THE ELECTRODE REACTIONS
OF SODIUM FORMALDEHYDE SULFOXYLATE SOLUTIONS

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ABSTRACT

A study of the electrode reactions of sodium formaldehyde sulfoxylate (SFS) was made using polarographic techniques. The project was undertaken to determine the possible mechanisms of these reactions and the number of electrons transferred in each process. The investigation was made over a wide range of pH. The results obtained indicate that in basic media the SFS is oxidized at the dropping mercury electrode (DME). In acidic media, the SFS undergoes decomposition, and its reactions form part of the complex dithionous acid-sulfurous acid system of electrode reactions.

INTRODUCTION

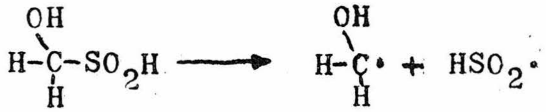
Sodium formaldehyde sufoxylate (SFS), which finds wide use in the dying industry, has been the subject of few detailed investigation.

Furness[1] mentioned that SFS can be oxidized irreversibly at a stationary platinum electrode in a citrate buffer of pH 4, but no anodic wave in this medium can occur at the dropping mercury electrode (DME). Goebring[2] reported that SFS was stable in neutral and alkaline solutions.

Work has been reported by Kunim[3] and Meyer[4] on the thermal decomposition of SFS. Kunim found the initial decomposition reaction

$$NaHSO_2 \cdot HCHO \rightarrow NaHSO_2 + HCHO$$

between 70° and 120°C. Meyer proposed a free radical mechanism for the initial decomposition. The suggested decomposition reaction is



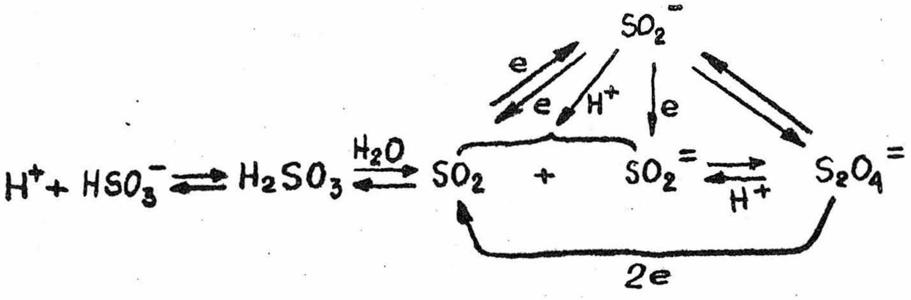
$$H\text{-}C(OH)(H)\text{-}SO_2H \longrightarrow H\text{-}\dot{C}(OH)(H) + HSO_2\cdot$$

Both Kunim's and Meyer's investigations were carried out in basic solutions.

It is well known that SFS is unstable in acidic solutions. The reactions of its inorganic group should be similar or related to those of sulfite, bisulfite, and dithionite ions. The kinetics of the electrode reactions of sodium dithionite and sodim bisulfite aqueous solutions have been the subject of much controversy over the past twenty years. Numerous investigators have studied the problem by means of polarography and chronopotentiometry.

Cermak[5,6] has formulated a scheme of electrode reactions and chemical equilibria which seems to explain satisfactorily the polarographic behavior of the dithionous-sulfurous acid system in basic and acidic solutions.

His scheme is as follows:



His work showed that in a basic solution $S_2O_4^=$ dissociates to produce the free-radical ion SO_2^-, which can either be oxidized reversibly to SO_2 or reduced irreversibly to $SO_2^=$. He also found that $S_2O_4^=$ can be oxidized directly to SO_2 by the reaction

$$S_2O_4^= + H_2O \longrightarrow 2H^+ + S_2O_5^= + 2e^-$$

where $S_2O_5^=$ decomposes into sulfite and sulfur dioxide.

