographic method are discussed.

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P A R T III

CHAPTER I TO CHAPTER IV

CHAPTER I

A.C. POLAROGRAPHIC STUDIES OF NITROBENZENE IN AQUEOUS AND NONAQUEOUS MEDIA

PAPER No. 1

A.C. POLAROGRAPHY OF NITROBENZENE IN AQUEOUS MEDIA

(Proc. Nat. Inst. Sci. India, 1965, 31A, 375)

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A.C. POLAROGRAPHY OF NITROBENZENE IN AQUEOUS MEDIA

by

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and

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A.C. POLAROGRAPHY OF NITROBENZENE IN AQUEOUS MEDIA

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(Communicated by K. S. G. Doss, F.N.I.)

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This investigation deals with the study of the reduction of nitrobenzene in aqueous medium and the effect of various factors which influence the peak potential and the magnitude of the peak by a.c. polarography. In buffered solution, the shift of peak potential to more negative values with increase in *p*H is linear. There is only one peak up to a *p*H of 10, but another small peak is obtained at $-0{\cdot}15$ volt *vs.* s.c.e. at *p*H $> 11{\cdot}0$ which has been confirmed to be due to the dissolved oxygen. The increase of the magnitude of the nitrobenzene peak with decrease in the amplitude of the a.c. ripple is also linear. The calibration curve of nitrobenzene is more sensitive in alkaline than in acidic medium. The magnitude of the peak depends on the nature of the anions and the concentration of the supporting electrolyte. Increase of the frequency of the a.c. ripple decreases the magnitude of the nitrobenzene peak and shows that the electrode process responsible for the reduction of nitrobenzene peak is faster than the electrode process corresponding to the oxygen peak at *p*H = 11·6. The causes of these variations have been discussed.

Introduction

Considerable work has been done on the reduction of nitrobenzene in aqueous medium by d.c. polarography, but no data are available on its reduction in the same medium by a.c. polarography. Breyer and Bauer (1956) showed that the nature of a.c. wave of nitrobenzene depends on whether or not a maximum is present on the d.c. polarographic step of nitrobenzene. The present investigation deals with the detailed study of the reduction of nitrobenzene and the effect of various factors which influence its peak potential and magnitude of the peak by a.c. polarography.

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. Mercury used for dropping electrode was purified by standard methods. All other chemicals used were of A.R., B.D.H. quality. The d.c. potentials were applied with respect to the saturated calomel electrode and the experiments were carried out at a constant temperature of $30 \pm 0{\cdot}5°$ C.

The apparatus employed in the present investigation is the same as that which has been described in literature (Doss and Gupta 1952), keeping the

The fact that the magnitude of the reduction peak increases with increase in *p*H may be due to the increased amounts of the reducible species present at the mercury surface at higher *p*H values. This is probably due to the greater extent of adsorption of the organic compounds at the mercury surface at higher *p*H values, as compared to that at low *p*H values, thus giving the 'composite' peak (Breyer 1953), which is supported by the observation that the per cent diminution of the double-layer capacity also increases at higher *p*H values. The same behaviour of the effect of *p*H on the peak potential as well as on the magnitude of the reduction peak of the nitrobenzene has also been noticed in other supporting electrolytes, viz. potassium perchlorate and potassium chloride in buffered solutions.

2. *Effect of the amplitude of a.c. ripple*

Table I gives the effect of the amplitude of the a.c. ripple on the peak potential and magnitude of the nitrobenzene peak. It is seen that the magnitude of the peak (per cent increase in a.c.) increases with decrease in the amplitude of the a.c. ripple up to 20 mV (r.m.s.) and becomes practically

TABLE I

Effect of the amplitude of the a.c. ripple on the nitrobenzene peak

Indifferent electrolyte = 0·1 *M* LiCl
Nitrobenzene = $4 \cdot 10^{-4}$ *M*
Frequency = 50 c/sec; *p*H = 6·8
Temp. = 30±0·5° C

S. No.	a.c. ripple in mV (r.m.s.)	Peak potential volts (*vs.* s.c.e.)	Peak magnitude (% increase in a.c.)
1	10	0·82	155·5
2	20	0·81	159·6
3	40	0·81	141·3
4	60	0·79	121·7
5	80	0·77	95·06
6	100	0·74	66·2

constant below 20 mV. This increase in the magnitude of the peak with decrease in the amplitude of the a.c. ripple within the range 20 to 100 mV is almost linear and follows the following equation:

$$Y = -1 \cdot 166X + 187 \cdot 5,$$

where Y is the per cent increase in a.c. and X is the amplitude of the a.c. ripple in mV (r.m.s.). Further, the peak potential is practically independent of the amplitude of the a.c. ripple up to 40 mV (r.m.s.) and becomes slightly less cathodic at higher values of a.c. ripples. The width of the peak also

becomes shorter, thereby making the peak more sharp at lower values of a.c. ripples. It may be noted here that, although it is usual to find an increase in the a.c. corresponding to peak height with increase in the amplitude of the superimposed a.c. voltage, the per cent increase in the a.c. corresponding to the same peak height diminishes with increase in the amplitude of the superimposed a.c. voltage. This is due to the fact that base currents are considerably enhanced with larger amplitude of the superimposed a.c. ripple, and hence the per cent increase in a.c., corresponding to peak height which involves in its calculation the base currents' decreases with increase in the amplitude of the superimposed a.c. voltage.

3. *Effect of concentration of the reducible species*

Fig. 1 gives the calibration curves of nitrobenzene at *p*H values of 11·7 and 2·0. Curve 1 refers to the negative peak (more cathodic), whereas curve 2 refers to the positive peak (less cathodic) at *p*H = 11·7. Curve 3 gives the calibration curve at *p*H = 2·0 without gelatin. It can be seen that in alkaline *p*H, the calibration curve is linear between the concentration range 4×10^{-5}

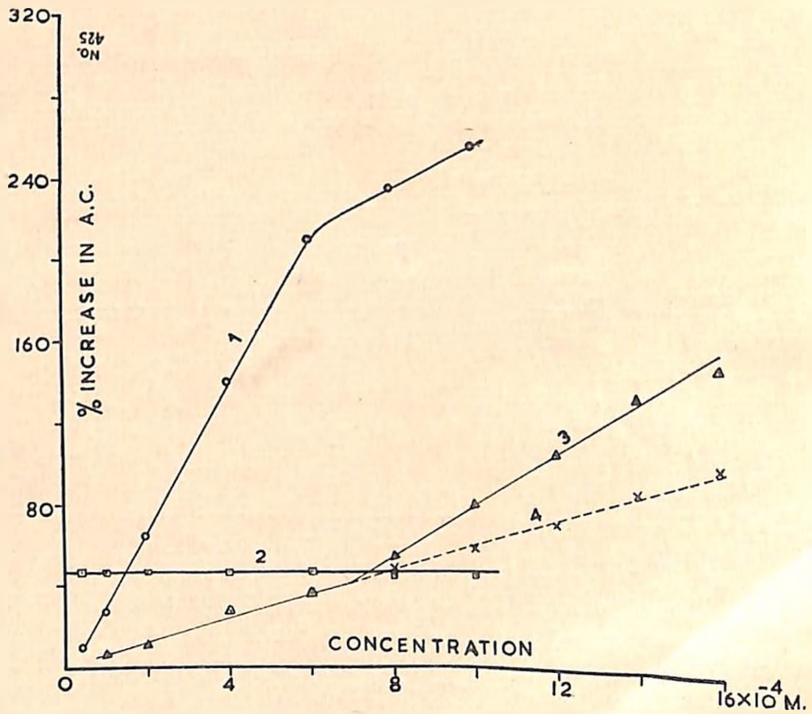

Fig. 1. Curves relating the magnitude of the nitrobenzene peak with its concentration:
Curve 1—*p*H = 11·6 (negative peak).
Curve 2—*p*H = 11·6 (positive peak).
Curve 3—*p*H = 2·0 (without gelatin).
Curve 4—*p*H = 2·0 (with 0·01 per cent gelatin).

and 6×10^{-4} M and tends to saturate at still higher concentrations which can be explained in terms of adsorption processes. The fact, that the magnitude of the positive peak (curve 2) is practically independent of the concentration of the nitrobenzene, suggests that the nature of these two peaks is quite different. At pH 2·0, the calibration curve 3 shows enhanced currents at concentrations higher than 6×10^{-4} M which are suppressed by 0·01 per cent

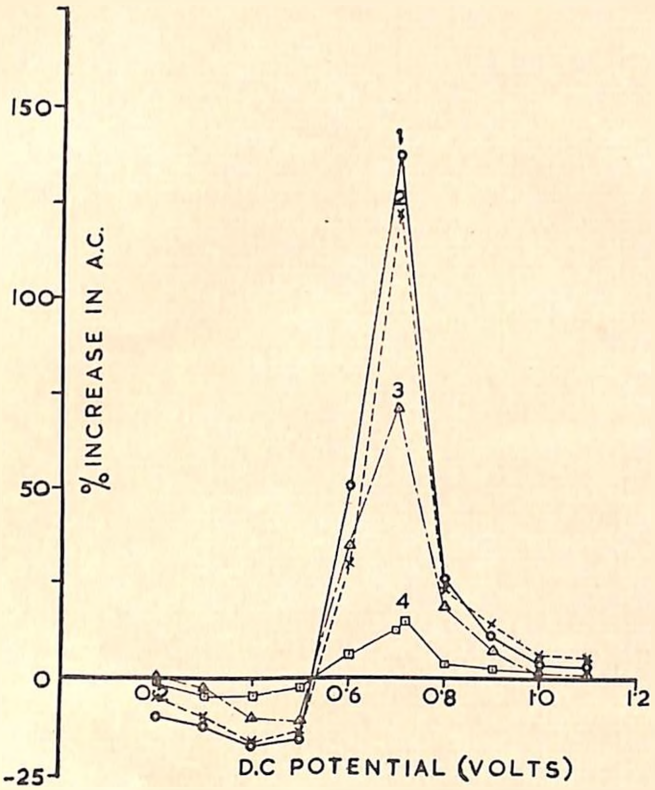

FIG. 2. Effect of the anions of the indifferent electrolytes on the magnitude of the nitrobenzene peak:
Nitrobenzene = 4×10^{-4} M; pH = 10·8.
Curve 1—0·1N $KClO_4$.
Curve 2—0·1N KCl.
Curve 3—0·1N KCNS.
Curve 4—0·1N KI.

gelatin and the calibration curve (curve 4) becomes linear even up to a concentration of $1·6\times10^{-3}$ M. It is difficult to explain the cause of these enhanced currents at present, but it seems probable that it has something to do with the electrocapillaryphoresis at the d.m.e. (Doss 1959). The calibration curve at lower pH is less sensitive than the one at higher pH and may be used for analytical purposes within the concentration range 4×10^{-5} M to

6×10^{-4} *M*. Further, there is practically no change in peak potential with the concentration of the nitrobenzene.

4. *Effect of nature and concentration of indifferent electrolyte*

Fig. 2 gives the effect of 0·1 *M* $KClO_4$, KCl, KCNS and KI on the magnitude and position of the reduction peak of nitrobenzene. Here the cation of the electrolytes is the same and the anion has been varied. It

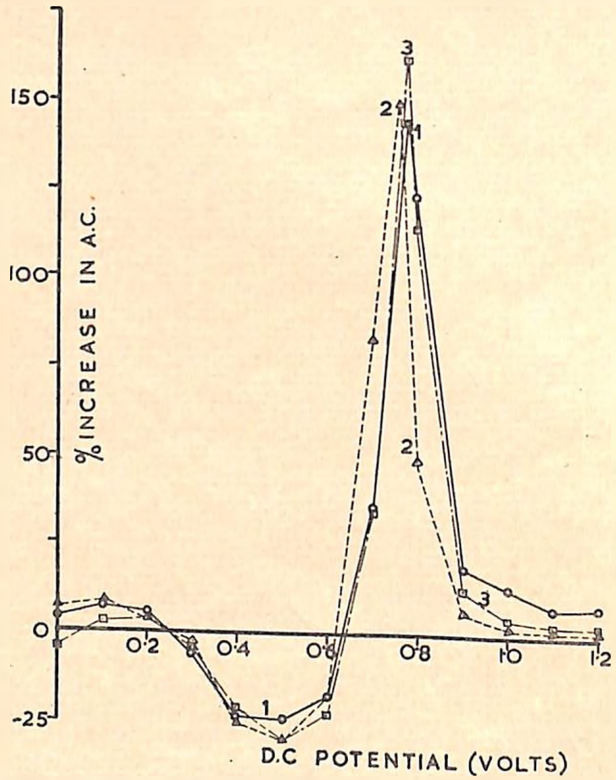

Fig. 3. Effect of the cations of the indifferent electrolytes on the magnitude of the nitrobenzene peak:
Nitrobenzene = 4×10^{-4} *M*; *p*H = 9·3.
Curve 1—0·1*N* LiCl.
Curve 2—0·1*N* NaCl.
Curve 3—0·1*N* KCl.

can be seen that the magnitude of the peak diminishes in the order KI > KCNS > KCl > $KClO_4$ whereas the peak potential remains constant and is independent of the nature of the anion of the electrolyte. This diminution in the magnitude of the peak may be explained on the basis of the surface active nature of the anions of the electrolytes and their specific hindrance on the electrode processes.

It can also be seen from Fig. 3 that the magnitude as well as position of the nitrobenzene peak are practically independent of the nature of the cations of the univalent electrolytes, which may be due to the non-surface active nature of the cations of the electrolytes.

Fig. 4 gives the effect of various concentrations of the indifferent electrolyte (i.e. KCl) on the position and magnitude of the reduction peaks of

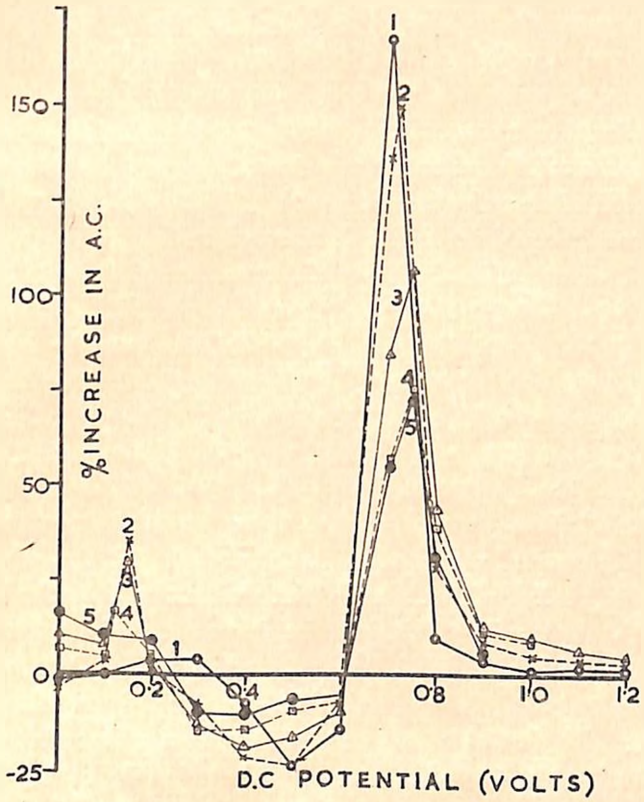

Fig. 4. Effect of concentration of the indifferent electrolyte on the magnitude of the nitrobenzene peaks :

Nitrobenzene = $4 \times 10^{-4} M$; pH = 11·6.
Curve 1—1N KCl.
Curve 2—0·1N KCl.
Curve 3—0·01N KCl.
Curve 4—0·005N KCl.
Curve 5—0·002N KCl.

nitrobenzene at a pH of 11·6. It is seen that the magnitude of the negative peak of nitrobenzene decreases with decrease in concentration of KCl up to a concentration of 0·005N and becomes practically constant below this concentration. The positive peak disappears at very high concentrations of the order of 1·0N KCl and at very low concentrations of the order of 0·002N

KCl, whereas its magnitude diminishes with decrease in concentration of KCl within the range 0·1*N* to 0·005*N*. There is a slight shift in peak potential of the negative peak to more cathodic values with decrease in concentration of the electrolyte, whereas there is practically no shift in peak potential of the positive peak under the same conditions.

The decrease in the magnitude of the negative peak with decrease of concentration of the indifferent electrolyte seems to be due to the effect of increased resistance of the supporting electrolyte with dilution. We have already seen that the magnitude of the reduction peak diminishes by increasing the series resistance, which in this case is obtained by decreasing the concentration of the indifferent electrolyte. This explanation is supported by the observation that almost similar magnitudes of the peak are obtained, whether the concentration of the electrolyte is 0·01 *M* KCl or 1 *M* KCl with an extra resistance in series equal to the difference of resistances between 1 *M* and 0·01 *M* KCl solutions under similar conditions.

The fact, that the positive peak has disappeared completely when the concentration of the supporting electrolyte is 1 *M*, may be due to the large amounts of Cl ions which are capillary active and get adsorbed at the mercury-aqueous interface to such an extent that they practically hinder the electrode process, thereby eliminating the positive peak. This is confirmed by the observation that there is no positive peak in 0·1 *M* Kl as the supporting electrolyte. The iodide ions possess larger surface activity than the chloride ions and therefore even lower concentrations of the iodide ions are sufficient to eliminate this peak. This chloride film does not affect the negative peak because at higher cathodic potentials the desorption of the film takes place. At a concentration of 0·1 *M* KCl, the concentration of Cl ions is not sufficient to hinder the electrode process and thus the peak is obtained which goes on diminishing with decrease in the concentration of the electrolyte due to the increased resistance with dilution.

5. *Effect of frequency of the a.c. ripple*

Fig. 5 gives the effect of frequency of the a.c. ripple on the magnitude and position of the negative and positive peaks. In general, it can be seen that the magnitudes of both the peaks diminish with increase in frequency of the a.c. ripple. The negative peak is completely suppressed by 500 c/sec, whereas the positive peak is eliminated by even 100 c/sec. This shows once again that the nature of these two peaks is different and throws light on the rates of the processes corresponding to these peaks. It appears that the rate of the process corresponding to the negative peak is faster than the rate of the electrode process corresponding to the positive peak. It may further be stated that the peak potential of either of these peaks is independent of the change in frequency of the a.c. ripple.

In order to differentiate the nature of the positive peak with that of the negative peak of nitrobenzene at pH $\geqslant$ 11, some more organic compounds, viz. ortho, meta and para nitrobenzoic acids, benzaldehyde, benzene and benzoic acid, were tried at a pH of 11·6 using the same concentrations, i.e. 4×10^{-4} M, under similar conditions. Surprisingly it was found that a similar positive peak was obtained with other organic substances tried at the same potential. This showed that the positive peak was independent of the nature of the organic compound. It was, therefore, thought that this peak might be due to the dissolved oxygen in the solution under investigation. In order to prove this, experiments were tried with de-aerated solution and also with

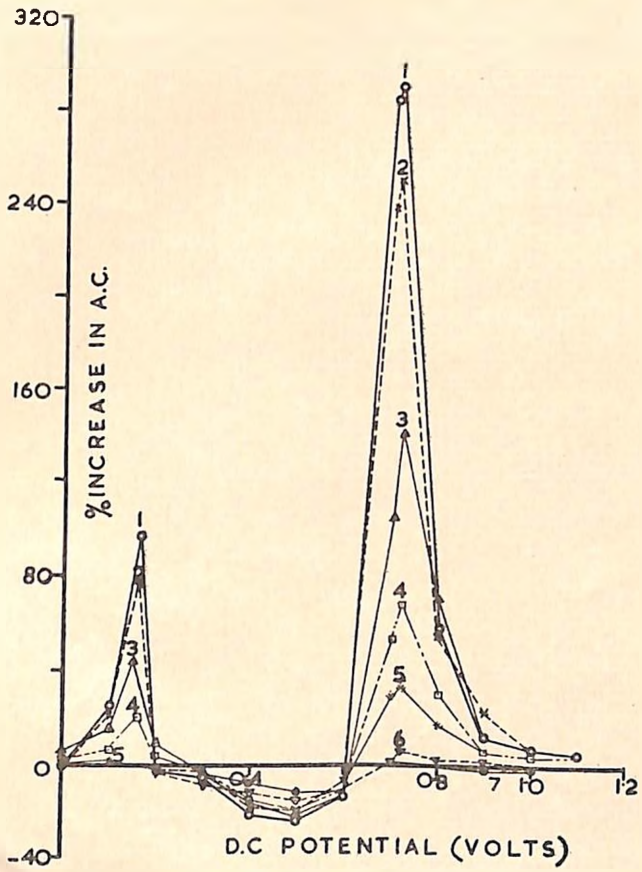

Fig. 5. Effect of the frequency of the A.C. ripple on the magnitude of the nitrobenzene peaks: Nitrobenzene = 4×10^{-4} M; pH = 11·6.
Curve 1—20 c/sec.
Curve 2—30 c/sec.
Curve 3—50 c/sec.
Curve 4—100 c/sec.
Curve 5—200 c/sec.
Curve 6—400 c/sec.
Curve 7—500 c/sec.

solution saturated with oxygen containing the same amount of nitrobenzene. It can be seen from Fig. 6 that the positive peak is completely eliminated by de-aerating the solution, whereas it is enhanced by saturating the solution with oxygen. This observation confirms that the positive peak is due to the dissolved oxygen which is quite different from the negative peak of nitrobenzene at the same *p*H. This is also confirmed from Fig. 1, curve 2, in which the magnitude of the positive peak is independent of the concentration of nitrobenzene because the amount of the oxygen dissolved is constant and does not vary by changing the concentration of nitrobenzene. It may also be recorded that the positive peak is completely eliminated by using very high concentrations of the organic compounds, which may be due to the adsorption of these organic compounds at the mercury surface to such an extent that they hinder the electrode process responsible for the peak.

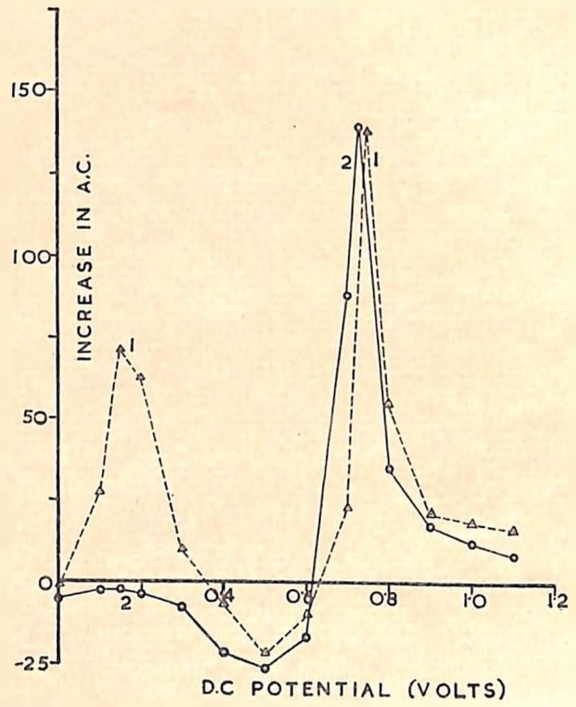

Fig. 6. Effect of oxygen on the nitrobenzene peak:
Nitrobenzene = 4×10^{-4} *M*; *p*H = 11·6.
Curve 1—Saturating the solutions with oxygen.
Curve 2—De-aerating the solution.

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PAPER No. 2

ORGANIC A.C. POLAROGRAPHY AND TENSAMMETRY IN NON-AQUEOUS MEDIA

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Short Communication

Organic a.c. polarography and tensammetry in non-aqueous media

Considerable work has been done on a.c. polarography of organic compounds and tensammetry in aqueous media in recent years but so far no data is available in the literature for the same studies in non-aqueous media. BREYER[1] distinguished between a.c. polarography of organic compounds and tensammetry in aqueous media, by showing that tensammetric peaks are the outcome of the adsorption and desorption processes occurring at the electrode whereas a.c. polarographic reduction peaks of organic compounds are due to two processes *i.e.*, (i) electron transfer and (ii) adsorption–desorption phenomena, occurring simultaneously at the electrode. He introduced the term *rearrangement current* to designate the sum of both the electron transfer and the adsorption-desorption current and called such peaks *composite peaks*. So far no method has been described by which the composite character of these peaks could be eliminated and their nature distinguished completely from tensammetric peaks.

The present work gives the results obtained in the study of a.c. polarography of organic cc ·ounds and tensammetry in methanolic medium.

The bromothymol blue used was B.D.H. indicator quality. Nitrobenzene (B.D.H., A.R.) was redistilled in an all-glass fractionating column and the middle one-third of the distillate was used for the experiments. Lithium chloride was prepared by recrystallising May & Baker Analysed Reagent and methanol was of B.D.H., A.R. quality. Mercury used for the dropping electrode was purified by passing it through Meyer's column, after which it was washed several times with distilled water, dried, passed through a sintered glass filter and finally distilled under vacuum.

The technique of the measurements is the same as that described earlier[2] the only modification being that the series resistance was made as small as possible. This technique consists in applying to the D.M.E., a 50 c/sec a.c. ripple of ± 20 mV (r.m.s.) on the d.c. potential and observing the alternating component of the resulting pulsating current. As the capacitative impedance of the D.M.E. is much higher than the impedance of the rest of the system, the magnitude of the alternating current gives a measure of the D.M.E. capacity.

0.1 *M* LiCl solutions in conductivity water and in pure methanol were used as aqueous and non-aqueous supporting electrolytes and the effects of bromothymol blue and nitrobenzene were investigated as representative of tensammetric and organic reduction peaks respectively. Negative d.c. potentials were applied to the D.M.E. with respect to the saturated calomel electrode. Pure nitrogen was used to de-aerate the solutions and the experiments were carried out at a constant temperature of $30 \pm 0.5°$ and at pH 6.8. The constants of the D.M.E. were: $m = 4.564$ mg/sec and $t = 1.8$ sec per drop in 0.1 *M* KCl, open circuit.

Figure 1 gives the a.c. *versus* potential curves of 0.004% bromothymol blue in aqueous and methanolic supporting electrolytes together with the respective base currents.

Figure 2 gives the corresponding curves for $4 \cdot 10^{-4}$ M nitrobenzene in the same electrolytes with the respective base currents. It can be seen from Fig. 1 that although bromothymol blue shows considerable adsorption as well as a desorption peak in aqueous medium, there is practically no adsorption or desorption peak in methanolic

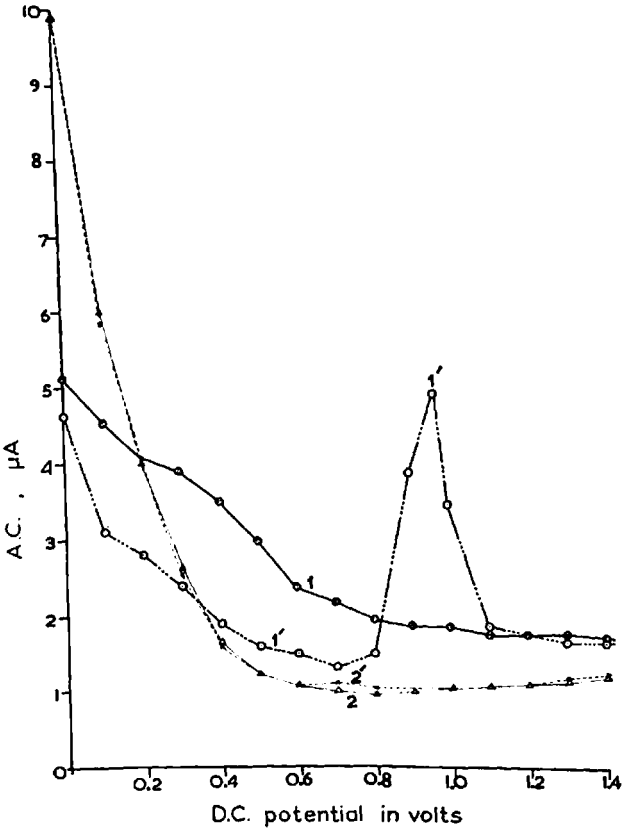

Fig. 1. Effect of the medium on the tensammetric peaks, air-free solutions. 1, base current in aqueous medium; 1', 0.004% bromothymol blue in aqueous medium; 2, base current in non-aqueous medium; 2', 0.004% bromothymol blue in non-aqueous medium.

medium. Similarly it can be observed from Fig. 2 that nitrobenzene shows adsorption as well as a reduction peak in aqueous medium. There is, however, practically no adsorption but a considerable enhanced reduction peak in methanolic medium.

The base currents are considerably reduced in methanolic medium thereby making a.c. polarography of organic compounds in this medium more sensitive than in aqueous medium. It is possible to estimate nitrobenzene in methanolic medium almost down to a concentration of 10^{-5} M whereas it is not possible to estimate amounts below 10^{-4} M in aqueous medium under present conditions. The observation, that there is considerable adsorption in aqueous medium but practically

no adsorption in non-aqueous medium, can be explained by the fact that water has a high surface tension compared to methanol and consequently most solutes will decrease the surface tension of methanol to a much less extent than that of water.

The fact that tensammetric peaks are practically absent and reduction peaks are

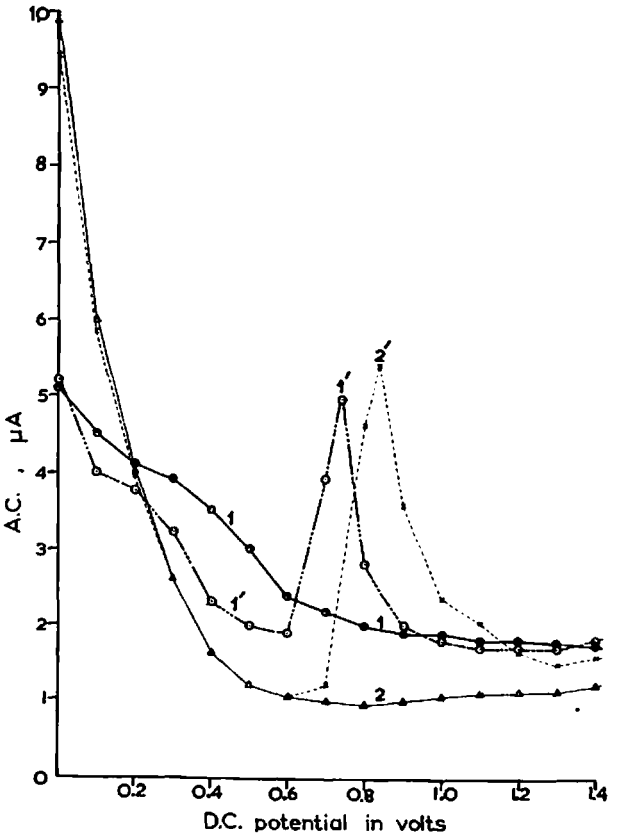

Fig. 2. Effect of the medium on the reduction peaks, air-free solutions. 1, base current in aqueous medium; 1', $4 \cdot 10^{-4}$ *M* nitrobenzene in aqueous medium; 2, base current in non-aqueous medium; 2', $4 \cdot 10^{-4}$ *M* nitrobenzene in non-aqueous medium.

enhanced in methanolic medium, can be used to advantage in determining the nature of the a.c. peaks observed with organic compounds at the D.M.E. This has not so far been a success in aqueous supporting electrolytes.

The fact that adsorption phenomenon is practically absent in non-aqueous media and the peaks due to organic compounds are reduction peaks, may be utilized in the elucidation of the electrode kinetics and in the resolution of peaks from a mixture of organic compounds which would have been complicated in aqueous media by adsorption processes. The a.c. polarography of organic compounds in non-aqueous media may also prove useful because of the limited solubilities of organic compounds in aqueous media.

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PAPER No. 3

A.C. POLAROGRAPHY OF NITROBENZENE IN NONAQUEOUS MEDIA

A.C. POLAROGRAPHY OF NITROBENZENE IN NONAQUEOUS MEDIA

It has been observed that the effect of pH and concentration of the supporting electrolyte on the magnitude of the peak and peak potential of nitrobenzene in nonaqueous medium is practically the same as that in aqueous medium, but the magnitude and peak potential remain practically unaffected with increase in temperature of the solution. This is unlike the behaviour of nitrobenzene in aqueous medium in which with increase of temperature the peak magnitude increases although the peak potential remains practically constant. The effects of various organic hydroxylic and non-hydroxylic solvents on the magnitude and peak potential of nitrobenzene have also been studied. In general the magnitude of the peak increases and the peak potential shifts to more negative values as we change the medium from aqueous to nonaqueous. In nonaqueous buffered systems the magnitude of the peak usually decreases and the peak potential becomes less cathodic than those in unbuffered solutions. In a buffered solution of homologous series of primary alcohols the magnitude of the nitrobenzene peak progressively decreases and the peak potential becomes more negative with increasing number of CH_2 groups in the solvent molecule. In non-hydroxylic solvents the peak potential is generally more cathodic than those in hydroxylic

solvents. The causes of these effects have been discussed.

Considerable amount of work has been done on the a.c. polarography of nitrobenzene in aqueous medium[1-5]. Gupta et al.[6] studied the a.c. polarographic behaviour of nitrobenzene in methanol and stated that tensammetric peaks are practically absent and reduction peaks are enhanced in methonlic medium, which can be used to advantage in determining the nature of the a.c. peaks observed with organic compounds at the dropping mercury electrode (d.m.e.).

The present investigation gives the effect of pH, concentration of the supporting electrolyte and temperature on the reduction of nitrobenzene in methanol as well as the extension of such studies in various protic and aprotic solvents.

EXPERIMENTAL

Nitrobenzene (B.D.H., A.R.) was redistilled at 209°C in all glass fractionating column and the middle one third of the distillate was used for the experiments. Methanol and all other organic solvents used were of B.D.H. quality and were fractionally distilled and the middle one third of the distillates were used for the experiments. Mercury used for the dropping electrode was purified by standard methods[7]. The d.c. potentials were applied with respect to the saturated calomel electrode and the experiments were carried out at a constant temperature of 20 ± 0.5°C, except where mentioned.

The apparatus employed in the present investigation is the same as that has been described earlier.

0.1 M lithium chloride and sodium perchlorate were used as indifferent electrolytes. The d.m.e. was cathodic throughout the measurements. The constants of the d.m.e. were:

m = 4.564 mg/sec.

t = 1.8 sec. per drop in 0.1 M KCl, open circuit.

