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TECHNICAL REPORT 3331

POLAROGRAPHIC STUDY

OF

NITRATE ESTERS

I. REDUCTION OF PENTAERYTHRITOL MONONITRATE

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I. Reduction of Pentaerythritol Mononitrate.

by

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ABSTRACT

The polarographic reduction of pentaerythritol mononitrate in un-buffered aqueous solution at pH 1-4, gave two well defined waves which are shown to be diffusion controlled. However from examination of the wave equation the electrode processes in each case are found to be irreversible. The first wave, not pH dependent, has a mean half wave potential, $E_{\frac{1}{2}}$ = -0.439 volt and is assigned to the electrode reduction of the nitrate function, through a two-electron change. The second wave which appears at a more negative potential, approximately -1.0 volt, is pH dependent and is shown to arise from the reduction of nitrous acid through a four electron change. This wave disappears at pH's above 4.

In buffered solutions under acidic conditions the first wave has a mean half wave potential, $E_{\frac{1}{2}}$ = -0.416 volt. Under basic conditions, however, $E_{\frac{1}{2}}$ shifts to more negative values. This shift in $E_{\frac{1}{2}}$ is interpreted as arising from complex formation of pentaerythritol mononitrate and the borate anion of the buffering system.

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CONCLUSION

Both waves observed from the polarographic reduction of pentaerythritol
mononitrate (PEMN) at low pH values, i.e. pH 1 - 4 are amenable to quantita-
tive determination as demonstrated by the rate of change of the diffusion
current with concentration. Hence polarography should be considered as an
efficient technique for the quantitative determination of pentaerythritol
mononitrate on microsize samples. The ability of pentaerythritol mononi-
trate to participate in complex formation with the borate anion which re-
sults in significant shift in the half wave potential, $E_{\frac{1}{2}}$ should provide a
valuable tool in the identification of this nitrate ester when admixed with
other nitrates.

Since our major concern however is to gather sufficient experimental
data so that a thorough understanding of the reduction process is acquired,
it is evident that considerably more work is needed to meet this objective.
Before we can assess for example the magnitude of structural and substituent
effects on the free energy of reduction we must first critically examine ex-
traneous influences on the process of reduction such as solvent and ionic
strength.

RECOMMENDATIONS

The data already obtained in aqueous solutions should be complemented
with additional experiments on the binary solvent, water-ethanol. The
solubility spectrum of the pentaerythritol nitrates varies greatly with the
number of nitrate groups. While pentaerythritol mononitrate (PEMN) is quite
soluble in water, pentaerythritol tetranitrate (PETN) on the other hand is

practically insoluble but does have a broad range of solubility in organic solvents including ethyl alcohol. Consequently in order to study these nitrates on a comparative basis we must not only find a solvent mixture common to all nitrate esters of pentaerythritol but also determine the effect of solvent composition on the reduction process.

INTRODUCTION

Our interest in organic nitrate esters led us to explore the merits of Polarography as an analytical tool in the study of these compounds. Of even greater importance to us was the belief that possibly some correlation between the half wave potential, $E_{\frac{1}{2}}$, of ni   ate esters and such well known effects as inductive, mesomeric or steric could be observed. Indeed linear free energy relationships have been reported for other families of compounds (Ref. 1-4). Any structural correlation that could be found between $E_{\frac{1}{2}}$ and neighboring substituents should give some greater insight in the mechanism of reduction. We also rationalized that since $E_{\frac{1}{2}}$ for the reduction and oxidation processes must be related to the bond energies of the function, the polarographic behavior of various nitrate compounds should to a first approximation correlate with other properties of interest such as thermal stability and vibrational energy.

The first polarographic study of nitrate esters was reported in 1952 by Kaufman and co-workers who studied the reduction at the dropping mercury electrode of ethyl and cyclohexyl nitrates (Ref. 5). A two electron reduction mechanism with alcohol and nitrite ion as products was established and found to be consistent with the experimental data. This mechanism seems to have been tacitly accepted by all workers who have since reported results on other organic nitrate esters. The list of nitrate esters so far studied comprises the following: pentaerythr ol tri- and tetranitrate, glycerol trinitrate, ethylene glycol dinitrate, mannitol hexanitrate, n-butyl nitrate, ethyl nitrate

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and cyclohexyl nitrate (Ref. 5 - 11). The bulk of this work however has been essentially analytical in nature with little concern regarding the fundamental mechanism of reduction or the effect of structure on the half wave potential, $E_{\frac{1}{2}}$.

For a number of reasons presented below the nitrate esters of pentaerythritol appeared attractive for the initial phase of our study. Every molecule, from pentaerythritol to pentaerythritol tetranitrate (PETN), has a tetrahedral configuration around a central carbon atom with little steric crowding of the functional groups (Ref. 12, 13). Molecular models also show that although the overall symmetry of the molecule decreases in going from the tetra- to the mono-nitrate, even the latter approaches the shape of a spherical body and consequently the Stokes-Einstein equation can be applied with sufficient confidence in the determination of diffusion coefficients. Consequently this series provides us with four different molecules having a different number of nitrate functions which however are subjected to the same electronic and steric environment. Lastly, of the four nitrate esters in this series, the di-, tri-, and tetranitrate were available in sufficient purity for the polarographic study. Thus, our efforts in the preparation of these compounds would be limited to the synthesis of pentaerythritol mononitrate. In the present communication we will concern ourselves solely with the synthesis and polarographic reduction of pentaerythritol mononitrate (PEMN).

RESULTS AND DISCUSSION

A. Preparation of Pentaerythritol Mononitrate (PEMN).

Three different methods were investigated for the preparation of PEMN.
The first two. controlled nitration of pentaerythritol and hydrolytic de-
nitration of pentaerythritol trinitrate (PETriN), although very attractive
because of their simplicity, did not yield the desired product. There is
however not enough ground to believe at this time from the limited number
of experiments conducted that these routes should be considered impractical.
The third approach which proved to be successful, the reductive denitration
of pentaerythritol tetranitrate (PETN), was suggested to us from a publication
which appeared in 1962 (Ref. 14). All three approaches are briefly described
below.

Controled Nitration of Pentaerythritol (PEOH)

The preparation of PETriN through a controlled nitration of Pentaeryth-
ritol with mixed acids (HNO_3 + H_2SO_4 + H_2O) is a well established manufactur-
ing process and leads to relatively high yields and purity of the desired
trinitrate. It seemed that this procedure with minor modifications could be
extended to the preparation of the mononitrate which could subsequently be
separated from the mixture of nitrates by column chromatography on silica gel.
This method of preparation was consequently tried in a few experiments but all
attempts failed to yield enough PEMN for characterization. The use of 98%
nitric acid diluted in methylene chloride was also briefly explored with no
better results. In every case, these approaches favored the formation of the

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higher nitrates even under conditions which resulted in high percentage of unreacted pentaerythritol.

Denitration of Pentaerythritol Trinitrate (PETriN)

A calculated quantity of aqueous sodium hydroxide was added to an ethanolic solution of PETriN and the mixture was left standing at room temperature. At various intervals of time, aliquots of this solution were withdrawn and analyzed for residual base. When it was judged that the hydrolyzis had proceeded far enough the mixture was worked up and separated into its various components. Besides unreacted PETriN and small amounts of the dinitrate (PEDN), only solid polymeric material melting above 300°C was recovered. This procedure was modified by using an alcoholic solution of potassium hydroxide as the hydrolytic agent. After working up the product mixture the results seemed to parallel those obtained above. Only the higher nitrates and some condensation polymers could be detected.

Reductive Denitration of Pentaerythritol Tetranitrate (PETN)

Simecek (Ref. 14) in 1962 described the .eaction of pentaerythritol tetranitrate (PETN) with hydrazine hydrate which yields all four nitrates in various proportions depending on the stoichiometry of the reactants. A graph showing the variation in products distribution with the ratio of $N_2H_4.H_2O$ to PETN used was also given. Based upon this graph the maximum yield of mononitrate was predicted at a $N_2H_4.H_2O$/PETN ratio of 3/1 moles per mole. Using this procedure at this ratio of the reactants we have not been able to produce PEMN. Under these conditions we have obtained only PETriN, the dinitrate

PEDN as the major product, and also a yellow oil which on the basis of nitrogen analysis is believed to be a mixture of higher molecular weight nitrate esters arising possibly through condensation reactions.

This procedure was repeated with the following modifications: a) The ratio of $N_2H_4.H_2O$/PETN was raised to 3.5/1 moles per mole, b) Also the residue from the acidified solution (see experimental p. 24) was given a more thorough extraction consisting in _refluxing_ with several ether portions which were subsequently combined, dried, and evaporated. These modifications resulted in a signigicant decrease in the proportion of PETriN in the products. However PEDN was still the major product and in addition only a non-crystallizable yellow oil having a nitrogen content of 4.81% could be recovered (Calculated for PEMN 7.73%N).

A third attempt followed with these further changes in the procedure: a) The ratio $N_2H_4.H_2O$/PETN was raised to 4.5/1, b) In order to minimize the formation of condensation polymers under strongly acidic conditions, the acidification step (see experimental, p.24) was controlled by means of a pH meter to a minimum pH 3.9 and the evaporation of the acidified solution was stopped as soon as a noticeable increase in viscosity was observed. With this modified procedure PETriN was absent in the products mixture and the quantity of polymeric material was sensibly decreased. Pentaerythritol mononitrate as an oil, which crystallized upon standing, was obtained from both ether extracts in a 25% yield. Recrystallization from chloroform yielded pure crystals, m.p. 78.0 - 78.5°C, percent nitrogen: found 7.66% calculated 7.73%.

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B. Polarographic Study of Pentaerythritol Mononitrate (PEMN).

Initial experiments were conducted on a solution of the supporting electrolyte alone at different pH's for the purpose of establishing: a) The magnitude of the residual current and its rate of increase with increasing applied potential, b) The half wave potential of the hydrogen ion and its variation with concentration, c) The appearance potential of the supporting electrolyte discharge.

The residual current increases very slowly and regularly with an increase in potential up to the discharge of the electrolyte which begins at -1.9 volts. At this potential the residual current reaches a maximum value of 0.30 microamperes which is less than 10% of the current produced by the reducible specie. Consequently errors arising in the correction of the residual current should be negligeable. A wave is observed prior to the discharge of the electrolyte whose diffusion current (i_d) and half wave potential ($E_{\frac{1}{2}}$) are function of the solution pH as shown in Fig. 1 & 2. At pH's above 4 this wave disappears. The fact that the i_d increases in a near linear relationship with the hydrogen ion concentration leaves little doubt that this wave arises from the reduction of hydrogen ions.

Aqueous solutions of the supporting electrolyte varying in pH from 1 to 12 and containing 5×10^{-4}M of pentaerythritol were also polarographed in order to determine if this substance when present as an impurity during the determinations of the nitrates would interfere with the electrode process. Furthermore since the first three nitrates of pentaerythritol, PEMN, PEDN, and

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PETriN possess besides the nitrate function from one to three hydroxyl groups in their molecular structure, a knowledge of the behavior of pentaerythritol at the dropping mercury electrode would indirectly establish if the hydroxyl function itself interferes in the reduction process. It was found that pentaerythritol under these conditions is completely inert at the dropping mercury electrode as shown in the polarograms which parallelled those obtained with the supporting electrolyte alone.

Reduction of Pentaerythritol Mononitrate (PEMN) in Unbuffered

Aqueous Solutions.