In acidic solution, Cermak found that $S_2O_4^=$ produces SO_2^- and SO_2 at first, then SO_2 can be reduced to SO_2^- and $SO_2^=$. At low pH values the reduction of SO_2 to SO_2^- attains a wave height corresponding to a two-electron process due to the coupling:

$$2\ SO_2 + 2e^- \longrightarrow 2SO_2^-$$

$$2SO_2^- \rightleftharpoons S_2O_4^=$$

$$S_2O_4^= \rightleftharpoons SO_2 + SO_2^=$$

which adds up to

$$SO_2 + 2e^- \longrightarrow SO_2^=$$

These different mechanisms were considered to be solely dependent on the pH values but a chemical explanation of this dependence was not found. The results obtained by Cermak are partially confirmed by the work of Kolthoff and co-workers[7,8,9,10], Bolsaitis[11] and Dunitz[12]. Kolthoff found that a solution of dithionite buffered at pH 7 produces four polarographic waves: 1) A very positive, diffusion-controlled, anodic wave with $E_{\frac{1}{2}} = 0.0$v. vs. SCE, characteristic of sulfite and corresponding to the following reversible electrode reaction

$$Hg + 2SO_3^= \longrightarrow (SO_3)_2Hg^= + 2e^-$$

2) A second anodic wave with $E_{\frac{1}{2}} = -0.485$v.vs. SCE, kinetically controlled, and corresponding to the direct oxidation of dithionite to sulfur dioxide. 3) A diffusion-controlled anodic-cathodic wave corresponding to the reversible reduction of SO_2, with $E_{\frac{1}{2}} = -0.7$ v. vs. SCE.

$$SO_2 + e^- \longrightarrow SO_2^-$$

$$SO_2^- \longrightarrow SO_2 + e^-$$

4) A kinetically controlled cathodic wave corresponding to the irreversible reduction of SO_2^- to $SO_2^=$ appears at $E_{\frac{1}{2}} = -1.21$ v. vs. SCE.

More recently Liu[13] has proposed the following mechanism for the oxidation of the sulfoxylate ion:

$$SO_2^= \xrightarrow{-e} SO_2^- \xrightarrow{-e} SO_2 \quad \text{at pH} \quad 3.88$$

$$SO_2^= \xrightarrow{-2e} SO_2 \quad \text{at pH} \quad 2.77$$

The specific role of the H^+ ion is also unclear in this scheme.

This project investigates the electrode reactions of SFS in basic and acidic media. Quantitative results have been obtained for the polarographic behavior of SFS in basic media which permit formulation of a reaction mechanism. The data obtained for acidic solutions are only qualitative but they permit a meaningful discussion of the chemical species present in acidic solutions of SFS.

THEORY[15, 16]

Polarographic analysis, invented in 1920 by Jaroslav Heyrovsky at the Charles University in Prague, rests on the properties of current-potential curves obtained with a dropping mercury electrode (DME) or other microelectrodes.

If a well-stirred solution containing an electroactive substance is electrolyzed between two large inert metal electrodes, the current-voltage curve will have the form shown in Figure 1a. If the potential applied to the cell is less than the decomposition potential of the solution, E_d, only a very small current flows, while at higher potential the current is given by Ohm's law: $i = E-E_{d/R}$. Under these conditions the current is limited only by the electrolytic resistance of the solution. The concentration of the electroactive substance at the surface of the electrode is kept equal to that in the body of the solution: no concentration polarization exists.

But if the electrode is very small and if the solution is unstirred, the current voltage curve will have the form shown in Figure 1b. Increasing the applied potential decreases the concentration of the electroactive substance at the microelectrode surface until it becomes practically zero. A further increase of the applied potential can no longer increase the current, which is now governed by the rate of supply of the electroactive substance to the electrode surface by a process whose rate is more or less independent of the electrode potential. The electrode is then said to be concentration polarized.

In general, the electroactive substance is supplied to the electrode surface by either a mass transfer process, or by a reaction in the solution producing it from some other substances. In the latter case one speaks of a "kinetic current". In the former case, the limiting current is the sum of three components: the residual current, the migration current, and the diffusion current.