Ammonium acetate and boric acid were used for maintaining the buffer capacity in acidic and alkaline media respectively and the required pH was adjusted by adding a few drops of concn. HCl & KOH respectively. The pH measurements were made with glass electrode using a Beckman pH meter, model H2.

Pure nitrogen was used for deaerating the solutions.

RESULTS AND DISCUSSION

(1) Effect of pH

Table I gives the effect of pH on the peak potential and magnitude of the reduction peak observed with nitrobenzene in methanolic medium. It can be seen that the peak potential of the nitrobenzene peak in buffered methanolic solutions increases to more cathodic values with increase in pH of the solution. But unlike the pH studies of nitrobenzene in aqueous medium the plot of summit potential vs. pH is non-linear. The increase of the peak potential with increase in pH may be explained by the fact that as pH increases the concentration

Table I

Effect of pH

Nitrobenzene in buffered methanolic medium

20 mV(r.m.s.); 50 c/s; Temp. = 20 ± 0.5°C; Concn. = 4×10^{-4}M

Supporting electrolyte = 0.1 M LiCl

Sl.No.	pH	Peak potential V	Peak magnitude μA
1.	2.20	0.50	1.19
2.	4.38	0.72	1.44
3.	6.90	0.84	2.23
4.	7.90	0.87	3.295
5.	9.80	0.91	4.00

Table II

Effect of supporting electrolyte concentration

20 mV(r.m.s.); 50 c/s; Temp. = 20 ± 0.5°C; Concn.= 4×10^{-4}M

pH = 6.8

Sl.no.	Concn. of supporting electrolyte in moles	Peak potential V	Peak magnitude μA
1.	1.000	0.84	5.83
2.	0.500	0.86	4.84
3.	0.100	0.88	3.73
4.	0.010	0.93	1.754
5.	0.002	1.00	1.62

of hydrogen ion in solution decreases and more energy will be required for the reduction process. The peak potential will, therefore, be shifted to more negative values.

It can also be seen that the magnitude of the peak increases with increase in pH of the solution. This may be due to the fact that the reduction peak of nitrobenzene becomes more reversible in alkaline than in acidic pH values[8].

(2) Effect of the concentration of indifferent electrolyte

Table II gives the effect of various concentrations of indifferent electrolyte (LiCl) on the position and magnitude of the reduction peak of nitrobenzene in methanolic medium at a pH of 6.8. It can be seen that the magnitude of the nitrobenzene peak diminishes with decrease in concentration of LiCl upto a concentration of 0.002 M. There is quite an appreciable shift in peak potential of nitrobenzene peak to more cathodic values with the decrease in concentration of the supporting electrolyte. The lowering of the magnitude of the nitrobenzene peak with decrease in concentration of the indifferent electrolyte seems to be due to the effect of increased resistance of the supporting electrolyte solution with dilution. It has already been observed that the magnitude of the reduction peak diminishes by increasing the series resistance[9] which in this case is obtained by decreasing the concentration of the supporting electrolyte.

Similarly the shift of peak potential to more cathodic values with decrease in concentration of the electrolyte is due to the iR drop.

(3) Effect of Temperature

Table III gives the effect of temperature on the magnitude of the a.c. peak and its peak potential observed with nitrobenzene in methanolic medium. It is seen from the table that the magnitude of the peak remains practically constant with the increase in temperature. Further, the peak potential is independent of temperature. This is unlike the behaviour of nitrobenzene in aqueous medium in which with increase of temperature the peak height increases although the peak potential remains practically constant.

(4) Effect of solvents

Tables IV and V give the effect of different organic solvents on the peak potential and magnitude of the reduction peak observed with nitrobenzene. In all the solvents studied, which are polar in character, practically no adsorption of nitrobenzene at the electrode surface is observed. In general the magnitude of the peak increases and the peak potential shifts to more negative values as we change the medium from aqueous to nonaqueous.

There is considerable lowering of the base current in the deaerated nonaqueous medium as compared to that in aqueous medium and hence the a.c. reduction peaks in such medium become more enhanced as compared to those in aqueous medium.

In nonaqueous buffered systems the magnitude of the peak usually diminishes and the peak potential becomes less

Table III

Effect of Temperature

20 mV(r.m.s.); 50 c/s; pH = 6.8; Concn. = 4×10^{-4} M

0.1 M LiCl as the supporting electrolyte

Sl.No.	Temperature in °C	Peak potential V	Peak magnitude µA
1.	10	0.88	3.68
2.	15	0.88	3.77
3.	20	0.89	3.77
4.	25	0.89	3.72
5.	30	0.90	3.77

Table IV

20 mV(r.m.s.); 50 c/s; pH=6.6; Concn.=2×10^{-4}M; Temp.=20 ± 0.5°C

Supporting electrolyte 0.1 M LiCl

Sl. No.	Solvent	Buffered solutions		Unbuffered solutions	
		Peak potential V	Peak Magnitude µA	Peak potential V	Peak Magnitude µA
1.	Methanol	0.81	1.74	0.87	2.35
2.	Ethanol	0.81	1.07	0.90	2.03
3.	n-Propanol	0.83	0.68	0.88	1.536
4.	iso-Propanol	0.84	0.57	0.90	1.016

Table V

20 mV(r.m.s.); 50 c/s; pH=6.6; Concn.=2×10^{-4}M; Temp.=20 ± 0.5°C

Supporting electrolyte 0.1 M $NaClO_4$

Sl. No.	Solvent	Peak potential V	Peak magnitude μA
1.	Methanol	0.87	2.218
2.	Ethanol	0.89	1.850
3.	iso-propanol	0.88	1.427
4.	n-propanol	0.89	0.970
5.	Acetone	0.98	2.980
6.	Methyl ethyl ketone	0.97	2.730
7.	Acetonitrile	1.00	2.990
8.	Demethylformamide	1.00	1.770
9.	Pyridine	0.97	0.730
10.	Water	0.73	1.420

cathodic than those in unbuffered solutions. This may be due to the fact that all the organic reduction peaks are very much dependent upon the pH of the solution and buffer capacity. As the hydrogen ions are involved in the reduction process, in the immediate vicinity of the electrode the pH of the unbuffered solution increases and therefore the peak height increases as well as peak potential becomes more cathodic, whereas in buffered solution the depletion of hydrogen ions do not cause any change in pH of the solution in the vicinity of the electrode. Hence the magnitude of the peak is greater and the peak potential is more negative in unbuffered solutions as compared to buffered solutions in the same medium.

The solvents tried in the investigation can be broadly divided into two types - (i) non-hydroxylic (ii) hydroxylic solvents. The non-hydroxylic solvents tried are acetone, methyl ethyl ketone, acetonitrile, dimethylformamide and pyridine and the hydroxylic solvents are methanol, ethanol, n-propanol and iso-propanol.

Geske and Maki[10] observed in conventional polarography that nitrobenzene undergoes a one electron reduction in acetonitrile at the dropping mercury electrode which is reversible. Further reduction of this compound in aprotic solvents was not possible due to the nonavailability of the protons in this solvent. The reduction of nitrobenzene in other aprotic solvents may also be proceeding in the same way, which is suggested from the similarity of the peak potentials of nitrobenzene in these solvents.

It can be seen from Table V that the reduction potential of nitrobenzene in hydroxylic solvents is approximately 100 mV more positive than that in non-hydroxylic solvents including pyridine. This behaviour may be attributed to the protic and aprotic nature of these two groups of solvents. The alcohols are known to be proton active solvents because of their power of releasing the hydrogen of the OH group as free hydrogen ions or protons, whereas the non-hydroxylic solvents, as has already been stated, are aprotic or non-proton active, So more energy will be needed for the reduction process to occur in aprotic solvents than in protic solvents.

The effect of hydroxylic solvents on the peak potential and peak magnitude of nitrobenzene can be attributed to the protic nature of these solvents, the surface active nature of the solvents and their viscosities. It can be seen that the peak potential of nitrobenzene shifts to more negative values in alcoholic buffered solutions and as we go from methanol to n-propanol the peak potential becomes more negative. The shift in the peak potential is in the order n-propanol > iso-propanol > ethanol > methanol. This may be due to the fact that in a homologous series of primary alcohols the tendency of the COH group to break as C-O$\frac{|}{|}$H is greatest in methanol and as we increase the number of CH_2 groups, the CH_2 group being electron releasing, the bond strength of C-O becomes weaker and the tendency of COH group to break as C$\frac{|}{|}$O-H becomes greater. Therefore, the ease with which a proton can be released from C-OH is greatest in methanol and least in n-propanol.

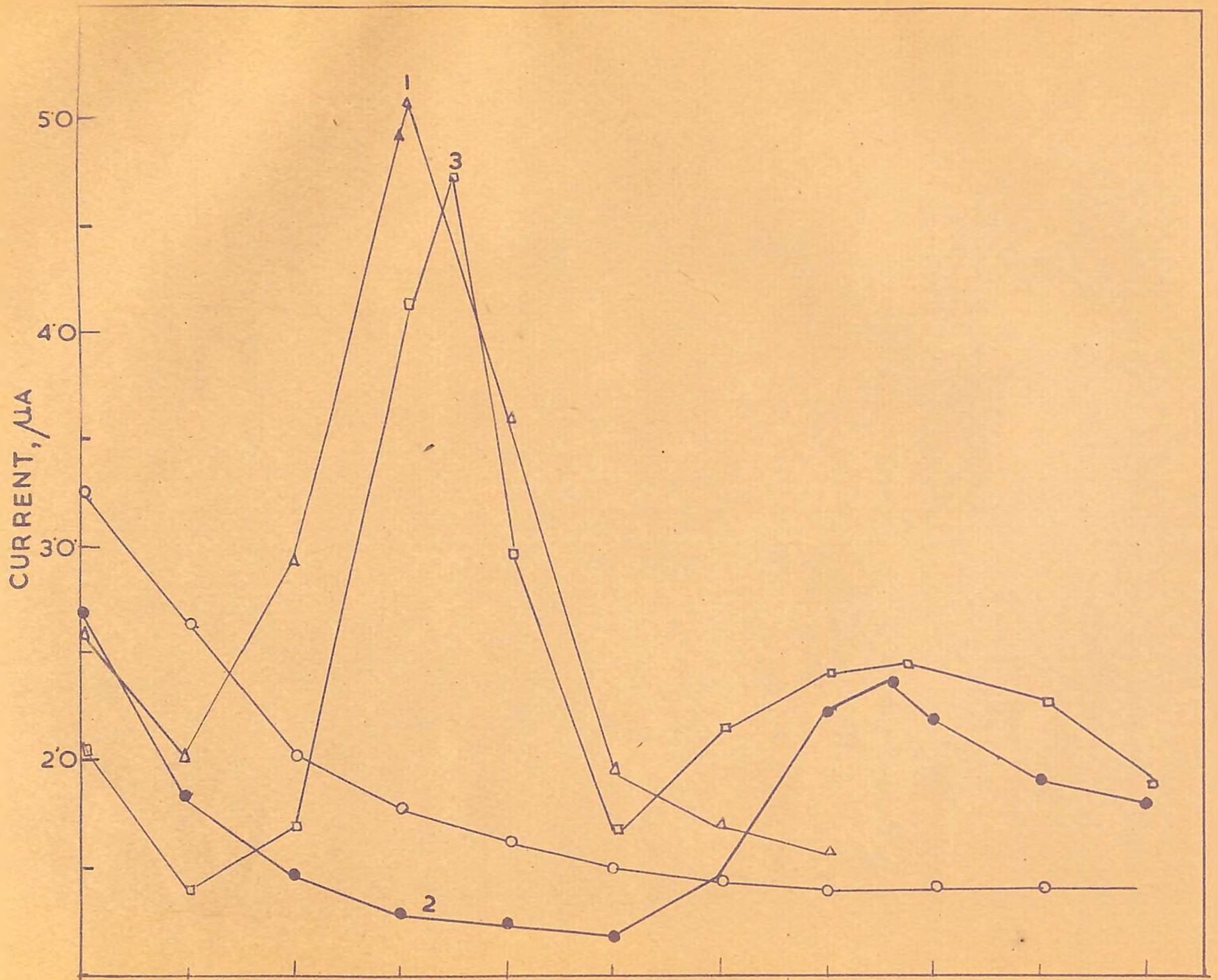

FIG. 1.

LEGEND OF FIGURE

Fig. 1: Effect of pyridine on the peak potential and magnitude of the peak observed with nitrobenzene in aqueous media.

Curve 1: 6×10^{-4}M nitrobenzene

Curve 2: 0.4% pyridine

Curve 3: Mixture of 6×10^{-4}M nitrobenzene and 0.4% pyridine.

The magnitude of the peak diminishes with increase in CH_2 group in the solvent. This is indicated by the homologous series of alcohols and ketones. It may be due to the fact that the aprotic nature of the solvent increases with increase in CH_2 group thereby decreasing the reversibility of the process and consequently diminishing the magnitude of the peak and also due to the increase in viscosity of the solvent with increase in CH_2 group, thereby decreasing the diffusion coefficient of the solute.

It may be mentioned here that the magnitude of the nitrobenzene peak is very much diminished in pyridine as compared to dimethylformamide as solvent having similar viscosities. This may be due to some interaction between pyridine and nitrobenzene which is indicated by the fact that the mixture of nitrobenzene and pyridine in aqueous medium gives the peak whose peak potential is different from the individual peak potentials of both nitrobenzene and pyridine (Fig. 1).

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PAPER No. 4

EFFECT OF CONCENTRATION OF SOME OF THE ORGANIC NITRO COMPOUNDS ON THEIR PEAK POTENTIALS BY A.C. POLAROGRAPHY

(Jour. B.I.T.S., in press)

EFFECT OF CONCENTRATION OF SOME OF THE ORGANIC NITRO COMPOUNDS ON THEIR PEAK POTENTIALS BY A.C. POLAROGRAPHY

It has been observed, with some of the organic nitro compounds which give reduction peaks at the d.m.e., that in certain cases the peak potential changes to more cathodic values by increasing the concentration of the solute whereas in other cases there is no shift in the peak potential with change in the concentration of the solute. Nitrobenzene, ortho and meta nitrobenzoic acids and para nitrophenol peaks do not shift with concentration at alkaline pH values (pH = 11.3), whereas the peak potentials of ortho and meta nitrophenols, di and tri nitrophenols, ortho and meta nitrotoluenes and meta and para nitroanilines progressively shift to more cathodic values with increase of their concentrations. In acidic pH value (pH = 3.5) the peak potentials of all the nitro compounds tried shift to more cathodic values with increase in concentration of the solute. This shift of peak potentials with increase in concentration of the solute may be related to the greater tendency of the irreversible nature of the electrode process. The causes of these effects have been discussed.

The effect of organic compounds on the d.m.e. capacity in pulsating field is responsible for the peaks observed, The peaks may be broadly classified into those caused by - (a) adsorption - desorption and (b) chemical reactions (reduction or oxidation). According to Hacobian[1] these two classes of peaks can be distinguished by the fact that the peak potential of the chemical peaks does not very with the concentration of the surface active solute, whereas the peak potential varies continuously with the logarithm of the concentration in the case of desorption peaks. The general theory proposed by Doss and Gupta[2] indicates, however, that the desorption peaks can also occur at a fixed potential irrespective of the concentration of the solute.

In course of our studies with some of the organic nitro compounds at the d.m.e. which give reduction peaks, we observed that in certain cases the peak potential changes to more cathodic values by increasing the concentration of the solute, whereas in other cases there is no shift in the peak potential with change in the concentration of the solute. This investigation therefore gives the results obtained in such studies by a.c. polarography.

EXPERIMENTAL

Nitrobenzene and all other liquid organic compounds were of B.D.H. and E. Merck quality and were redistilled in all glass fractionating column and the middle one third of the distillates were used for the experiments. The organic solid compounds were recrystallised samples of B.D.H. Mercury

used for the dropping electrode was further purified by the method described in literature[3]. The d.c. potentials were applied with respect to the saturated calomel electrode. All the experiments were carried out at a constant temperature of 30 ± 0.5°C.

The apparatus employed in the present investigation is the same as that has been described earlier. 0.1 M potassium chloride solution was used as indifferent electrolyte. The d.m.e. was cathodic throughout the measurements. The constants of the d.m.e. were as follows:-

m = 4.564 mg/sec.

t = 1.8 sec. per drop in 0.1 M KCl, open circuit.

Mixtures of (i) Ammonium acetate and HCl and (ii) NaOH were used as buffers for acidic and alkaline media respectively. The pH measurements were done with glass electrode using Beckman pH meter model H2.

RESULTS AND DISCUSSION.

Table I gives the effect of concentration of nitro compounds on peak potentials at pH 11.3 and 3.5. At pH 11.3, it can be seen that nitrobenzene, o-nitrobenzoic acid,m-nitrobenzoic acid, 3:5 dinitrobenzoic acid, sym-trinitrobenzoic acid and p-nitrophenol produce no change in peak potentials with increase in concentration of the solute whereas with ortho and meta nitrophenols, 2:4 dinitrophenol, 2:4:6 tri-

Table I

Effect of concentration on the peak potentials of organic reduction peaks

± 20 mV; 50 c/sec.; Temperature = 30 ± 0.5°C; 0.1 M KCl as the supporting electrolyte

Name of the compound	Peak Potential, Volts																				
	pH = 11.3											pH = 3.5									
	Concentrations in millimdes											Concentrations in millimoles									
	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.4	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.4
* Nitrobenzene	0.72	0.72	0.73	0.73	0.73	-	-	-	-	-	-	0.38	0.39	0.39	0.41	0.42	0.425	-	0.43	-	0.43	0.43
o-nitrobenzoic acid	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	-	-	-	-	0.335	0.335	0.335	0.34	0.345	0.355	0.365	0.37	-	-
* m-nitrobenzoic acid	0.72	-	0.73	0.73	0.73	0.73	-	-	-	-	-	-	0.34	0.36	0.37	0.385	0.385	0.385	0.385	-	-	-
3:5 dinitrobenzoic acid	-	-	0.62	0.63	0.63	0.63	-	-	-	-	-	-	-	-	0.18	0.20	0.21	0.23	-	-	-	-
	0.70	0.70	0.73	0.74	0.74	0.74	-	-	-	-	-	-	0.34	0.36	0.365	0.37	0.38	0.38	-	-	-	-
*Sym-trinitrobenzoic acid	0.70	0.70	0.70	0.70	0.70	0.70	0.70	-	-	-	-	0.40	0.40	0.35	0.37	0.40	-	-	-	-	-	-
	-	0.84	0.84	0.845	0.85	0.85	0.85	-	-	-	-											
* o-nitrophenol	0.785	0.795	-	0.82	-	0.84	-	0.855	-	0.865	0.865	0.355	0.38	0.385	0.395	0.40	0.41	0.41	-	-	-	-
* m-nitrophenol	0.79	0.79	0.80	0.805	-	0.81	-	0.82	-	0.825	0.825	0.355	0.36	0.375	0.395	0.415	0.42	0.42	0.43	0.44	-	-
p-nitrophenol	0.94	0.94	-	0.94	-	0.94	-	0.94	-	0.94	0.945	0.43	0.43	0.44	0.46	0.46	0.46	-	-	-	-	-
* 2:4 dinitrophenol	0.835	0.835	0.84	0.855	0.86	0.87	0.87	-	-	-	-	-	0.28	0.29	0.29	0.29	0.29	0.29	0.29	-	-	-
	0.955	0.965	0.975	0.99	1.00	1.02	1.02	-	-	-	-	-	0.50	0.52	0.52	0.54	0.56	0.57	0.57	-	-	-
* 2:4:6 trinitro-phenol	0.70	0.71	0.72	0.73	0.73	0.735	0.745	0.76	-	-	-	0.25	0.255	0.265	0.29	0.30	0.315	0.315	-	-	-	-
	0.965	0.985	1.01	1.03	1.04	1.05	1.07	1.09	-	-	-											
o-nitrotoluene	0.79	0.80	0.81	0.82	0.835	0.84	-	-	-	-	-	0.44	0.46	0.465	0.47	0.47	0.475	-	-	-	-	-
m-nitrotoluene	0.75	0.765	0.78	0.795	0.795	0.795	-	-	-	-	-	0.39	0.40	0.41	0.415	0.43	0.44	0.44	-	-	-	-
* m-nitroaniline	0.75	0.765	0.805	0.805	0.81	0.81	-	-	-	-	-	0.40	0.40	0.40	0.41	0.425	0.425	0.425	0.44	0.44	-	-
* p-nitroaniline	0.875	0.88	0.89	0.895	0.895	-	-	-	-	-	-	0.49	0.52	0.56	0.58	0.60	0.61	0.615	0.615	-	-	-

* 0.01% Gelation added at pH 3.5.

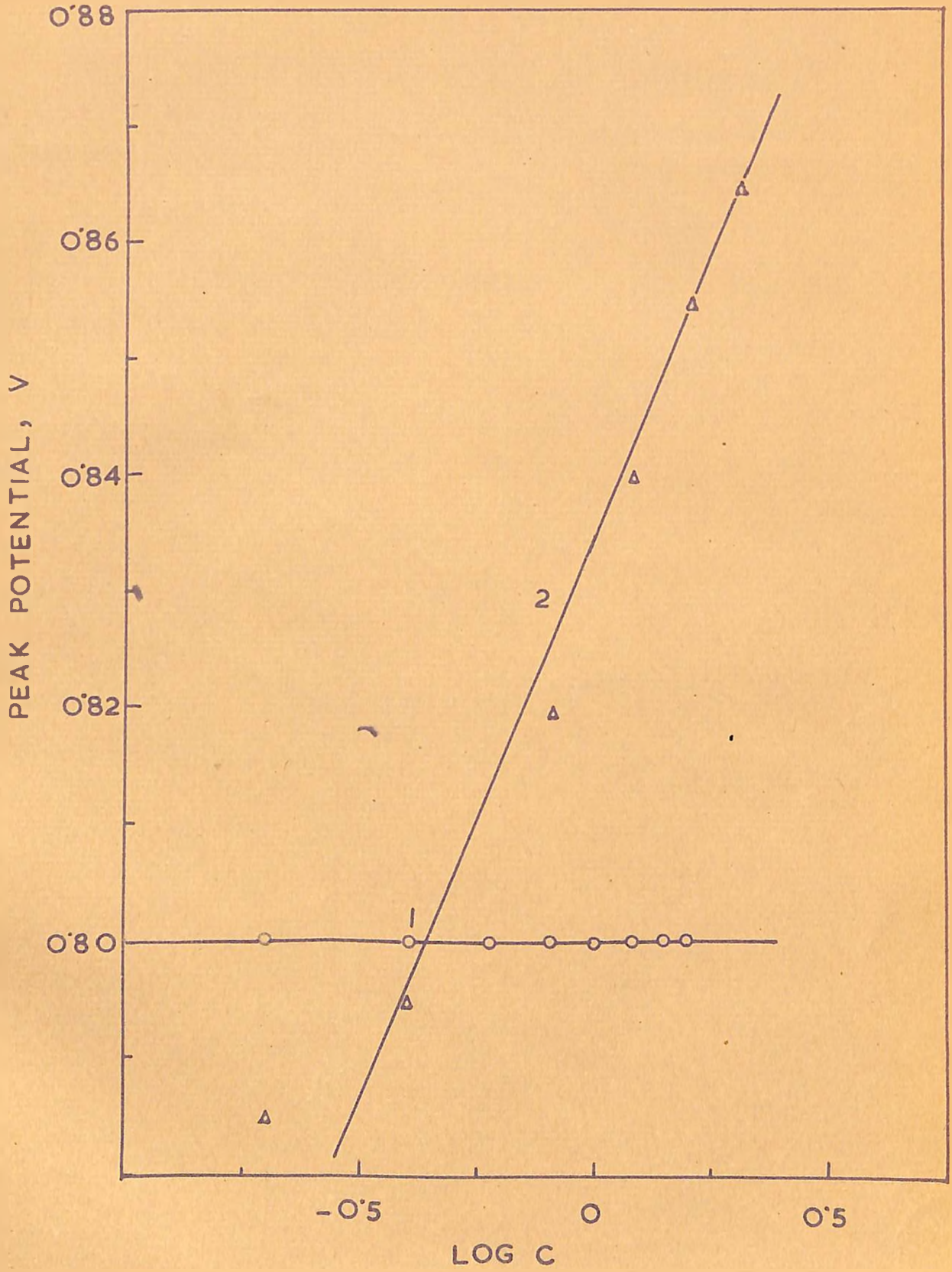

FIG. 1.

LEGEND OF FIGURES

Fig. 1: Effect of concentration of o-nitrobenzoic acid and o-nitrophenol on their peak potentials.

Curve 1: o-nitrobenzoic acid.

Curve 2: o-nitrophenol.

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tion is in agreement with the fact that at lower pH values more electrons are needed for reduction process than at alkaline pH.

At alkaline pH the shift of peak potential in certain compounds with increase in concentration of the solute may be explained on the basis of structural effects of the substituent groups on the reduction of nitrobenzene.

In case of nitrobenzoic acids we find no change of peak potential with increase in concentration of the solute at alkaline pH value. Further, the peak potentials almost correspond to the reduction potential of nitrobenzene, which suggests that COOH group has no effect on the reduction of NO_2 group. However, the reduction potential of o-nitrobenzoic acid and the second peak of sym-trinitro benzoic acid are more negative, which may be due to the hydrogen bonding between COOH and NO_2 groups in the ortho position.

The nitrophenols are reduced at the d.m.e. as follows:-

$$HO.C_6H_4NO_2 + 2e + 2H^+ \longrightarrow HO.C_6H_4.NO + H_2O$$

which is a 2 electron irreversible process. $HO.C_6H_4.NO$ is further reduced reversibly to $HO.C_6H_4.NHOH$:-

$$HO.C_6H_4.NO + 2e + 2H^+ \rightleftharpoons HO.C_6H_4.NHOH.$$

This hydroxylamine is stable in acidic medium. In alkaline medium the unstable hydroxylamine rearranges to:-

$$HO.C_6H_4.NHOH \rightleftharpoons O = C_6H_4 = NH + H_2O$$

which is further reduced reversibly to:-

$$O = C_6H_4 = NH + 2e + 2H^+ \rightleftharpoons HO.C_6H_4.NH_2.$$

The overall reduction process although irreversible, has a tendency to be more reversible in alkaline medium. At alkaline pH o-nitrophenol and p-nitrophenol both can form the quinonoid structure as given in the above equation, but m-nitrophenol cannot do so. The reduction of m-nitrophenol will thus be more irreversible than ortho - and para nitrophenols. This is confirmed by the fact that the peak potentials of p-nitrophenol remains unchanged even at very high concentration of the reducible species at alkaline pH. The shift in peak potential in o-nitrophenol at the same pH may be due to the complications of NO_2 group being in the ortho position.

The reductions of 2:4 dinitrophenol and 2:4:6 trinitrophenol are more complicated becuase of the fact that in these compounds more than one nitro group is involved. As one of the nitro groups in dinitrophenol is reduced to amine at both pH values[6] the quinonoid structure is possible only with one nitro group. The overall reduction process therefore becomes more irreversible than those involved in the mono-nitrophenols.

In nitrotoluenes and nitroanilines although the reduction process involves only one nitro group and the process is similar to that of nitrobenzene, the presence of CH_3 group and NH_2 group in the nucleus makes the reduction more irreversible than that of nitrobenzene at alkaline pH. p-nitroaniline which can give a quinonoid structure with the phenylhydroxylamine tends to

increase the reversibility of the reduction process at alkaline pH. This is evident from the effect of concentration on the peak potential of p-nitroaniline, where the shift is only 20 mV within the concentration range of 2.0×10^{-4} M to 1.0×10^{-3} M.

It can therefore be seen that a.c. reduction peaks of organic nitro compounds can also vary with change in concentration of the solute. This shift of peak potentials with increase in concentration of the solute may be related to the irreversible nature of the electrode process.

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CHAPTER II

A.C. POLAROGRAPHIC STUDIES ON ELECTRODE PROCESSES IN PRESENCE OF ADSORBED FILMS

PAPER No. 5

A.C. POLAROGRAPHIC STUDIES OF THE MIXTURES OF REDUCIBLE ORGANIC COMPOUNDS

A.C. POLAROGRAPHIC STUDIES OF THE MIXTURES OF REDUCIBLE ORGANIC COMPOUNDS

The influence of organic reduction waves on one another, has been studied by a.c. polarography. p-nitrophenol can be estimated quantitatively from its mixture with nitrobenzene as well as with o-nitrophenol or m-nitrophenol and vice-versa within specified concentration ranges. The magnitude of nitrobenzene and p-nitrophenol peaks progressively decrease with increasing concentration of benzaldehyde and p-nitroaniline. Magnitude and peak potential of benzaldehyde and p-nitroaniline are not influenced by increasing the concentration of nitrobenzene or p-nitrophenol. When nitrobenzene is mixed with o-nitrophenol or m-nitrophenol, the individual peaks disappear and instead a new peak appears whose peak potential and magnitude differ from the individual peaks. The causes of these effects have been discussed.

Gupta and Sharma[1] studied the influence of tensammetric waves on reduction peaks of inorganic compounds. They[2] also investigated the influence of tensammetric waves on one another. As no data are available in literature on the influence of organic reduction waves on one another, the present investigation

gives in detail the results obtained on such studies by a.c. polarography.

EXPERIMENTAL

Nitrophenols (ortho, meta and para) (B.D.H.) and p-nitroaniline (B.D.H.) were recrystallised before use. Nitrobenzene (B.D.H., A.R.) and benzaldehyde (B.D.H.) were redistilled in an all glass fractionating column, middle one third of the distillate was used for experiments. Other chemicals used were of AnalaR quality of B.D.H. Mercury used for the pool and the dropping electrode was purified by standard methods.

The experimental set up and technique of measurement were same as described earlier. The d.c. potentials were expressed with reference to the saturated calomel electrode and all the experiments were carried out at a constant temperature of $30 \pm 0.5^{\circ}$. The d.m.e. was cathodic throughout the measurements and its constants were as follows:-

$m = 4.564$ mg/sec.

$t = 1.8$ sec. per drop in 0.1 M KCl, open circuit.

0.1 M potassium chloride solution was used as supporting electrolyte and was invariably shaken and kept in contact with mercury and mercurous chloride.

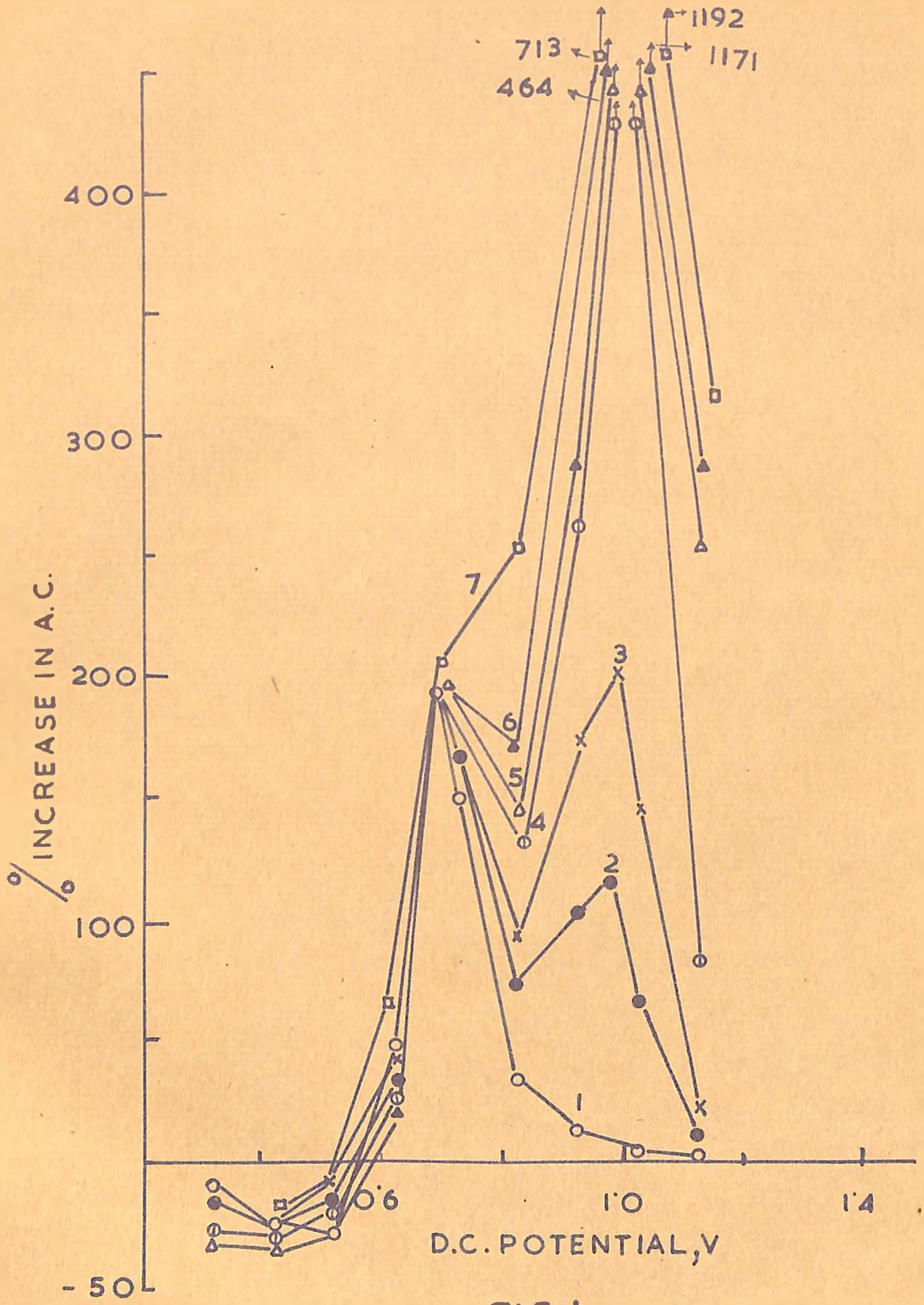
RESULTS AND DISCUSSION

Figure 1 shows the effect of various concentrations of

p-nitrophenol at pH 10.8 on the reduction peak of nitrobenzene (4×10^{-4}M). It is seen that the magnitude and peak potential of nitrobenzene peak are not influenced up to a concentration of 4×10^{-3}M p-nitrophenol, but with concentrations greater than this only p-nitrophenol peak is obtained. Similarly Fig.2 shows the effect of various concentrations of nitrobenzene on the reduction peak of p-nitrophenol (4×10^{-4}M) at the same pH. Here also the magnitude and the peak potential of p-nitrophenol peak are not influenced up to a concentration of 2×10^{-3}M nitrobenzene but concentrations greater than this produce only nitrobenzene peak. It seems, therefore, possible to estimate quantitatively nitrobenzene and p-nitrophenol from a mixture of 4×10^{-4}M nitrobenzene and 4×10^{-3}M p-nitrophenol as well as 4×10^{-4}M p-nitrophenol and 2×10^{-3}M nitrobenzene respectively.