In this medium the reduction of PEMN gives rise to two waves in acid solution (pH 1-3) while at higher pH's only the first wave remains. The experimental data are summarized in Table I. This wave, which as shown below, varies linearly with the concentration of PEMN is believed to be due to the reduction of the nitrate function. The average position of the half wave potential ($E_{\frac{1}{2}}$) for the range of pH's studied is at -0.430 volt with a standard deviation of 0.016 volt[1]. Although this wave does not appear to be pH dependent a rather broad range in the value of $E_{\frac{1}{2}}$ is observed, i.e., 0.044 volt. We should certainly anticipate better constancy in half wave potential values. The presence of small quantities (five drops of a 0.1% solution) of the maximum suppressor methyl red which was added to every polarographic solution might be responsible for this erratic behavior. The quantity, $E_{3/4} - E_{1/4}$ included in Table I gives a measure of the steepness of the rise of the polarographic wave. Suffice to say in connection with the quantity $E_{3/4} - E_{1/4}$ that its magnitude appears to vary with the position of $E_{1/2}$. When $E_{1/2}$ shifts to more negative values, $E_{3/4} - E_{1/4}$ increases in magnitude.

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[1] The potential values reported in Table I are those of the applied potential which were not corrected for the cell resistance. We have measured the cell resistance under these conditions and found it to be 1700 Ω. This resistance would lower the $E_{\frac{1}{2}}$ values only by a maximum of three millivolts for the first wave and five millivolts for the second wave.

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It was noted that the height of the first wave is a linear function of the PEMN concentration as shown in Fig. 3 & 4 where the limiting current was plotted vs. the concentration in PEMN for both acidic (pH 2) and basic (pH 9) media respectively. It is deduced therefore that the electrode process is diffusion controlled. The number of electrons transferred at the electrode was calculated from the Ilkovic equation below.

$$n = \left[\frac{i_d}{.C \, m^{2/3} t^{1/6}} \right] \left[\frac{1}{607 \, D^{1/2}} \right] \tag{1}$$

n = Number of electrons consumed by the electroactive species.

D = Diffusion coefficient of the electroactive species (cm^2.sec.).

C = Concentration of the electroactive species (moles/liter.).

m = Average rate of flow of mercury through the capillary (mg./sec.).

t = Drop time (sec.).

i_d = Average diffusion current (microamperes).

In this equation only the diffusion coefficient D needs to be measured in a separate experiment, or alternatively the value of D can be calculated by means of the Stokes-Einstein relation (2).

$$D = \frac{2.96 \times 10^{-7}}{\eta \, (V_m)^{1/3}} \, cm.^2 sec.^{-1} \quad at \; 25^{O}C \tag{2}$$

η = Viscosity of the medium at 25°C.

V_m = Apparent molar volume of the reducible species in the pure solid state. (mol.wt./density).

This relationship will give an accurate value of D provided that the reducible

specie is essentially a spherical molecule and that it is sufficiently larger than the solvent molecules so that all retarding forces may be treated as frictional. It is believed that for PEMN both these criteria are met. Using as an approximate value of viscosity for the aqueous medium that of water at $25^{\circ}C$, i.e., 8.94×10^{-3} dyne cm. and from the measured density of PEMN (d=1.48g./cc.) a value for the diffusion coefficient of PEMN of 6.67×10^{-6} cm.^{2}sec.$^{-1}$ was obtained.

The number of electrons transferred for the electrode process which gives rise to the first reduction wave as calculated from equation (1) is very closed to two for all pH's studied (Table 1). Consequently the result of the present study are in agreement with the previous findings of Kaufman (Ref. 5). Having established that the electrode process occurs with the transfer of two electrons it is then possible from the Ilkovic equation (1) to obtain an experimental value of the diffusion coefficient D which could be compared with the value 6.67×10^{-6} cm^2 sec.$^{-1}$ ca@culated from the Stokes-Einstein equation (2). Referring to Fig. 3 & 4 where the limiting current was plotted vs. the concentration in PEMN the experimental diffusion coefficient of PEMN is found to be 7.45×10^{-6} cm^2 sec.$^{-1}$ at pH 2.0 and 6.91×10^{-6} cm^2 sec.$^{-1}$ at pH 9.0. The deviation from the calculated value (equation 2) is 11.7% at pH 2.0 and 3.5% at pH 9.0. In our views this is a reasonable agreement between experimental and calculated values.

In order to obtain further insight into the reaction mechanism we have examined the polarographic data obtained in light of the wave equation(4).

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$$E_{d.e.} = E_{\frac{1}{2}} - \frac{0.0591}{an} \quad \log i/i_d\text{-}i \qquad\qquad (4)$$

$E_{d.e}$ = Reduction potential at the dropping mercury electrode
   corresponding to the reduction current, i.

a   - Transfer coefficient for the electrode reaction.

n   - Number of electrons involved in the rate determining electron-
   transfer step.

i_d - Diffusion current or maximum current of the polarographic wave.

From a plot of log i/i_d-i versus the corresponding potential $E_{d.e.}$ it
is found that the points do not fall on a straight line but a strong curvature
of the experimental line is usually observed in the neighborhood of $E_{\frac{1}{2}}$. Two
typical plots are shown in Fig 5 & 6 for reductions carried out at pH's 1.0
and 10.1. In fact two straight lines can be drawn which meet at about $E_{\frac{1}{2}}$.
From the slope of these lines the value of the product, **an**, was calculated
and these values for the whole range of pH's investigated are given in Table II.
The value of the product, an, being much lower than two, the number of elect-
rons transferred at the electrode, demonstrates the irreversibility of the over-
all electrode process.

It is tempting to give a mechanistic significance to the fact that a
change in slope is observed in the neighborhood of the half wave potential,
$E_{\frac{1}{2}}$. One wonders if this behavior does not reveal two consecutive one-electron
steps at the electrode instead of a single two-electron step. As shown in
equation (5) the primary electrode process would be the transfer (reversible)
or irreversible) of one electron to the nitrate function followed by abstraction

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of a proton either from the hydronium ion or a water molecule. The second

step at the electrode would involve another transfer of one electron to

the intermediate (I) with the subsequent rearrangement of species (II) to

yield the products, alcohol and nitrous acid.

$$R - O - N\underset{\displaystyle O}{\overset{\displaystyle O}{\big\langle}} \cdot + \ e \ + \ H_3^+O \ \ or \ H_2O \ \underset{k_1}{\overset{k_1}{\rightleftharpoons}} \ R - O - N\underset{\displaystyle O}{\overset{\displaystyle OH}{\big\langle}} \qquad (5)$$
$$\phantom{R - O - N\underset{\displaystyle O}{\overset{\displaystyle O}{\big\langle}} \cdot + \ e \ + \ H_3^+O \ \ or \ H_2O \ \underset{k_1}{\overset{k_1}{\rightleftharpoons}} \ R - O - N} I$$

$$R - O - N\underset{\displaystyle O}{\overset{\displaystyle OH}{\big\langle}} \ + \ e \ \overset{k_2}{\longrightarrow} \ R - \overset{\curvearrowleft}{O} - N\underset{\displaystyle \mathbb{C}O}{\overset{\displaystyle OH}{\big\langle}} \ \longrightarrow \ R - \overset{-}{O} \ + \ HO - NO \qquad (6)$$
$$\phantom{R - O - N\underset{\displaystyle O}{}}I \phantom{\ + \ e \ \overset{k_2}{\longrightarrow} \ R - \overset{\curvearrowleft}{O} - N\underset{\displaystyle \mathbb{C}O}{}}II$$
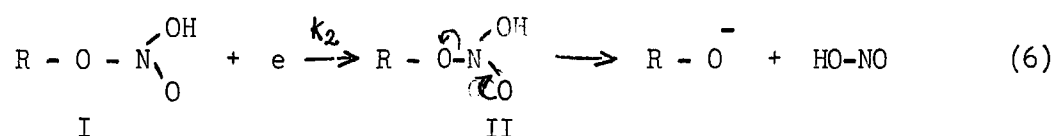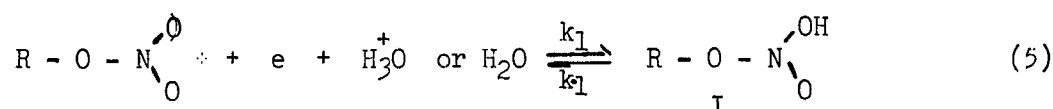
If both electron transfer steps are irreversible this situation then reduces

to a case of two consecutive electrochemical reactions. On the other hand

if the first step consists of a reversible electron transfer the overall

electrode reaction would involve a potential determining step. Both cases

have been treated by Delahay in his theory of irreversible polarographic

waves (Ref. 21).

A very convenient way to obtain values of $\underline{an}$ is shown in equation (7).

(Ref. 23) This relation is derived from the equation of a totally irreversible

$$E_{3/4} - E_{1/4} \ = \ - \ \frac{0.05172}{an} \ v. \qquad (7)$$

wave involving only a single rate determining electron-transfer step at $25^{\circ}C$

(Ref. 22). Applying equation (7) to the case under study gave values of $\underline{an}$

shown in Table III. These new $\underline{an}$ values calculated from equation (7) are

much closer to those of an_2 than an_1 (Table II). Possibly then, the second

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step in the proposed mechanism for the reduction of PEMN (equation 6) is rate determining. In addition since the magnitude of the transfer coefficient is generally closed to 0.5 we may infer from our results that only one electron is involved in the rate determining electron-transfer step.

The second wave observed in the reduction of pentaerythritol mononitrate is located in the neighborhood of -1.0 volt. The analysis of this wave which is observed only in acidic media is rendered difficult by the close proximity of the intense hydrogen wave. The second wave appears more or less as a shoulder on the steep rising portion of the hydrogen wave. Consequently in the absence of a well defined plateau, accurate estimation of the diffusion current, i_d, for the second wave rests of course a great deal on the judgement of the experimentalist. The interpretation offered in the following discussion is arrived at with full awareness of this limitation in the precision of the experimental data.

The second wave has the following features: a) Only at pH's below 4 is this intense and well defined wave observed; b) The half wave potential, $E_{\frac{1}{2}}$, is pH dependent, shifting to more negative values with an increase in pH (Fig. 7); c) The value of $E_{3/4} - E_{1/4}$ increases with increasing pH's (Fig. 8); d) Plots of $E_{d.e.}$ versus log i/i_d-i yield curves consisting of two segments which meet in the neighborhood of $E_{\frac{1}{2}}$ (Fig. 9); e) The values for the product, an, obtained from these curves are much less than one and decrease with increasing pH (Table IV).

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All this information points to the fact that this wave is related to
a process which must involve the hydrogen ion in the rate determining step.
Using relation (7) for an irreversible process new values of the product, an,
for this wave are obtained (Table V) which check quite closely with the an_2
values obtained from the wave equation (Table IV). The limiting current on
the other hand does not appear to follow any regular pattern with the change
in pH. It seems consequently that this limiting current at high negative
potentials is not controlled by some electrode kinetic process but is a true
diffusion current which would depend entirely on the rate of mass transfer
to the electrode. This was confirmed by measuring the change of the limiting
current with the concentration of PEMN. As shown in Fig. 10, a plot of the
limiting current versus the concentration of PEMN gives a straight line which
passes through the origin. Since this current is diffusion controlled we
can by means of the Ilkovic equation (8) determine the number of electrons

$$n = \frac{i_d}{607 \ C \ D^{\frac{1}{2}} \ m^{2/3} t^{1/6}}$$

transferred at the electrode surface. The value of the diffusion coefficient
D for the reducible specie or intermediate which gives rise to this wave
must by necessity be the same as the diffusion coefficient of its precursor,
i.e., PEMN which was found to be $7.45 \times 10^{-6} \ cm^2.sec^{-1}$ at the same pH. In-
serting this value into equation (8) and solving for $\underline{n}$ gives 3.9 for the
number of electrons participating in the electrode process. If this wave
arises from the reduction at the electrode surface of nitrous acid (equation 6)
the consumption of four electrons during this process could then indicate that

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the electrode process is the reduction of nitrous acid to hydroxylamine as shown in equation (9). (Ref. 18, 19, 20)

$$HO-NO \quad + \quad 4e^- \quad + \quad 4H^+ \longrightarrow HO-NH_2 \quad + \quad H_2O \qquad (9)$$
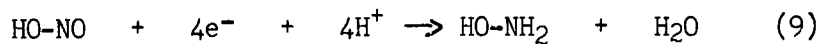
Returning to Table I, it is seen that a third wave is present at pH 3.1. From its position, $E_{\frac{1}{2}} = -1.470$, there is not much doubt that this wave arises from the reduction of H^+ in the medium. It's value interestingly enough corresponds to a hydrogen ion concentration (Fig. 1) of 1×10^{-4} or to a pH4. This confirms the general view that in unbuffered solutions the hydrogen ion concentration at the electrode surface decreases relative to the bulk concentration during the reduction process.