The residual current is the small current which would flow even in the absence of any electroactive substance. Since it is due to convection, and this is an exceedingly difficult process to interpret quantitatively, it is fortunate that it does not play a significant role when polarographic measurements are made with the DME. Convection does influence the current observed with solid microelectrodes, in either quiet or stirred solutions, which is one of the reasons why the use of such electrodes entails greater interpretative complexities than the DME.

With the DME, diffusion and electrical migration are the only important mass transfer processes. Electrical migration is restricted to ionic substances or dipolar molecules capable of undergoing directed movement in an electric field. In the case of ions, the contribution to the limiting current by electrical migration depends directly on the transference number of the ion in the solution and on the electrical potential gradient (mostly iR) in the vicinity of the electrode surface. Depending on whether the reducible or oxidizable ion is a cation or anion, electrical migration may either augment or oppose diffusion. The migration current should be eliminated because it is sensitive to small changes in electrolyte composition in very dilute electrolytic solutions. This is accomplished by addition of a relatively high concentration ($\sim$100 times larger than the concentration of the substance being determined) of a "supporting electrolyte", a salt whose ions are neither reduced nor oxidized at the microelectrode within the potential range being studied. Under these conditions, the transference number of the electroactive ion is decreased practically to zero, and the resistance of the solution, and thus the iR drop through it, is made desirably small.

The limiting current is then controlled entirely by diffusion. The rate of diffusive transfer to the electrode depends directly on the extant concentration gradient at the surface of the electrode, or roughly on the difference in concentration between the bulk of the solution and the electrode surface. As the applied potential is increased above the decomposition potential and the current increases, the demand for the electroactive substance at the electrode increases, but its concentration at the electrode surface decreases. Consequently, the rate of diffusive transfer increases. Ultimately a condition is reached in which the electroactive substance is reduced or oxidized as rapidly as it diffuses to the electrode surface and its concentration at the electrode sinks to a minimal value which remains practically constant with still further increase in potential. The rate of diffusive transfer, dependent on the difference in concentration between the electrode surface and the solution, thus becomes constant, and correspondingly a diffusion-controlled limiting current results.

There are several advantages to the use of the DME. The continually refreshed surface is conductive to a high degree of reproducibility of the current-potential curve, independent of the previous history of the electrolysis. Each drop attains an accurately reproducible size which depends on the geometry of the capillary and the interfacial tension between the mercury and the solution.

The continuously increasing area during the drop life causes a corresponding increase in current with time which results from the growth of the diffusion layer away from the electrode surface so that the net result is a complex current-time function. However, the current oscillations are so very uniform that it is no more difficult to observe their average than to observe a steady current. This is facilitated by using a recorder whose period is two or three times longer than the drop time. Thus, while the current oscillates from practically zero to a maximal value, as each mercury drop grows and falls, the recorder pen oscillates over a very much smaller range than the true current oscillation, but its mean value corresponds very closely to the average value of the current.

Stationary microelectrodes are very sensitive to vibrations. On the DME, because of the periodic dropping the diffusion layer on each mercury drop remains quite thin, and thus is relatively insensitive to disruption by convection in the solution. Consequently, in spite of the more complex geometry, quantitative interpretation of the current at the DME is actually simpler than at a solid electrode where mass transfer occurs by a combination of both diffusion and convection. With DME it is easy to predict quantitatively the influence of all factors which influence the diffusion current, but, except for the special case of a plane electrode to which diffusion is restricted to be normal to the surface, such quantitative prediction is, as yet, not possible with solid microelectrodes.

With the DME, the average current becomes constant inmmediately after each change of the applied potential, whereas with a solid microelectrode time must elapse for the establishment of a steady state of diffusion-convection before the current stabilizes.

Another virtue of the DME is the very large hydrogen overpotential on mercury. This, combined with the decreased free energy of reduction resulting from amalgamation of some deposited metals with mercury, makes it possible to secure well-defined waves for ions whose standard potentials lie far above that of hydrogen ion.

On the other hand, the relative ease with which mercury itself is oxidized to produce an unlimited increase in anodic current, limits the accessible anodic range in comparison with a platinum or gold microelectrode. Anodic polarography with the DME is thus limited to relatively easily oxidized substances whose current-potential curves are developed below the potential of the anodic dissolution of mercury.