Similarly p-nitrophenol can be estimated quantitatively from its mixture with o-nitrophenol or m-nitrophenol within the concentration range of 4×10^{-4}M p-nitrophenol and 1×10^{-3}M ortho or meta nitrophenols respectively and vice-versa. Ortho and meta nitrophenols cannot be estimated from their mixture under similar conditions, probably, because their peak potentials are close together. Similar results are obtained in methanolic medium (vide Figs. 3 and 4).

Figure 5 shows the effect of various concentrations of benzaldehyde at pH 5.8 on the reduction peak of nitrobenzene (4×10^{-4}M). It is seen that the magnitude of the nitrobenzene peak progressively decreases with increase in concentration of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6
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0·6
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D.C. POTENTIAL, V

FIG. 1.

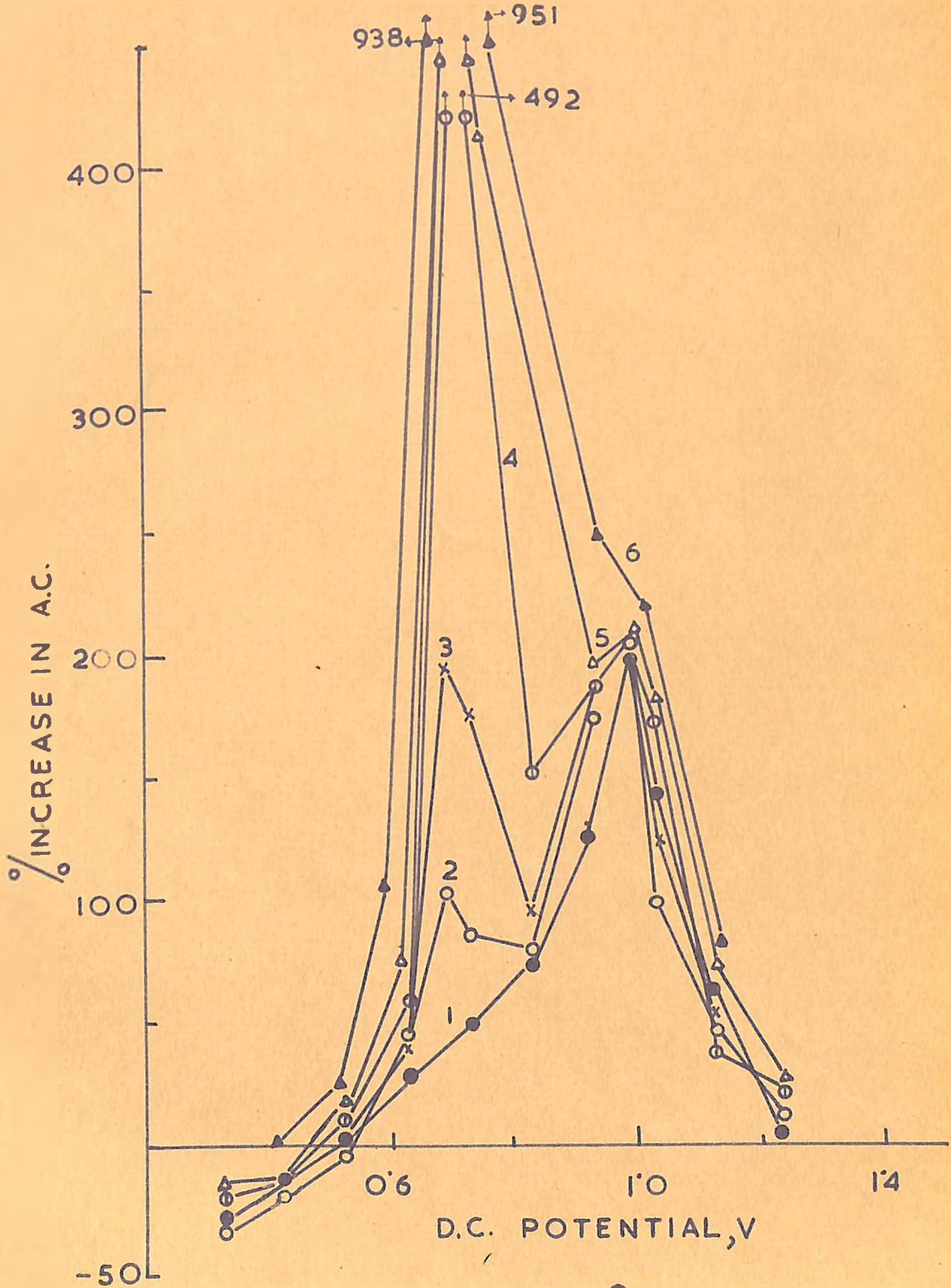
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FIG. 2.

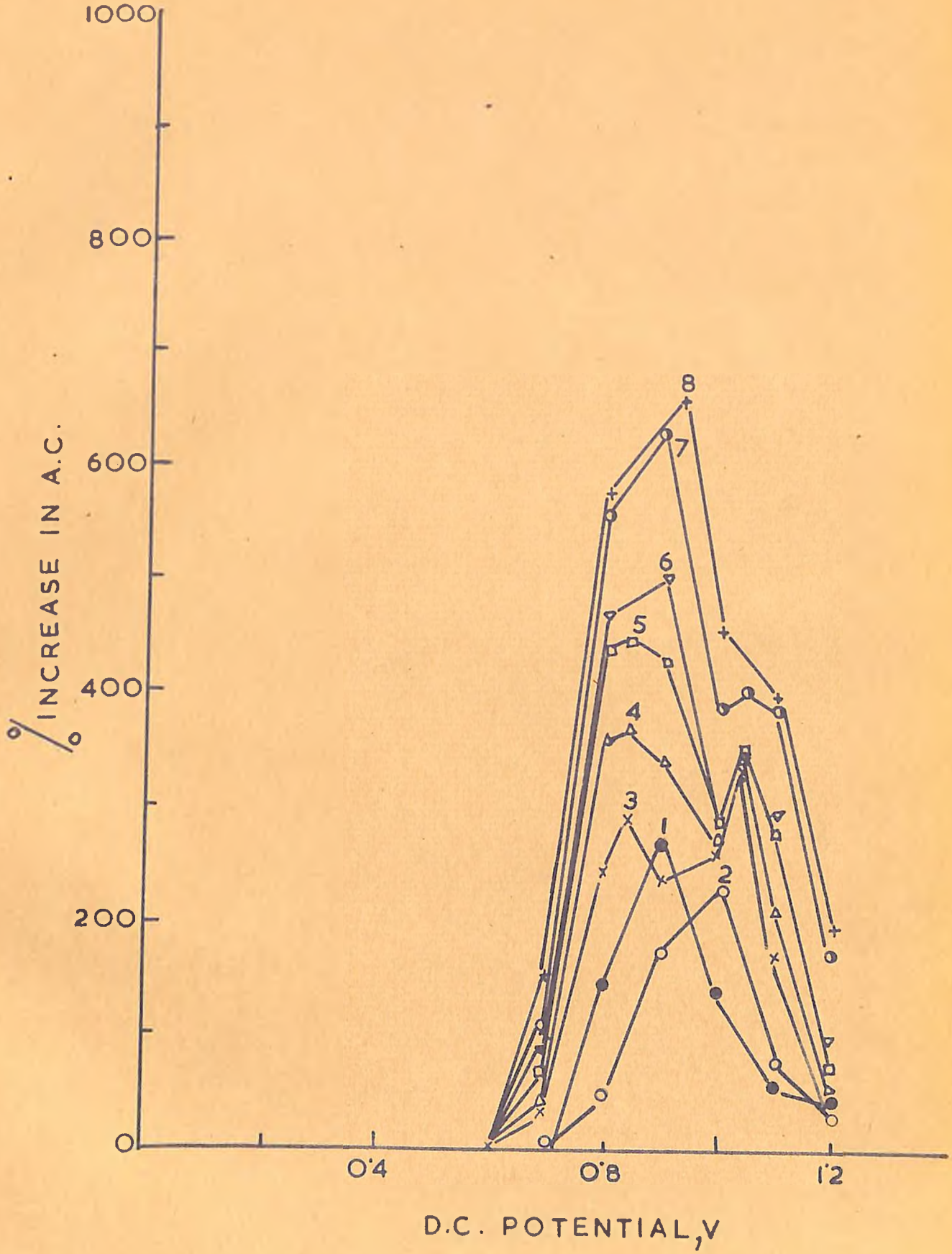
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FIG. 3.

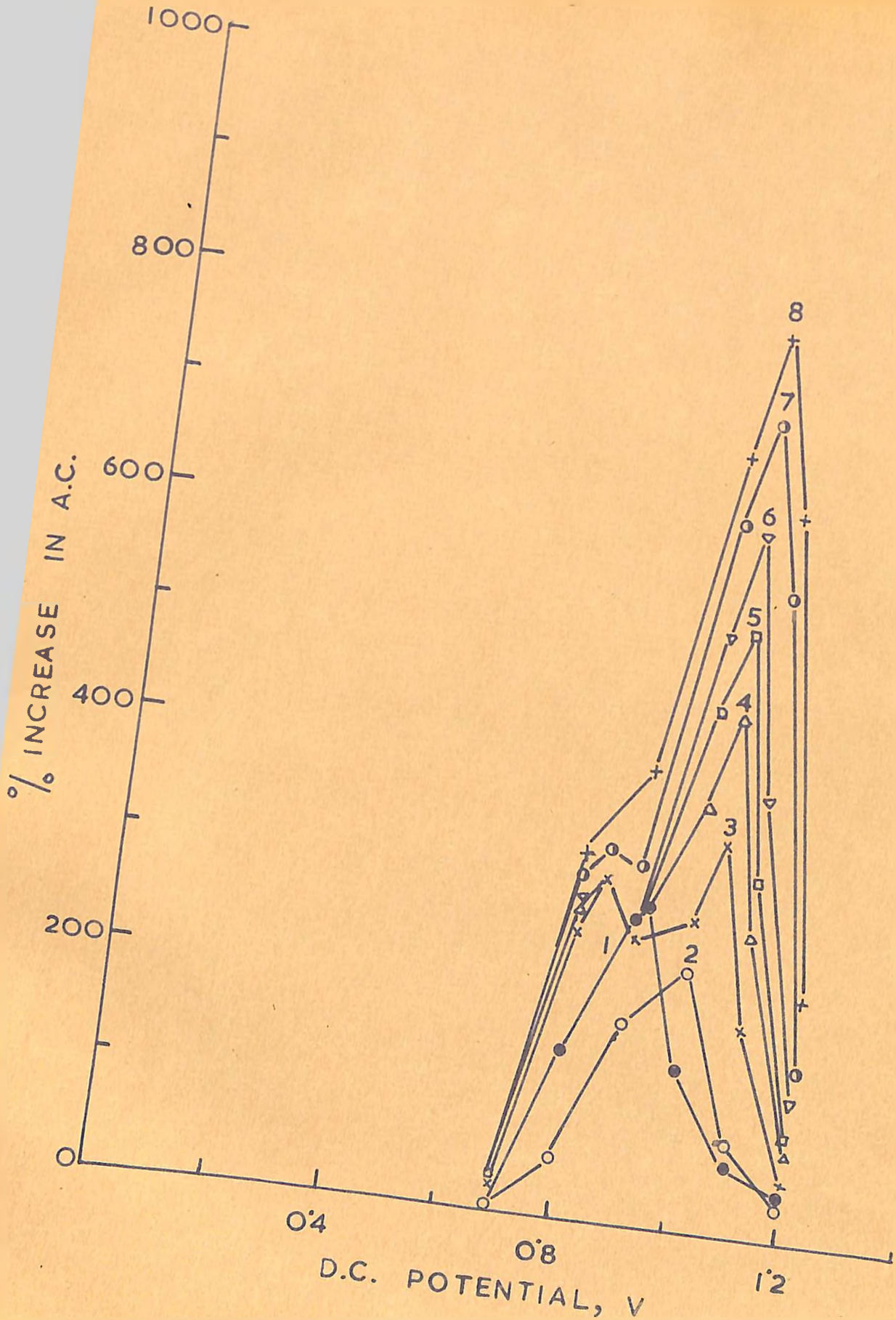
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FIG. 4

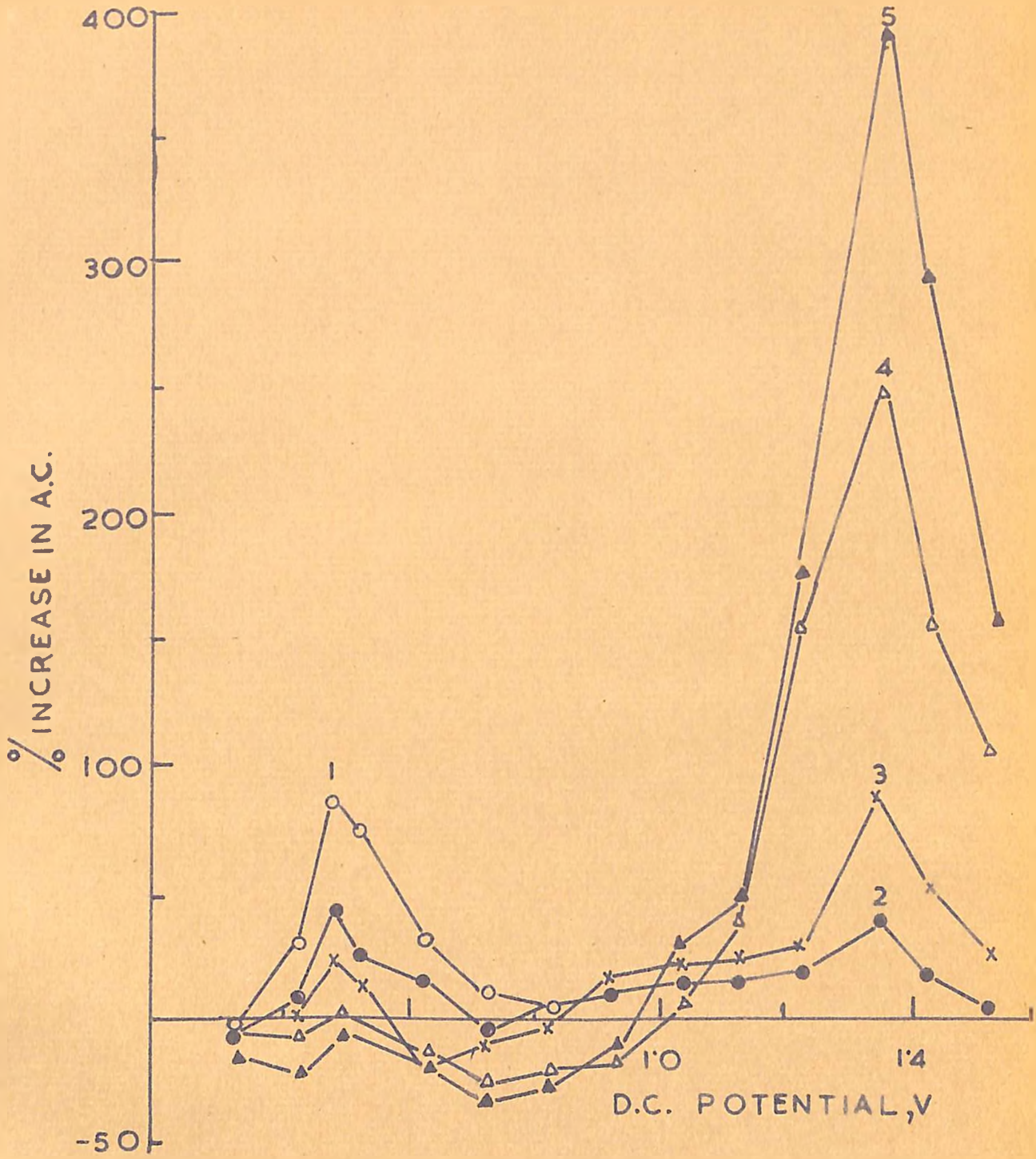

FIG.5.

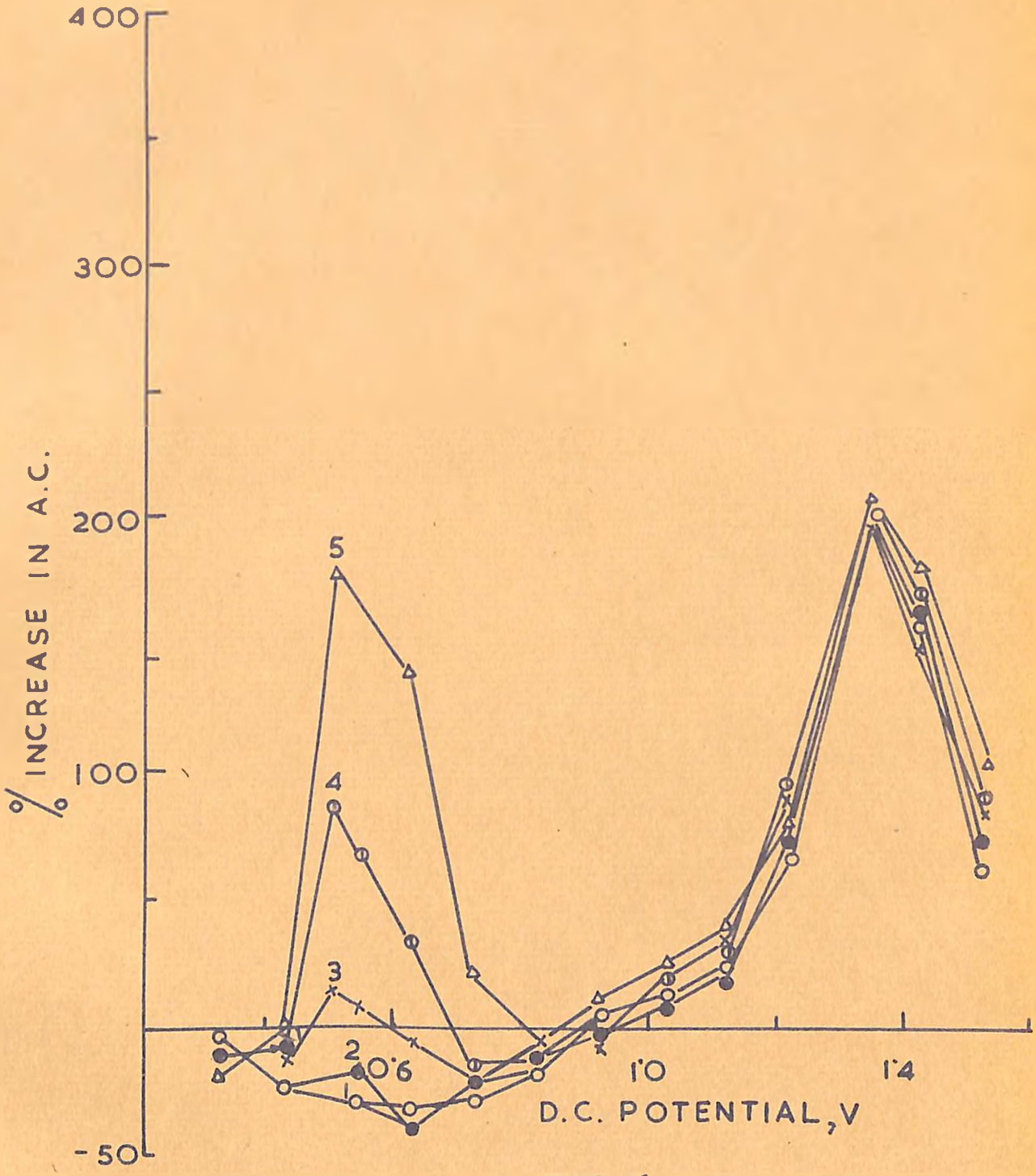

FIG.6.

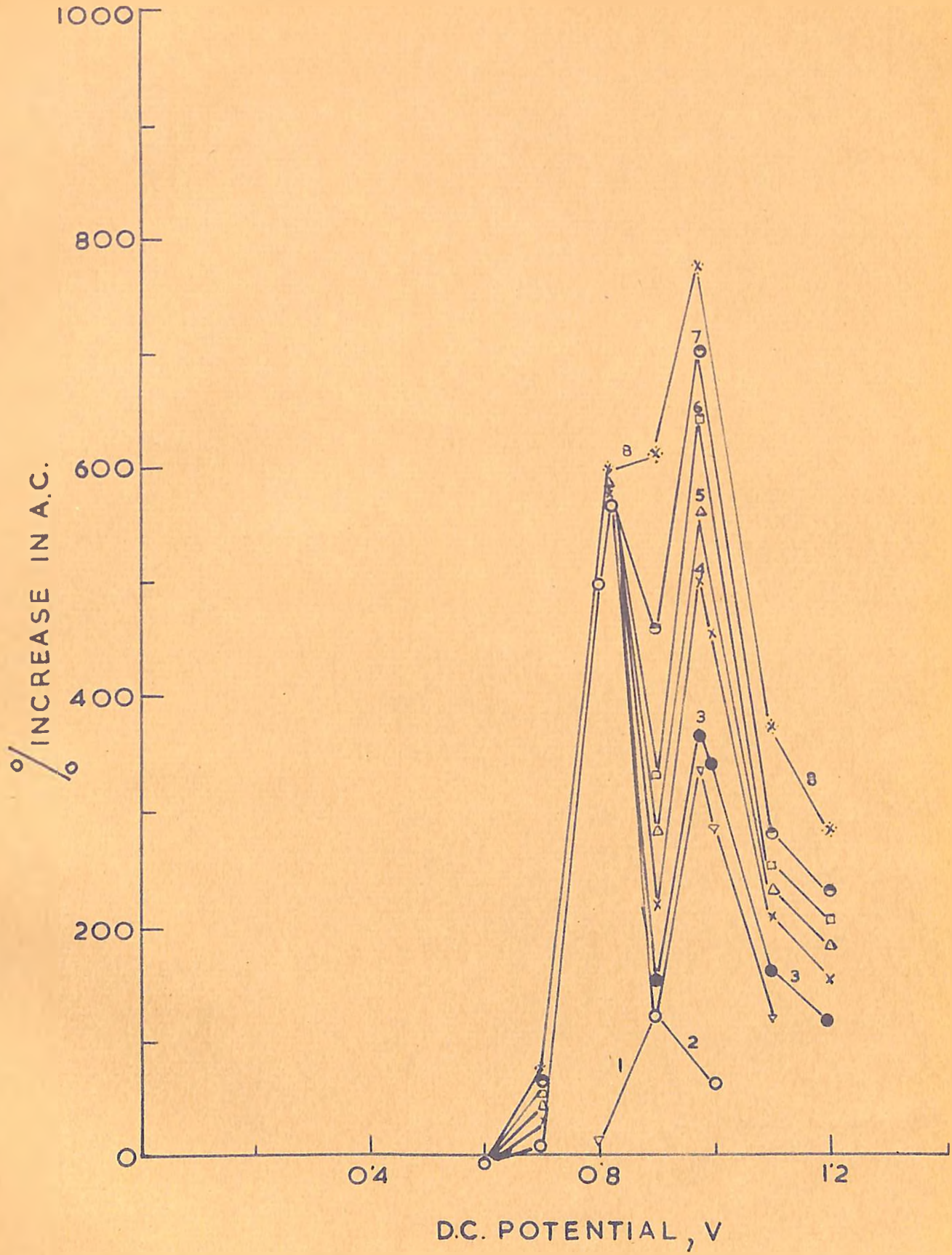
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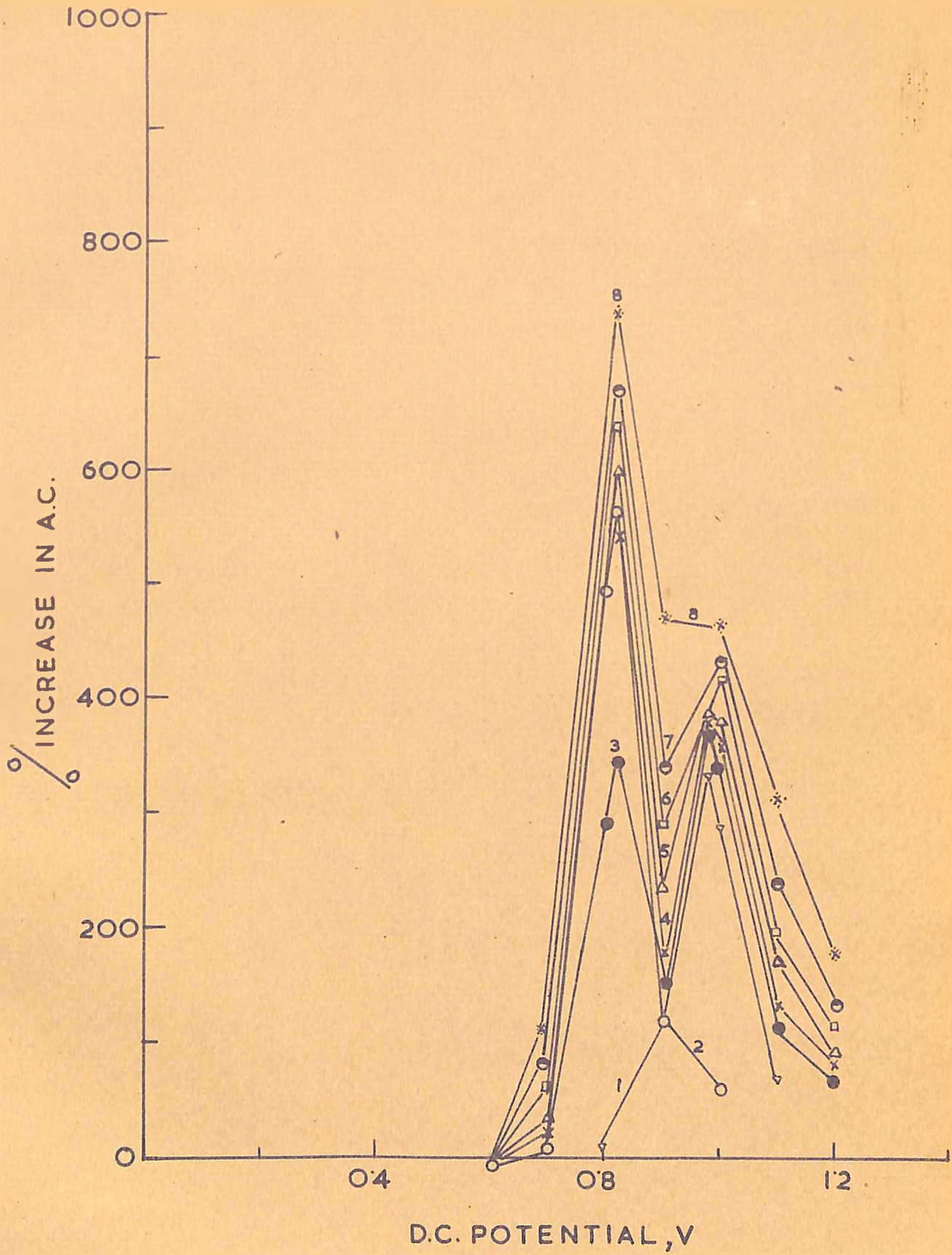
FIG.7.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% INCREASE IN A.C.
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D.C. POTENTIAL, V
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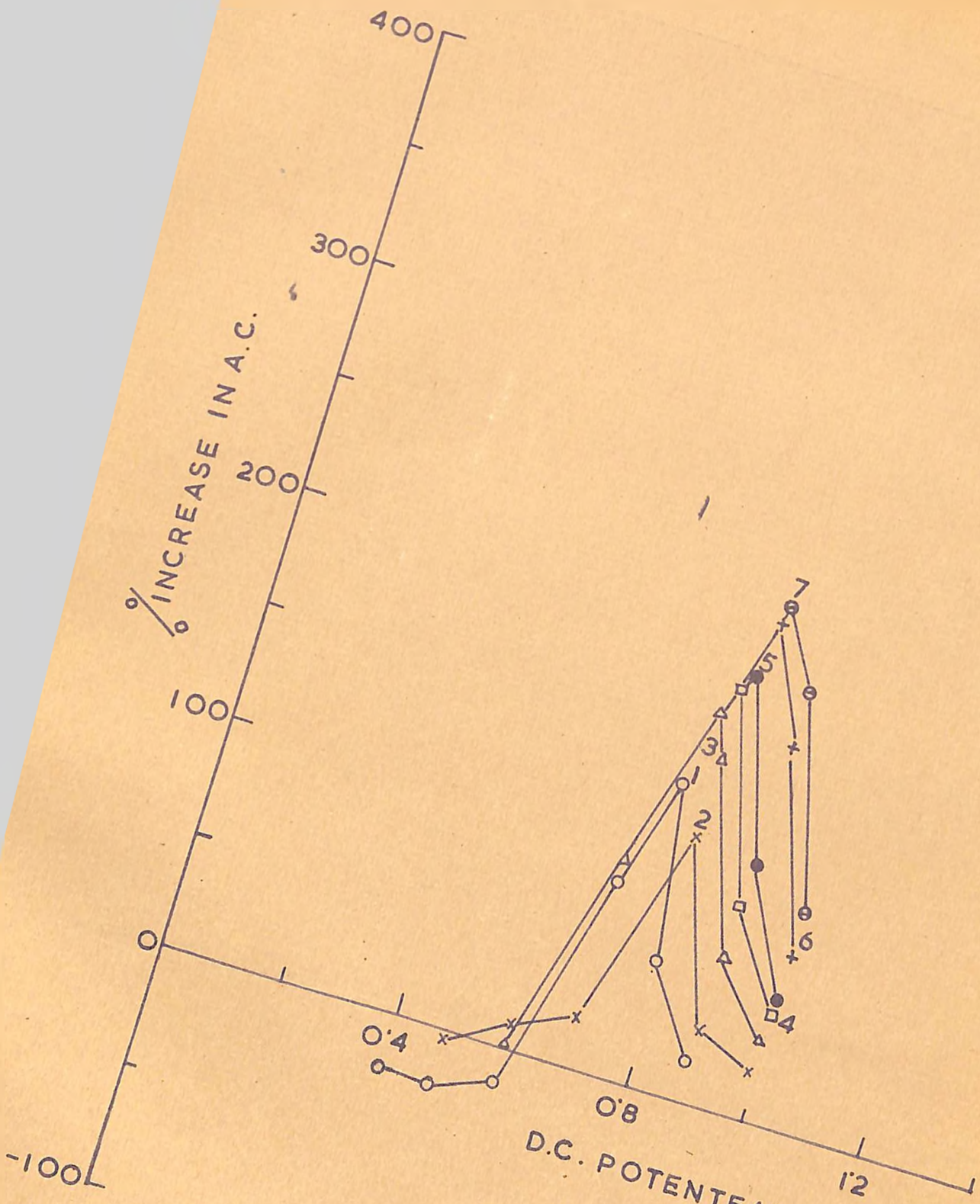
FIG. 8.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% INCREASE IN A.C.
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D.C. POTENTEAL, V
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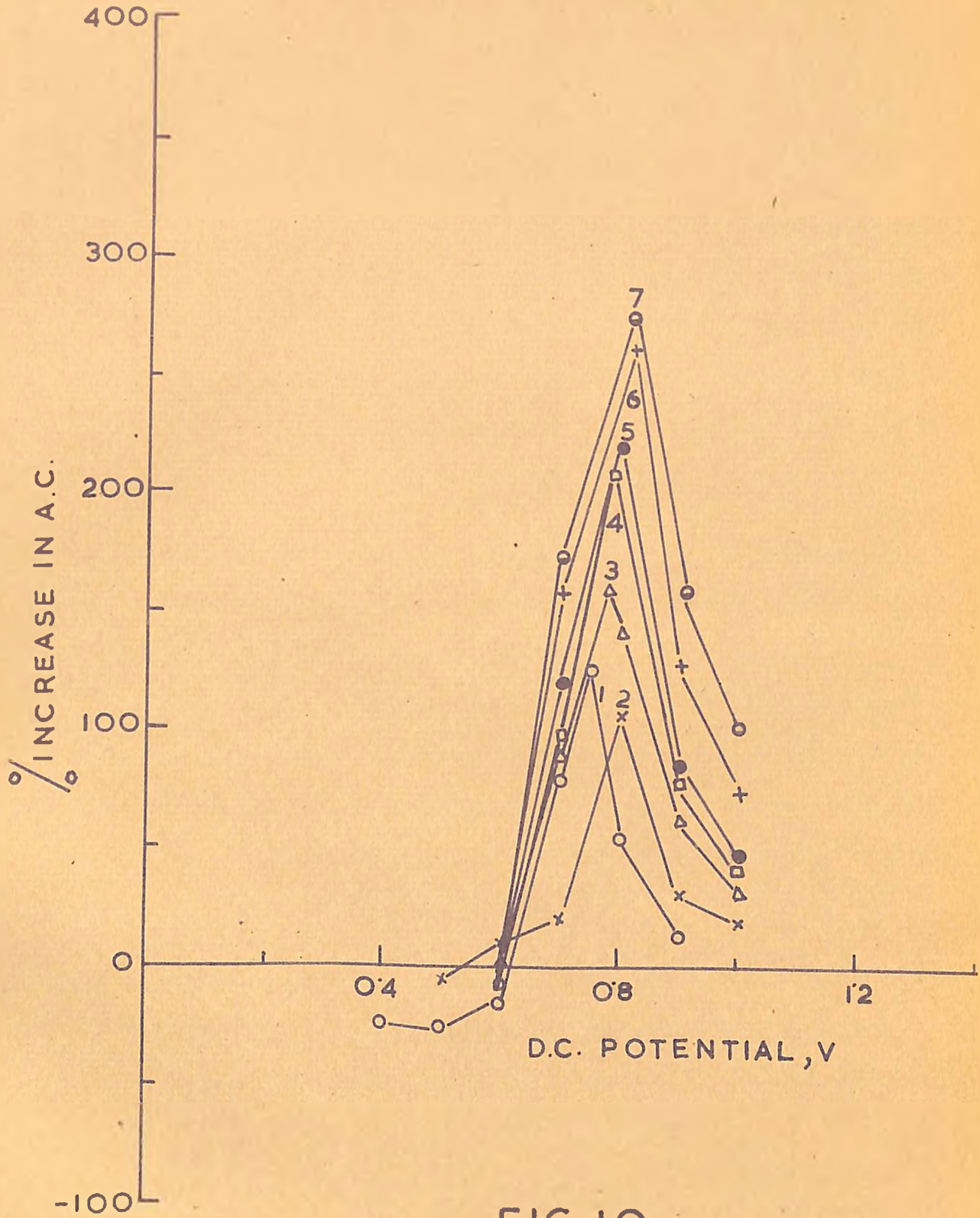
FIG. 9.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% INCREASE IN A.C.
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D.C. POTENTIAL, V
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FIG. 10.