Reduction of Pentaerythritol Mononitrate (PEMN) in Buffered Aqueous
Solutions

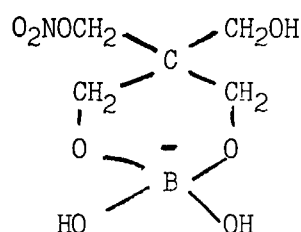As shown above when working with unbuffered solutions there is always
the danger that the hydrogen ion concentration in the immediate vicinity of
the electrode surface becomes depleted making virtually impossible a study
of the effect of pH on the reduction process. In buffered systems on the
other hand, any change in concentration of H^+ would be immediately com-
pensated through the buffering mechanism and consequently constancy in pH
at the electrode surface results. Three buffers were chosen to cover the
pH range of 1 to 12. The results of PEMN reduction under these conditions
are given in Table VI. Up to and including pH 5.90 the first wave appears
at an average of -0.418 volt with a standard deviation of 0.015 volt. This
wave then appears at more positive potential than that observed in the un-
buffered system discussed previously. Since the ionic strength in both
series of experiments was kept the same, this difference in the average
value of $E_{\frac{1}{2}}$ (Δ = 0.013 volt) must be traced to nature of the different sup-
porting electrolytes used in these two series and more specifically to the
different cations used, $(CH_3)_4N^+$ for unbuffered and K^+ for buffered solutions.
The diffusion constant, $i_d/Cm^{2/3}t^{1/6}$ is also slightly lower on the average in
the buffered medium by approximately 3% relative to the unbuffered medium.
In one respect the behavior of the reduction in buffered solutions is in
direct contrast to what had been observed in unbuffered solutions. Whereas
in the latter, the function $E_{3/4} - E_{1/4}$ was found to increase with more

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negative half wave potentials, in buffered solutions, $E_{3/4} - E_{1/4}$ decreases with increasing half wave potentials as shown in Fig. 11. No satisfactory explanation can be offered at this time for this behavior. The characteristics of the second wave observed at pH's below 4 parallel the previous findings in unbuffered solutions (Fig. 12) except for the diffusion constant which is found to increase with the pH of the solution (Table VI). In unbuffered solutions (Table I) the diffusion constant did not vary in a regular fashion with the pH of the solution. However as mentioned previously the absence of a well defined plateau in the profile of the second wave throws some doubt in the validity of the diffusion current measurements. From pH's between 8 and 12 use was made of boric acid-borate electrolyte and this change in the buffering system has a significant effect on the half wave potential, the diffusion constant and the function $E_{3/4} - E_{1/4}$. The magnitude of these effects is shown in Table VI and Fig. 13 and 14. This behavior is indicative of the formation of a charge complex with PEMN. This should not be too surprising since it is well known that polyhydroxy alcohols and borate ions interact in solution to form complexes (Ref. 15) The formation of these complexes is not limited to vicinal diols but include also 1,3-diols, consequently PEMN whose structure is shown below would be anticipated to complex with the borate ion.

$$O_2NOCH_2 \diagdown \qquad \diagup CH_2OH$$
$$C$$
$$HOCH_2 \diagup \qquad \diagdown CH_2OH$$

1,3
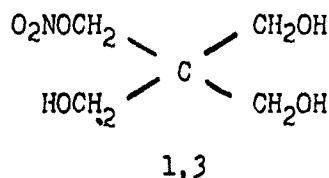
By analogy with Hermans' proposed structure for polyhydroxyborate complexes (Ref. 16, 17) we can postulate for PEMN-Borate complex the following structure.

$$O_2NOCH_2 \diagdown \quad \diagup CH_2OH$$
$$C$$
$$CH_2 \diagup \quad \diagdown CH_2$$
$$O \qquad O$$
$$\diagdown \; \overset{-}{} \; \diagup$$
$$B$$
$$HO \diagup \quad \diagdown OH$$

The presence of a negative charge in the structure should certainly raise the energy barrier for the reduction process occurring at a negative electrode and thus a shift in $E_{\frac{1}{2}}$ to more negative potential would be predicted. Also since complex formation leads to an increase in molecular weight this should be reflected in a decrease in the diffusion coefficient, hence a lowering in the diffusion current, i_d. Superimposed will be the dragging effect from the presence of a negative charge in the structure. Both i_d and $E_{\frac{1}{2}}$ experimental values are in qualitative agreement with these views.

There is no doubt that both free PEMN and its complex co-exist in the solution at the pH's we have studied. This is very nicely indicated by the spreading in the values of $E_{3/4} - E_{1/4}$, which suggests that we are indeed dealing with a composite wave rather than a single wave. The function $E_{3/4} - E_{1/4}$ could thus be a valuable tool for estimating the extent of complex formation.

Analysis of the waves (equations 4) obtained in buffered system yielded plots similar to those obtained in the unbuffered system. The $\underline{an_1}$ and $\underline{an_2}$ values are given in Table VII and Table VIII. It will be observed that the

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transfer coefficient $\underline{a}$ decreases significantly in the presence of the borate buffer at high pH. This is substantiated by calculating $\underline{an}$ values using equation (7) as shown in Table IX.

EXPERIMENTAL

1. Preparation of Pentaerythritol Mononitrate (PEMN)

Reductive Denitration of Pentaerythritol Tetranitrate (PETN)

Into a 500 mls. r.b. flask equipped with a condenser and addition funnel was placed 63.2g. (0.20 mole) of PETN dissolved in a mixture of 120 mls. of ethanol and 120 mls. of dioxane. An aqueous solution of hydrazine hydrate, $H_2H_4 \cdot H_2O(85\%)$ containing 35.3g. (0.60 mole) of base was transferred into the addition funnel and added dropwise over a period of one hour to the reaction flask which had been previously heated to $74^{\circ}C$. After the addition was completed the mixture was heated and kept under reflux ($79^{\circ} - 80^{\circ}C$) for two and one half hours. The solvent was removed at $35-40^{\circ}C$ under a reduced pressure of 15mm. and the residue was taken up in water. Pentaerythritol trinitrate (PETriN) separated as a reddish oil (Product I).

The aqueous layer was extracted several times with diethyl ether and the combined ether extracts were dried over sodium sulfate and after removal of the solvent yielded a yellow oil identified as pentaerythritol dinitrate (PEDN). Percent nitrogen: found 12.11% Calculated for PEDN, 12.39%. (Product II).

The water layer was next acidified with 2N H_2SO_4 until the gas evolution ceased. The acidified solution was then extracted several times with diethyl ether, and the ether extracts were combined and dried over sodium sulfate. Removal of the solvent yielded a yellow oil. Percent nitrogen: found 3.6%. (Product III). The same procedure was repeated with the following modifications: a) the ratio $N_2H_4 \cdot H_2O$/PETN was raised from 3/1 to 3.5/1 moles per mole, b) the

residue from the acidified solution was subjected to a more thorough extraction procedure which consisted in refluxing with several ether portions.

Product I - Reddish oil, which was characterized as PETriN was formed in lesser amounts than in the original procedure.

Product II - Yellow oil, identified as PEDN was still the major product.

Product III - Yellow oil which could not be crystallized. Nitrogen analysis: found 4.8%N.

The procedure was further modified as follows: a) the ratio $N_2H_4 \cdot H_2O$/PETN was raised to 4.5/1 moles per mole, b) the acidification step was monitored with a pH meter and not allowed to proceed beyond a pH 3.9, c) the evaporation of the acidified solution was stopped as soon as a noticeable increase in viscosity was observed.

Product I - No product separated at this step indicating the absense of both PETN and PETriN in the mixture.

Product II - Yellow oil, 25.31g. (0.112 mole) identified as PEDN possibly admixed with some PEMN, was still the major product. Nitrogen analysis: found 11.50%. Yield: 56.0%.

Product III - Yellow oil, 8.51g (0.047 mole) which crystallized upon standing. Recrystallization from chloroform gave colorless crystals, m.p. 78.0 - 78.5°C. Nitrogen analysis: found 7.66%, Calculated for PEMN, 7.73%. Yield 23.5%.

A summary of the stoichiometric conditions for these experiments is given below:

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Experiment	85% aqueous $N_2H_4 \cdot H_2O$ Wgt. (g.)	Mole	PETN Wgt. (g)	Mole	$N_2H_4 \cdot H_2O$/PETN Ratio
1	35.3	0.6	63.2	0.2	3/1
2	41.2	0.7	63.2	0.2	3.5/1
3	53.0	0.9	63.2	0.2	4.5/1

2. Polarographic Study of Pentaerythritol Mononitrate (PEMN)

The polarograms were run on a Sargent Model XXI Polarograph used in the No. 1 damping position. A commercial H type polarographic cell was used for all reductions, with the cross-arm filled approximately to 1/3 with a 3% solution of agar saturated with KCl, acting as a salt bridge. Mercury, calomel and solid KCl were placed in the reference compartment which was filled with a saturated KCl solution, the whole forming a large-surface saturated calomel electrode against which all potentials were measured. Throughout the study the polarographic cell was kept in a thermostated water bath maintained at $25^\circ \pm 0.1^\circ$C. The concentration of PEMN for most experiments was chosen as 0.5 millimoles per liter and the solutions prepared by adding a calculated amount of a stock solution, 10^{-2} M in PEMN to a measured volume of the polarographic solution containing the electrolytes and five drops of alcoholic methyl red (0.1%) as the maximum suppressor. The pH's, measured on a Beckman Model 76 pH meter, were adjusted with small volumes of HCl, NaOH or $(CH_3)_4$NOH as needed. The ionic strength of the solutions was kept constant at 0.1M. The dropping electrode capillary characteristics, m and t, were set to give a value of $m^{2/3}t^{1/6}$ equal to 2.037 mg $^{2/3}$sec $^{-1/2}$.

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REFERENCES

1. Zuman P. "Organic Polarographic Analysis" International Series of Monographs on Analytical Chemistry, Vol. 12. Pergamon Press Book, The MacMillan Company, N. Y. 1964 p. 245.

2. Streituieser, Jr, A. and Perrin, Charles, J. Am. Chem. Soc., 86, 4938 (1964).

3. Coulson, Dale, M, Crowell, William R., and Tendick, S. Kathleen, J. Am. Chem. Soc., 79, 1354 (1957).

4. Geske, David H., Ragle John L, Bembenek, Mark A., and Balch Alan L., J. Am. Chem. Soc., 86, 987 (1964).

5. Kaufman, Frederick, Cook Helen J., and Davis, Stanley M., J. Am. Chem. Soc., 74, 4997 (1952).

6. Whitnack, Ferald C., Nielsen, Julien M., and Gantz, E. St. Clair, J. Am. Soc, 76, 4711 (1954).

7. Hetman, J. S., Anal.Chim. Acta, 28, 588-90 (1963).

8. Whitnack, Gerald C., Mayfield Margaret M., and Gantz E. St. Clair, Anal. Chem. 27, No. 6 899 (1955).

9. Hetman, J. S., Anal. Chem. 32. Vol. 32, No. 12, 1699 (1960).

10. Hetman, J. S., Talanta, Vol. 5, 267-71 (1960).

11. Williams, A. F., and Kenyon D., Talanta, Vol. 3, 160-71 (1959).

12. Barlow Evelyn, Barth Robert H., and Snow John E., "The Pentaerythritols", American Chemical Society Monograph Series, Reinhold Publishing Corporation, N. Y., 1958.