A brief theory of the diffusion current follows.

Assume that a small plane solid electrode is placed in a solution containing a reducible ion, and that these ions can reach the surface of the electrode from only one direction (linear diffusion). The observed diffusion current will be given by the equation

$$i_\tau = n F_y A C (D/\pi\tau)^{\frac{1}{2}} \tag{1}$$

where n is the number of faradays consumed per mole of substance reduced at the electrode (i.e., the number of equivalents per mole), F_y is the number of coulombs per faraday, A is the area of the electrode (cm^2), C is the concentration of reducible ion (moles/1000 cm^3), D is the diffusion coefficient of the reducible ion (cm^2/sec), τ is the length of time for which the electrolysis has proceeded (sec), and i is the current at that instant (amperes).

Since the drops produced by the DME are very nearly spherical, the volume of a drop τ seconds after it has begun to form is

$$V = 4/3\pi r^3 = m\tau/d$$

where r is the radius of the drop, m is the rate of flow of mercury into the drop (g/sec.) and d the density of mercury. The area of the drop is then

$$A = 4\pi r^2 = 4\pi(3m\tau/4\pi d)^{2/3}$$

Substitution into equation (1) gives

$$i_\tau = (36)^{1/3} \pi^{-1/6} d^{-2/3} n F_y D^{1/2} C m^{2/3} \tau^{1/6} \tag{2}$$

Changing the units of i to microamperes, of C to millimoles per liter, and of m to mgs/sec, and introducing the numerical values of d and F_y gives

$$i_\tau = 464 \; n D^{\frac{1}{2}} C m^{2/3} \tau^{1/6}$$

We may now secure the average current by integrating over the life of the drop, to secure the number of microcoulombs which flow during that time, and dividing the result by the drop time $\underline{t}$, which is the length of time that elapses between the instants at which two succesive drops fall. This gives

$$(3) \qquad i_d = \frac{1}{t}\int_0^t i_\tau \, d\tau = 398 \quad n \, D^{\frac{1}{2}} \quad C \quad m^{2/3} \, t^{1/6}$$

In this derivation it is assumed that the reducible ions reaching each small segment of the drop surface come from only one direction, parallel to the axis of a cylinder. Actually, however, they come from points whithin a cone whose apex is at the center of the drop: that is, the diffusion is rather radial than linear. Since the volume bounded by the cone is greater than that bounded by the cylinder, the current predicted by equation (3) is too small. Much better agreement with experimental results is secured by multiplying the right hand side of equation (3) by $(7/3)^{\frac{1}{2}}$ giving

$$(4) \qquad i_d = 607 \quad n \, D^{\frac{1}{2}} \quad C \, m^{2/3} \quad t^{1/6}$$

which is known as the Ilkovic equation[16].

Equation (4) fails badly at low drop times (below 2 seconds) because the rapid growth and frequent fall of drops cause stirring of the solution around the capillary tip, so that excessive amounts of reducible material reach the drop surface and the observed currents are too high.

Equation (4) may be rewritten to permit comparison of data secured under otherwise identical conditions but with different capillaries.

$$(5) \qquad I = \frac{i_d}{C \, m^{2/3} \, t^{1/6}} = 607 \quad n \quad D^{\frac{1}{2}}$$

where I is the "diffusion current constant".

It can be shown that $m^{2/3} \, t^{1/6}$, and therefore i_d is proportional to the square root of the effective presure of mercury. This is the basis for ascertaining whether the height of a wave is diffusion controlled. If $i_d/(h_{Hg})^{\frac{1}{2}}$ is not constant within experimental error over a wide range of mercury pressures, the current must be partially or wholly governed by the rate of some process other than diffusion to the electrode surface. The occurrence of such a kinetic current depends on the existence of an equilibrium, $X \rightleftarrows Y$, where Y is reducible at a lower applied potential than X, or where X is not reducible at all at the DME. If the transformation of X into Y at the drop surface is rapid compared to the electroreduction of X, the observed current will be controlled by the rate of diffusion of X to the electrode surface and will obey the Ilkovic equation with respect to the effects of mercury pressure, total concentration, temperature, etc.