LEGEND OF FIGURES

Fig. 1: Effect of various concentrations of p-nitrophenol on the nitrobenzene peak.

1 - 4×10^{-4}M nitrobenzene;

2 - 4×10^{-4}M nitrobenzene + 2×10^{-4}M p-nitrophenol;

3 - 4×10^{-4}M nitrobenzene + 4×10^{-4}M p-nitrophenol;

4 - 4×10^{-4}M nitrobenzene + 1×10^{-3}M p-nitrophenol;

5 - 4×10^{-4}M nitrobenzene + 2×10^{-3}M p-nitrophenol;

6 - 4×10^{-4}M nitrobenzene + 4×10^{-3}M p-nitrophenol;

7 - 4×10^{-4}M nitrobenzene + 5×10^{-3}M p-nitrophenol.

Fig. 2: Effect of various concentrations of nitrobenzene on the p-nitrophenol peak.

1 - 4×10^{-4}M p-nitrophenol;

2 - 4×10^{-4}M p-nitrophenol + 2×10^{-4}M nitrobenzene;

3 - 4×10^{-4}M p-nitrophenol + 4×10^{-4}M nitrobenzene;

4 - 4×10^{-4}M p-nitrophenol + 1×10^{-3}M nitrobenzene;

5 - 4×10^{-4}M p-nitrophenol + 2×10^{-3}M nitrobenzene;

6 - 4×10^{-4}M p-nitrophenol + 3×10^{-3}M nitrobenzene.

Fig. 3: Effect of various concentrations of m-nitrophenol on the p-nitrophenol peak in methanolic medium.

pH = 7.0; 1.0 M LiCl in methanol.

1 - 4×10^{-4}M m-nitrophenol;

2 - 4×10^{-4}M p-nitrophenol;

3 - 4×10^{-4}M m-nitrophenol + 4×10^{-4}M p-nitrophenol;

4 - 6×10^{-4}M m-nitrophenol + 4×10^{-4}M p-nitrophenol;

5 - 8×10^{-4}M m-nitrophenol + 4×10^{-4}M p-nitrophenol;

6 - 1×10^{-3}M m-nitrophenol + 4×10^{-4}M p-nitrophenol;

7 - 1.5×10^{-3}M m-nitrophenol + 4×10^{-4}M p-nitrophenol;

8 - 2×10^{-3}M m-nitrophenol + 4×10^{-4}M p-nitrophenol.

Fig. 4: Effect of various concentrations of p-nitrophenol on the m-nitrophenol peak in methanolic medium.
pH = 7.0; 1.0 M LiCl in methanol.
1 - 4×10^{-4}M m-nitrophenol;
2 - 4×10^{-4}M p-nitrophenol;
3 - 4×10^{-4}M m-nitrophenol + 4×10^{-4}M p-nitrophenol;
4 - 4×10^{-4}M m-nitrophenol + 6×10^{-4}M p-nitrophenol;
5 - 4×10^{-4}M m-nitrophenol + 8×10^{-4}M p-nitrophenol;
6 - 4×10^{-4}M m-nitrophenol + 1×10^{-3}M p-nitrophenol;
7 - 4×10^{-4}M m-nitrophenol + 1.5×10^{-3}M p-nitrophenol;
8 - 4×10^{-4}M m-nitrophenol + 2.0×10^{-3}M p-nitrophenol;

Fig. 5: Effect of various concentrations of benzaldehyde on the nitrobenzene peak.
1 - 4×10^{-4}M nitrobenzene;
2 - 4×10^{-4}M nitrobenzene + 4×10^{-4}M benzaldehyde;
3 - 4×10^{-4}M nitrobenzene + 8×10^{-4}M benzaldehyde;
4 - 4×10^{-4}M nitrobenzene + 3×10^{-3}M benzaldehyde;
5 - 4×10^{-4}M nitrobenzene + 4×10^{-3}M benzaldehyde.

Fig. 6: Effect of various concentrations of nitrobenzene on benzaldehyde peak.
1 - 2×10^{-3}M benzaldehyde;
2 - 2×10^{-3}M benzaldehyde + 2×10^{-4}M nitrobenzene;
3 - 2×10^{-3}M benzaldehyde + 4×10^{-4}M nitrobenzene;
4 - 2×10^{-3}M benzaldehyde + 1×10^{-3}M nitrobenzene;
5 - 2×10^{-3}M benzaldehyde + 2×10^{-3}M nitrobenzene.

Fig. 7: Effect of various concentrations of p-nitroaniline on nitrobenzene peak.

pH = 7.0; 1.0 M LiCl in methanol.

1 - 4×10^{-4}M p-nitroaniline;

2 - 4×10^{-4}M nitrobenzene;

3 - 4×10^{-4}M p-nitroaniline + 4×10^{-4}M nitrobenzene;

4 - 6×10^{-4}M p-nitroaniline + 4×10^{-4}M nitrobenzene;

5 - 8×10^{-4}M p-nitroaniline + 4×10^{-4}M nitrobenzene;

6 - 1×10^{-3}M p-nitroaniline + 4×10^{-4}M nitrobenzene;

7 - 1.2×10^{-3}M p-nitroaniline + 4×10^{-4}M nitrobenzene;

8 - 1.6×10^{-3}M p-nitroaniline + 4×10^{-4}M nitrobenzene;

Fig. 8: Effect of various concentrations of nitrobenzene on the p-nitroaniline peak in methanolic medium.

pH = 7.0; 1.0 M LiCl in methanol.

1 - 4×10^{-4}M p-nitroaniline;

2 - 4×10^{-4}M nitrobenzene;

3 - 4×10^{-4}M p-nitroaniline + 2×10^{-4}M nitrobenzene;

4 - 4×10^{-4}M p-nitroaniline + 4×10^{-4}M nitrobenzene;

5 - 4×10^{-4}M p-nitroaniline + 6×10^{-4}M nitrobenzene;

6 - 4×10^{-4}M p-nitroaniline + 8×10^{-4}M nitrobenzene;

7 - 4×10^{-4}M p-nitroaniline + 1×10^{-3}M nitrobenzene;

8 - 4×10^{-4}M p-nitroaniline + 1.5×10^{-3}M nitrobenzene.

Fig. 9: Effect of various concentrations of m-nitrophenol on the nitrobenzene peak.

1 - 4 x 10^{-4}M nitrobenzene;
2 - 4 x 10^{-4}M m-nitrophenol;
3 - 4 x 10^{-4}M nitrobenzene + 4 x 10^{-4}M m-nitrophenol;
4 - 4 x 10^{-4}M nitrobenzene + 6 x 10^{-4}M m-nitrophenol;
5 - 4 x 10^{-4}M nitrobenzene + 8 x 10^{-4}M m-nitrophenol;
6 - 4 x 10^{-4}M nitrobenzene + 1.2x10^{-3}M m-nitrophenol;
7 - 4 x 10^{-4}M nitrobenzene + 1.6x10^{-3}M m-nitrophenol.

Fig.10: Effect of various concentrations of nitrobenzne on the m-nitrophenol peak.

1 - 4 x 10^{-4}M nitrobenzene;
2 - 4 x 10^{-4}M m-nitrophenol;
3 - 4 x 10^{-4}M nitrobenzene + 4 x 10^{-4}M m-nitrophenol;
4 - 6 x 10^{-4}M nitrobenzene + 4 x 10^{-4}M m-nitrophenol;
5 - 8 x 10^{-4}M nitrobenzene + 4 x 10^{-4}M m-nitrophenol;
6 - 1.2x10^{-3}M nitrobenzene + 4 x 10^{-4}M m-nitrophenol;
7 - 1.6x10^{-3}M nitrobenzene + 4 x 10^{-4}M m-nitrophenol.

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benzaldehyde till 3 x 10^{-3}M benzaldehyde suppresses the nitrobenzene peak in the positive side. Similarly, Fig. 6 gives the effect of various concentrations of nitrobenzene on the magnitude of benzaldehyde peak (2 x 10^{-3}M) at the same pH. It can be seen that nitrobenzene peak reappears and increases progressively with increasing concentration of nitrobenzene without affecting either the magnitude or peak potential of benzaldehyde peak. Similar effects are obtained with p-nitrophenol and benzaldehyde and vice-versa. Here it can be seen that the magnitude of the less cathodic peak is influenced by the substance corresponding to more cathodic reduction peak due to the adsorption of the latter on the electrode surface and thereby hindering the electrode process corresponding to less cathodic peak. It may be mentioned that benzaldehyde gives "composite peak" at acidic pH values which is indicative from its lowering of the differential double layer capacity to a large extent as compared to other reducible organic compounds. Similar results are obtained with nitrobenzene and p-nitroaniline in aqueous medium at alkaline pH. However, nitrobenzene and p-nitroaniline can be estimated quantitatively in their mixtures in methanolic medium (vide Figs. 7 and 8) where the adsorption effects of more cathodic peak on less cathodic peak are eliminated[3]. Figs. 9 and 10 give the effect of various concentrations of m-nitrophenol on nitrobenzene (4 x 10^{-4}M) and vice-versa respectively. Here it can be seen that the individual reduction peaks of 4 x 10^{-4}M nitrobenzene and m-nitrophenol (4 x 10^{-4}M) disappear and instead a new peak appears whose peak potential lies between the individual peaks of nitrobenzene and m-nitro-

phenol. The peak potential of the mixture shifts to more cathodic values with increase in concentration of either nitrobenzene or m-nitrophenol till it becomes constant. Similar behaviour is observed with the mixture of nitrobenzene and o-nitrophenol. It can be seen that in such cases the effect is quite different from that just discussed, which may be due to the chemical interaction between the two organic compounds to form a complex which is reduced at different potential.

In general, it can be concluded that the influence of organic reduction peaks on one another is threefold. In the first case, the peaks are free from any surface or chemical interaction effects. In such cases, various reducible organic compounds can be estimated quantitatively from their mixtures within specified concentration ranges which depends on the nature of compounds and the separation of their peak potentials. In the second case the less cathodic peaks are influenced by the more cathodic ones due to adsorption of the substance corresponding to more cathodic peak, whereas in the third case they are influenced by chemical interaction. In the last two cases, therefore, no quantitative estimations can be made.

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2. S.L. Gupta and S.K. Sharma, Electrochim. Acta, 1965, 10, 151.

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

PAPER No. 6

A.C. POLAROGRAPHIC STUDIES OF THE MIXTURES OF ORGANIC REDUCIBLE SPECIES AND SURFACE ACTIVE SUBSTANCES

A.C. POLAROGRAPHIC STUDIES OF THE MIXTURES OF ORGANIC REDUCIBLE SPECIES AND SURFACE ACTIVE SUBSTANCES

The effect of nature and concentration of the surface active substances (s.a.s.) on the a.c. reduction peaks of nitrobenzene and nitrophenols (ortho, meta and para) and vice-versa by a.c. polarography, have been studied. The magnitude of the reduction peak is not influenced up to a certain concentration of the s.a.s., but with concentrations higher than this, the magnitude of the reduction peak of nitrobenzene progressively decreases till it attains a certain minimum value whereas magnitudes of reduction peaks of nitrophenols (ortho, meta and para) diminish progressively till they are completely removed by surface active substances. Magnitude and the peak potential of the tensammetric peaks are not influenced by organic reducible substances. There is a linear relation between the concentration of the reducible substance and the optimum concentration of the s.a.s. just required to decrease the nitrobenzene peak to its minimum value. Ionic surfactants are more efficient in suppressing the reduction peak than non-ionic ones.

Breyer et al[1]. found that certain depolarizers freely

penetrate surface films and yield good a.c. waves even after addition of surface active substances such as p-nitrophenol in presence of octyl alcohol. Gupta and Sharma[2] studied the influence of tensammetric waves on reduction peaks of inorganic cations and found that magnitude of the reduction peak is not influenced up to a certain concentration of the s.a.s., but with concentrations higher than this, the magnitude of the reduction peak progressively diminishes till it is completely removed.

The purpose of the present investigation is to study in detail the influence of the tensammetric waves on a.c. reduction peaks of organic compounds and vice-versa at the dropping mercury electrode (d.m.e.) with a view to see the changes in the electrode processes in presence of adsorbed films.

EXPERIMENTAL

Bromothymol blue (B.T.B) was B.D.H. indicator quality. Cerfak (sodium naphthalene 2 dodecyl - 3 sulphonate) and cetylpyridinium bromide were commercial detergents. Organic solid compounds were either B.D.H. or Merck's quality and were recrystallised before use. Organic liquid substances were pure samples of either Merck or B.D.H. quality and were redistilled in an all glass fractionating column and the middle one third of the distillate was used for experiments. Inorganic chemicals used were AnalaR quality of B.D.H. Mercury used for pool and dropping electrode was purified by standard methods.

The experimental set up and the technique of measurement were same as described earlier. The d.c. potentials are expressed with reference to the saturated calomel electrode. All the experiments were done at a pH of 10.8 except where mentioned, and a temperature of 30 ± 0.5°. The d.m.e. was cathodic throughout the measurements and its constants were as follows:-

m = 4.564 mg/sec.

t = 1.8 sec. per drop in 0.1 M KCl, open circuit.

RESULTS

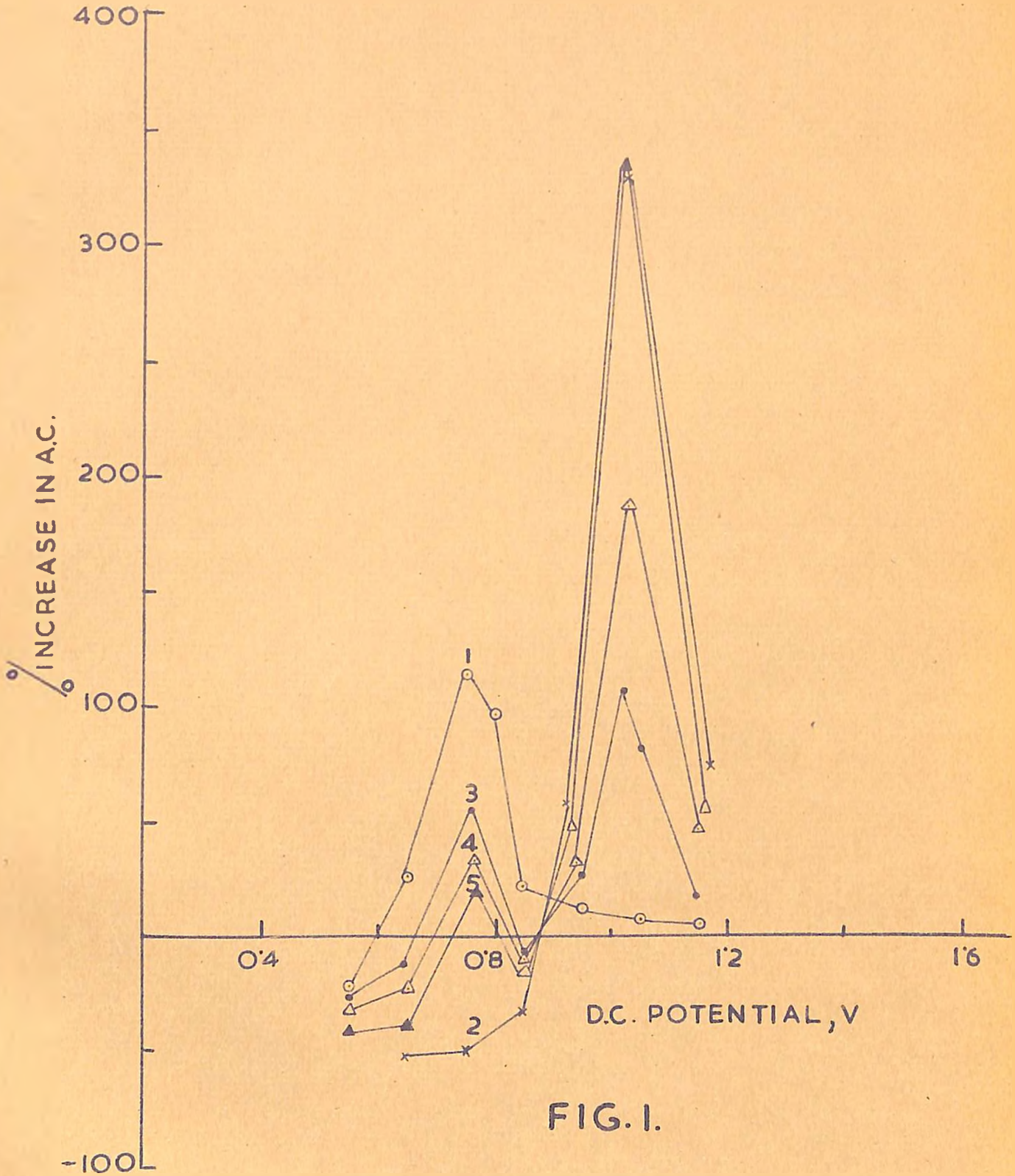
Figure 1 shows the effect of various concentrations of bromothymol blue on the reduction peak of nitrobenzene (2×10^{-4}M).. It is seen that the magnitude of the reduction peak is not influenced up to a certain concentration, known as the optimum concentration, of the surface active substance, but with concentrations higher than this the magnitude of the reduction peak progressively decreases till it attains a certain minimum value which is independent of further increase in concentration of BTB. The magnitude and the peak potential of the tensammetric peak of BTB show normal behaviour that would be expected without the presence of nitrobenzene. These observations are further supported by Table I which gives the effect of various surfactants on the reduction peak of nitrobenzene.

Figure 2 shows the effect of various concentrations of nitrobenzene on the tensammetric peak of 0.004% BTB. The

Table I

The Concentrations of Surfactants required just to Remove the Reduction peak or to Suppress it to its Maximum Extent on the Positive Side

Reduction Peak.	Concentration (mole/l)	Tensammetric peak.	Concentration needed for removing reduction peak or to suppress it to maximum extent (%)
Nitrobenzene	4×10^{-4}	Pyridine	20.0
Nitrobenzene	4×10^{-4}	n-amyl alcohol	Saturated
Nitrobenzene	4×10^{-4}	Benzaldehyde	0.2
Nitrobenzene	4×10^{-4}	Cerfak	0.14
Nitrobenzene	4×10^{-4}	Cetylpyridinium bromide	0.01
o-Nitrophenol	4×10^{-4}	Pyridine	1.0
m-Nitrophenol	4×10^{-4}	Pyridine	1.3
p-Nitrophenol	4×10^{-4}	Pyridine	0.5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% INCREASE IN A.C.
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D.C. POTENTIAL, V
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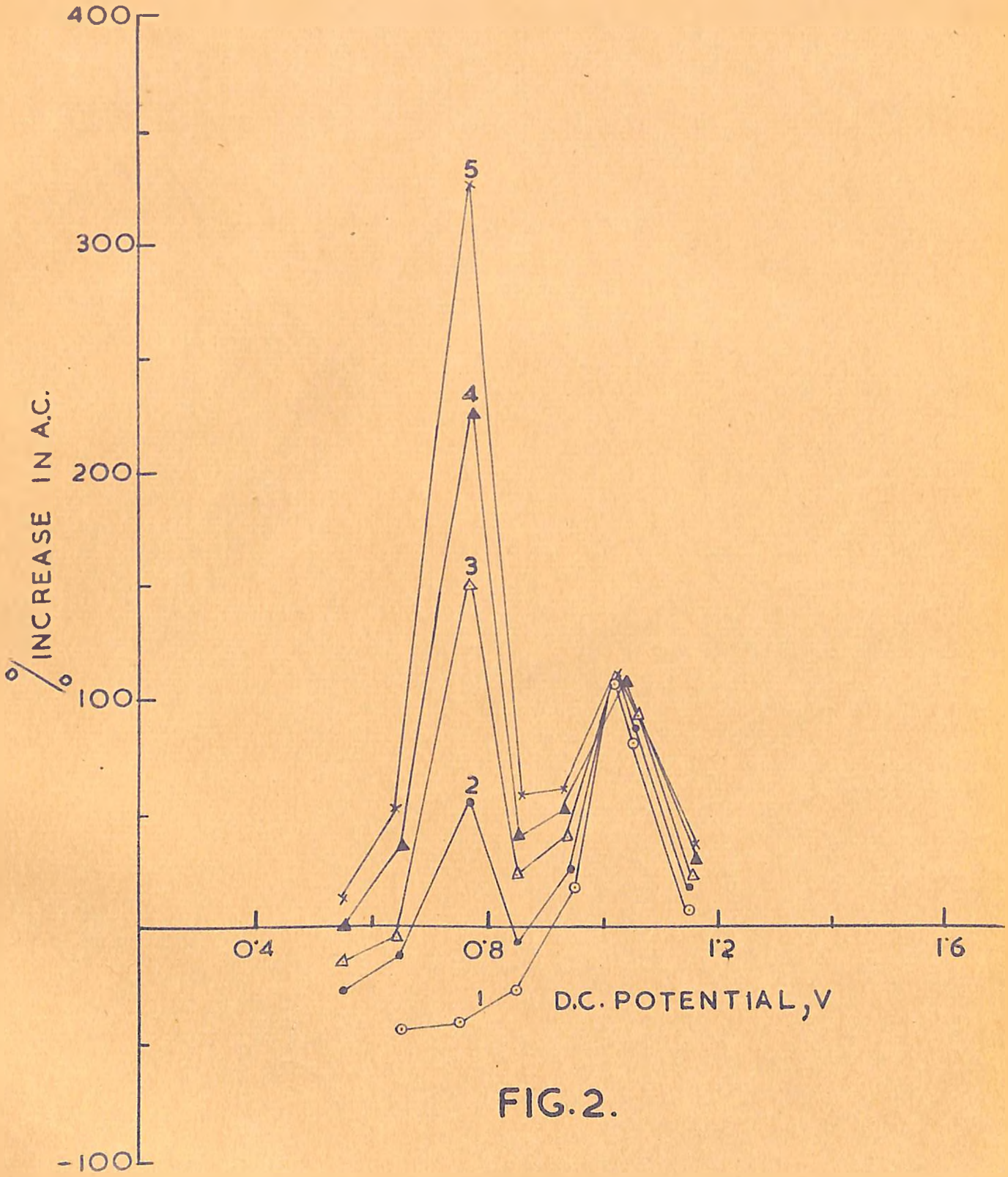
FIG. 1.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% INCREASE IN A.C.
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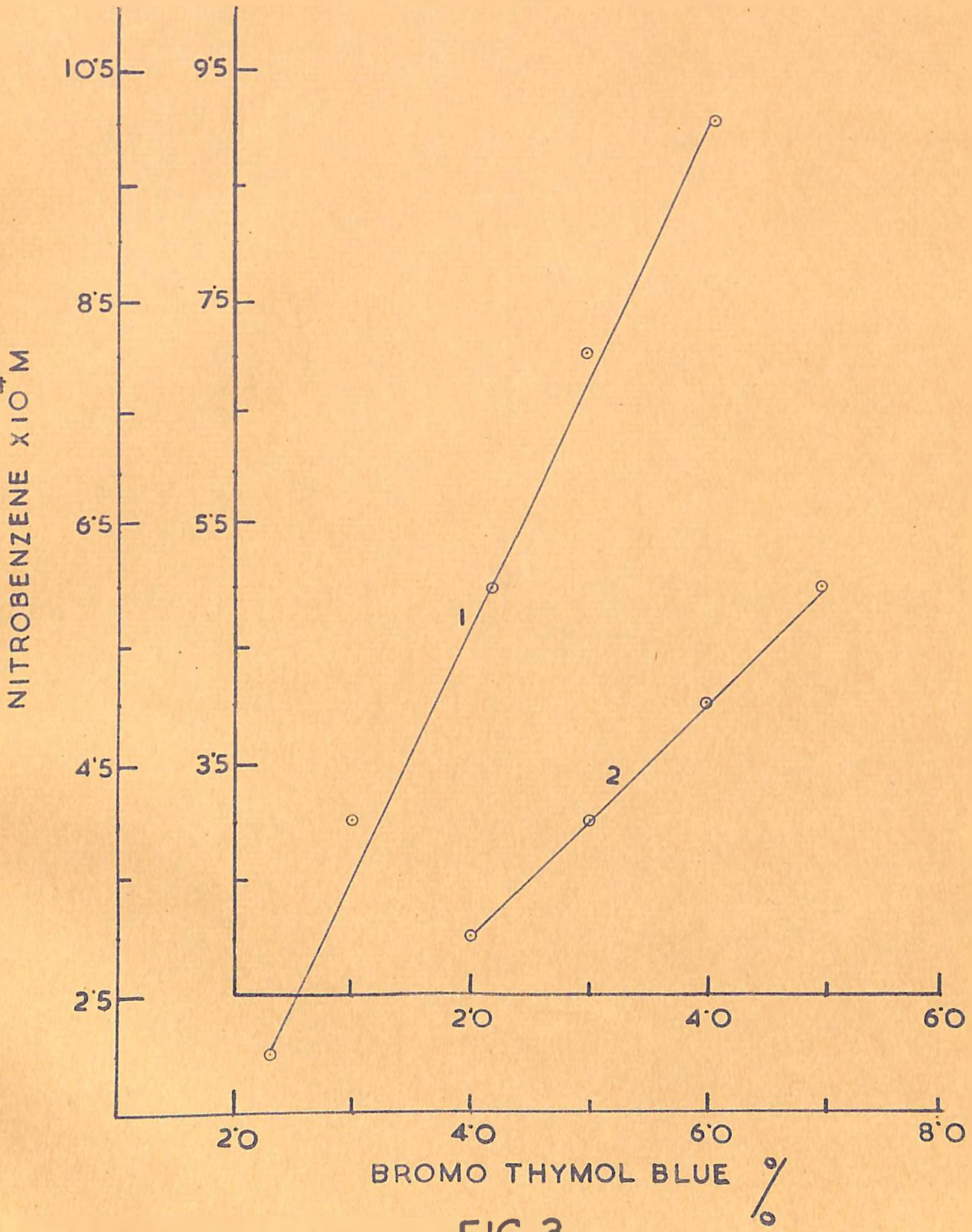
D.C. POTENTIAL, V

FIG. 2.


10·5
9·5
8·5
7·5
6·5
5·5
4·5
3·5
2·5
NITROBENZENE X 10⁻⁴ M
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2·0
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8·0
BROMO THYMOL BLUE %

FIG.3.

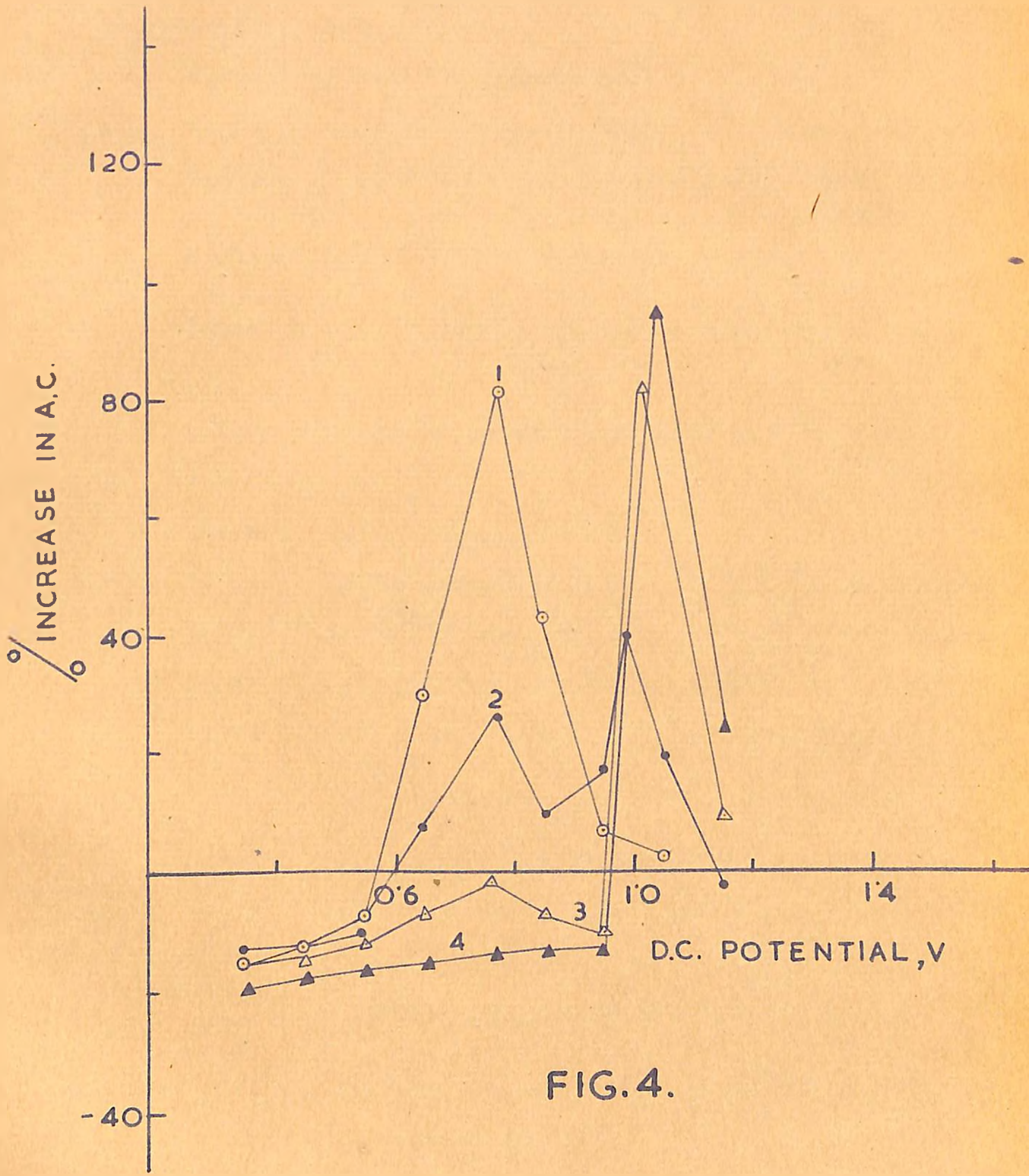

FIG. 4.

LEGEND OF FITURES

Fig. 1: Effect of various concentrations of BTB on the nitrobenzene peak.

Curve 1: 2 x 10^{-4}M nitrobenzene;

Curve 2: 0.02% bromothymol blue;

Curve 3: 2 x 10^{-4}M nitrobenzene + 0.004% bromothymol blue;

Curve 4: 2 x 10^{-4}M nitrobenzene + 0.01% bromothymol blue;

Curve 5: 2 x 10^{-4}M nitrobenzene + 0.02% bromothymol blue.

Fig. 2: Effect of various concentrations of nitrobenzene on the BTB peak.

Curve 1: 0.004% bromothymol blue;

Curve 2: 0.004% bromothymol blue + 2x10^{-4}M nitrobenzene;

Curve 3: 0.004% bromothymol blue + 4x10^{-4}M nitrobenzene;

Curve 4: 0.004% bromothymol blue + 6x10^{-4}M nitrobenzene;

Curve 5: 0.004% bromothymol blue + 1 x10^{-3}M nitrobenzene.

Fig. 3:

Curve 1: Optimum concentrations of BTB required for various concentrations of nitrobenzene.

Curve 2: Concentrations of BTB for reducing the nitrobenzene peak to its minimum value.

Fig. 4: Effect of various concentrations of n-amyl alcohol on the o-nitrophenol peak.

Curve 1: 4 x 10^{-4}M o-nitrophenol;

Curve 2: 4 x 10^{-4}M o-nitrophenol + 0.1% n-amyl alcohol;

Curve 3: 4 x 10^{-4}M o-nitrophenol + 0.15% n-amyl alcohol;

Curve 4: 4 x 10^{-4}M o-nitrophenol + 0.2% n-amyl alcohol.

magnitude of the reduction peak increases with increasing concentration of nitrobenzene without affecting either the magnitude or the peak potential of the tensammetric peak of BTB.

Curve 1 in Fig. 3 relates the optimum concentrations of BTB used for various concentrations of nitrobenzene. It can be seen that the relation is linear in the concentration range 2×10^{-4}M - 10^{-3}M of nitrobenzene. Further, curve 2 in the same figure, relating the concentration of BTB for reducing the nitrobenzene peak to its minimum value for various concentrations of nitrobenzene used, is also linear. The relation between the magnitude of the reduction peak and the molar concentration of the nitrobenzene is linear within the above range[3].

Figure 4 shows the effect of various concentrations of n-amyl alcohol on the reduction peak of 4×10^{-4} M o-nitrophenol. Here it can be seen that unlike nitrobenzene peak, the magnitude of the nitrophenol peak decreases progressively till it is completely removed by 0.2% n-amyl alcohol. Further, the peak potential and the magnitude of the tensammetric peak of 0.2% n-amyl alcohol remain unaffected by the presence of 4×10^{-4}M o-nitrophenol.