13. Troher James, Acta Cryst. 16, 698 (1963).

14. Simecek J., Collec. Czech, Chem. Commun. 27, 362-71 (1962).

15. Malcolm Earl. W., Green John W., and Swenson Harold A., J. Chem. Soc., 4669-76 (1964).

16. Hermans P.H., Z. Anorg. Allgem. Chem., 83, 142 (1923).

17. Swann W. D., McNabb W. M., and Hazel J. F., Anal. Chim. Acta., 28, 441-49 (1963)

18. Kolthoff & Lingane "Polarography" Vol. II, 2nd Edition, Interscience Publishers, N. Y., 1952 pp. 533-40.

19. Keilin Bertram, and Otvos John W., J. Am. Chem. Soc., 68, 2665 (1946).

20. Meites Louis, J. Am. Chem. Soc., 73. 4115-19 (1951).

21. Berzins Talivaldis., and Delahay Paul, J. Am. Chem. Soc., 75, 5716 (1953).

22. Meites L., and Israel Y., J. Am. Chem. Soc., 83, 4903 (1961).

23. Kolthoff, I. M., and Elving Philip J., "Treatise on Analytical Chemistry", Part I, Vol. 4, Chapter 46 "Voltammetry at the Dropping Mercury Electrode (Polarography)" by Louis Meites, Interscience Publishers, N. Y. 1963.

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TABLE I

Reduction of Pentaerythritol Mononitrate (PEMN) in Unbuffered

Aqueous Solutions

$C = 5 \times 10^{-4}M$, $0.1M(CH_3)_4NCl$, Capillary Constant, $m^{2/3}t^{1/6} = 2.037 \frac{mg^{2/3}}{} \sec^{-1/2}$

Diffusion Constant (I): $i_d/m^{2/3}t^{1/6}C$.

pH	$E_{1/2}$** (Volts)	i_d a	I	$E_{3/4}-E_{1/4}$ (Volts)	Electrons Transferred n
			First Wave		
1.0	-.438	3.60	3.54	-.127	2.3
2.0	-.422	3.40	3.34	-.120	2.1
3.1*	-.421	3.12	3.06	-.114	2.0
4.0	-.432	3.33	3.28	-.134	2.1
6.1	-.441	3.21	3.16	-.138	2.0
8.2	-.465	3.30	3.24	-.144	2.1
9.0	-.422	3.36	3.30	-.123	2.1
10.1	-.456	3.42	3.36	-.139	2.1
12.2	-.450	3.36	3.30	-.135	2.1
			Second Wave		
1.0	-.884	4.98	5.60	-.123	3.6
2.0	-.982	6.60	6.48	-.159	4.1
3.1	-1.050	6.03	5.92	-.184	3.8

*A third wave was observed at this pH with a $E_{\frac{1}{2}} = -1.470$ volt and i_d: 1.86 μa.

**vs. S.C.E.

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TABLE II

Reduction of Pentaerythritol Mononitrate (PEMN) in Unbuffered

Aqueous Solution

$$E_{d.e.} = E_{1/2} - \frac{0.0591}{an} \log i/id\text{-}i$$

pH	an_1	an_2
	First Wave	
1.0	0.52	0.38
2.0	0.53	0.37
3.1	0.54	0.33
4.0	0.50	0.37
6.1	0.46	0.39
8.2	0.52	0.40
10.1	0.53	0.37
12.2	0.51 Ave 0.51	0.33 Ave 0.37
	Second Wave	
1.0	0.51	0.49
1.9	0.45	0.33
3.1	0.40	0.30

an_1 - Value obtained from the lower segment of the curve (Fig. 5 & 6)

an_2 - Value obtained from the upper segment of the curve (Fig. 5 & 6)

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TABLE III

Reduction of Pentaerythritol Mononitrate (PEMN) in Unbuffered

Aqueous Solution

$$E_{3/4} - E_{1/4} = - \frac{0.05172}{an}$$

pH	Volt First Wave	an
1.0	−0.127	0.41
2.0	−.120	0.43
3.1	−0.114	0.45
4.0	−0.134	0.39
6.1	−0.138	0.37
8.2	−0.144	0.36
10.1	−0.139	0.37
12.2	−0.135	0.38 Ave. 0.40

pH	Volt Second Wave	an
1.0	−0.123	0.42
2.0	−0.159	0.33
3.1	−0.184	0.28

TABLE IV

Reduction of Pentaerythritol Mononitrate (PEMN) in Buffered

Aqueous Solutions

Capillary, $m^{2/3} t^{1/6} = 2.037 \text{ mg}^{3/2} \text{sec.}^{-1/2}$ $C = 5 \times 10^{-4} M$

Diffusion Constant $(I) = i_d/m^{2/3} t^{1/6} C.$

Ionic Strength 0.1M.

Buffer Salt	pH	$E_{1/2}$ Vs S.C.E.	I	$E_{3/4} - E_{1/4}$ Volts	Electrons Transferred
		First Wave			
KCl + HCl	1.0	-0.440	3.24	-0.108	2.1
KCl + HCl	2.1	-0.422	3.24	-0.138	2.1
KH_2PO_4 + HCl	2.9	-0.407	3.06	-0.153	2.0
KH_2PO_4 + HCl	4.1	-0.403	3.06	-0.162	2.0
KH_2PO_4	5.9	-0.417	3.24	-0.155	2.1
H_3BO_3 + NaOH	8.0	-0.460	3.12	-0.128	2.0
H_3BO_3 + NaOH	10.1	-0.500	2.65	-0.170	1.7
H_3BO_3 + NaOH	11.9	-0.623	2.65	-0.291	1.7
		Second Wave			
-	1.0	-0.910	5.6	-0.101	3.6
-	2.1	-1.035	6.20	-0.153	4.0
-	2.9	-1.090	6.60	-0.163	4.2

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TABLE V

Reduction of Pentaerythritol Mononitrate (PEMN) in Buffered

Aqueous Solution

$$E_{d.c.} = E_{1/2} - \frac{0.0591}{an} \log i/id-i$$

pH	an_1	an_2
	First Wave	
1.0	0.64	0.52
2.1	0.43	0.35
2.9	0.47	0.34
4.1	0.43	0.34
5.9	0.49	0.36
8.0	0.48	0.31
10.1	0.42	0.30
11.9	0.27	0.17
	Second Wave	
1.0	0.65	0.36
2.1	0.51	0.34
2.9	0.45	0.35

an_1 - Value obtained from the lower segment of the curve.

an_2 - Value obtained from the lower segment of the curve.

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TABLE VI

Reduction of Pentaerythritol Mononitrate (Pemn) In Buffered

Aqueous Solutions.

$$E_{3/4} - E_{1/4} = \frac{-0.05172}{an}$$

pH	$E_{3/4} - E_{1/4}$ Volt First Wave	an
1.0	-0.108	0.48
2.1	-0.138	0.37
2.9	-0.153	0.33
4.1	-0.162	0.32
5.9	-0.155	0.33
8.0	-0.128	0.40
10.1	-0.170	0.30
11.9	-0.291	0.18
	Second Wave	
1.0	-0.101	0.51
2.1	-0.153	0.34
2.9	-0.163	0.32
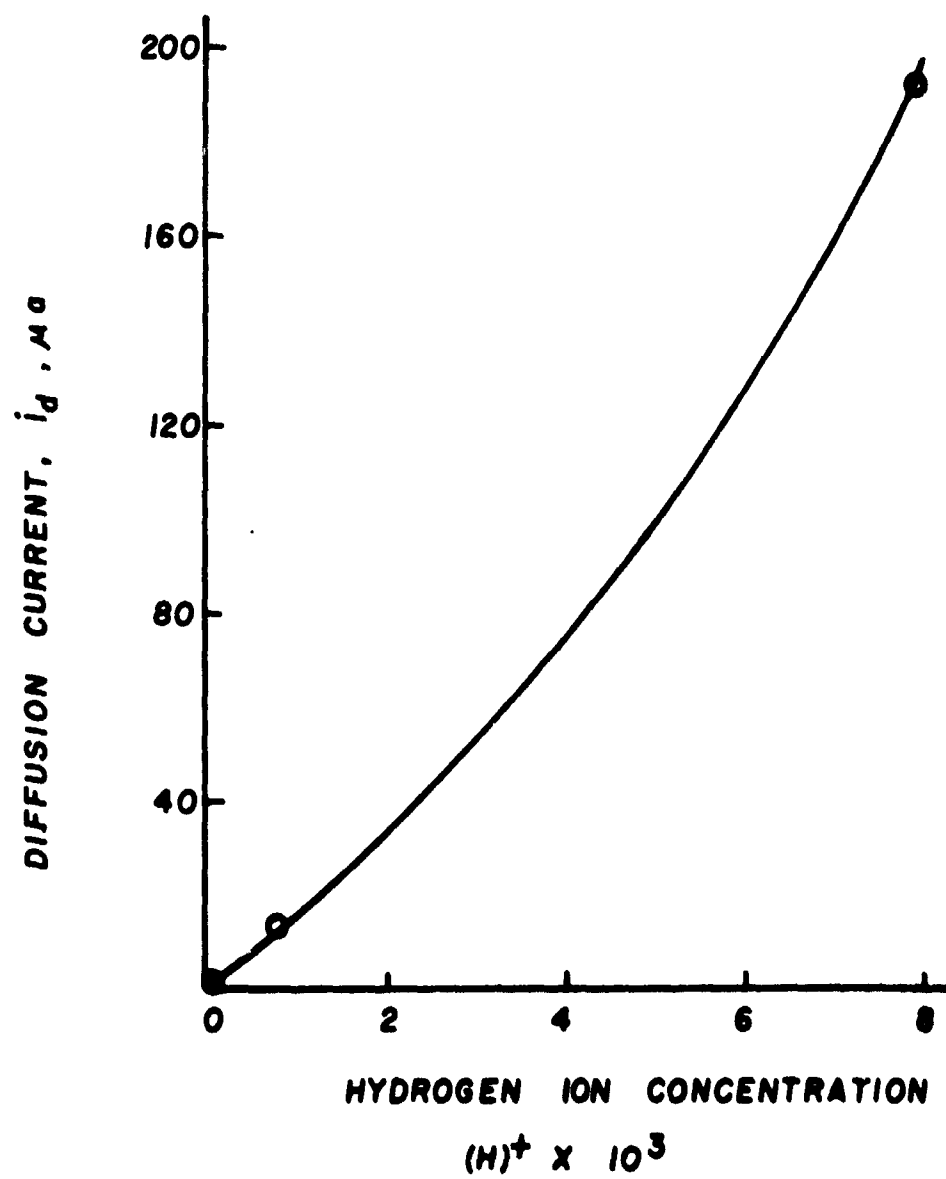
FIG. I VARIATION IN DIFFUSION CURRENT WITH
HYDROGEN ION CONCENTRATION