If, on the other hand, equilibrium in this reaction is attained so slowly that no appreciable amount of Y is produced in this way during the life of a drop, two waves will be secured, provided that X is also reducible at the DME. The ratio of the wave heights will then be equal to the ratio of the concentrations of X and Y in the solution, and both wave heights will be diffusion controlled.

Most often the rate of the chemical reaction is such that some, but not all, of the X present in the diffusion layer is converted into Y during the drop life at potentials on the plateau of the Y wave. If the equilibrium concentration of Y in the solution is negligibly small, the observed current at the potential at which Y alone is reducible will be entirely kinetic in nature. Otherwise this current will be the sum of the diffusion current of the Y already present in the solution and the kinetic current due to the reduction of the additional Y produced as a result of the displacement of the equilibrium in the diffusion layer. The first of these components is diffusion-controlled and proportional to $h^{\frac{1}{2}}$. The second is rate-controlled and independent of the above factors.

So, depending on the position of the equilibrium between X and Y, and the rate at which this equilibrium is attained, the observed current may show any behavior intermediate between that of a true diffusion current at one extreme and a pure kinetic current at the other. Thus the wave height may be proportional to $h^{\frac{1}{2}}$, independent of h, or may increase with increasing h but less rapidly than the one half-power relationship predicts.

Other kinds of waves can be detected at the DME, such as catalytic and adsorption waves, but their study is not pertinent to this report, since they have not been observed during the experimental work. An understanding of electrocapillary phenomena, and such related effects as the occurrence of maxima in polarographic waves is of good use in polarographic work; yet, these effects have not been observed either.

The equation of the polarographic wave and the criteria for reversibility of the electrode reaction will be considered next.

The simplest case of electrode reaction occurs when a substance undergoes reversible reduction to a product which is soluble in either the solution or the mercury (amalgam). The electrode reaction may be represented by

$$\text{ox.} + n\ e^- \longrightarrow \text{red.}$$

If the reaction proceeds reversibly, that is with little or no overpotential, the potential of the DME at any point on the polarographic wave will correspond to the concentrations, strictly activities, of the oxidized and reduced forms at the surface of the DME, according to the Nernst equation

$$(6) \qquad E = E^0 - (RT/nF)\ \ln\ C^0_{red}/C^0_{ox}$$

where $\underline{E^0}$ is the standard potential of the reaction against the particular reference electrode used to measure the potential of the DME. The potential $\underline{E}$ refers to the average value during the life of a mercury drop, and likewise for the concentrations.

As the potential at the DME is increased over the decomposition potential, the concentration of the oxidized form at the electrode surface decreases while that of the reduced form increases correspondingly; the magnitudes of these changes are directly proportional to the change in current. If $\underline{C}$ and $\underline{C^0}$ are the concentrations in the bulk of the solution and at the electrode surface, we have for the oxidized form

$$(7) \qquad C^0_{ox} = C_{ox} - k'i$$

where $\underline{i}$ is the current. When the current attains its limiting value i_d, C^0_{ox} may be set equal to zero in equation (7). Then,

$$k' = C_{ox}/i_d$$

and it is evident that the constant $\underline{k'}$ is equal to the reciprocal of $607\ n\ D^{\frac{1}{2}}_{ox}\ m^{2/3}\ t^{1/6}$. Representing this latter constant by k_{ox} we may rewrite equation (7) as

$$(8) \qquad C^0_{ox} = (i_d - i)/k_{ox} = C_{ox}(i_d\ i)/i_d$$

If the solution originally contains none of the reduced form, then

$$C^0_{red.} = i/k_{red}$$

where k_{red} is the ratio i_d/C_{red} for the anodic wave that would be observed with a solution of the reduced form, and is defined by the Ilkovic equation with $D = D_{red}$.