Figure 5 shows the effect of various concentrations of o-nitrophenol on the tensammetric peak of 0.4% n-amyl alcohol. It can be seen again that the o-nitrophenol peak reappears with higher concentrations of the depolarizer. Its magnitude then increases with increase in concentration of the o-nitrophenol

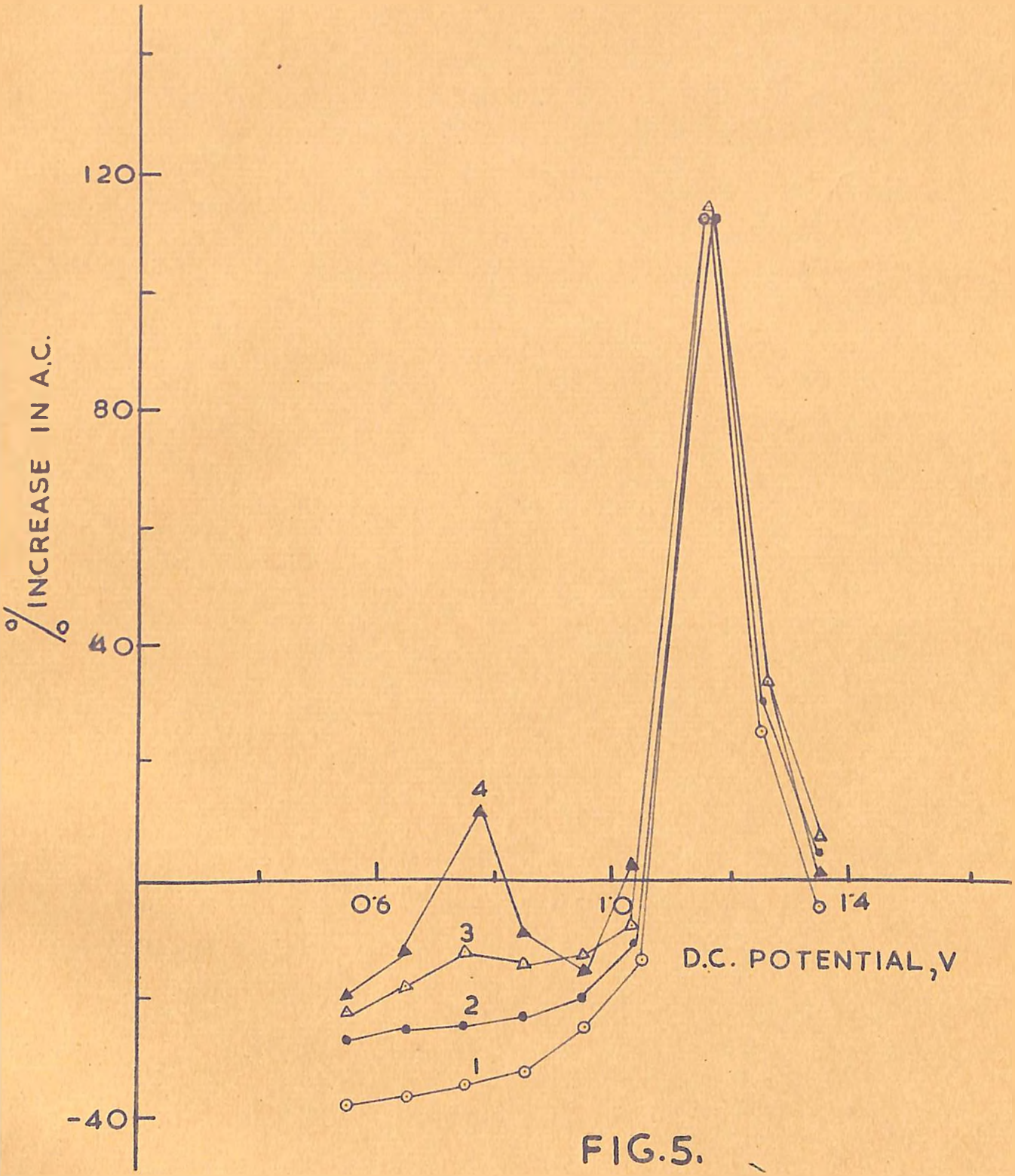

FIG.5.

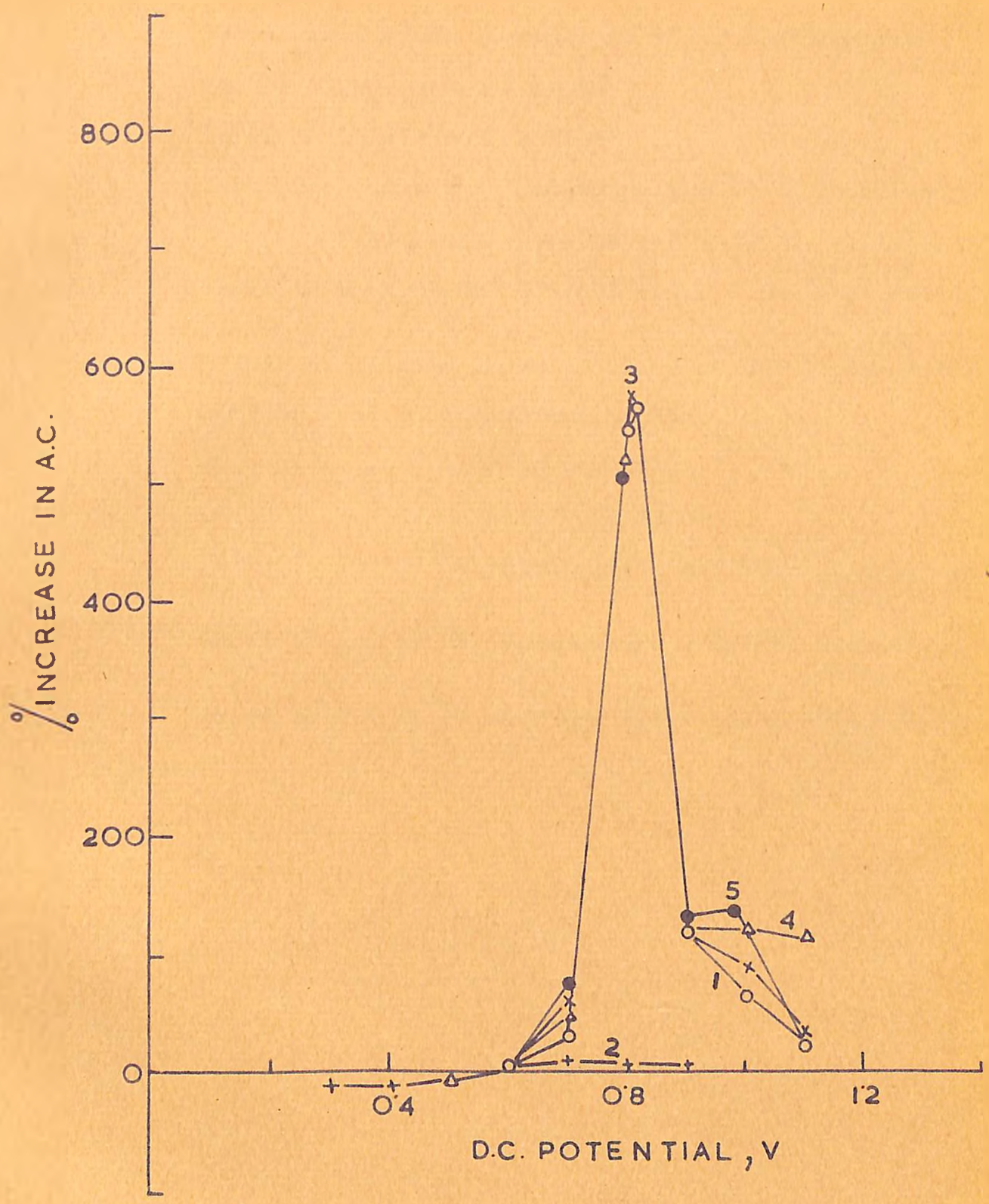

FIG. 6.

Fig. 5: Effect of various concentrations of o-nitrophenol on the n-amyl alcohol peak.

Curve 1: 0.4% n-amyl alcohol;

Curve 2: 0.4% n-amyl alcohol + 4×10^{-4}M o-nitrophenol;

Curve 3: 0.4% n-amyl alcohol + 8×10^{-4}M o-nitrophenol;

Curve 4: 0.4% n-amyl alcohol + 1.2×10^{-3}M o-nitrophenol.

Fig. 6: Effect of various concentrations of BTB on the nitrobenzene peak in methanolic medium.

pH = 7.0; 1.0 M LiCl in methanol.

Curve 1: 4×10^{-4}M nitrobenzene;

Curve 2: 4×10^{-4}M nitrobenzene + 0.004% bromothymol blue;

Curve 3: 4×10^{-4}M nitrobenzene + 0.008% bromothymol blue;

Curve 4: 4×10^{-4}M nitrobenzene + 0.01% bromothymol blue.

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without affecting either the magnitude or the peak potential of the tensammetric peak of 0.4% n-amyl alcohol. Similar observations are further confirmed by Table I, which gives the effect of n-amyl alcohol on the reduction peaks of meta and para nitrophenols.

DISCUSSION

Because the peak potential and the magnitude of the tensammetric peak corresponding to any particular amount of s.a.s. remain constant with and without depolarizer in all the cases studied, this suggests that the hindrance of the electrode process arises from film formation at the electrode surface and not from any chemical interaction between s.a.s. and the depolarizer. This is further confirmed from our studies of the mixtures of organic reducible compounds and s.a.s. in methanolic medium (vide typical Fig.6) where considerably large amounts of s.a.s. are required to affect the magnitude of the organic reduction peaks as compared to that in water. This behaviour is due to the fact that the extent of adsorption of s.a.s. on the d.m.e. in methanolic medium is diminished to a very large extent because the surface tension of methanol is much less than that of water and consequently most solute will decrease the surface tension of methanol to a much less extent than that of water. It appears that with concentrations up to the optimum concentration of the s.a.s., the amount of s.a.s. is not sufficient to cover the electrode surface to a sufficient extent to hinder the electrode process, but concentrations greater than

the optimum concentration progressively increase the extent of surface coverage within the life of the drop and increase the degree of hindrance of the electrode process, thereby diminishing the magnitude of the reduction peak. At higher concentrations of the s.a.s. corresponding to the removal of the reduction peak, it appears that most of the surface is covered with a unimolecular film.

In general, it can be concluded that nitrobenzene peak cannot be completely eliminated even by using very high concentrations of the surfactants at alkaline pH. Ionic surfactants are more effective in suppressing the nitrobenzene peak than the non-ionic surfactants. On the cathodic side of the electro capillary zero, cationic surfactants will be adsorbed more strongly than anionic surfactants and, therefore, the amount of citylpyridinium bromide (which is cationic) required to suppress nitrobenzene peak is much less than the amount of cerfak (which is anionic), vide Table I. That the nitrobenzene peak cannot be completely eliminated even with highest concentration of the surfactant used, might have something to do with its complicated nature of the electrode process at alkaline pH and is difficult to explain at present and needs further investigation. It may also be seen from Table I that the concentration of pyridine required to completely remove the peak of p-nitrophenol is much less than that for o-nitrophenol or m-nitrophenol although the magnitude of the p-nitrophenol peak is much higher than the magnitudes of o-nitrophenol or m-nitrophenol peaks. This may probably be due to the greater composite nature of the p-nitrophenol peak which shows larger depression in differential capacity

of the double layer as compared to ortho or meta nitrophenols using same concentrations.

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PAPER No. 7

A.C. POLAROGRAPHIC STUDIES OF THE MIXTURES OF INORGANIC AND ORGANIC REDUCIBLE SPECIES

A.C. POLAROGRAPHIC STUDIES OF THE MIXTURES OF INORGANIC AND ORGANIC REDUCIBLE SPECIES

The influence of organic reduction waves on a.c. reduction peaks of inorganic cations and vice-versa, has been studied by a.c. polarography. p-nitrophenol can be estimated quantitatively from its mixture with Cd^{+2} as well as Tl^{+} (ous) ions and vice-versa, within specified concentration ranges at pH 7.0. Benzaldehyde can be estimated from its mixture with Cd^{+2} at pH 3.8 but their estimations are not possible at pH 7.0. Nitrobenzene can be estimated in presence of Zn^{+2} and Ni^{+2} within specified concentration ranges. Estimations of Cd^{+2} and Pb^{+2} from their mixtures with m-nitroaniline and p-nitrophenol and m-nitrotoluene and p-nitrophenol respectively have also been made.

Gupta and Sharma[1] studied the influence of tensammetric waves on reduction peaks of inorganic cations. Gupta and Chatterjee[2,3] have also investigated the influence of organic reduction waves on one another and on tensammetric peaks. As no data are available in literature on the influence of organic reduction waves on reduction peaks of inorganic cations, the present investigation gives in detail the results obtained on such studies by a.c. polarography.

EXPERIMENTAL

p-nitrophenol (B.D.H.) was recrystallised before use. Nitrobenzene (B.D.H., A.R.) and Benzaldehyde (B.D.H.) were redistilled in an all glass fractionating column and the middle one third of the distillate was used for experiments. Pure recrystallised samples of zinc sulphate ($ZnSO_4,7H_2O$), nickel sulphate ($NiSO_4$, $6H_2O$), cadmium sulphate ($3CdSO_4,8H_2O$), thallons sulphate and lead sulphate were used. Other chemicals used were of AnalaR quality of B.D.H. Mercury used for the pool and the dropping electrode was purified by standard methods.

The experimental set up and technique of measurements were same as described earlier. D.C. potentials are expressed with reference to the saturated calomel electrode. All the experiments were carried out at a constant temperature of 30 $\pm$ 0.5°C. The d.m.e. was cathodic throughout the measurements and its constants were as follows:-

m = 4.564 mg/sec.

t = 1.8 sec. per drop in 0.1 M KCl, open circuit.

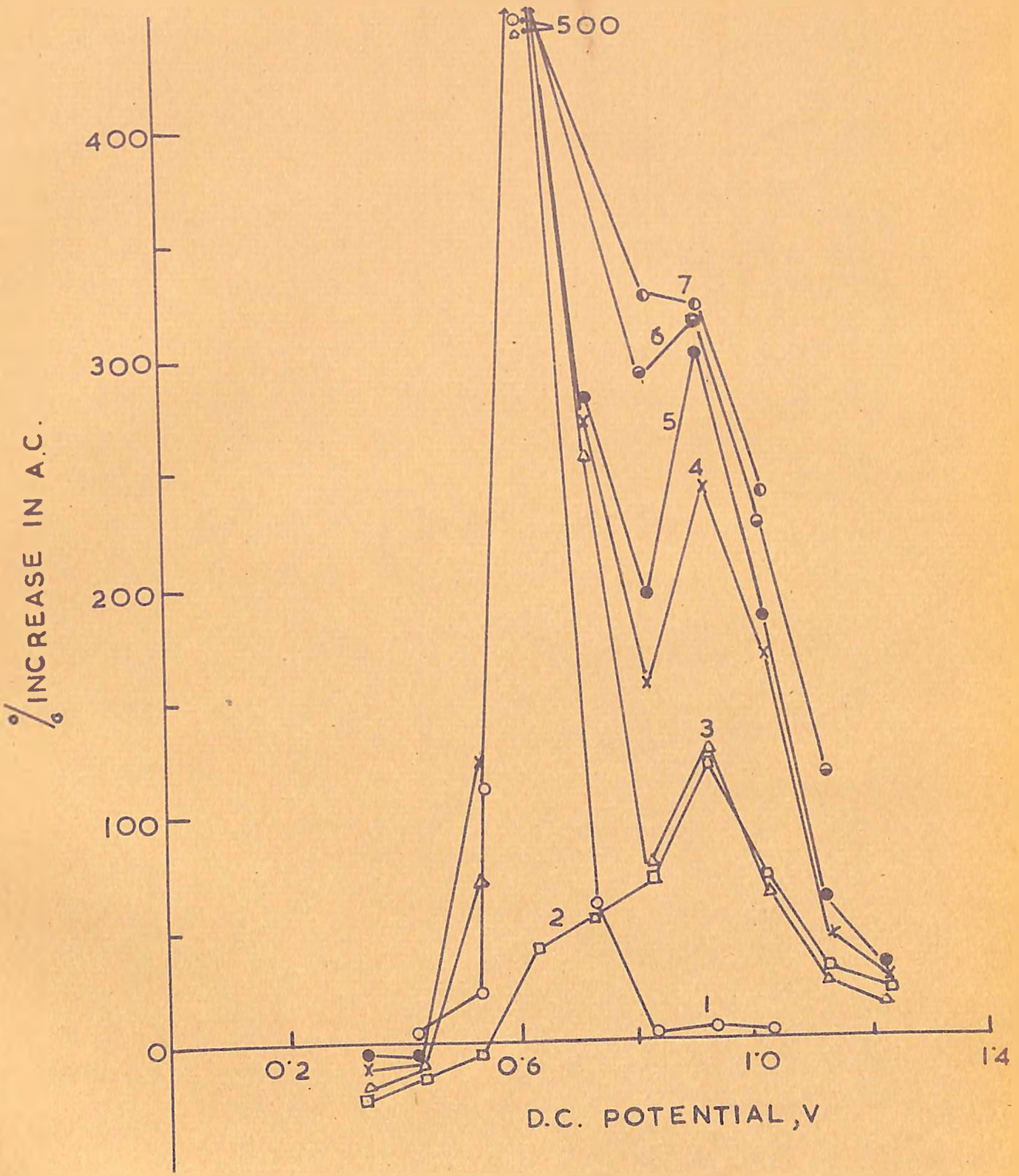
0.1 M potassium chloride solution was used as the supporting electrolyte and was invariably shaken and kept in contact with mercury and mercurous chloride.

RESULTS AND DISCUSSION

(1) Estimations when reduction peak of inorganic cations are at less cathodic potential than that of organic reducible species

Figure 1 shows the effect of various concentrations of p-nitrophenol at pH 7.0 on the reduction peak of Cd^{+2} (10^{-3} M). It is seen that magnitude and peak potential of Cd^{+2} peaks are not influenced up to a concentration of (2×10^{-3}M) p-nitrophenol, but with concentrations greater than this only Cd^{+2} peak is obtained. This seems to be due to the increase of the width of the cadmium wave with increase in concentration of the nitrophenol and also due to relatively little increase in the magnitude of the nitrophenol peak at concentration greater than 2×10^{-3} M which corresponds to the saturation value. Fig. 2 shows the effect of various concentrations of Cd^{+2} on the reduction wave of 4×10^{-4}M p-nitrophenol at the same pH. Here also the magnitude and peak potential of p-nitrophenol are not influenced up to a concentration of 3×10^{-3}M Cd^{+2} but concentrations greater than this give only Cd^{+2} peak due to large increase in the width of the Cd^{+2} wave. It seems therefore possible to estimate quantitatively Cd^{+2} and p-nitrophenol from a mixture of 10^{-3}M Cd^{+2} and 2×10^{-3} M p-nitrophenol as well as 4×10^{-4}M p-nitrophenol and 3×10^{-3}M Cd^{+2} at pH 7.0.

Similarly p-nitrophenol can be estimated quantitatively from the mixture with Tl^{+} in concentration range of 4×10^{-4}M p-nitrophenol and 2.5×10^{-3}M Tl^{+} and vice-versa at pH 7.0. Estimations of p-nitrophenol with Cd^{+2} as well as Tl^{+} are not possible at acidic pH values under similar conditions. This is due to the fact that organic reduction peaks shift to less cathodic potential with decrease in pH and hence the peak potential in the mixture becomes so close that they cannot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% INCREASE IN A.C.
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D.C. POTENTIAL, V
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FIG. 1.

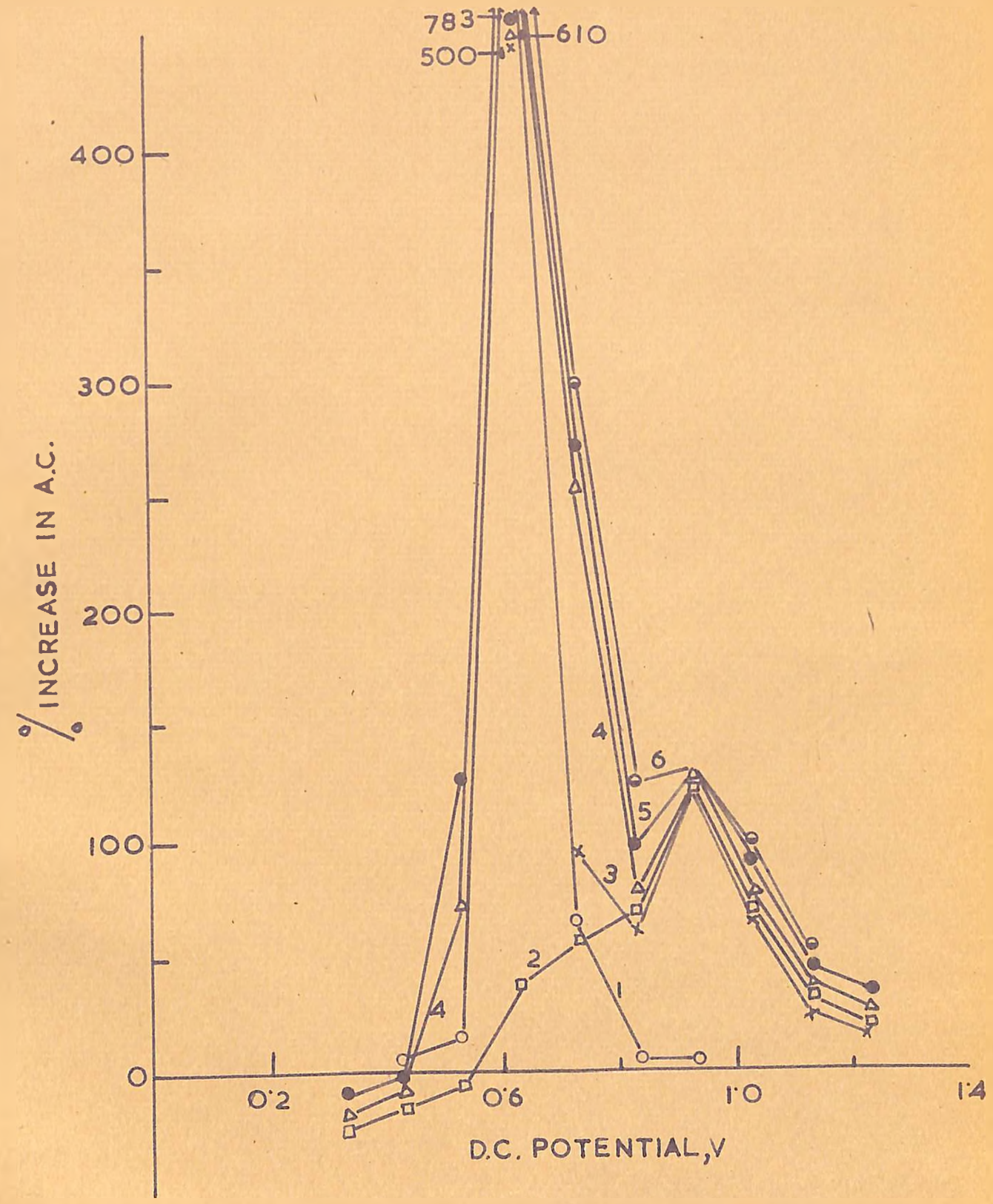
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FIG. 2.

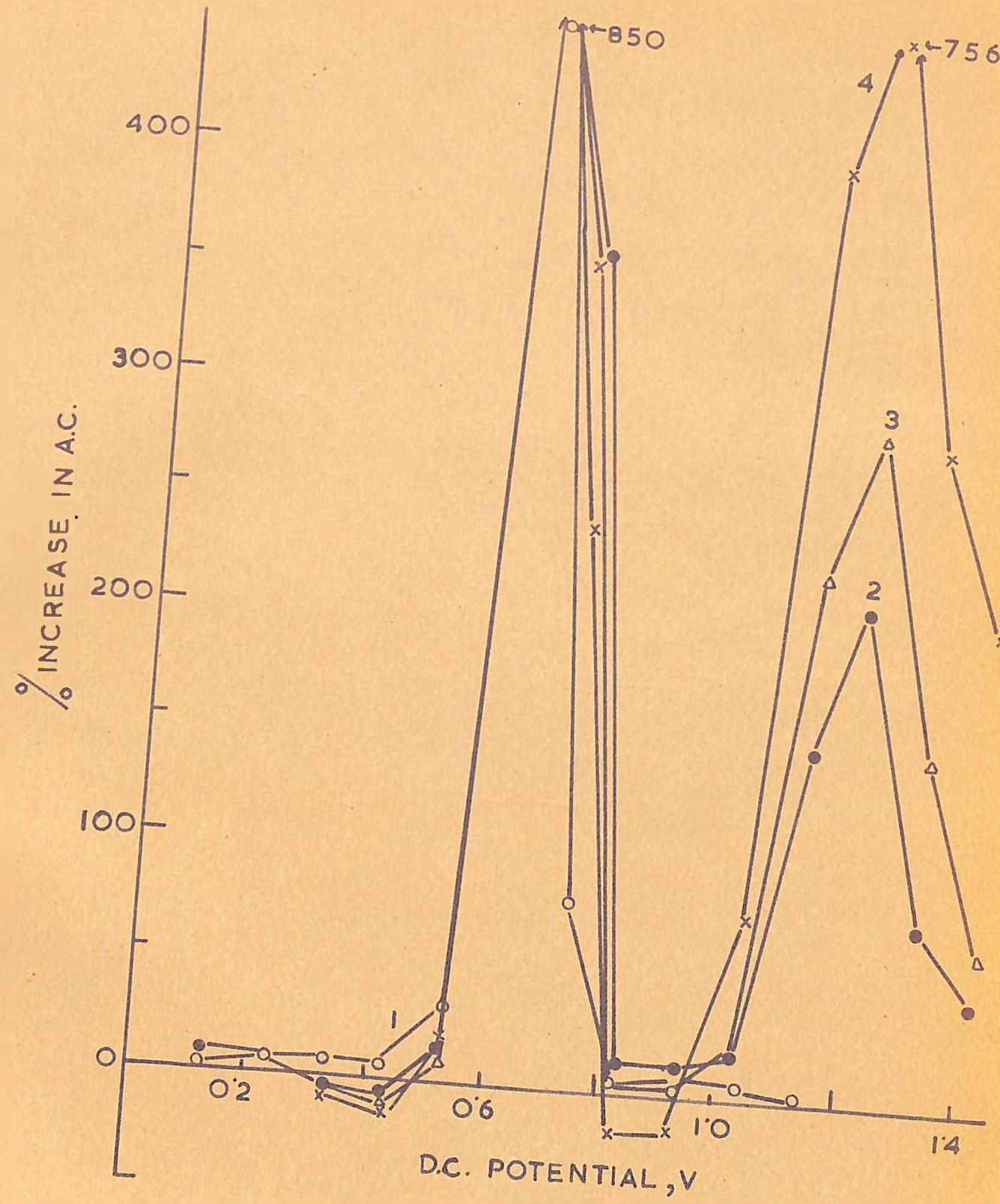
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FIG. 3.

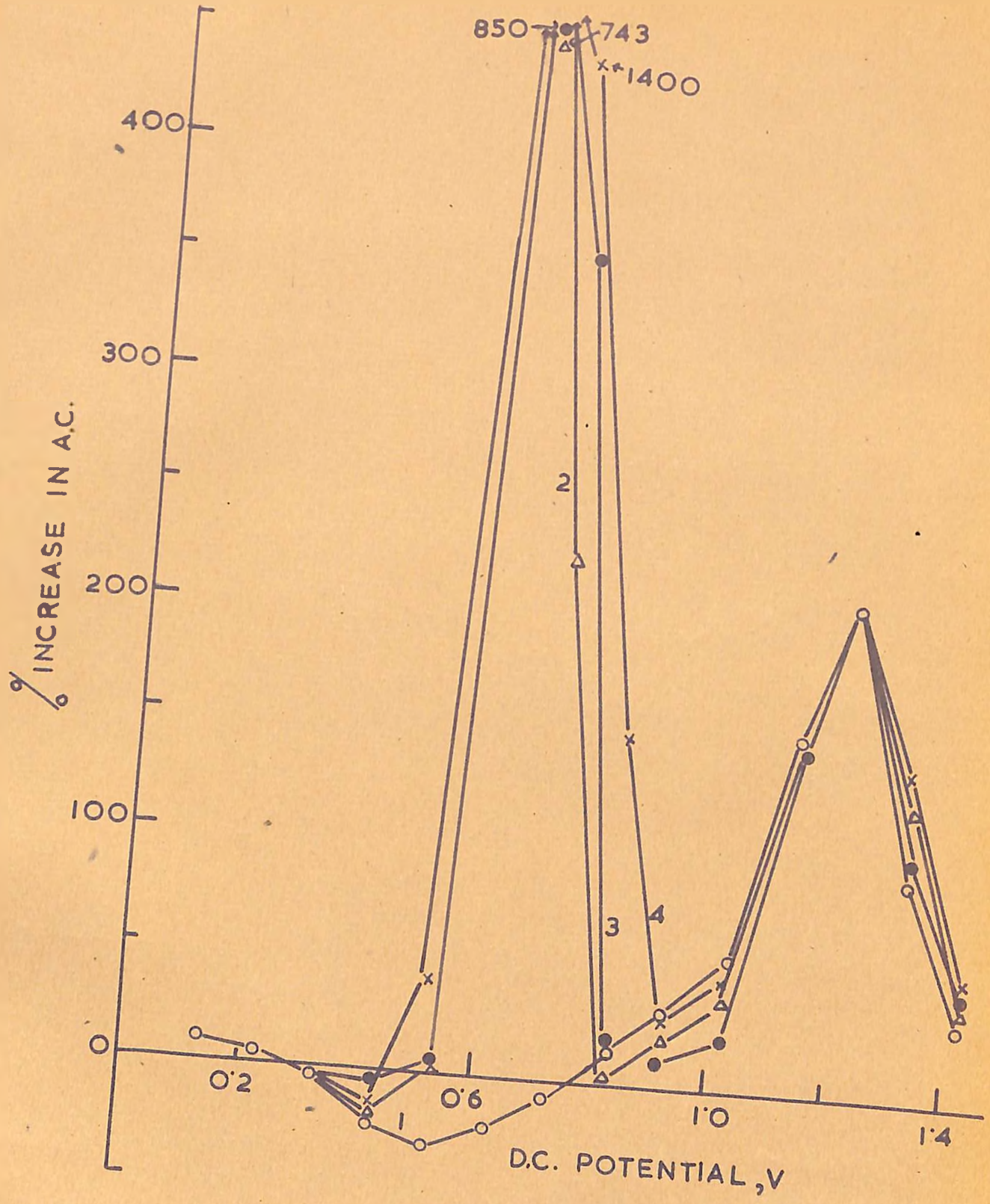
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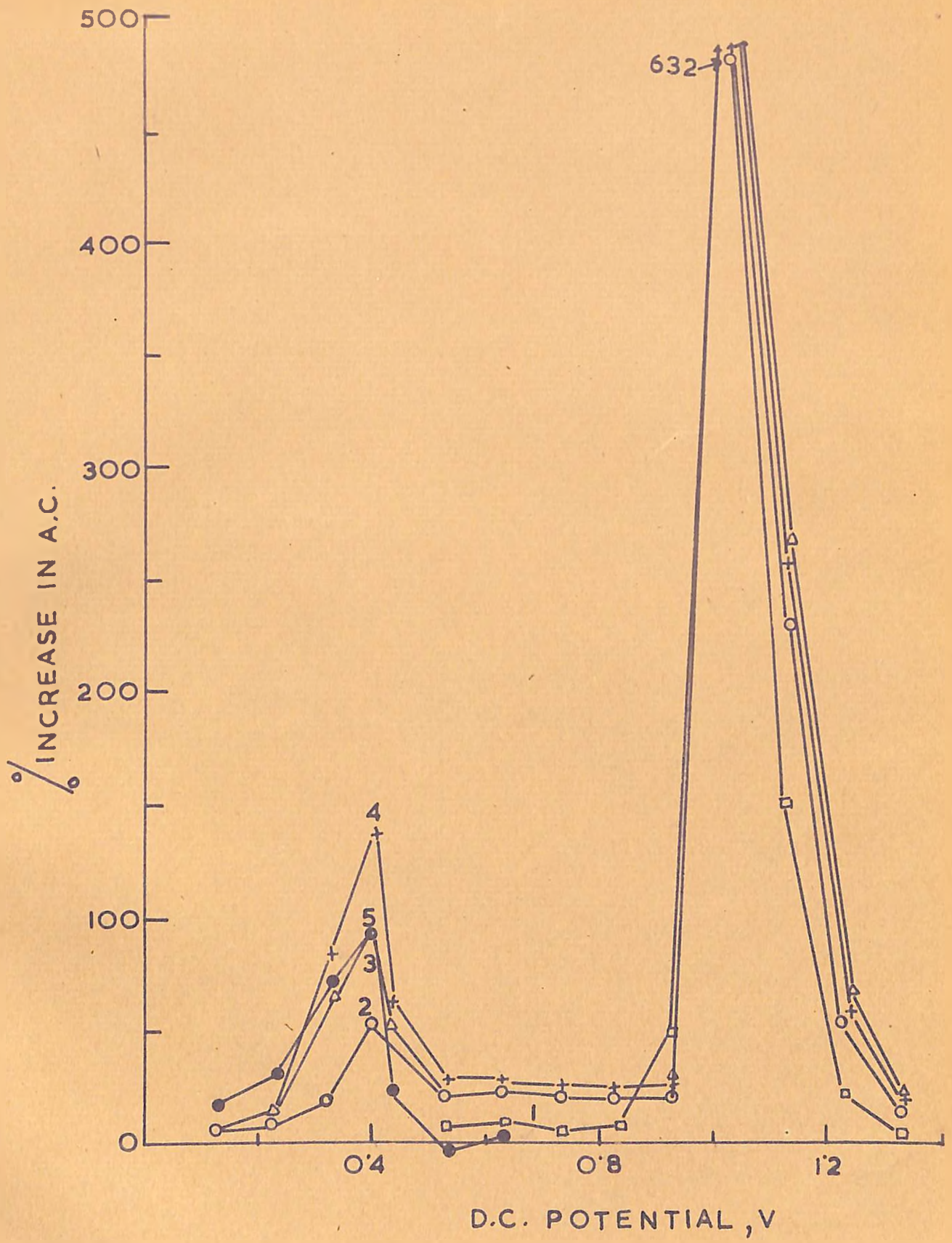
FIG. 4.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% INCREASE IN A.C.
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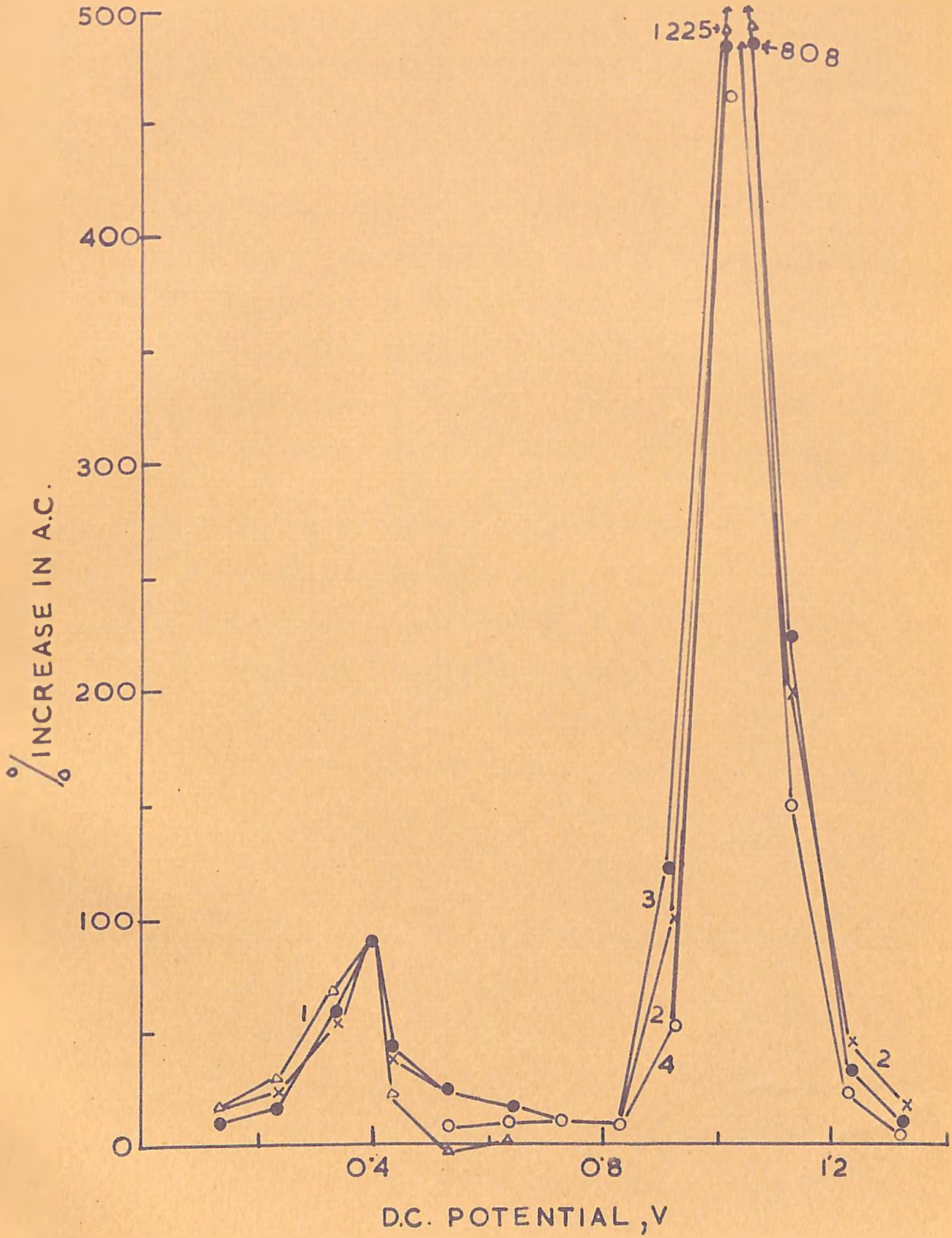
D.C. POTENTIAL, V

FIG.5.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808
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D.C. POTENTIAL, V
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2
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2

FIG. 6.