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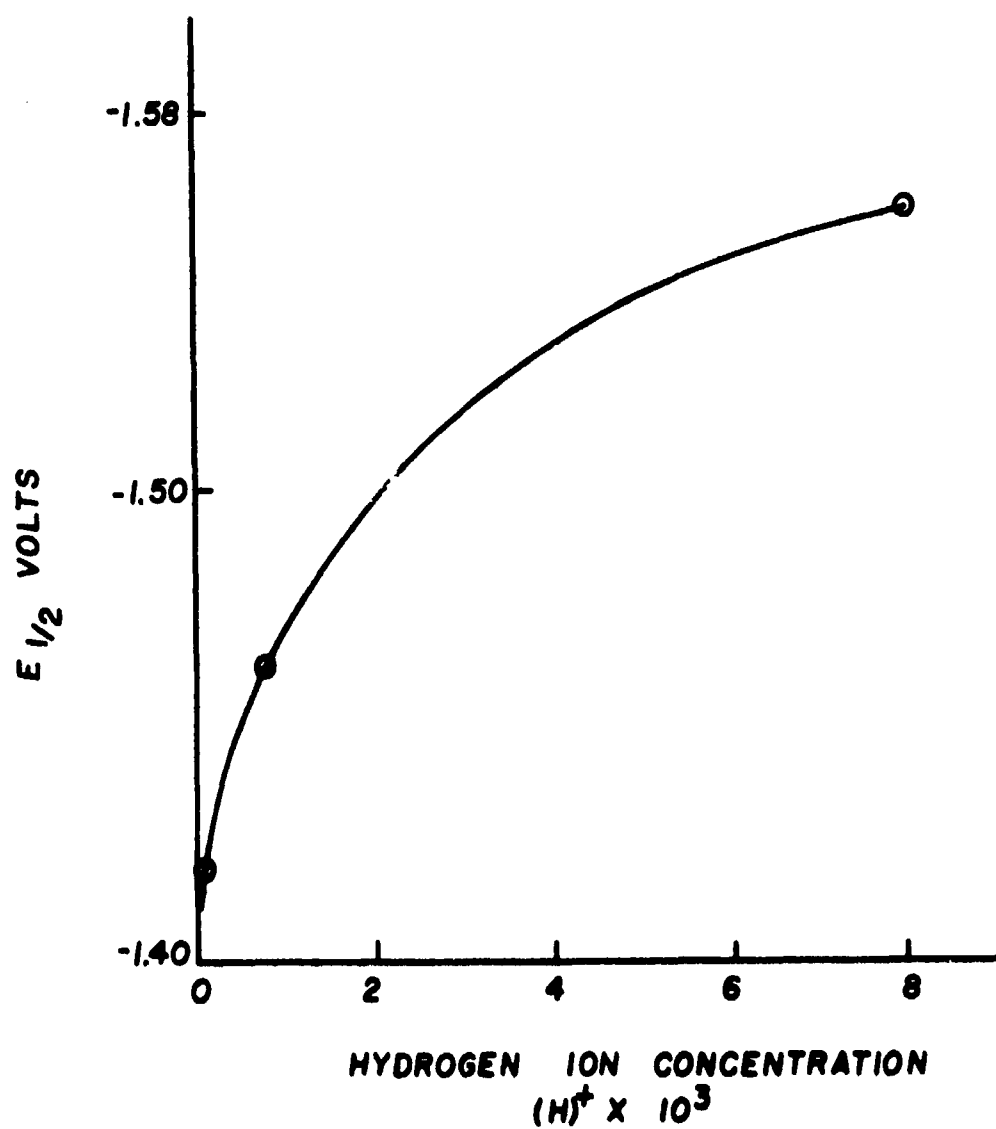
FIG. 2 VARIATION IN $E_{1/2}$ WITH HYDROGEN ION
CONCENTRATION

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PEMN
UNBUFFERED
pH 2.0
1st WAVE

$E_{1/2} = -.420$

$E_{1/2} = -.422$

$E_{1/2} = -.422$

$E_{1/2} = -.425$

$id = 607_n D^{1/2} CM^{2/3} T^{1/6}$

$M^{2/3} T^{1/6} = 2.037 mg^{2/3} SEC^{-1/2}$

$D = 7.450 \times 10^{-6} CM^2/SEC$

$E_{1/2} = -.415$

$E_{1/2} = -.426$

DIFFUSION CURRENT (id), μa

CONCENTRATION mM/LITER
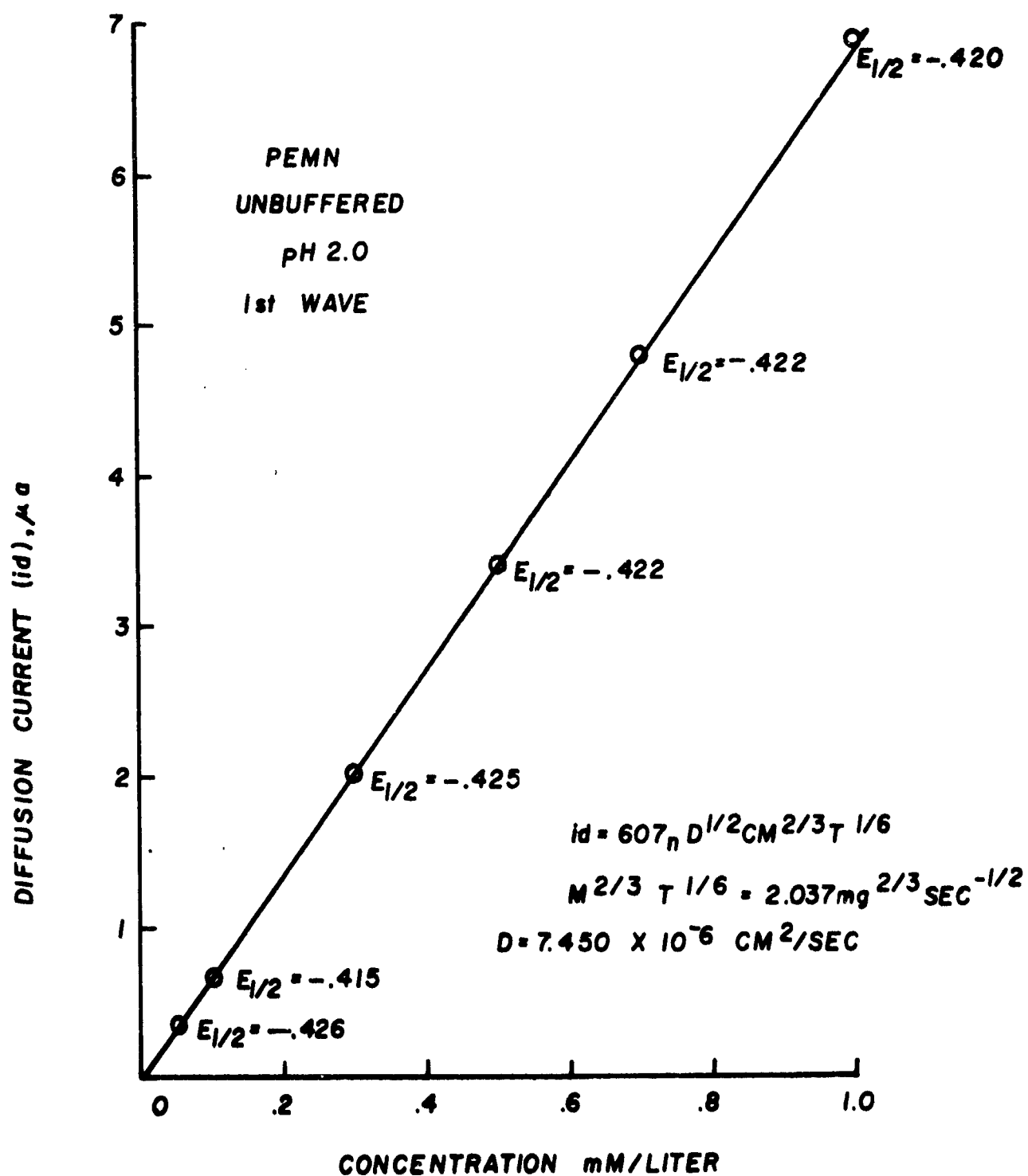
FIG 3   VARIATION IN DIFFUSION CURRENT (id) WITH THE
CONCENTRATION OF PENTAERYTHRITOL
MONONITRATE

35
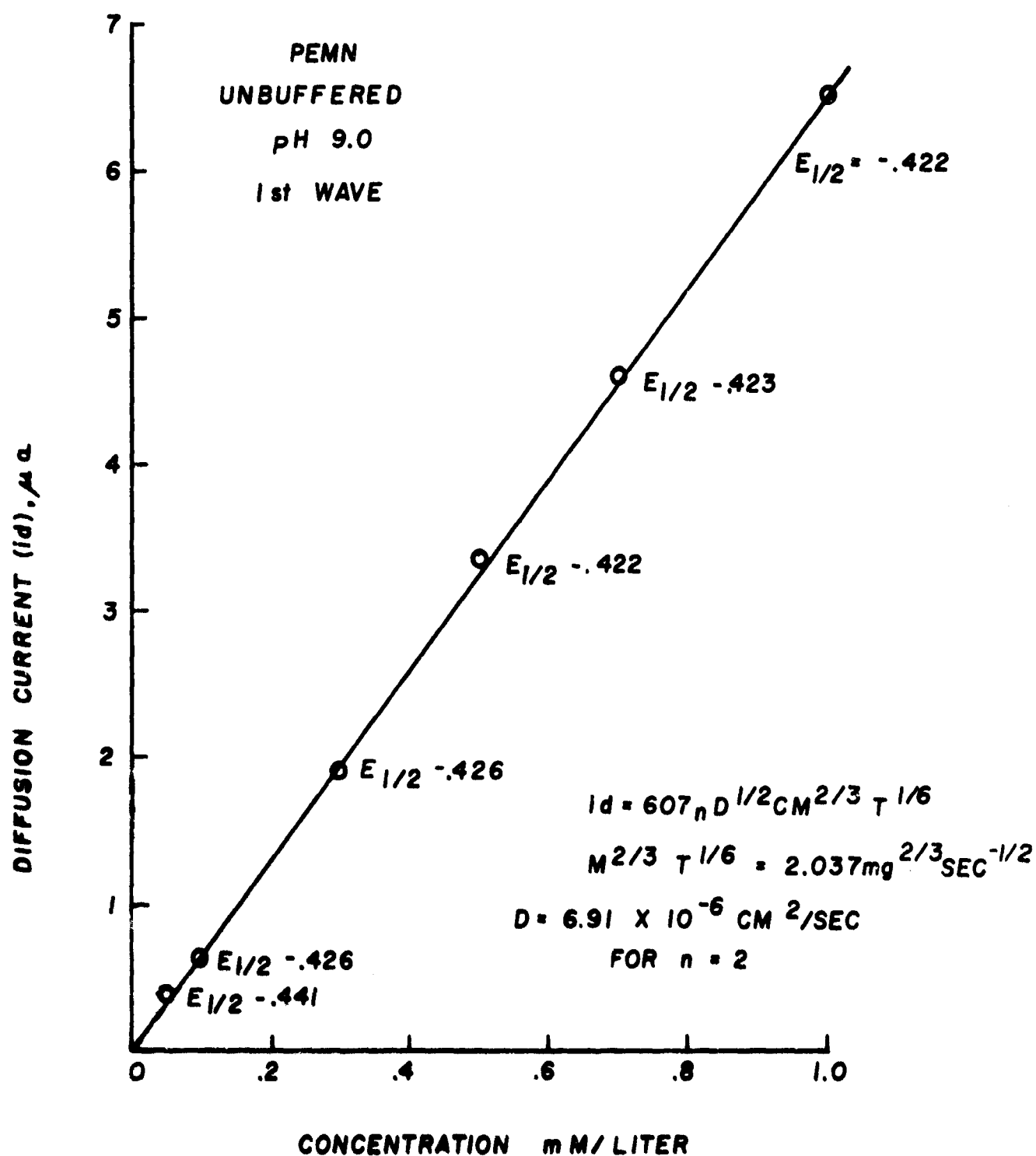
FIG. 4   VARIATION IN DIFFUSION CURRENT (id) WITH
THE CONCENTRATION OF PENTAERYTHRITOL
MONONITRATE