Substituting the expressions obtained for the concentrations at the electrode surface into the Nernst equation we obtain

$$E = E^{0} - (RT/nF)\ \ln\ (k_{ox}/k_{red}) - (RT/nF)\ \ln\ i/(i_{d}-i)$$

The potential at the DME at the midpoint of the wave where the current is one-half of the diffusion current is the "half-wave potential". Because when $i = i_{d}/2$ the last log term in the above equation vanishes and

$$E_{\frac{1}{2}} = E^{0} - (RT/nF)\ \ln(k_{ox}/k_{red})$$

and at 25°C, the equation takes the form

$$E = E_{\frac{1}{2}} - (0.0591/n)\ \log\ i/(i_{d}-i) \tag{9}$$

Thus, when the electrode reaction has the form

$$\text{ox.} + n\ e^{-} \longrightarrow \text{red.}$$

a plot of E versus log $i/(i_{d}-i)$ yields a straight line with a reciprocal slope of 1.059/n, provided the reaction proceeds reversibly. With irreversible reactions the plot log will either not be a straight line, or, if it is, the slopes will be larger than that predicted; i.e., the polarographic wave itself rises less steeply than for a reversible reaction.

The half-wave potential is characteristic of the particular electrode reaction, and thus can be used to identify it. If certain other, easily established conditions are satisfied the current-potential curve will exhibit a limiting current, controlled by diffusion, whose magnitude is directly dependent on the concentration of the electroactive species. This, with the use of the Ilkovic equation, permits the calculation of diffusion coefficients if the number n of electrons transferred is known. If the electrode reaction is reversible n can be found using Nernst equation for the polarographic wave. In any case a reasonable estimate of the diffusion coefficient can be made, and n found thereof. In the case of kinetically controlled currents careful study can lead to extensive knowledge of the chemical equilibria within the solution. These are the phenomena which make polarography such a versatile technique for the simultaneous qualitative and quantitative analysis of both aqueous and nonaqueous solutions of reducible and oxidizable substances.

APPARATUS AND PROCEDURE

The apparatus consisted of a polarograph and a cell system. The cell system was a Sargent H-type cell, S-29401, and a dropping mercury electrode. Their arrangement is shown in Fig. 2. The cell was mounted on a stand and cushioned with rubber to minimize vibration.

The cross member was almost filled with a 4% agar-saturated KCl gel. Once the gel was solidified, the saturated calomel electrode (SCE) was set up in the reference compartment. Mercury was added to 1-2 cms. deep; then an equal thickness of a paste made by stirring equal weights of Hg_2Cl_2 (calomel) and KCl with a little saturated solution of KCl; the tube was then filled with KCl solution and an excess of KCl crystals, and stoppered tightly. Electrical contact was made by means of a platinum wire sealed in at the bottom of a glass tube, which is half filled with mercury, and lowered into the reference compartment.

The solution compartment is provided with an outlet stopcock which facilitates draining, and with a tube that permits deaeration of the solution, by bubbling N_2 through it before running. By means of a two-way stopcock the gas is diverted over the solution during the runs.

The voltage between the SCE and the DME, and the current flowing in the cell were automatically recorded in a voltage-scanning Sargent Model XV Recording Polarograph, S-29310, at the rate of 0.1 volts per minute. Half-wave potential data and diffusion current data were obtained graphically from such records. See Fig. 6.

Nitrogen used for sweeping out oxygen was oxygen-free HPD grade (99.95% purity), and was purified further by bubbling through a standard chromous chloride solution, and vapor saturated by scrubbing with oxygen-free distilled water. SFS used was a commercial product, previously analysed by Meyer[4], and reported 87.7 ± 0.4% pure, its impurities being sodium sulfite and sodium thiosulfate. Formaldehyde used was a 30% solution. Mercury used was doubly distilled. All other chemicals used were of reagent grade.

The supporting electrolytes used were, in general, Britton-Robinson buffers. Values of pH from 2 to 12 can be obtained by mixing in adequate proportions a solution 0.2N in NaOH and a stock solution made 0.04M in acetic acid, 0.04M in phosphoric acid and 0.04M in boric acid[18]. The stock solutions were also made 0.1M in potassium chloride. The pH was measured immediately before the runs with a Beckman pH-meter.