LEGEND OF FIGURES

Fig. 1: Effect of various concentrations of p-nitrophenol on 10^{-3}M Cd^{+2} at pH 7.0.

Curve 1:- 10^{-3}M Cd^{+2}

Curve 2:- 4×10^{-4}M p-nitrophenol

Curve 3:- 10^{-3}M Cd^{+2} + 4×10^{-4}M p-nitrophenol

Curve 4:- 10^{-3}M Cd^{+2} + 8×10^{-4}M p-nitrophenol

Curve 5:- 10^{-3}M Cd^{+2} + 10^{-3}M p-nitrophenol

Curve 6:- 10^{-3}M Cd^{+2} + 2×10^{-3}M p-nitrophenol

Curve 7:- 10^{-3}M Cd^{+2} + 4×10^{-3}M p-nitrophenol

Fig. 2: Effect of various concentrations of Cd^{+2} on 4×10^{-4}M p-nitrophenol at pH 7.0.

Curve 1:- 4×10^{-4}M Cd^{+2}

Curve 2:- 4×10^{-4}M p-nitrophenol

Curve 3:- 4×10^{-4}M p-nitrophenol + 4×10^{-4}M Cd^{+2}

Curve 4:- 4×10^{-4}M p-nitrophenol + 10^{-3}M Cd^{+2}

Curve 5:- 4×10^{-4}M p-nitrophenol + 2×10^{-3}M Cd^{+2}

Curve 6:- 4×10^{-4}M p-nitrophenol + 3×10^{-3}M Cd^{+2}

Fig. 3: Effect of various concentrations of benzaldehyde on 10^{-3}M Cd^{+2} at pH 3.8.

Curve 1:- 10^{-3}M Cd^{+2}

Curve 2:- 10^{-3}M Cd^{+2} + 2×10^{-3}M benzaldehyde

Curve 3:- 10^{-3}M Cd^{+2} + 4×10^{-3}M benzaldehyde

Curve 4:- 10^{-3}M Cd^{+2} + 8×10^{-3}M benzaldehyde

Fig. 4: Effect of various concentration of Cd^{+2} on 10^{-3}M benzaldehyde at pH 3.8.

Curve 1: 10^{-3}M benzaldehyde

Curve 2: 10^{-3}M benzaldehyde + 4 x 10^{-4}M Cd^{+2}

Curve 3: 10^{-3}M benzaldehyde + 10^{-3}M Cd^{+2}

Curve 4: 10^{-3}M benzaldehyde + 2 x 10^{-3}M Cd^{+2}

Fig. 5: Effect of various concentrations of nitrobenzene on 10^{-3}M Zn^{+2} at pH 3.8.

Curve 1: 10^{-3}M Zn^{+2}

Curve 2: 10^{-3}M Zn^{+2} + 4 x 10^{-4}M nitrobenzene

Curve 3: 10^{-3}M Zn^{+2} + 8 x 10^{-4}M nitrobenzene

Curve 4: 10^{-3}M Zn^{+2} + 10^{-3}M nitrobenzene

Curve 5: 8 x 10^{-4}M nitrobenzene

Fig. 6: Effect of various concentrations of Zn^{+2} on 8 x 10^{-4}M nitrobenzene at pH 3.8.

Curve 1: 8 x 10^{-4}M nitrobenzene

Curve 2: 8 x 10^{-4}M nitrobenzene + 2 x 10^{-3}M Zn^{+2}

Curve 3: 8 x 10^{-4}M nitrobenzene + 4 x 10^{-3}M Zn^{+2}

Curve 4: 8 x 10^{-4}M nitrobenzene + 8 x 10^{-3}M Zn^{+2}

be separated[4]. Further, inorganic cations cannot be estimated in alkaline pH because of precipitation.

Benzaldehyde can be estimated quantitatively from its mixture with Cd^{+2} within concentration range of 10^{-3}M Cd^{+2} and 8 x 10^{-3}M benzaldehyde as well as 10^{-3}M benzaldehyde and 1.2 x 10^{-2}M Cd^{+2} at pH 3.8, vide Figs. 3 and 4. At pH 7.0 the effect of various concentrations of benzaldehyde on the reduction peak of Cd^{+2} (10^{-3}M) has been investigated and it is seen that the magnitude of Cd^{+2} peak progressively decreases with increase in concentration of benzaldehyde till 5 x 10^{-3}M benzaldehyde suppresses the Cd^{+2} peak. It is due to the fact that benzaldehyde gives a tensammetric peak in neutral or alkaline media[5] and hence the magnitude of the reduction peak of Cd^{+2} is suppressed by higher concentration of benzaldehyde.

(2) <u>Estimations when reduction peak of inorganic cations are at more cathodic potential than that of organic reducible species</u>

Figure 6 shows the effect of various concentrations of Zn^{+2} at pH 3.8 on the reduction wave of nitrobenzene (8x10^{-4}M). It is seen, again, that magnitude as well as peak potential of nitrobenzene are not influenced up to a concentration of 1.2 x 10^{-2}M Zn^{+2}. Similarly, Fig. 6 shows the effect of various concentrations of nitrobenzene on the reduction peak of Zn^{+2} (10^{-3} M) at the same pH value. The magnitude of the nitrobenzene peak increases with increasing concentration of notrobenzene without affecting either the magnitude or the peak potential of the reduction peak of 10^{-3}M Zn^{+2}. Therefore,

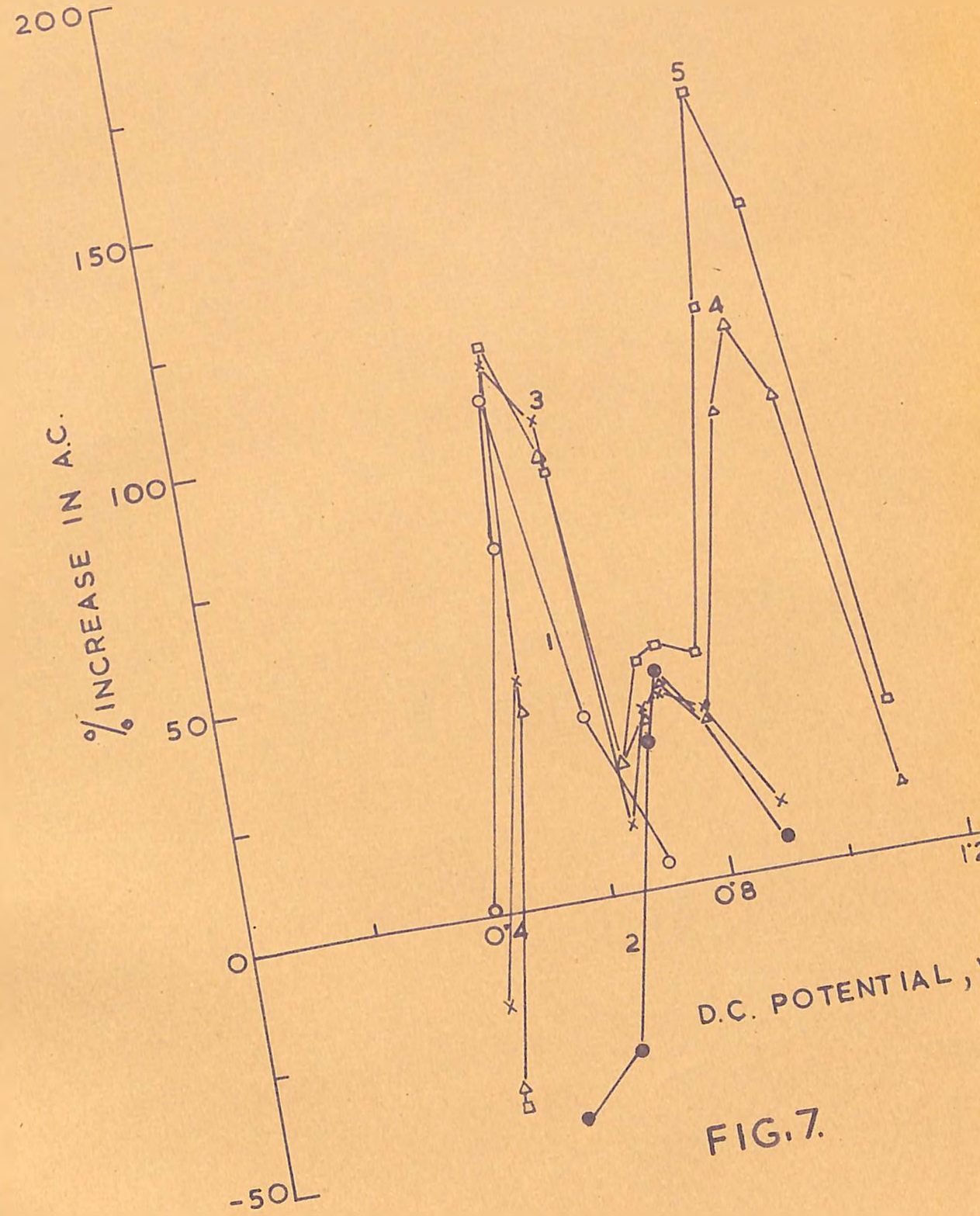

FIG. 7.

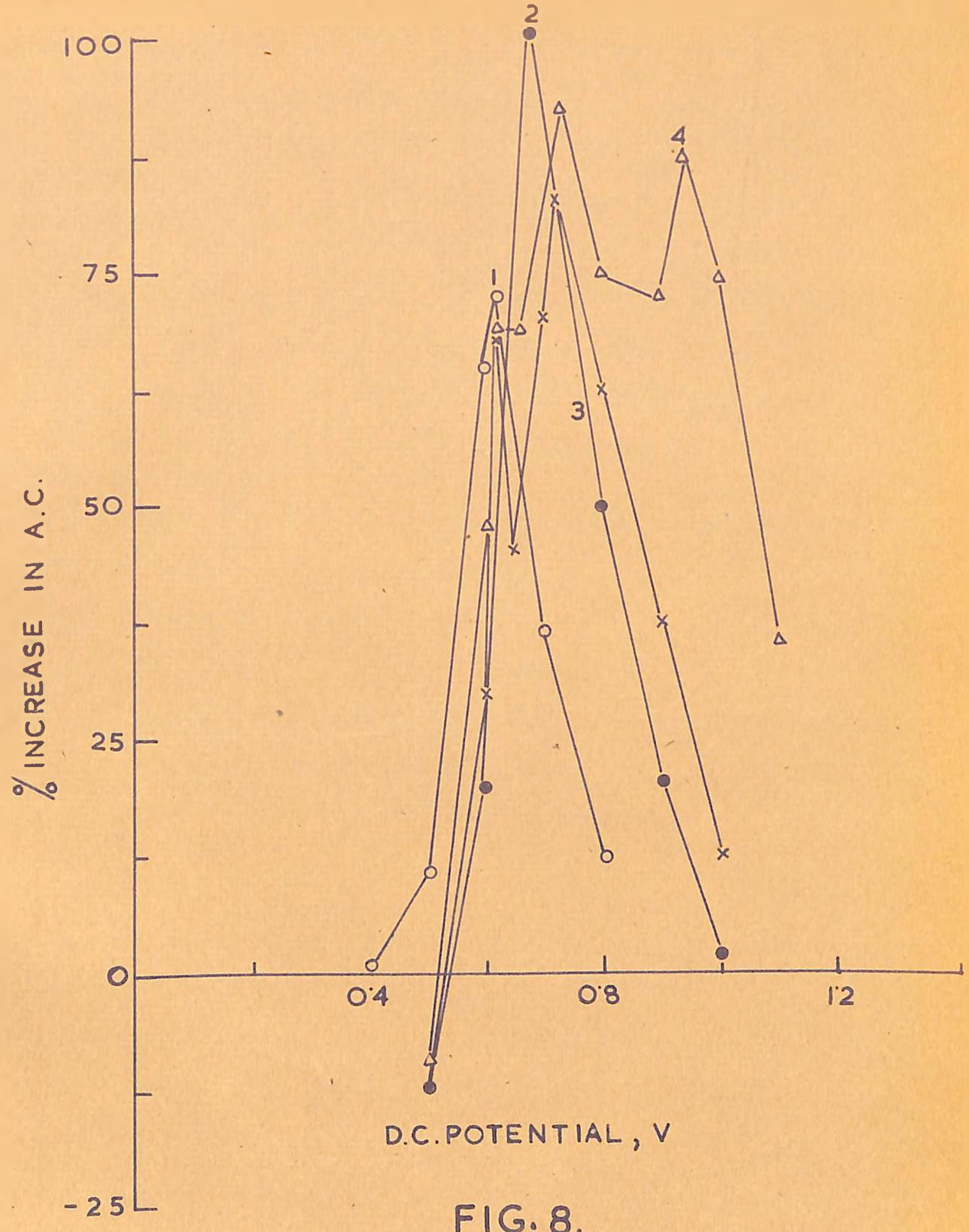

FIG. 8.

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Fig. 7: Estimation of Pb^{+2} from its mixture with m-nitrotoluene and p-nitrophenol.

Curve 1:- 2×10^{-4}M Pb^{+2}

Curve 2:- 2×10^{-4}M m-nitrotoluene

Curve 3:- 2×10^{-4}M Pb^{+2} + 2×10^{-4}M m-nitrotoluene

Curve 4:- 2×10^{-4}M Pb^{+2} + 2×10^{-4}M m-nitrotoluene + 4×10^{-4}M p-nitrophenol

Curve 5:- 2×10^{-4}M Pb^{+2} + 2×10^{-4}M m-nitrotoluene + 6×10^{-4}M p-nitrophenol.

Fig. 8: Estimation of Cd^{+2} from its mixture with m-nitroaniline and p-nitrophenol.

Curve 1:- 2×10^{-4}M Cd^{+2}

Curve 2:- 2×10^{-4}M m-nitroaniline

Curve 3:- 2×10^{-4}M Cd^{+2} + 2×10^{-4}M m-nitroahiline

Curve 4:- 2×10^{-4}M Cd^{+2} + 2×10^{-4}M m-nitroaniline + 2×10^{-4}M p-nitrophenol.

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it is possible to estimate nitrobenzene in presence of Zn^{+2} at pH 3.8. Nitrobenzene and Zn^{+2} cannot be estimated from their mixture under similar conditions at pH 7.0, because their peak potentials are close together at this pH value.

Similarly it is possible to estimate quantitatively nitrobenzene and Ni^{+2} from a mixture of 6×10^{-3}M nitrobenzene and 10^{-3}M Ni^{+2} as well as 8×10^{-3}M Ni^{+2} and 3×10^{-4} M nitrobenzene.

Further, Cd^{+2} (2×10^{-4}M) and Pb^{+2} (2×10^{-4}M) can also be estimated from their mixtures of 2×10^{-4}M m-nitroaniline and 2×10^{-4}M p-nitrophenol as well as 2×10^{-4} M m-nitrotoluene and 6×10^{-4}M p-nitrophenol respectively (vide Figs. 7 and 8).

In general, it can be concluded that influence of organic reduction wave on reduction peaks of inorganic cations depends on pH of the buffer solution and also on the concentrations of the reducible species. Reducible organic compounds can be estimated quantitatively from their mixtures with inorganic cations within specified concentration ranges which depends on the nature of the reducible species and the separation of their peak potentials. Estimations of inorganic cations in presence of organic reducible compounds at particular pH values suggest that peaks are free from surface effects or chemical interaction.

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2. S.L. Gupta and M.K. Chatterjee,(Unpublished).

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CHAPTER III

A.C. POLAROGRAPHIC STUDIES ON THE STRUCTURAL INFLUENCE ON THE PEAK POTENTIALS OF A SERIES OF NITRO COMPOUNDS

PAPER No. 8

A.C. POLAROGRAPHIC STUDIES OF NITROBENZENE AND ITS DERIVATIVES WITH SPECIAL REFERENCE TO THE STRUCTURAL INFLUENCE ON PEAK POTENTIAL IN AQUEOUS AND METHANOLIC MEDIA

A.C. POLAROGRAPHIC STUDIES OF NITROBENZENE AND ITS DERIVATIVES WITH SPECIAL REFERENCE TO THE STRUCTURAL INFLUENCE ON PEAK POTENTIAL IN AQUEOUS AND METHANOLIC MEDIA

The different substituent groups tried are NO_2, COOH, CHO, Cl, NH_2 and CH_3. The influence of their substitutions in the parent nitrobenzene molecule have been studied at the para position in aqueous and methanolic media. The effect of these substituents in different positions of the nitrobenzene molecule has also been observed. Substituents like NO_2, COOH, CHO and Cl shift the peak potential to less cathodic values, whereas groups like OH and NH_2 shift it to more cathodic values as compared to the peak potential of nitrobenzene. In general the reduction of nitrobenzene becomes more difficult in the para position with the substituents in the order $NO_2 > Cl > CHO > COOH > CH_3 > OH > NH_2$. The effect of position isomers has also been studied. The behaviour of different substituents on the nitrobenzene peak potential has been explained by the inductive and tautomeric effects of the substituted groups. Hammett's free energy relationship between the peak potentials of the substituted nitrobenzenes and their substitution constant values has also been established in methanolic medium.

Lot of work has been done on the influence of substituents on the half wave potential of organic compounds in conventional polarography[1-6]. The correlations between the half wave potentials and the Hammett total polar substituent constants 'σ' are also well established. Geske and Maki[7] found a correlation between the half wave potentials of different substituted nitrobenzenes and their electron spin resonance values in acetonitrile. They have also applied the modified Hammett's equation to their studies. However, no data are available in literature on such studies by a.c. polarography. The present investigation, therefore, reports the work done on the reduction of nitrobenzene and its derivatives in aqueous medium with special reference to the structural influence on peak potential by a.c. polarography with a view to see if this technique can be used successfully for such studies. Further, the work has been extended in methanolic medium to ascertain if it has any advantage over aqueous medium.

EXPERIMENTAL

Organic solid compounds used were of either B.D.H. or Merck's quality and were recrystallised before use. Organic liquid compounds were also extra pure samples of either B.D.H. or Merck's quality and were redistilled in all glass fractionating column and the middle one third of the distillates were used for the experiments. The mercury used for the dropping electrode was purified by the standard methods.

The apparatus employed in the present investigation was

the same as that described earlier. The d.c. potentials have been expressed with reference to the saturated calomel electrode. The constants of the d.m.e. were:

m = 4.564 mg/sec.

t = 1.8 sec. per drop in 0.1 M KCl, open circuit.

0.1 M lithium chloride (B.D.H.) solution in water and methanol were used as supporting electrolytes. Pure nitrogen was used to deaerate the methanolic solutions and the experiments were carried out at a constant temperature of $30\pm0.5^{o}C$. 0.1 M ammonium acetate in water and methanol was used to keep the buffer capacity. The pH of the measurements was 6.8 throughout. The dropping mercury electrode was cathodic throughout the measurements.

RESULTS AND DISCUSSION

Changes in the structure of organic substances can be frequently followed by measurements of the shifts in peak potentials. Usually the shifts of peak potentials are due to (a) an introduction of a substituent into the parent compound, (b) an exchange of the polarographically active groups. In the present work all the substances involved possess the same skeleton 'A', the same reducible group 'R' and the substances only differ in the type of substituent 'X'.

Nitrobenzene has been taken as the parent compound with the reducible group NO_2 and the effects of different substituent groups like OH, COOH, NH_2, CH_3, etc.,have been studied.

(1) Effect of different substituents on the peak potential of nitrobenzene in aqueous medium

(a) Effect of substituent groups:

Table I gives the effect of the substitution of functional groups, viz., OH, COOH, NH_2, CH_3, etc., on the reduction of nitrobenzene at a pH 6.8. The concentration of all the organic compounds was kept constant and the peak potentials of the reduction peaks were compared. Reduction of nitrobenzene becomes easier if the functional groups are introduced in the meta position of nitrobenzene. m-nitrotoluene is most easily reduced and m-nitrophenol is the least. The substitution in the para position of OH and NH_2 groups increases the reduction potential of nitrobenzene but COOH group reduces the reduction potential. Substitution of NH_2 group in ortho position shifts the peak potential to more negative values whereas OH, COOH and CH_3 shift it to less negative values.

(b) Effect of position isomers

In the study of the substitution of various groups in different positions of the nucleus of nitrobenzene, the nitrophenols maintain a regular order - ortho is most easily reduced and para is most difficulty reduced, but in nitrobenzoic acids the substitution at the ortho or para positions makes it more easily reducible than the meta. If a methyl group is introduced to nitrobenzene nucleus then the meta substituted compound is more easily reduced than the ortho substituted. In nitroanilines also the meta substituted derivative is more easily reduced than ortho or para.

Table I

Effect of substituents on the peak potential of nitrobenzene

0.1 M LiCl as the supporting electrolyte

± 20 mV(r.m.s.); 50 c/s; Temp. = 30 ± 0.5°C; pH = 6.8

Concn. = 4×10^{-4}M

Sl. No.	Compound	Peak Potential in Volts	
		Aqueous medium	Methanolic medium
1.	Nitrobenzene	0.68	0.84
2.	m-dinitrobenzene	-	0.58; 0.83
3.	o-nitrobenzoic acid	0.55	0.80
4.	m-nitrobenzoic acid	0.62	0.80
5.	p-nitrobenzoic acid	0.56	0.76
6.	2:5-dinitrobenzoic acid	-	0.40; 0.92
7.	Sym-trinitrobenzoic acid	-	0.37;0.63; 0.89
8.	o-nitrophenol	0.62	0.75
9.	m-nitrophenol	0.66	0.81
10.	p-nitrophenol	0.73	0.89
11.	2:4-dinitrophenol	0.52; 0.79	0.58; 0.91
12.	o-nitroaniline	0.73	0.87
13.	m-nitroaniline	0.63	0.78
14.	p-nitroaniline	0.74	0.90
15.	o-nitrotoluene	0.67	0.83
16.	m-nitrotoluene	0.61	0.77
17.	p-nitrotoluene	-	0.79
18.	m-nitrobenzaldehyde	-	0.74
19.	p-nitrobenzaldehyde	-	0.74
20.	p-chloronitrobenzene	-	0.71

(2) Effect of different substituents on the peak potential of nitrobenzene in non-aqueous medium

The results are summarized in Table I. In general the peak potentials of nitrobenzene and its derivatives are more negative in methanolic medium than that in aqueous medium. This may be due to the large value of liquid junction potential associated with the non-aqueous system. The effect of the substituted groups on the peak potential of nitrobenzene is the same as that in aqueous medium. As regards the effect of position isomers, the effect is also same except that in nitrobenzoic acid, the substitution at the para position makes it more easily reducible than ortho and meta positions. Further, quite a few compounds which cannot be studied in aqueous medium because of their insolubility could be studied in methanolic medium. The reduction of the original nitro group is facilitated by the addition of more nitro groups in the compound as shown in case of m-dinitrobenzene when compared with nitrobenzene or dinitro or trinitrobenzoic acids when compared with nitrobenzoic acids.

It can be seen from the Table that the substituent groups NO_2, COOH, Cl and CH_3 in para position facilitate the reduction of nitrobenzene whereas the substituent groups OH and NH_2 hinder the reduction of nitrobenzene under similar conditions. The decrease in the reduction potential of nitrobenzene with substituent groups NO_2 and COOH can be explained on their -I and -T effects. Chloro group has -I and +T effects. The fact that this substituent group facilitates the reduction of nitrobenzene suggests that -I effect predominates +T effect. The observation

that the Cl group is more effective in decreasing the reduction potential than COOH group may be explained on the ground that the tautomeric effect is further reduced at neutral pH[8] and Cl group is more electronegative than COOH group. The CH_3 group has +I and +T effects and hence it should increase the reduction potential of nitrobenzene, but we find that it decreases the reduction potential of nitrobenzene. It is difficult to explain this behaviour at the moment and needs further investigation.

Similarly the increase of the reduction potential of nitrobenzene with substituent groups NH_2 is due to its +I and +T effects. OH group has -I and +T properties and the +T effect is so much powerful than the -I effect at the para position that it increases the reduction potential of nitrobenzene.

In general the reduction becomes more difficult in the para position with the substituents in the order $NO_2 > Cl > CHO > COOH > CH_3 > OH > NH_2$.

NO_2 and COOH groups show -I and -T effects. Both of these effects decrease the electron density around nitrogen thus facilitating the reduction of the nitro group. The -T effect would have greater influence in the ortho and para isomers. Consequently, the meta isomer should be reduced with greatest difficulty and this can be observed with the nitrobenzoic acids, except o-nitrobenzoic acid, which shows abnormal behaviour presumably due to hydrogen bonding. The methyl group exhibits +I and +T effect and hence increases the electron density around the ortho and para positions relative to the meta position and therefore the

meta isomer is to be readily reduced. NH_2 which shows +I and +T effects also behaves in a similar way as is observed with the studies of nitroanilines.

OH group has -I and +T effects. But as +T effect dominates the -I effect the results are similar to that of the behaviour of CH_3 or NH_2 group as far as the para isomer is concerned. The fact that ortho nitrophenol is easily reduced than either meta or para isomers is due to the hydrogen bonding which takes place between NO_2 group and OH group in the ortho position.

(3) Application of Hammett's equation

The effects of substituents can also be treated by a linear free energy relationship.. The most general postulate on which these treatments are based, is that the shift of the half-wave potentials ($\Delta E_{1/2}$) relative to that of the parent compound is due to the more or less independent contributions of the polar 'P' steric 'S' and mesomeric 'M' effects of the substituents[9].

$$\Delta E_{1/2} = P + S + M.$$

The most generally used special form of this expression is the Hammett's equation[9,10]:-

$$\Delta E_{1/2} = \rho_{\pi}.R \cdot \sigma x.$$

Where ' ρ' is the reaction constant characterising the reducible group R and 'σ' is the substituent constant. If the

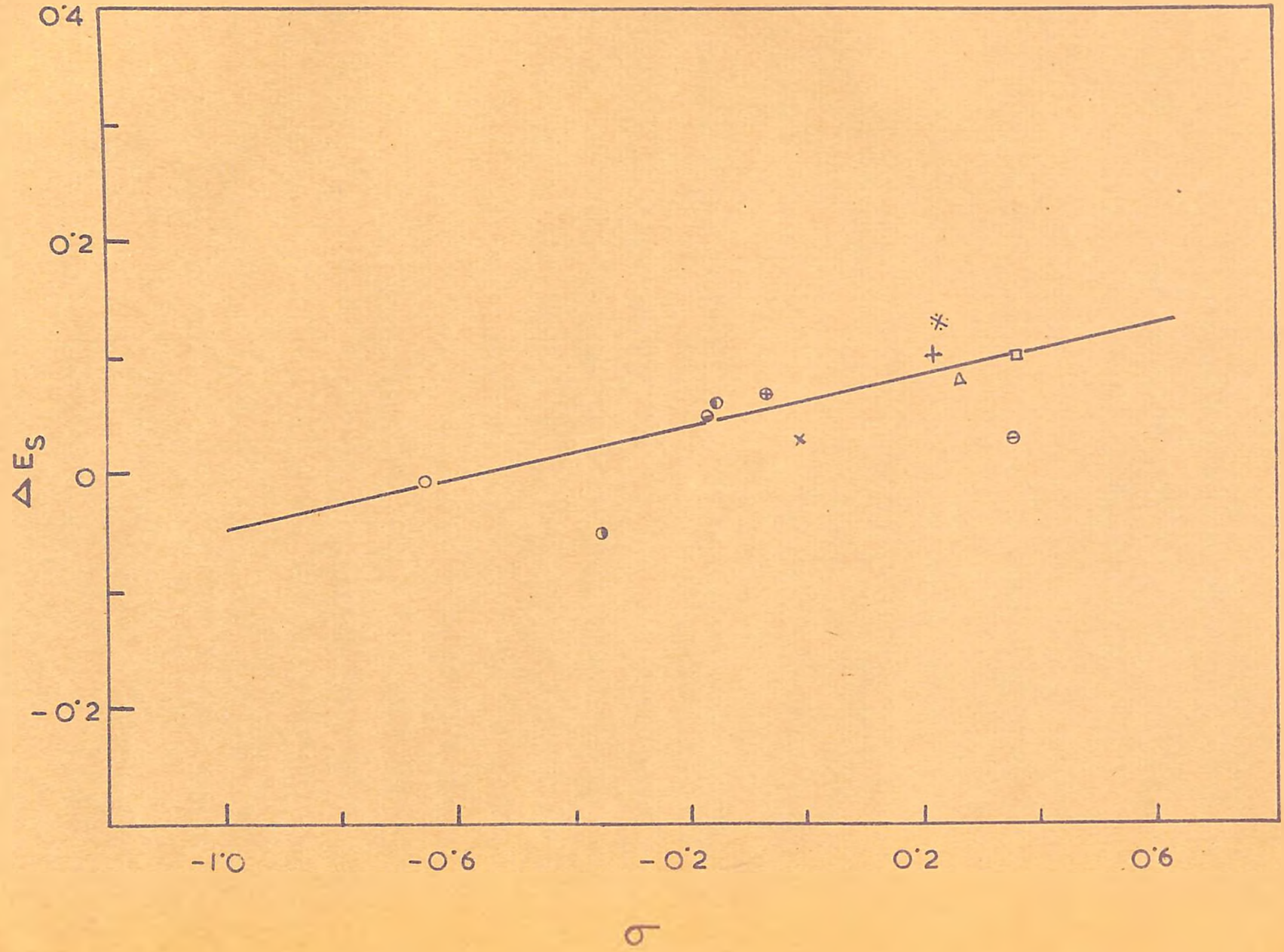

FIG. 1

LEGEND OF FIGURE

The correlation between the summit potentials and Hammett's total polar substituent constants 'σ' for nitrobenzene and its derivatives

⊖ m-nitrobenzoic acid,

⊕ m-nitrotoluene,

◐ m-nitroaniline,

× m-nitrophenol,

▫ m-nitrobenzaldehyde,

✲ p-chloronitrobenzene

▵ p-nitrobenzoic acid

◒ p-nitrotoluene

○ p-nitroaniline

◑ p-nitrophenol

+ p-nitrobenzaldehyde

---

shift in half-wave potential $\Delta E_{1/2}$ be replaced by the peak potential of the reduction of the organic compounds by a.c. polarography, then this equation can be applied to the structural studies of the organic nitro compounds by a.c. polarography. The modified equation then becomes:-

$$\Delta E_S = \rho_{\pi} \cdot R \cdot \sigma x \cdot$$

If in the a.c. polarographic studies of the nitro compounds in aqueous medium the peak potentials are plotted against the substituent constant values then the behaviour seems to be very much irregular, indicating that the reaction process does not follow the Hammett's equation. The reason for this may be due to the fact that the organic compounds get adsorbed at the mercury surface in aqueous medium and the reduction peaks are of composite nature[11]. However, in the studies of the organic compounds in non-aqueous medium the adsorption part is completely eliminated[12] and the reduction processes may be very much similar to that in conventional polarography. If the peak potentials of these compounds in non aqueous medium are plotted against the substituent constant σ^{11} then we obtain a straight line (Fig. 1) showing thereby that they follow the Hammett's rule.