36
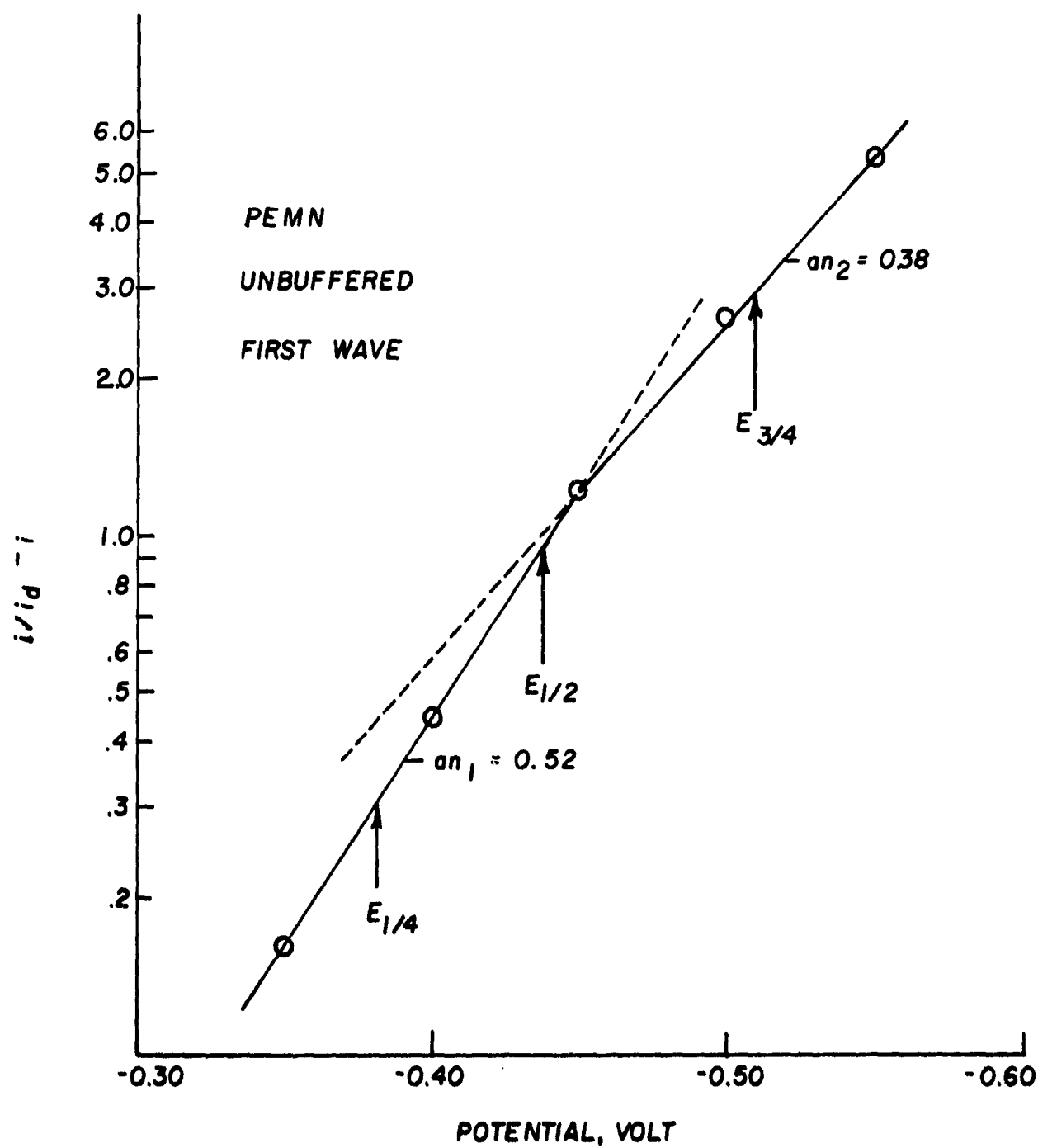
FIG. 5 – APPLICATION OF THE WAVE EQUATION TO THE REDUCTION OF PENTAERYTHRITOL MONONITRATE IN UNBUFFED SOLUTION (pH 1.0)

FIG. 6 - APPLICATION OF THE WAVE EQUATION TO THE REDUCTION OF
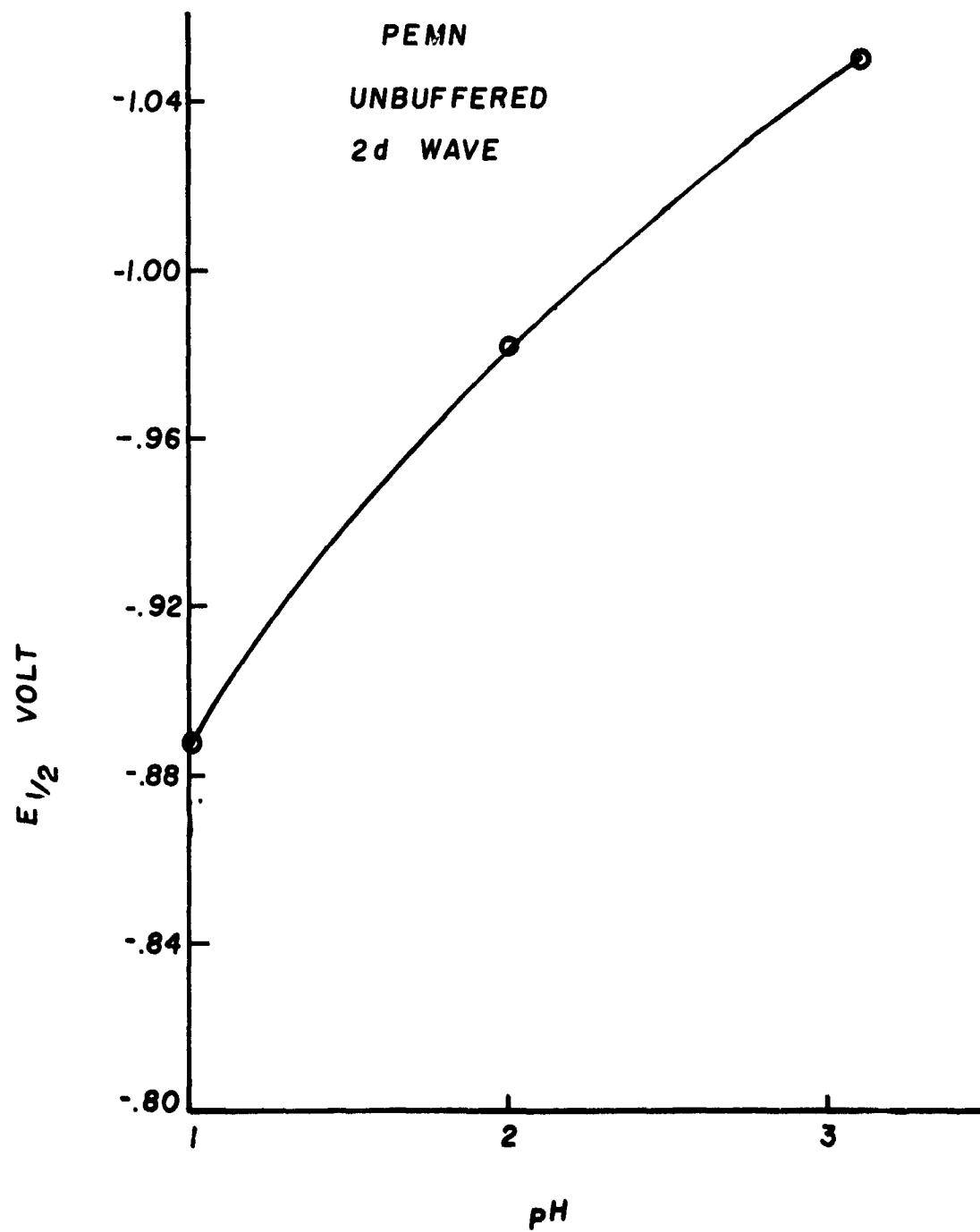PENTAERYTHRITOL MONONITRATE IN UNBUFFERED SOLUTION
(pH 10.1)

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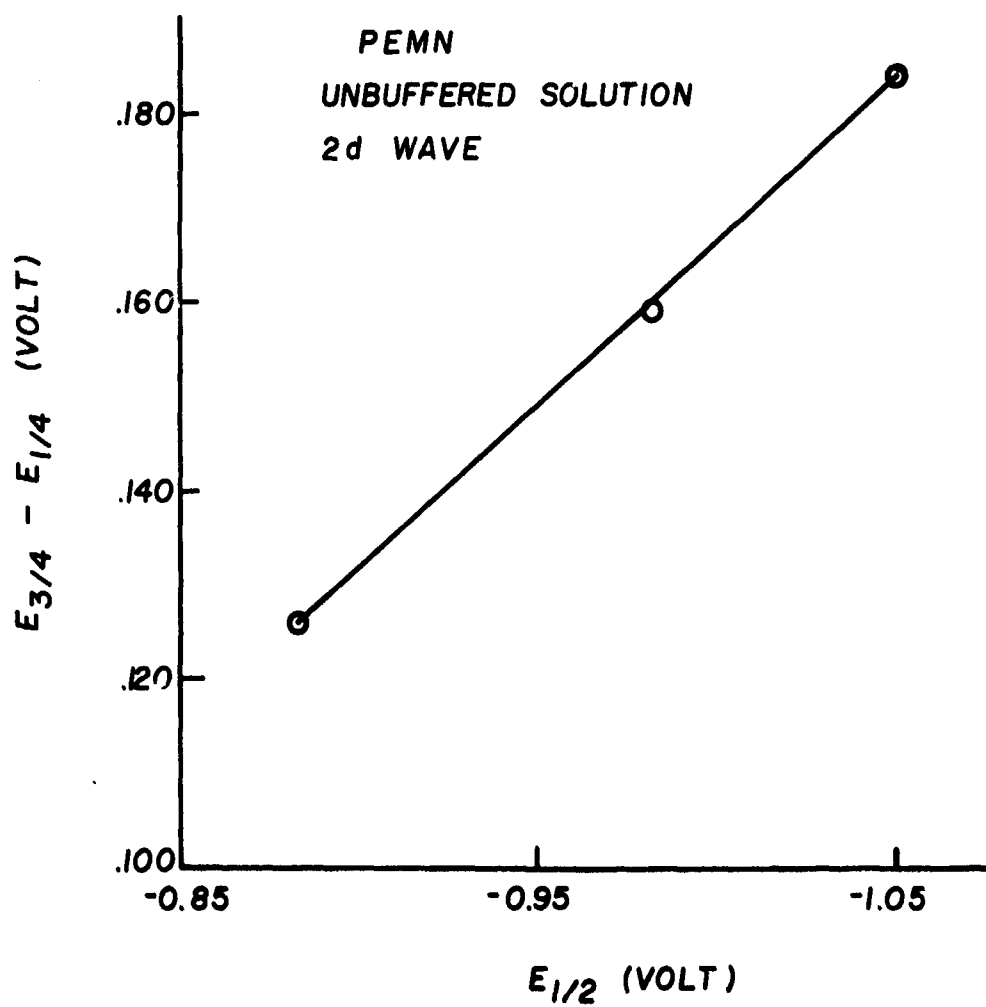FIG. 7   VARIATION IN $E_{1/2}$ WITH THE pH   OF THE
POLAROGRAPHIC   SOLUTION