For each run, the solution side of the cell was thoroughly rinsed with distilled water and allowed to drain. Then, 25.00 ml. of the buffered electrolyte were pipetted in and N_2 bubbled through the solution for at least 15 minutes. Weighed amounts of the substance under study were added, and helped to dissolve by brief further bubbling.

The drop time was measured simply by timing 10 drops with a stopwatch, with the DME polarized at the same potential at which the diffusion current is measured. The rate of mercury flow is measured by weighing the mercury collected from the DME over a measured time interval.

The cell was not thermostated, but room temperature remained nearly constant during the experiments at 25 ± 1° C.

RESULTS AND DISCUSSION

In solutions of SFS approximately 10^{-3} M, well-defined anodic waves were observed in the pH range from 7 to 12. No cathodic waves were observed in this range. The value of the half-wave potential was found independent of the SFS concentration.

The value of the half-wave potential was found dependent on the pH of the solution (Fig. 3). The half-wave potentials became more negative with increasing hydroxyl concentration, indicating that the free energy of oxidation decreases with increasing basicity. Thus OH^- ions should be present on the left side of the equation for the electrode oxidation.

The effect of added formaldehyde on the SFS electrode oxidation was studied qualitatively. Addition of even comparable concentrations of formaldehyde to a basic SFS solution did not change the value of the diffusion current or alter the nature of the anodic wave in any detectable way. Thus, a mechanism of the type proposed by Meyer[4],

$$CH_2OHSO_2^- \longrightarrow HSO_2^- + HCOH$$

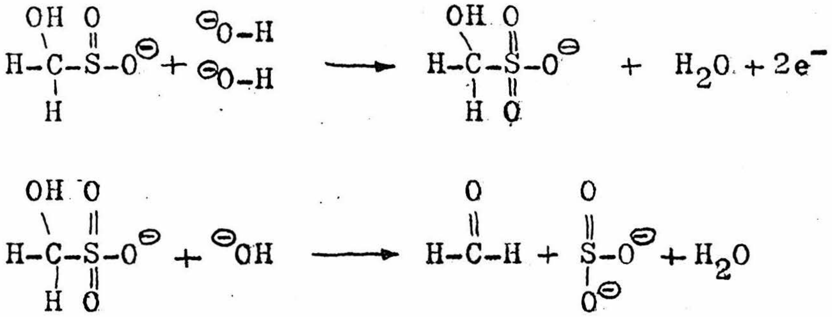
where the initial reaction is the intermediate formation of HSO_2^-, can be discarded since in that case an excess of formaldehyde would affect the characteristics of the waves.

The variation of the diffusion current with SFS concentration was measured at pH 11.6. The wave height was found to be linearly proportional to the SFS concentration (Table 1 and Fig. 4). This means that the limiting current is actually diffusion-controlled, and the Ilkovic equation can be applied. No measurements were made of the variation of wave-height with mercury pressure.

The criterion for reversibility was applied to the anodic waves of SFS. At pH 10.75, it was found that the reaction is irreversible (Table 2 and Fig. 5). Thus the number <u>n</u> of electrons transferred may not be determined directly using the Nernst equation for the polarographic wave. However, the final product of the decomposition of SFS in basic media is sulfite[3,4]. Thus, $n = 2$ is indicated for the number of electrons transferred.

The diffusion current constant was found to be $I = 3.73$. Using the Ilkovic equation and assuming a two-electron transfer reaction, the diffusion coefficient, <u>D</u>, is found to be 0.95×10^{-5} cm.^{2}/sec. This value is close to the value reported by Kolthoff[10] for the two-electron oxidation of dithionite to sulfur dioxide. This should be so in as much as the substances are similar and the number of electrons transferred is identical.