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CHAPTER IV

APPLICATION OF THE TECHNIQUE TO THE STUDY OF THE SOLUBILITY OF THE SPARINGLY SOLUBLE SALTS AND COMPLEX METAL IONS

PAPER No. 9

DETERMINATION OF THE SOLUBILITY OF SPARINGLY SOLUBLE SALTS AND CALCULATION OF THE COMPOSITION AND STABILITY CONSTANT OF THE COMPLEX FROM SOLUBILITY DATA BY A.C. POLAROGRAPHY

(Trans. Soc. Adv. Electrochem. Sci. Tech. India, in Press)

DETERMINATION OF THE SOLUBILITY OF SPARINGLY SOLUBLE SALTS AND CALCULATION OF THE COMPOSITION AND STABILITY CONSTANT OF THE COMPLEX FROM SOLUBILITY DATA BY A.C. POLAROGRAPHY

Solubility of sparingly soluble salts like lead sulfate, lead iodide, cadmium oxalate and thallous bromide were determined by a.c. polarography applying the method of standard addition at three different temperatures. From the solubility of lead hydroxide at different concentrations of sodium hydroxide the composition and stability constant of the complex between lead and sodium hydroxide was determined a.c. polarographically. The composition of the complex was found to be $[HPbO_2]^-$ and the stability constant 0.5×10^{12}.

Saxena and Mittal[1] applied the method of standard addition to study the solubilities of thallous vanadates in aqueous medium by conventional polarography. No data are available in literature for such studies by a.c. polarography.

The present investigation was taken up, therefore, to see if a.c. polarography could be applied to determine the solubilities of some of the sparingly soluble salts, like

lead sulfate, lead iodide, thallous bromide and cadmium oxalate, in aqueous medium. The studies were also extended to elucidate the composition and stability constant of the lead hydroxide - sodium hydroxide complex by a.c. polarography from solubility data.

EXPERIMENTAL

The experimental set up and the technique of measurement employed in the present investigation was the same as described before. Negative d.c. potentials were applied to the d.m.e. with respect to the saturated calomel electrode. All the experiments were carried out at a constant temperature of $30^{\circ} \pm 0.5^{\circ}C$, except where mentioned.

The chemicals used were of B.D.H., A.R. and E. Merck quality and were used after repeated recrystallisation. The sparingly soluble salts - lead sulfate, lead iodide, cadmium oxalate and thallous bromide - were precipitated from the freshly prepared solutions of the respective metal salts by suitable precipitating agents, filtered, washed several times with distilled water, then dried in vacuum. Saturated solutions of these salts were prepared in conductivity water and kept over-night at a constant temperature of $30^{\circ} \pm 0.5^{\circ}C$.

Triple distilled A.R. mercury was used for the dropping electrode. Decimolar potassium nitrate in conductivity water was used as the supporting electrolyte.

The constants of the dropping electrode were -

m = 4.564 mg/sec.

t = 1.8 sec. per drop in 0.1 M KCl, open circuit.

RESULTS AND DISCUSSION

(i) Solubility of sparingly soluble salts

The standard addition method, as in conventional polarography[2] was used with following modifications to determine the solubilities in grams per litre of the sparingly soluble salts. A known amount of the saturated solution of the sparingly soluble salt was taken in 25 c.c. measuring flask and the volume was made up by conductivity water. Potassium nitrate with an effective concentration of 0.1 M was used as supporting electrolyte. The polarogram of this solution was recorded; then a known volume of a standard solution of some soluble salt of the same metal ion was added to this unknown solution and the polarogram was recorded again. If 'V' is the volume of the unknown solution, 'C_u' its concentration in moles and 'i_1' its peak height and if 'i_2' is the peak height secured after the addition of 'v' ml. of a standard solution of the soluble salt whose concentration is 'C_s', then we have -

$$C_u = i_1.v.C_s/\left[i_2.v + (i_2 - i_1)\, V\right] \qquad \ldots \quad 1$$

wherefrom 'C_u' in moles can be calculated. Then solubility in grams per litre can be obtained by multiplying 'C_u' by 'M' the molecular wt. of the substance.

Table I

Solubility of the sparingly soluble salts at different temperatures. ± 20 mV(r.m.s.); 50 c/s; 0.1 M KNO_3 as supporting electrolyte.

Sl.No.	Substance	Solubilities in gm. per litre.		
		30°C	40°C	50°C
1.	$PbSO_4$	0.0398	0.0721	0.1101
2.	PbI_2	0.8706	1.2100	1.4300
3.	TlBr	0.3260	0.5930	0.9440
4.	CdC_2O_4	0.0567	0.1333	0.2182

Table II

Complex studies by a.c. polarography. $Pb(OH)_2$ - NaOH system. ± 20 mV(r.m.s.); 50 c/s; 0.1 M KNO_3 as supporting electrolyte

Temp. = 30° ± 0.5°C.

Sl. No.	Concn.of NaOH in moles (c)	Solubility of $Pb(OH)_2$ in moles (s)	log(c)	log(s)	n
1.	0.045	2.183×10^{-3}	-1.3486	-2.6609	
					0.64
2.	0.095	2.750×10^{-3}	-1.0233	-2.5607	
3.	0.145	2.970×10^{-3}	-0.8386	-2.5273	
					0.79
4.	0.195	3.338×10^{-3}	-0.7100	-2.4765	

The results are calculated mathematically and are summarized in Table I. It can be seen from the Table that for all the salts studied their solubilities in grams per litre agree fairly well with the standard values[3] at various temperatures.

(ii) Composition and stability constant of the complex

In previous publications Dey et al.[4] derived simple expressions enabling the direct calculation of the composition and stability constant of complexes in aqueous solutions from solubility data. In a system of complex of the type -

$$MX_p + n\ Y^{-b} \rightleftharpoons \left[M(Y)_n\right]^{(p-nb)} + X^{-1}$$

in equilibrium, 'MX_p' is a sparingly soluble salt of the metal ion M^{p+} and 'Y' is the complexing ion, we may write -

$$\beta_n = \left[M(Y)_n^{(p-nb)}\right]\left[M^{p+}\right]^{-1}\left[Y^{-b}\right]^{-n} \quad \ldots \quad 2$$

where 'β_n' is the stability constant of the complex $\left[M(Y)_n\right]^{(p-nb)}$.

Now, if 's' is the concentration of MX_p dissolved in aqueous solution of 'Y' of concentration 'c', then we can calculate 'n' and 'β_n' from the following relationships -

$$n = \frac{2 \log s/s'}{\log c/c'} \quad \ldots \quad 3$$

and $$K_s \cdot \beta_n = \frac{s^2 f_i^2}{(c-ns)^n} \quad \ldots \quad 4$$

where $K_s = \left[M^{p+}\right]\left[X^{-1}\right]$, i.e., the solubility product of 'MX_p' and 'f_i' the activity coefficient calculated from the relationship:-

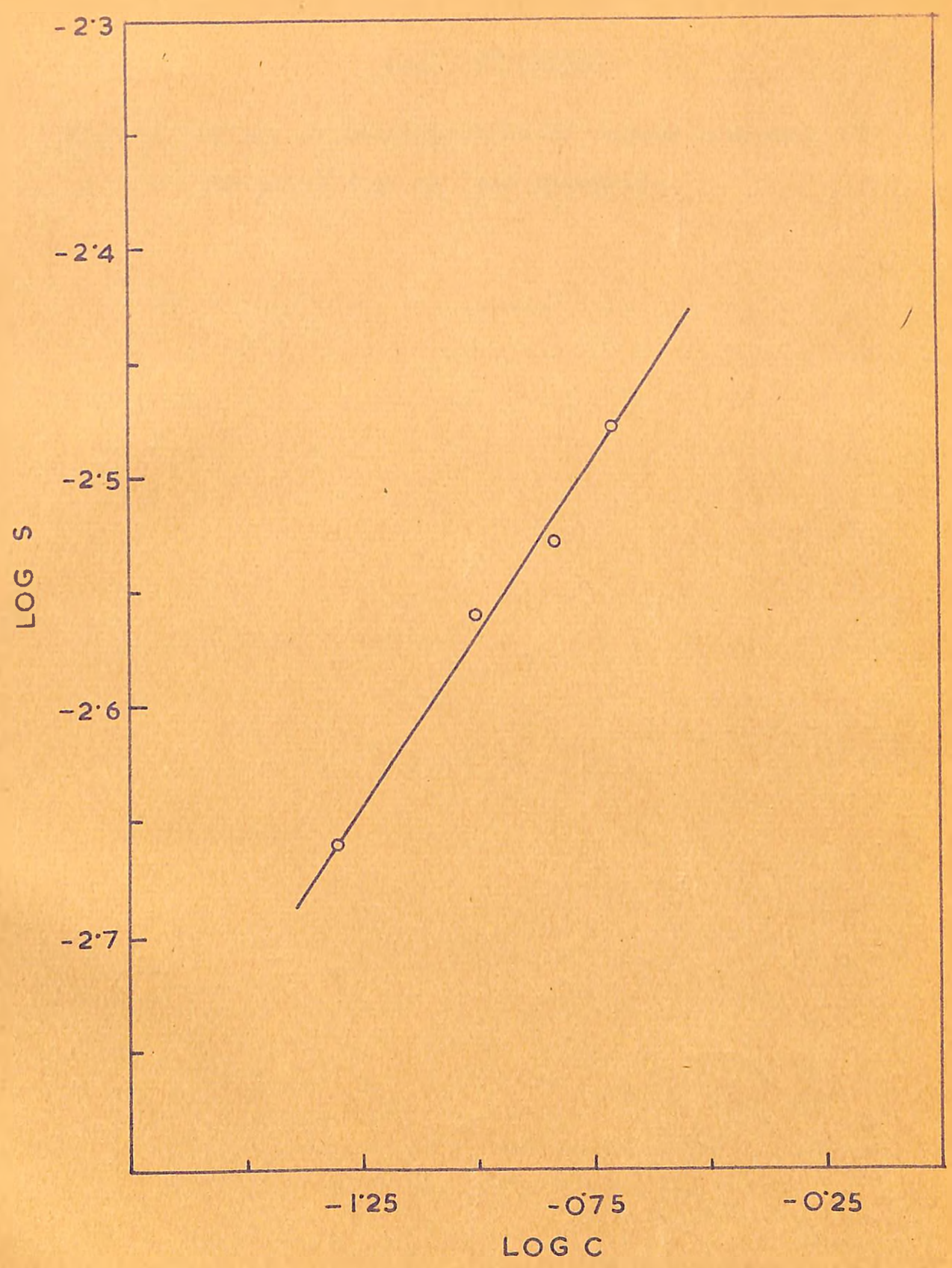

FIG. 1.

LEGEND OF FIGURE

Fig. 1: Effect of concentration of sodium hydroxide on the solubility of lead hydroxide.

$$-\log f_i = 0.5\ Z^2 \sqrt{\mu}.(1 + \sqrt{\mu})^{-1}$$

where 'μ' = s; 'n' is obtained from a plot of 'log c' versus 'log s', where the value of 'n' is twice the slope of the curve.

The solubilities of the sparingly soluble salt lead hydroxide in different concentrations of the complexing agent, sodium hydroxide, for the system of the complex $Pb(OH)_2$ - NaOH have been found out by the method of standard additions as has been described earlier in this paper. The results are tabulated in Table II. The plot of 'log s' versus log concentration of NaOH (Fig. 1) gives a straight line, the slope of which when multiplied by two approximates to unity, giving the possible equation to be -

$$Pb(OH)_2 + NaOH == Na(H\ PbO_2) + H_2O.$$

The stability constant as calculated from Eqn. 4 gives a value of 0.500×10^{12} which agrees fairly well with the value of 4.9×10^{12} found by the method of a.c. polarography[5].

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PAPER No..10

A.C. POLAROGRAPHY OF COMPLEX METAL IONS

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Short Communications

A.c. polarography of complex metal ions

ie conventional polarographic method can be applied advantageously to the study complex metal ions since the half-wave potentials of metal ions are shifted usually more negative values by complex formation. Quantitative information regarding e formula and dissociation constant of the complex can be obtained by measuring is shift as a function of the concentration of the complexing agent provided the luction or oxidation of the metal ion complex takes place reversibly at the opping mercury electrode[1]. However, no data is available in the literature for such antitative studies regarding the formula and dissociation constant of complexes by :. polarography.

The purpose of the present investigation is, therefore, to ascertain if a.c. polaro-iphy can be applied to determine the formula and dissociation constant of the mmino-cadmium complex.

Cadmium sulphate (3 $CdSO_4 \cdot 8H_2O$) used was B.D.H., A.R. quality. Standard utions of ammonia (B.D.H.) were used as the complexing agent. Mercury for the opping electrode was purified by passing it through Meyer's column, after which was washed several times with distilled water, dried, passed through a sintered-ss filter and finally distilled under vacuum.

The technique was the same as that described earlier[2,3], the only modification being t the series resistance was made as small as possible. This consists in applying to D.M.E., a 50 c/sec. a.c. ripple of 20 mV (r.m.s.) on the d.c. potential and observing alternating component of the resulting pulsating current.

A 0.1 *M* potassium nitrate (B.D.H., A.R.) solution in conductivity water was supporting electrolyte. Negative d.c. potentials were applied to the D.M.E. with pect to the saturated calomel electrode. The experiments were carried out at a nstant temperature of 30 ± 0.5°. The constants of the D.M.E. were: $m = 4.564$ g/sec and $t = 1.8$ sec per drop in 0.1 *M* KCl, open circuit.

The technique of the alternating current polarography is based on the investigation electrode processes by the use of a small (of the order of millivolts or tens of llivolts) sinusoidal alternating potential superimposed on the steady polarising tential. The alternating current produced under these conditions is measured and orded as a function of the applied steady potential, and the resulting graph is led an "a.c. polarogram". When a reversible redox process is being studied, the in characteristic of an alternating current polarogram is that a maximum alter-ing current can be observed at steady potentials. This is referred to as E_p (peak ential) and corresponds to $E_{\frac{1}{2}}$ (half-wave potential) in the conventional polaro-m.

According to KOLTHOFF AND LINGANE[1] the formula and dissociation constant of complex ion of a metal that is soluble in mercury may be given by the following ıtions:

$$\frac{\Delta(E_{\frac{1}{2}})c}{\Delta \log C_X} = -p\,\frac{0.0591}{n} \qquad (1)$$

$$(E_{\frac{1}{2}})c - (E_{\frac{1}{2}})s = \frac{0.0591}{n}\log K_C - p\,\frac{0.0591}{n}\log C_X \qquad (2)$$

where $(E_{\frac{1}{2}})c$ and $(E_{\frac{1}{2}})s$ refer to the reversible half-wave potentials of the complex metal ion and simple metal ion respectively; C_X is the concentration of the complexing agent; p is the co-ordination number of the complex metal ion; n is the number of electrons involved in reduction to metal amalgam and K_C refers to the dissociation constant of the complex.

The above equations can be applied for deriving the formula of the complex by a.c. polarography as well as its dissociation constant if $(E_{\frac{1}{2}})c$ and $(E_{\frac{1}{2}})s$ are replaced by $(E_p)c$ and $(E_p)s$, *i.e.*, their peak potentials, respectively.

Figure 1 gives a straight line on plotting $(E_p)c$ *vs.* log ammonia concentration with a slope of -0.121 V. From this slope, using eqn. (1), the value of p is found to be 4.1 with $n = 2$ showing that the formula of the complex is $Cd(NH_3)_4^{2+}$.

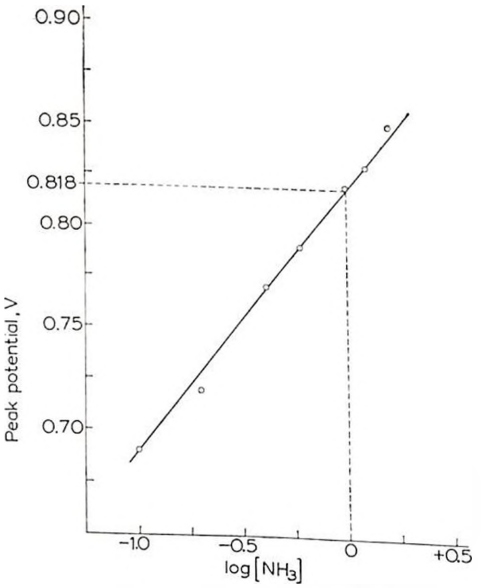

Fig. 1. Effect of ammonia concn. on the peak potential of the ammino cadmium complex in 0.10 M KNO_3.

From the equation for the straight line through the experimental points, it is found that $(E_p)c$ is -0.818 V at an ammonia concentration of 1.00 M. From this value and the measured peak potential of the simple cadmium ion in 0.1 M KNO_3 containing no added ammonia (-0.60 V *vs.* S.C.E.), the value of K_C was calculated from eqn. (2) as 0.397×10^{-7} which agrees fairly well with the value of 1×10^{-7} for K_C obtained from conventional polarography[4].

The complexes of cadmium with thiocyanate, iodide and oxalate ions have also been studied by a.c. polarography and the details will be published elsewhere.

It may, therefore, be concluded that a.c. polarography can be successfully used for the quantitative study of complex metal ions. The method has the following advantages over the conventional polarographic method.

(i) It is unnecessary to analyse the polarogram for its reversibility as in conventional polarography, since a.c. polarograms will be obtained only for reversible oxidation and reduction processes.

(ii) Oxygen need not be removed from the solution as it does not interfere in a.c. polarography provided it does not react chemically with the reducible species as in the case of lead[5].

(iii) Peak potentials can be determined more conveniently and accurately than half-wave potentials.

(iv) Measurement can be made more rapidly and with an improved all round reproducibility.

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PAPER No. 11

STUDIES ON THE COMPLEXES OF COPPER WITH AMMONIA & PYRIDINE BY ALTERNATING CURRENT POLAROGRAPHY

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Studies on the Complexes of Copper with Ammonia & Pyridine by Alternating Current Polarography

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Manuscript received 10 *September* 1964

Alternating current polarography has been successfully used for the quantitative study of the complexes of copper and ammonia involving two reduction peaks. The dissociation constants of cupric and cuprous complexes of ammonia, represented as $[Cu^{II}(NH_3)_4]^{2+}$ and $[Cu^{I}(NH_3)_2]^{+}$ are $0{\cdot}415 \times 10^{-14}$ and $0{\cdot}219 \times 10^{-11}$ respectively; these values agree fairly well with literature values. Copper forms only one complex with pyridine, $[Cu^{I}(Py)_2]^{+}$; the dissociation constant of the complex is $7{\cdot}266 \times 10^{-9}$ which has also been confirmed by conventional polarographic studies.

RECENTLY Gupta and Chatterjee[1] have shown that a.c. polarography can be used with advantage for the quantitative study of the complex formed between cadmium and ammonia, involving one reduction peak. With a view to ascertaining the applicability of a.c. polarography for the quantitative study of the complexes involving two reduction peaks, such as the ones formed between copper and ammonia the present investigation was undertaken. Also the composition of the complex between copper and pyridine as well as its confirmation by conventional polarography have been determined since no data are available in literature about the complexes.

Experimental Procedure

Copper sulphate ($CuSO_4.5H_2O$) used was BDH (AR) quality. A standard solution of ammonia (BDH) and redistilled pyridine (E. Merck) were used as complexing agents. A fresh sample of cuprous chloride was prepared as described earlier[2]. Mercury used for the dropping electrode was purified by passing it through Meyer's column, after which it was washed serveral times with distilled water, dried, passed through a sintered glass filter and finally distilled under vacuum.

The technique of measurement is the same as that described earlier[3,4], the only modification being that the series resistance was made as small as possible. This consists in applying to the DME, a 50 cycles/sec. a.c. ripple of 20 mV. (r.m.s.) on the d.c. potential and observing the alternating component of the resulting pulsating current.

Ammonium nitrate ($2{\cdot}0M$) and pyridinium chloride ($0{\cdot}1M$) in conductivity water were used as the supporting electrolytes. Negative d.c. potentials were applied to the DME with respect to the saturated calomel electrode. The experiments were carried out at a constant temperature of $30 \pm 0{\cdot}5°C$. The constants of the DME were $m = 4{\cdot}564$ mg./sec. and $t = 1{\cdot}8$ sec. per drop in $0{\cdot}1M$ KCl, open circuit.

Results and Discussion

The main characteristic of an a.c. polarogram when a reversible redox process is being studied is the observation of a maximum a.c. at a steady potential (E_p) corresponding to ($E_{1/2}$) in the conventional polarogram. According to Kolthoff and Lingane when the free energies of the various possible oxidation states of a complex metal ions are sufficiently different, reduction from a higher to lower oxidation state can proceed in stages at the dropping electrode to produce a polarogram consisting of two or more separate waves. For a polarogram consisting of two waves, such a stepwise reduction in eomplex can be represented by two equations[5]

$$CuX_p(2-p)^+ + e \rightleftharpoons CuX_q(2-1-q)^+ + (p-q)X^{-1} \quad \ldots (1)$$

$$CuX_q(2-1-q)^+ + e + Hg \rightleftharpoons Cu(Hg) + qX^{-1} \quad \ldots (2)$$

where $E^{I}_{1/2}$ and $E^{II}_{1/2}$ are the standard potentials of the two reactions.

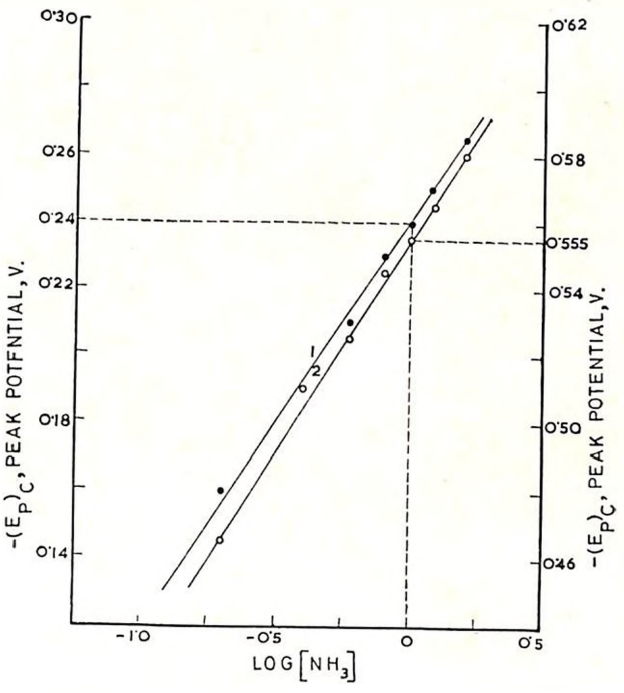

Fig. 1 — Effect of ammonia concentration on the peak potentials of the copper-ammonia complexes in $2{\cdot}0M$ ammonium nitrate by a.c. polarography [Curve 1, cupric-ammonia complex; and curve 2, cuprous-ammonia complex]

The same equations can be applied for deriving the formula of the complex by a.c. polarography if $(E^{I}_{1/2})$ and $(E^{II}_{1/2})$ are replaced by (E^{I}_{p}) and (E^{II}_{p}), i.e. their peak potentials respectively.

The curves 1 and 2 in Fig. 1 represent the straight-line plots of $(E^{I}_{p})_c$ and $(E^{II}_{p})_c$ versus log concentration of ammonia, each having a slope of −0·120 and −0·127 respectively. From the slopes, the values of the number of ammonia molecules combined with one cupric and one cuprous ions come out to be 4·17 and 2·14 with $n = 1$ respectively. The corresponding structures may be then represented as $[Cu^{II}(NH_3)_4]^{2+}$ and $[Cu^{I}(NH_3)_2]^{+}$ which agree with the structures obtained by Von Stackelberg and Von Freyhold[6] using conventional polarography. Further, the dissociation constants of cupric and cuprous complexes of ammonia as calculated are $0{\cdot}415\times10^{-14}$ and $0{\cdot}219\times10^{-11}$ respectively. These agree fairly well with the values of $4{\cdot}56\times10^{-14}$ for cupric ammonia and $1{\cdot}35\times10^{-11}$ for cuprous ammonia complexes given in literature[7].

In the study of the complex between copper sulphate and pyridine by a.c. polarography, it is seen that only one peak is obtained whose peak potential $(E_p)_c$ shifts to more cathodic side with increase in concentration of pyridine. This peak corresponds to the reduction of Cu^{+} ion to Cu(Hg). The reduction of Cu^{2+} to Cu^{+} seems to be irreversible under these conditions and that is why no peak is obtained for this reduction by a.c. polarography. Curve 1 in Fig. 2 gives a straight line on plotting $(E_p)_c$ using copper sulphate versus log pyridine concentration. From the slope of this straight line which is −0·130, the number of pyridine molecules, combined with one cuprous ion comes to be 2·19 with $n = 1$ showing that the structure of the complex is $[Cu^{I}(Py)_2]^{+}$.

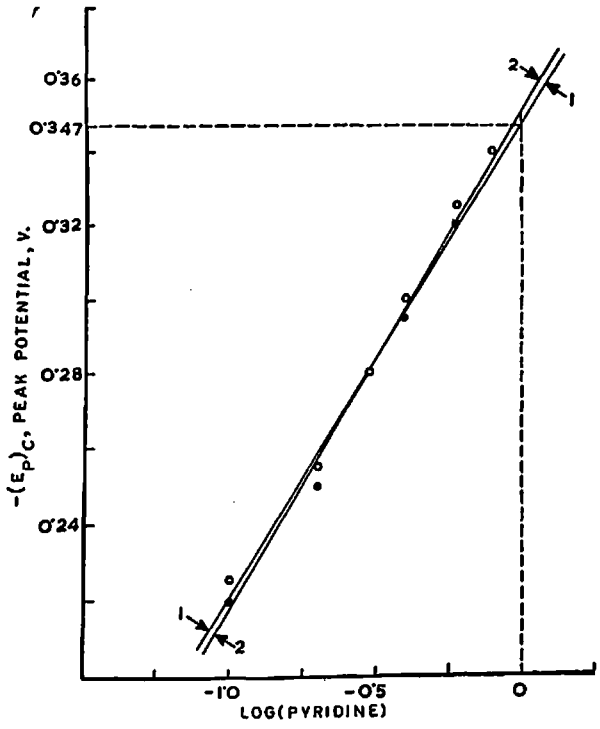

Fig. 2 — Effect of pyridine concentration on the peak potentials of cuprous-pyridine complex in 0·1*M* pyridinium chloride by a.c. polarography [Curve 1, copper sulphate-pyridine complex; and curve 2, cuprous chloride-pyridine complex]

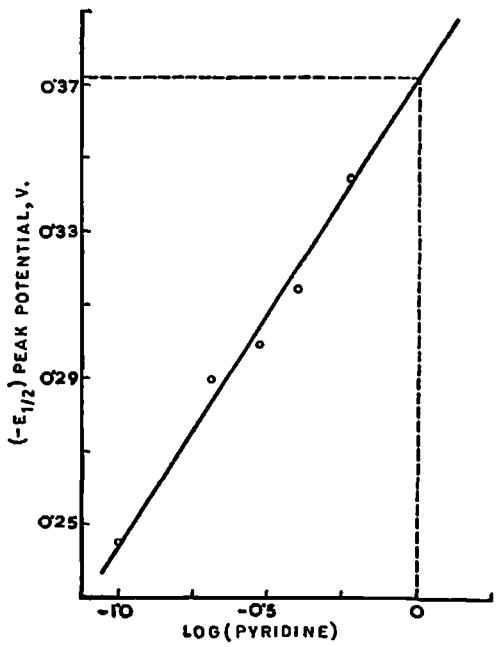

Fig. 3 — Effect of pyridine concentration on the peak potentials of cuprous-pyridine complex in 0·1*M* pyridinium chloride by conventional polarography

The fact that the peak in a.c. polarography is due to the reduction of Cu^{+} to Cu(Hg) and the composition of the complex is $[Cu^{I}(Py)_2]^{+}$ is confirmed by curve 2 (Fig. 2) which gives a straight line plot of $(E_p)_c$ against log pyridine concentration using cuprous chloride with slope equal to −0·134 and the number of pyridine molecules combined with one cuprous ion as 2·26. The above structure of copper-pyridine complex is also confirmed by conventional polarography where the slope of the straight line plot of $(E_{1/2})_c$ versus log pyridine concentration is −0·128 and the number of pyridine molecules combined with one cuprous ion comes out to be 2·16 (Fig. 3).

From the equation for the straight line through the experimental points (curve 1; Fig. 2), it is found that $(E_p)_c$ is −0·347 V. versus SCE at pyridine concentration of 1·0*M*. From this value and the value of $(E_p)_s$ calculated from thermodynamic data[8], i.e. 0·134 V. versus SCE (the equilibrium between simple cuprous ion and copper amalgam is not accessible to experimental measurement), the value of K_c was calculated as $7{\cdot}266\times10^{-9}$ which agrees fairly well with the value of $2{\cdot}965\times10^{-9}$ obtained by conventional polarography (Fig. 3).

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PAPER No. 12

A.C. POLAROGRAPHY OF COMPLEX METAL IONS

(Rev. Polarog., Japan, 1967, 14, 49.)

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A.C. POLAROGRAPHY OF COMPLEX METAL IONS

It is shown that a.c. polarography can be applied with advantage for the determination of the formula and dissociation constant of the complex involving one reduction peak such as cadmium-ammonia, cadmium-thiocyanate, cadmium-iodide, lead-hydroxide, lead-oxalate and cupric -β -resorcylic acid complexes as well as two reduction peaks such as copper-ammonia complex. Copper forms only one complex with pyridine having composition $\left[Cu^{I}(Py)_2\right]^{+}$ and stability constant 1.376 x 10^8 which agrees fairly well with the value of 1.608 x 10^8 obtained by conventional polarography.

The technique has also been used to study the systems of complexes such as cadmium-oxalate and zinc-thiocyanate in step equilibrium. It is shown that cadmium forms three complexes with oxalate whereas zinc gives four complexes with thiocyanate. The stability constants of various complexes have been determined and they agree fairly well with the values given in the literature. The advantages of the method over conventional polarographic method are discussed.

The conventional polarographic method can be applied to the study of complex metal ions since the half wave potentials

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

Provided all the reactions at the d.m.e. are reversible and very rapid as compared with rates of ionic diffusion, it can be shown that the shift in half wave potential due to the formation of a metal complex $MX^{(n-pb)+}$ for a solvated cation M^{n+} and a ligand X^{-b} is given approximately by[1]:-

$$\Delta E_{1/2} = (E_{1/2})_s - (E_{1/2})_c = \frac{0.0591}{n} \log \beta_p + \frac{0.0591}{n} p \log C_x \quad \ldots 1$$

where, $(E_{1/2})_s$ and $(E_{1/2})_c$ are the half wave potentials for the reduction of the simple and complex ions respectively. C_x is the total concentration of the complexing ligand 'X' and 'β_p' is the stability constant of the complex 'MX_p'.

However, as no data are available on such studies by a.c. polarography, the present investigation has, therefore, been taken up with a view to ascertain if a.c. polarography can be applied with advantage to determine the formulae and stability constants of the complexes. This investigation, therefore, gives the results obtained in the study of the complexes involving one reduction peak as well as two reduction peaks. These studies have also been extended to the systems of complexes in step equilibrium.

EXPERIMENTAL

Various chemicals used were pure recrystallised samples of AnalaR quality. Ammonia and pyridine were of B.D.H. and E.Merck samples respectively. Stanandrd solutions of potassium oxalate, potassium thiocyanate, ammonia, β-resorcylic acid and pyridine in conductivity water were used as complexing agents. Triple distilled A.R. mercury was used for the experiments.

The experimental set up and technique of measurement were same as described earlier. The ionic strength was maintained constant throughout the measurements with potassium nitrate solution. Negative d.c. potentials were applied to the d.m.e. with respect to the saturated calomel electrode. The experiments were carried out at a constant temperature of 30 ± 0.5°C. The constants of the d.m.e. were

$m = 2.3006$ mg/sec.

and $t = 3.5$ sec. per drop in 0.1 M KCl, open circuit.

RESULTS AND DISCUSSION

1. Complexes involving one reduction peak

Eq. 1 can be applied for deriving the coordination number of the complex "p" and the stability constant "β_p" by a.c. polarography if $(E_{1/2})_c$ and $(E_{1/2})_s$ are replaced by $(E_p)_c$ and $(E_p)_s$, i.e., their peak potentials respectively. Then the modified equation becomes:

$$\Delta E_p = (E_p)_s - (E_p)_c = \frac{0.0591}{n} \log \beta_p + \frac{0.0591}{n} p \log C_x \quad \ldots 2$$

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

The above equation is applied to the study of complexes like cadmium - ammonia[2a,2b], cadmium - thiocyanate[2b], cadmium - iodide[2c], lead - hydroxide[2d], lead - oxalate[2e], and cupric - β-resorcylic acid[2f,2g], all involving only one reduction peak. The experimental results, summarised in Table I, show the existence of only one complex and their stability constants agree fairly well with the values obtained by conventional polarographic studies.

Further, Fig. 1 gives typical curves depicting the results obtained with the studies of the complexes between lead and sodium hydroxide and lead and potassium oxalate, showing the existence of the complexes $\left[H\ PbO_2\right]^-$ and $\left[Pb(C_2O_4)_2\right]^{-2}$, with stability constants 4.902×10^{12} and 0.714×10^6 respectively.