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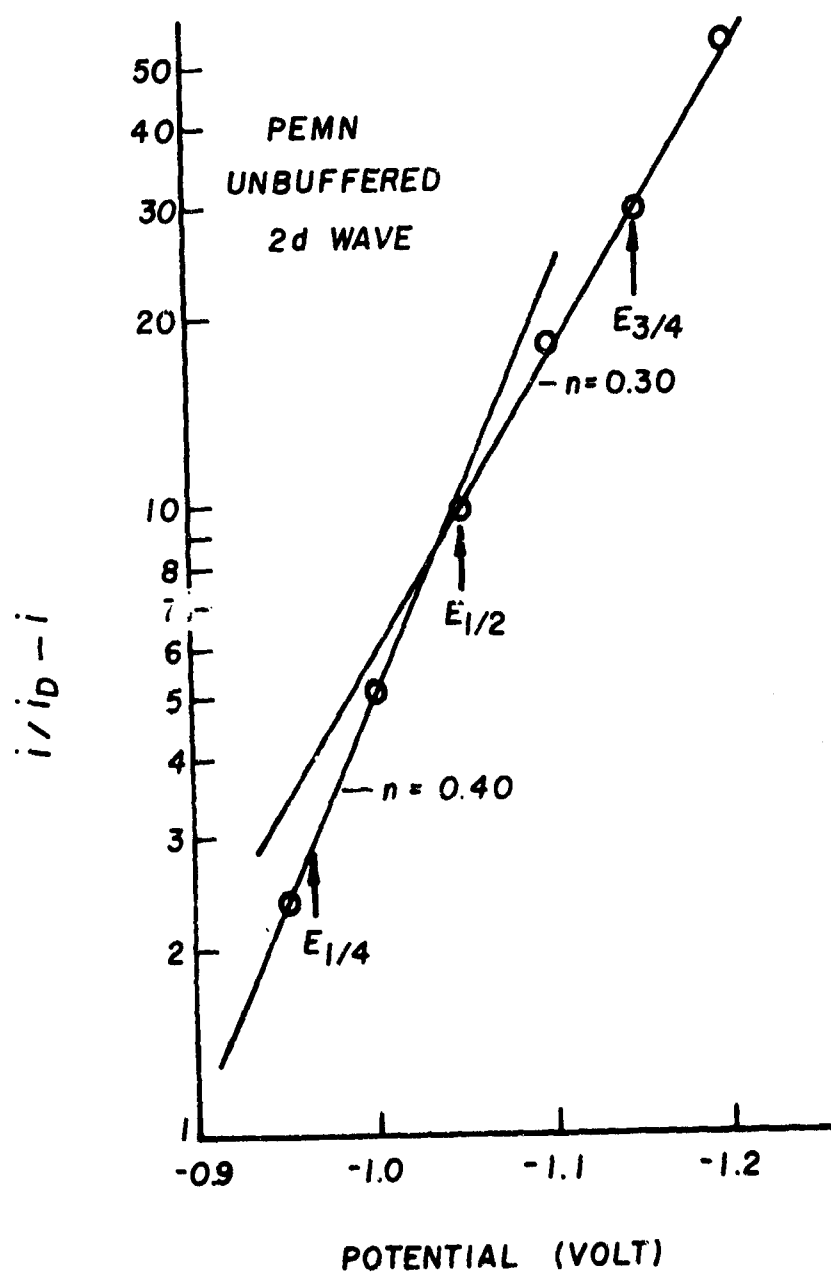FIG. 8 VARIATION OF $E_{3/4, 1/4}$ WITH $E_{1/2}$

40

FIG. 9 APPLICATION OF THE WAVE EQUATION TO
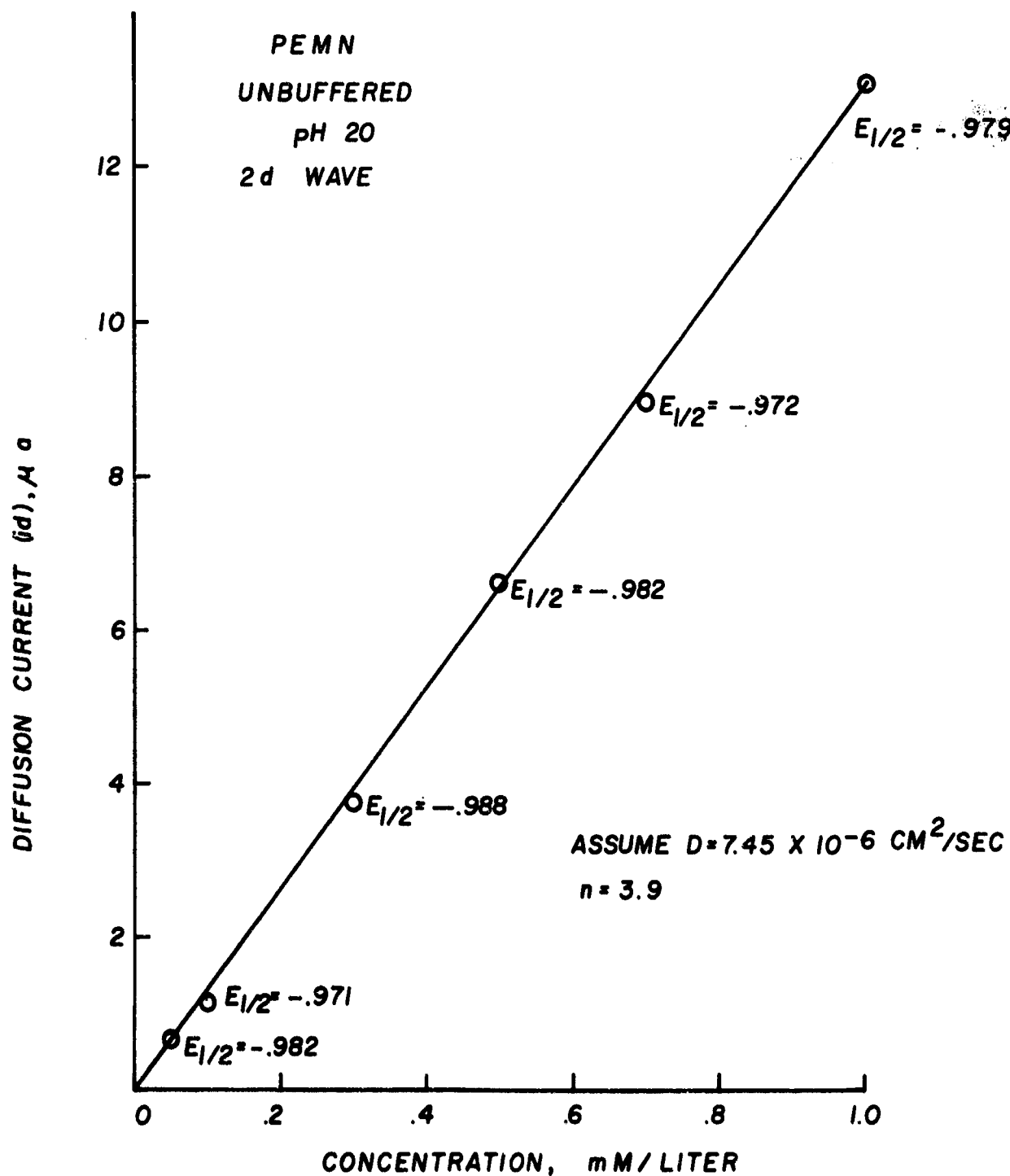THE REDUCTION OF PENTAERYTHRITOL
MONONITRATE AT pH 3.1

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FIG. 10   VARIATION IN DIFFUSION CURRENT (id) WITH THE
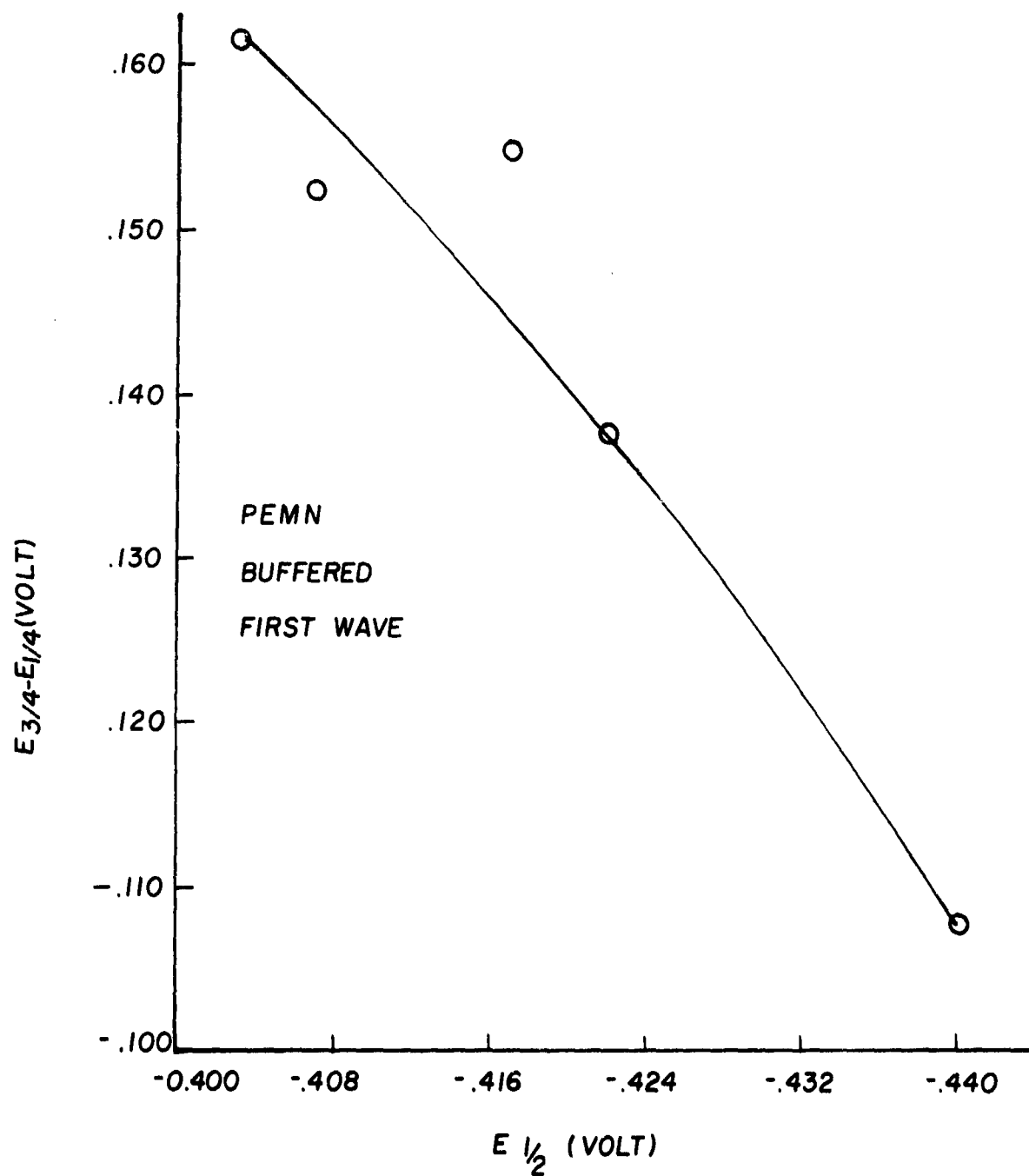CONCENTRATION OF PENTAERYTHRITOL MONONITRATE

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FIG. 11- VARIATION IN $E_{3/4} - E_{1/4}$ WITH THE HALF WAVE POTENTIAL
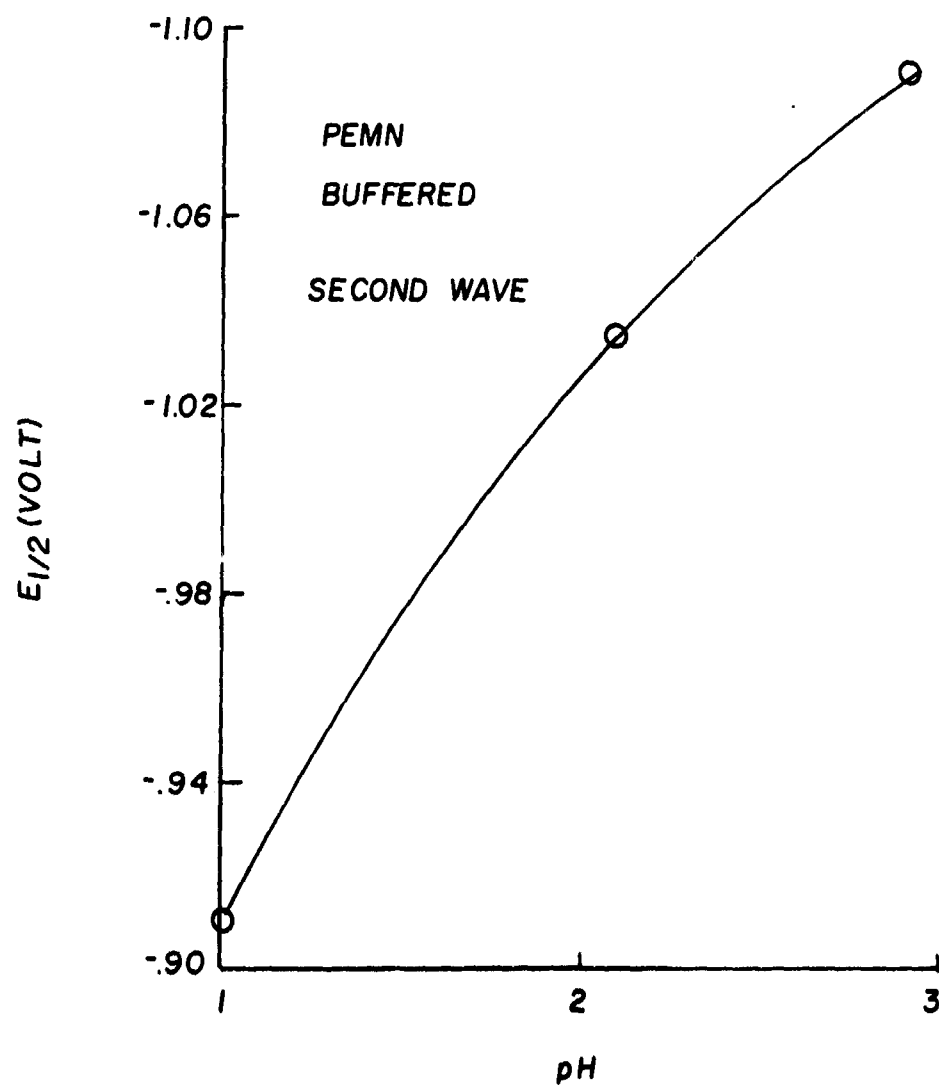
43

FIG. 12 - VARIATION IN HALF WAVE POTENTIAL WITH THE pH OF
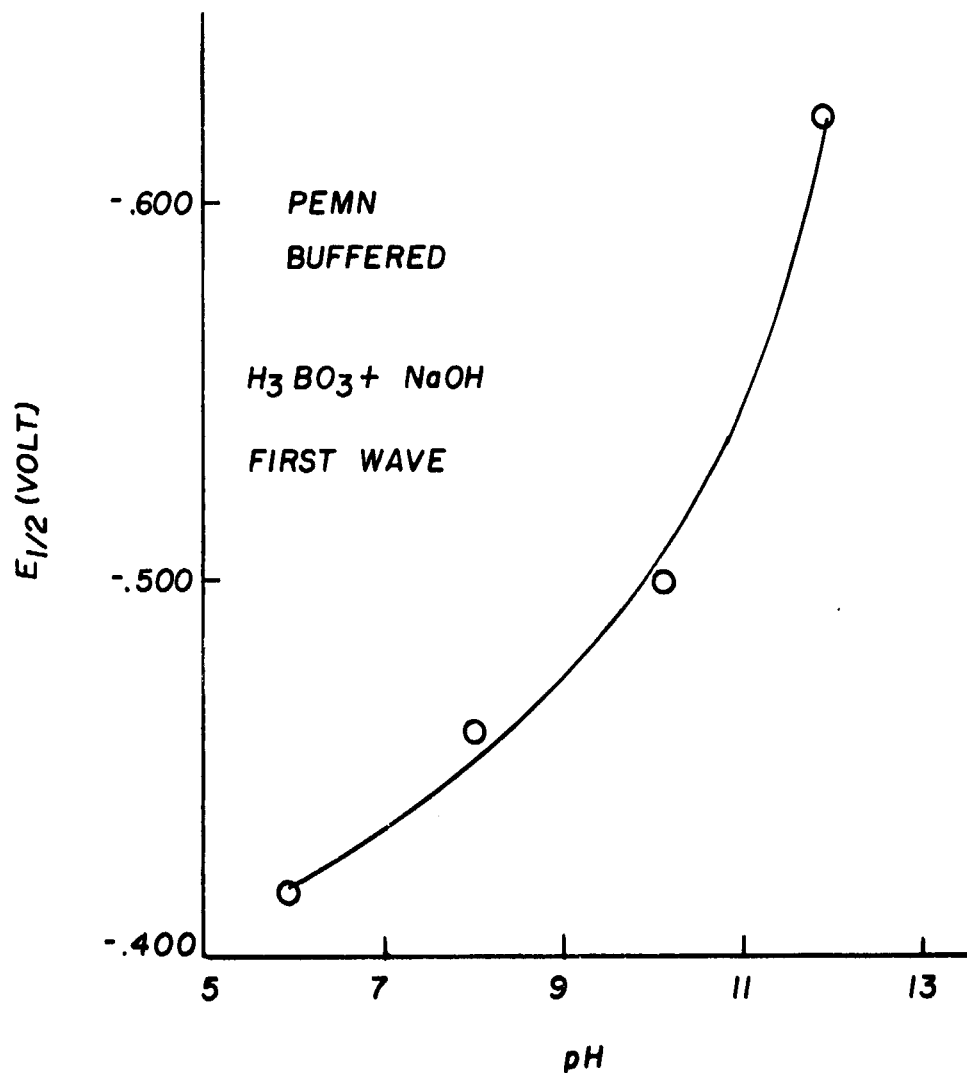THE POLAROGRAPHIC SOLUTION

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FIG. 13 - VARIATION IN HALF WAVE POTENTIAL WITH pH IN
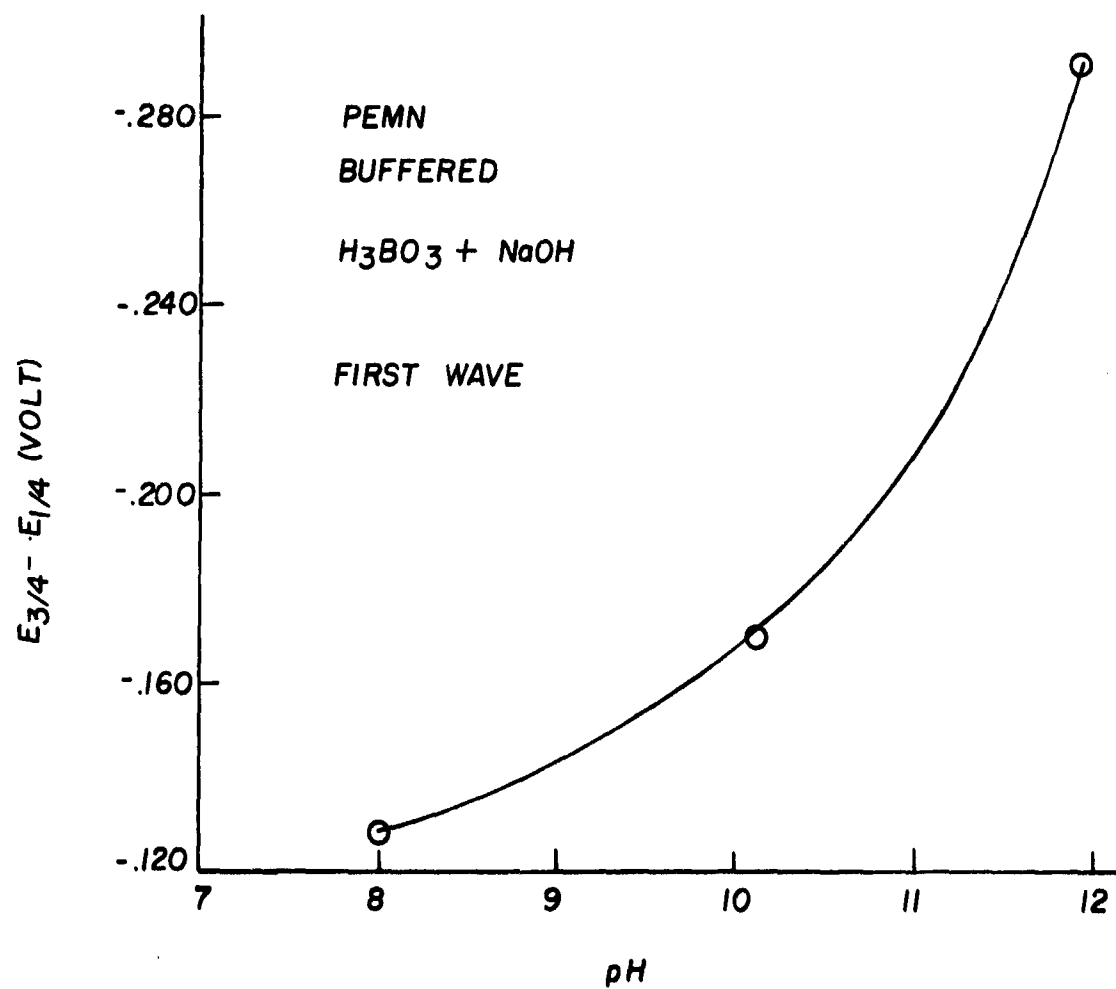BUFFERED SOLUTION CONTAINING BORATE ION

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FIG. 14 − VARIATION IN $E_{3/4} - E_{1/2}$ WITH pH IN BUFFERED SOLUTION CONTAINING BORATE ION

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13. ABSTRACT

The polarographic reduction of pentaerythritol mononitrate in unbuffered aqueous solution at pH 1-4, gave two well defined waves which are shown to be diffusion controlled. However from examination of the wave equation the electrode processes in each case are found to be irreversible. The first wave, not pH dependent, has a mean half wave potential, $E_{\frac{1}{2}} = -0.439$ volt and is assigned to the electrode reduction of the nitrate function, through a two-electron change. The second wave which appears at a more negative potential, approximately -1.0 volt, is pH dependent and is shown to arise from the reduction of nitrous acid through a four electron change. This wave disappears at pH's above 4.

In buffered solutions under acidic conditions the first wave has a mean half wave potential, $E_{\frac{1}{2}} = -0.416$ volt. Under basic conditions, however, $E_{\frac{1}{2}}$ shifts to more negative values. This shift in $E_{\frac{1}{2}}$ is interpreted as arising from complex formation of pentaerythritol mononitrate and the borate anion of the buffering system.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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