2. Complex involving two reduction peaks

According to Kolthoff and Lingane[3] when the free energies of the various possible oxidation states of a complex metal ion are sufficiently different, reduction from a higher to lower oxidation state can proceed in stages at the d.m.e. to produce a polarogram consisting of two or more separate waves. For a polarogram consisting of two waves such a stepwise reduction in complex can be represented by two equations:

$$MX_p^{(n-pb)+} + e \rightleftharpoons MX_q^{(n-1-qb)+} + (p-q)\ X^{-b} \qquad \ldots 3$$

$$MX_q^{(n-1-qb)+} + e + Hg \rightleftharpoons M(Hg) + q\ X^{-b} \qquad \ldots 4$$

where $(E_{1/2}^{I})$ and $(E_{1/2}^{II})$ are the standard potentials of the two reactions. The same equations can be applied for deriving the formula of the complex by a.c. polarography if $(E_{1/2}^{I})$ and $(E_{1/2}^{II})$ are replaced by (E_p^{I}) and (E_p^{II}), i.e., their peak potentials respectively.

The results show the existence of two complexes (vide Table I) and their stability constants agree fairly well with the values obtained by conventional polarography[4a,4b].

In the study of the complex between copper sulphate and pyridine by a.c. polarography it is seen that only one peak is obtained which shifts to more cathodic values with increase in concentration of pyridine. This peak corresponds to the reduction of Cu^{+} to (Cu(Hg) and the formula of the complex is found to be $\left[Cu^{I}(Py)_2\right]^{+}$. These observations are further confirmed by using cuprous chloride instead of copper sulphate and by conventional polarography. The value of the stability constant for $\left[Cu^{I}(Py)_2\right]^{+}$ obtained by two methods agree fairly well[4b].

3. Complex in step equilibrium

For many ligands - notably those which do not form very stable complexes - the plot of $(E_{1/2})_c$ vs. log C_x is a nonlinear continuous curve indicating the presence of more than one complex

Sl. No.	Structure of the Complex
1.	$\left[Cd(NH_3)_4\right]^{+2}$
2.	$\left[Cd\ CNS\right]^{+}$
3.	$\left[Cd\ I_3\right]^{-}$
4.	$\left[H\ PbO_2\right]^{-}$
5.	$\left[Pb(C_2O_4)_2\right]^{-2}$ (inert atmosphere)

Table I

Coordination Number 'p'	Stability constant	
	A.C.Polarography	D.C.Polarography
4.100	2.732×10^{7}	1.000×10^{7}
1.040	3.069×10^{2}	0.500×10^{2}
2.940	2.513×10^{5}	0.454×10^{5}
2.830	4.902×10^{12}	6.546×10^{12}
2.206	0.714×10^{6}	3.448×10^{6}
0.970	0.671×10^{2}	1.538×10^{2} (Spectrophotometrically)
4.170	2.410×10^{14}	0.219×10^{14}
2.140	4.566×10^{11}	0.740×10^{11}

of varying stabilities. DeFord and Hume[5,6] obtained the following relations between the change in half wave potential and the free ligand concentration for a reversible metal deposition:-

$$\text{Antilog}_{10}\left[\frac{0.4343\ nF}{RT}\Delta E_{1/2} + \log_{10}\frac{I_s}{I_c}\right] = \gamma_M \sum_0^N \frac{\beta_j [X]^j \gamma_X{}^j}{\gamma_{MX_j}} \quad \ldots 5$$

$$= \beta_0 + \beta_1[X]\frac{\gamma_M \gamma_X}{\gamma_{MX}} \ldots + \beta_N[X]^N \frac{\gamma_M(\gamma_X)^N}{\gamma_{MX_N}} \quad \ldots 6$$

($\beta_0 = 1$ for the zero complex and $[X]$ = free ligand concentration). If all the measurements are made at the same ionic strength and the activity quotients dropped from Eq. 5, the right hand side may be denoted by $F_0[X]$, indicating that it is a function of free ligand concentration and written as follows:-

$$F_0[X] = \beta_0 + \beta_1[X] + \beta_2[X]^2 + \ldots + \beta_N[X]^N \quad \ldots 7$$

A new function $F_1[X]$, may be defined by:

$$F_1[X] = \left[\frac{F_0[X] - \beta_0}{[X]}\right] = \beta_1 + \beta_2[X] + \beta_3[X]^2 + \ldots 8$$

in a similar manner, other functions may be derived, giving finally:

$$F_N[X] = \left[\frac{F_{N-1}[X] - \beta_{N-1}}{[X]}\right] = \beta_N .$$

Now, if $(E_{1/2})_s$ and $(E_{1/2})_c$ can be replaced by their respective peak potentials $(E_p)_s$ and $(E_p)_c$ and the ratio of the diffusion current constants by the ratio of the peak currents $(i_p)_s$ and $(i_p)_c$ of the simple and the complex metal ions, then Eq. 5 can

be applied for the study of such complexes by a.c. polarography. The modified equation then becomes:

$$F_o\,[X] = \text{Antilog}_{10}\left[\frac{0.4343\ nF}{RT}\Delta E_p + \log_{10}\frac{(i_p)_s}{(i_p)_c}\right] \qquad \ldots 9$$

If the values of $F_o\,[X]$ obtained from the above equation for different values of C_x, the total ligand concentration, are plotted against C_x, then a nonlinear continuous curve is obtained. The value of $F_o\,[X]$ for this curve at $C_x = 0$ gives the value of β_o and the slope at $C_x = 0$ gives β_1. Substituting this value for β_o (β_o assumed to be equal to unity) in Eq. 8 and calculating $F_1\,[X]$ for different values of C_x and plotting against C_x, we obtain another nonlinear curve whose value for $F_1\,[X]$ at $C_x = 0$ gives β_1 and the slope at $C_x = 0$ gives β_2. Proceeding similarly we should ultimately reach a function $F_{j-1}\,[X]$, which when plotted against C_x will give straight line with positive slope, and the last function $F_j\,[X]$ should give a line parallel to the C_x axis with an intercept equal to β_j.

Again, if C_M denotes the total concentration of the metal present in solution in presence of the complexing ligand and number of complexes by 'j', then C_M should be equal to the sum of the concentration of all the complexes and free metal ion:

$$C_M = [M] + [MX] + [MX_2] + \ldots + [MX_N] \qquad \ldots 10$$

Now, by definition we know that

$$[MX_j] = \beta_j [M]\,[X]^j \cdot \gamma_M (\gamma_X)^j / \gamma_{MX}$$

$$\text{or} \quad C_M = [M]\left\{1 + \beta_1[X]\frac{\gamma_M \gamma_X}{\gamma_{MX}} + \ldots\right\} = [M]\, F_o[X]$$

$$\text{or} \quad [M] = \frac{C_M}{F_o[X]} \; ; \quad [M] = \text{concentration of the free metal}$$

ion present in the solution.

Similarly, the fraction of the total metal present as another complex, e.g., as MX_j, will be given by:

$$\frac{[MX_j]}{C_M} = \frac{\beta_j [X]^j \gamma_M (\gamma_X)^j / \gamma_{MX_j}}{F_o[X]}$$

neglecting the activity coefficient terms:

$$\frac{[MX_j]}{C_M} = \frac{\beta_j [X]^j}{F_o[X]} .$$

(i) Cadmium - oxalate system:

The experimental results and calculations are summarized in Table II. The plot of $F_o[X]$ vs. concentration of the ligand (Fig.2, curve 1) essentially gives a curve indicating the presence of more than one complex system. Extrapolation of the plot to zero oxalate concentration yielded a value almost equal to unity for $F_o[X]$. Using unity for $F_o[X]$ and calculating $F_1[X]$ resulted the curve 2 in the same figure which on extrapolation leads to a value of 4.0×10^2 for β_1. When the values of $F_2[X]$ were calculated using this value of for β_1 and plotted against C_x the points approximated to a straight line with a positive slope, which gave $\beta_2 = 9.467 \times 10^3$.

Table II

Cadmium -Oxalate System

$\pm$20 mV(r.m.s.); 50 c/s; Temp. = 30 $\pm$ 0.5°C; Cadmium concn. = 3.0×10^{-4}M

Ionic strength = 1.5.

Oxalate (M)	Peak Potential V	Current μA	$F_0[X]$	$F_1[X]$	$F_2[X]$	$F_3[X]$
0.00	- 0.585	3.98				
0.05	- 0.635	3.78	48.50	950	11000	
0.10	- 0.658	3.98	266.70	2657	22570	131300
0.15	- 0.673	2.88	1162.00	7740	48933	263106
0.20	- 0.680	2.80	1753.00	8760	41800	161665
0.30	- 0.690	2.72	4511.00	15033	48776	131030
0.40	- 0.700	3.01	8776.00	21937	53842	110937
0.50	- 0.710	2.70	21060.00	42118	83436	147940

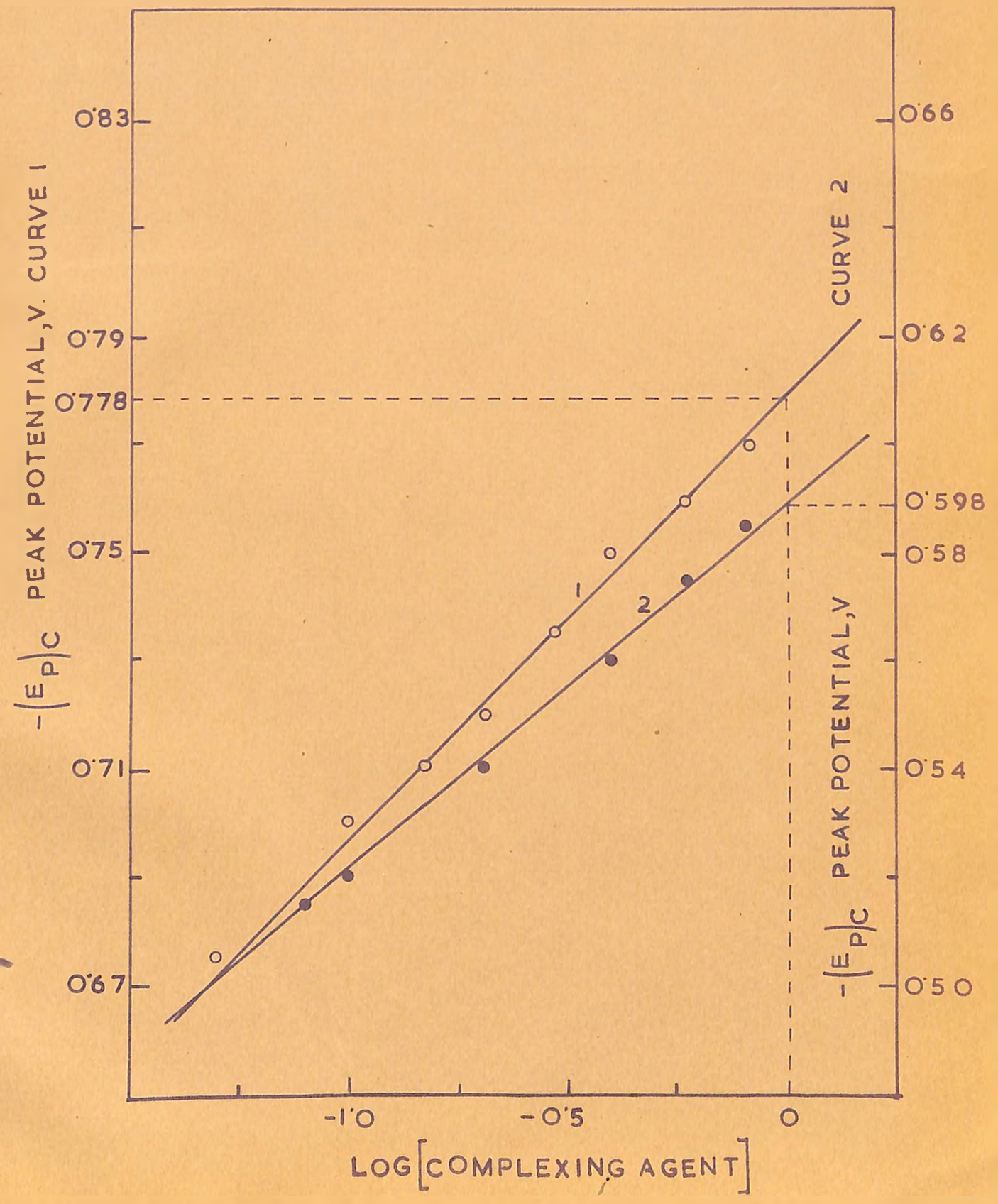
0·83
0·79
0·778
0·75
0·71
0·67
0·66
0·62
0·598
0·58
0·54
0·50
-(Ep)c PEAK POTENTIAL, V. CURVE 1
CURVE 2
-(Ep)c PEAK POTENTIAL, V
1
2
-1·0
-0·5
0
LOG [COMPLEXING AGENT]

FIG. 1.

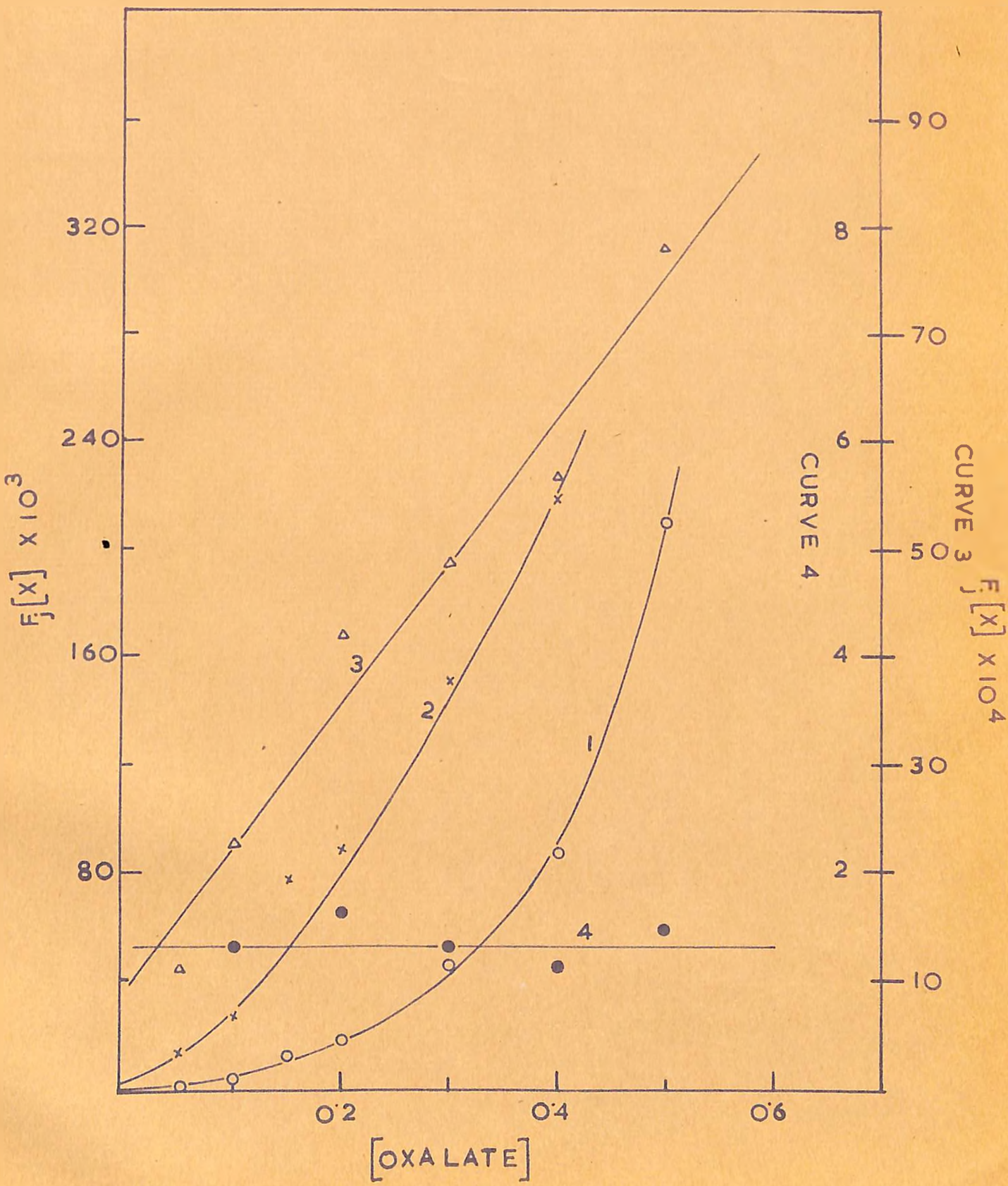
320
240
160
80
$F_j[X] \times 10^3$
90
8
70
6
50
4
30
2
10
$F_j[X] \times 10^4$
CURVE 4
CURVE 3
1
2
3
4
0·2
0·4
0·6
[OXALATE]

FIG. 2.

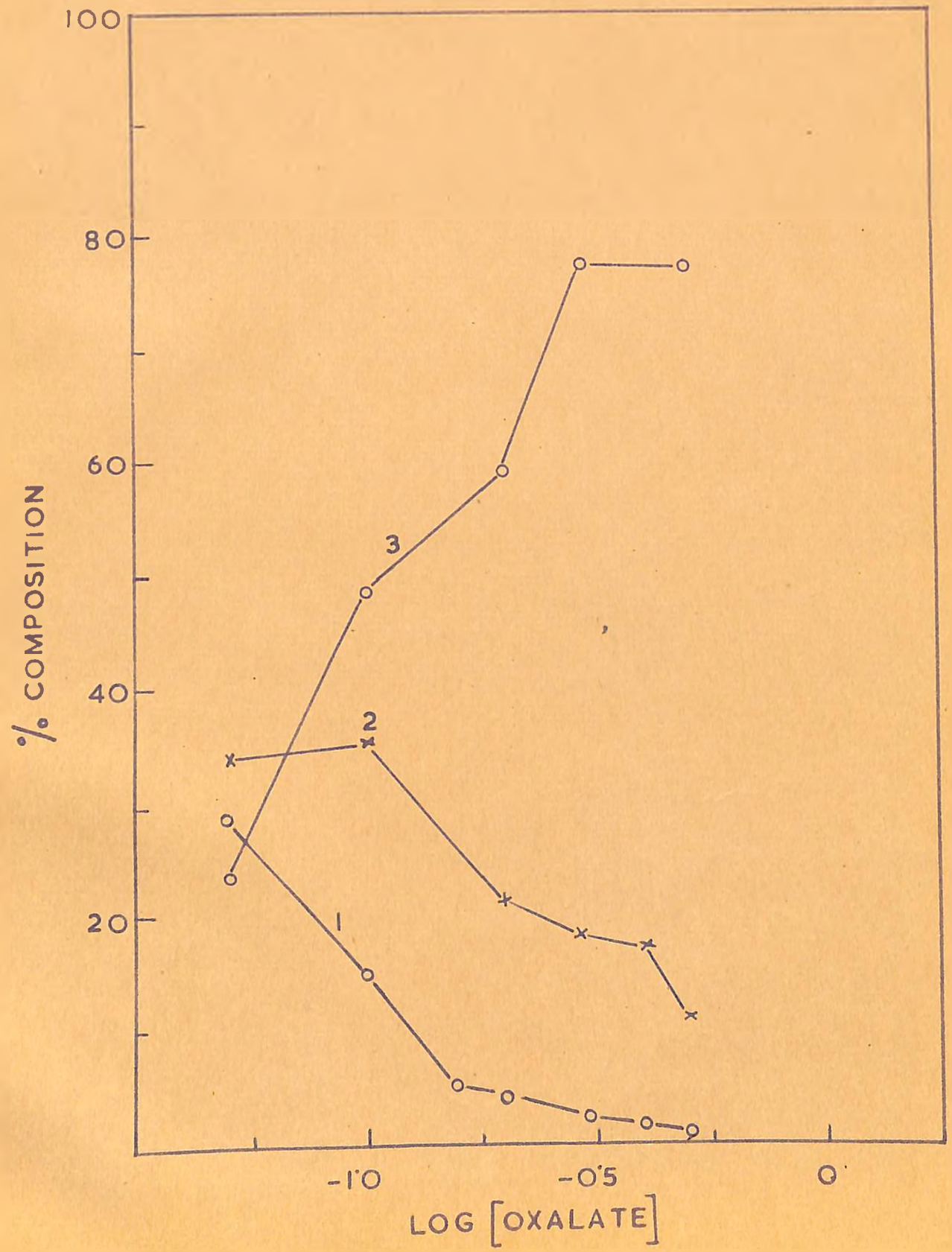

FIG. 3.

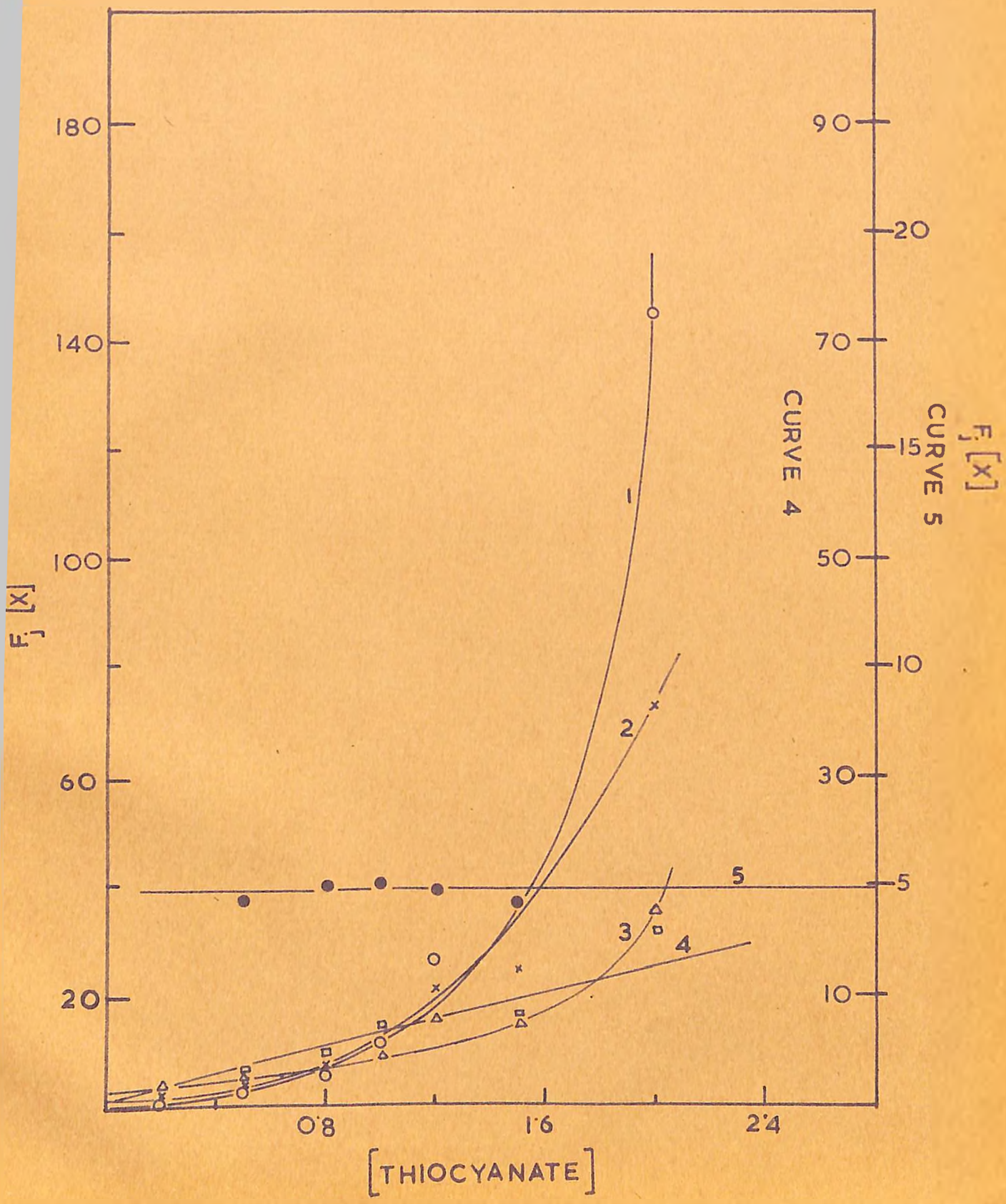
180
140
100
60
20
90
70
50
30
10
20
15
10
5
10
$F_j[X]$
CURVE 4
CURVE 5
$F_j[X]$
1
2
3
4
5
0·8
1·6
2·4
[THIOCYANATE]

FIG.4.

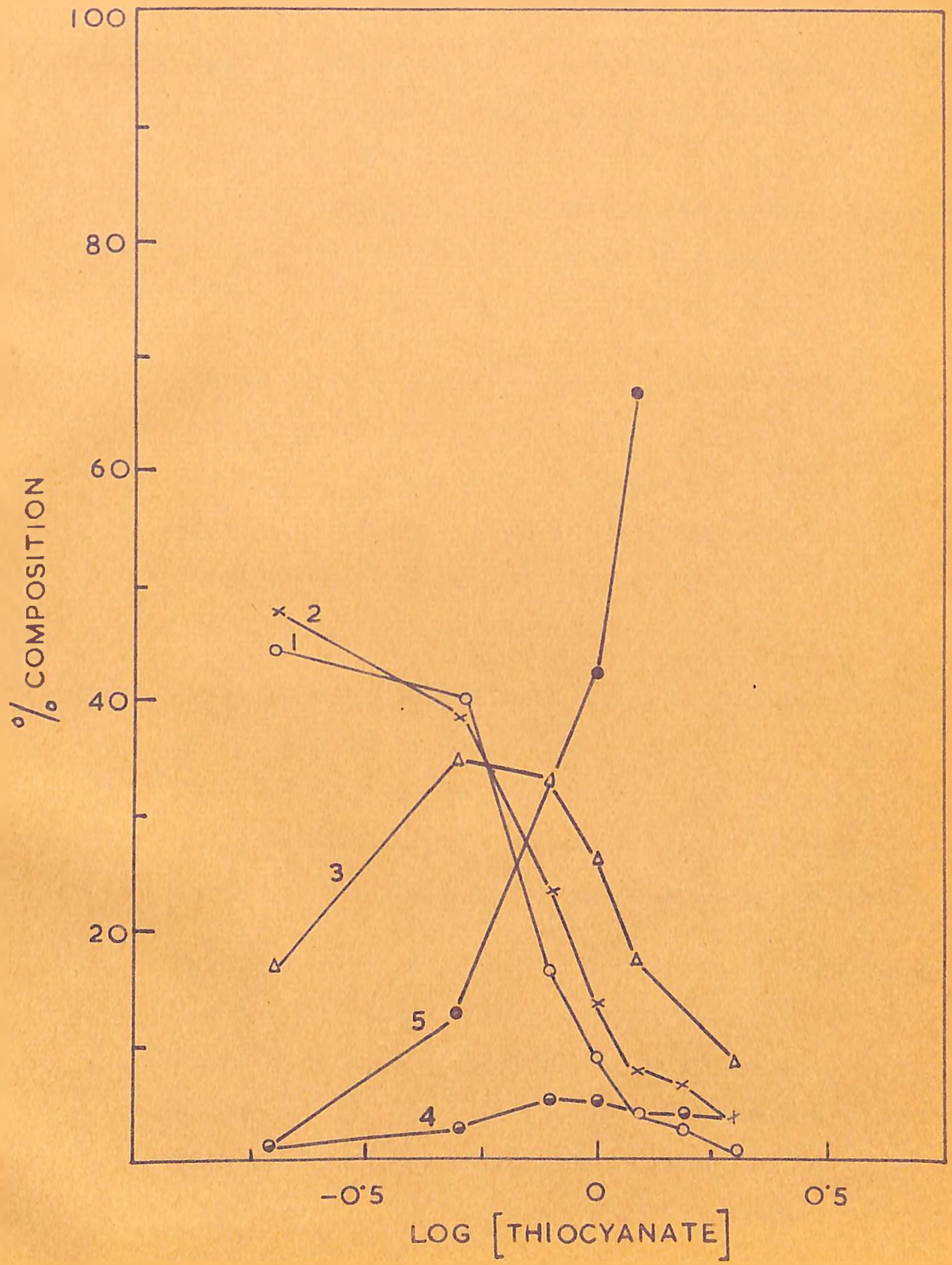

FIG. 5.

LEGEND OF FIGURES

Fig. 1: Curve 1: Effect of sodium hydroxide concentration on the peak potentials of lead-hydroxide complex in 0.1 M KNO_3.

Curve 2: Effect of potassium oxalate concentration on the peak potentials of lead-oxalate complex in 0.1 M KNO_3(inert atmosphere).

Fig. 2: Values of $F_j[\bar{X}]$ for cadmium as a function of oxalate ion concentration. Ionic strength 1.5.

Curve 1: $F_o[\bar{X}]$ vs. oxalate concentration.

Curve 2: $F_1[\bar{X}]$ vs. oxalate concentration.

Curve 3: $F_2[\bar{X}]$ vs. oxalate concentration.

Curve 4: $F_3[\bar{X}]$ vs. oxalate concentration.

Fig. 3: Percentage of cadmium in various figures as a function of oxalate ion concentration.

Curve 1: Cd(oxalate) vs. oxalate concentration.

Curve 2: $Cd(Oxalate)_2$ vs. oxalate concentration.

Curve 3: $Cd(Oxalate)_3$ vs. oxalate concentration.

Fig. 4: Values of $F_j[\bar{X}]$ for Zinc as a function of thiocyanate ion concentration. Ionic strength 2.0.

Curve 1: $F_o[\bar{X}]$ vs. thiocyanate concentration.

Curve 2: $F_1[\bar{X}]$ vs. thiocyanate concentration.

Curve 3: $F_2[\bar{X}]$ vs. thiocyanate concentration.

Curve 4: $F_3[\bar{X}]$ vs. thiocyanate concentration.

Curve 5: $F_4[\bar{X}]$ vs. thiocyanate concentration.

Fig. 5: Percentage of Zinc in various forms as a function of thiocyanate ion concentration.

Curve 1: Zinc vs. thiocyanate concentration.

Curve 2: $Zn(CNS)$ vs. thiocyanate concentration.

Curve 3: $Zn(CNS)_2$ vs. thiocyanate concentration.

Curve 4: $Zn(CNS)_3$ vs. thiocyanate concentration.

Curve 5: $Zn(CNS)_4$ vs. thiocyanate concentration.

A plot of the values of $F_3[X]$ using this value of β_2 gave a horizontal straight line with an intercept of 1.3103×10^5, corresponding to the value of β_3. Although there was a considerable scatter of points no trend from the horizontal could be ditected.

The conclusion is therefore drawn that in solutions containing free oxalate ions in concentration up to 0.5 M only the species Cd^{+2}, $[Cd(OX)]$, $[Cd(OX)_2]^{-2}$ and $[Cd(OX)_3]^{-4}$ exist. The distribution of cadmium among the above four species for various concentrations of free oxalate ion has been calculated and is plotted in Fig. 3.

It is observed that the values of the stability constants for the various complex species obtained by this method agree fiarly well with the data obtained for $\beta_1 = 4.10 \pm 0.15 \times 10^2$, for $\beta_2 = 1.29 \pm 0.15 \times 10^4$ and for $\beta_3 = 1.15 \pm 0.15 \times 10^5$ by McMasters et al.[7] using conventional polarography.

(ii) Zinc-thiocyanate system:

The resulting data are analysed methamatically and summarized in Table III. Fig. 4 Curves 1 to 5 show the plots of $F_j[X]$ values as a function of thiocyanate concentration. The stability constants are calculated by the method as described in cadmium-oxalate system. The values obtained are $\beta_1 = 1.78$, $\beta_2 = 3.19$, $\beta_3 = 0.62$ and $\beta_4 = 4.8$.

It is therefore confirmed that in solutions containing free thiocyanate ion in concentration up to 2.0 M the species

Table III

Zinc-Thiocyanate system

±20 mV(r.m.s.); 50 c/s; Temp.=30 ± 0.5°C; Zinc Concn. = 1.0×10^{-3}M; Ionic strength = 2.0

Thiocyanate (M)	Peak Potential V	Current μA	$F_o[X]$	$F_1[X]$	$F_2[X]$	$F_3[X]$	$F_4[X]$
0.00	- 1.00300	1.15					
0.20	- 1.11333	3.37	0.7525	2.42	3.42		
0.50	- 1.02849	3.48	2.3230	4.11	4.66	2.92	4.60
0.80	-1 .04157	3.59	6.0890	7.28	6.90	4.62	5.00
1.00	- 1.04975	3.65	11.2700	11.00	10.22	7.00	6.38
1.20	- 1.06000	3.56	26.4600	21.80	16.00	10.70	8.36
1.50	- 1.06425	3.43	36.4200	24.10	14.80	7.90	4.80
2.00	- 1.08244	3.43	145.2000	72.40	35.11	15.94	7.66

Zn^{+2}, $[Zn(CNS)]^{+}$, $[Zn(CNS)_2]$, $[Zn(CNS)_3]^{-}$ and $[Zn(CNS)_4]^{-2}$ exist. The formation constants determined agree fairly well with the values found by Frank and Hume[8] using conventional polarography.

The zinc complexes, as might be expected are quite less stable as can be seen from the stability constant data. The distribution of zinc among several species as a function of equilibrium thiocyanate ion concentration has been calculated and is plotted in Fig. 5 Curves 1 to 5.

CONCLUSION

It can therefore be concluded that a.c. polarography can be applied with advantage for the determination of the formulae and stability constants of the complexes involving one and two reduction peaks as well as systems of complexes in step equilibrium. The method has the following advantages over the conventional polarographic method:

(1) It is unnecessary to analyse the polarogram for its reversibility as in conventional polarography, since a.c. polarograms will be obtained only for reversible oxidation and reduction processes.

(2) Oxygen need not be removed from the solution as it does not interfere in a.c. polarography provided it does not react chemically with the reducible species as in the case of lead.

(3) Peak potentials can be determined more conveniently

and accurately than the half wave potentials.

(4) Measurements can be made more rapidly and with an improved all round reproducibility.

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