A mechanism is proposed for the anodic reaction of SFS for which the initial step is the direct two-electron oxidation of the sulfoxylate to the sulfite, followed by the separation of formaldehyde,



$$\mathrm{H{-}\underset{H}{\overset{OH}{C}}{-}\overset{O}{S}{-}O^{\ominus} + {}^{\ominus}O{-}H + {}^{\ominus}O{-}H \longrightarrow H{-}\underset{H}{\overset{OH}{C}}{-}\underset{O}{\overset{O}{S}}{-}O^{\ominus} + H_2O + 2e^-}$$

$$\mathrm{H{-}\underset{H}{\overset{OH}{C}}{-}\underset{O}{\overset{O}{S}}{-}O^{\ominus} + {}^{\ominus}OH \longrightarrow H{-}\overset{O}{C}{-}H + \underset{O^{\ominus}}{\overset{O}{S}}{-}O^{\ominus} + H_2O}$$

which add up to

$$CH_2OH\cdot SO_2^- + 3\ OH^- \longrightarrow SO_3^= + HCOH + 2H_2O + 2e^-$$

The data gathered for acidic SFS solutions is qualitative. A tabulated summary is presented in Table 3.

Acidification of a SFS solution produces sulfoxylate ions. At pH 5 the dominant species is SO_2^-. The monomer of dithionous acid is detected in solution by the cathodic wave at $E_{\frac{1}{2}} = -1.20$ v. vs. SCE. This cathodic wave, due to the reduction of SO_2^- to $SO_2^=$, disappears below pH=4.85. At these pH's, SO_2 is directly reduced to $SO_2^=$, with consumption of SO_2^- because of the equilibrium

$$2\ SO_2^- \rightleftharpoons SO_2 + SO_2^=$$

which is displaced to the right in acid medium. At these pH's the equilibrium

$$S_2O_4^= \rightleftharpoons SO_2 + SO_2^=$$

is also displaced to the right. The anodic oxidation of $S_2O_4^=$ to SO_2 at $E_{\frac{1}{2}} = -0.49$ v. vs. SCE is not detectable in SFS solutions because at pH 6.00 or higher, when the concentration of $S_2O_4^=$ could be significant, there are not many $SO_2^=$ ions produced by the SFS, which becomes stable with small basicity. These conclusions, based on the data presented, can be predicted from the scheme proposed by Cermak for the dithionous acid-sulfurous acid system. They fail, however, to explain in detail the role of the hydrogen ion.

With increasing acidity, $SO_2^=$ tends to become the dominant species in solution. In a 0.1 N HCl solution of SFS, $S_2O_3^=$ and $S_4O_6^=$ are present.

Presumably

$$2\ SO_2^{=} + 2H^+ \longrightarrow 2\ S_2O_3^{=} + H_2O$$

and it is known that the thiosulfate can be easily oxidized to tetrathionate ion[18].

Eventually, formation of sulfur would be expected through the reaction

$$S_2O_3^{=} + 2\ H^+ \longrightarrow SO_2 + S + H_2O$$

The sulfur in the above reaction could be detected by the appearance of milkiness, and so it was. The smell of H_2S was also detected in 0.1 N HCl solutions of SFS after about one hour of standing in the solution compartment of the H-cell. Marshak[19] has found the reaction

$$2SO_2^{=} + 6\ H^+ \xrightarrow[+2e^-]{} SO_2 + H_2S + 2\ H_2O \quad .$$

CONCLUSIONS

Sodium formaldehyde sulfoxylate (SFS) yields well-defined anodic waves in the pH range from 7 to 12. The diffusion coefficient at 25±1° C is 0.95×10^{-5} cm^2/sec. The half-wave potential is pH dependent. The electrode reaction is the two-electron transfer irreversible oxidation of sodium formaldehyde sulfoxylate to sulphite and free formaldehyde.

The chemical equilibria in acidic solutions of sodium formaldehyde sulfoxylate are those of the dithionous acid-sulfurous acid system. At pH 5, the monomer of dithionous acid is the dominant species; at pH's between 5 and 2, the sulfoxylate ion also becomes important; at pH 2, sulfoxylate ion is the dominant species. In 0.1 N acid, thiosulfate and tetrathionate ions are present and the eventual products of decomposition are sulfur dioxide, free sulfur, and hydrogen sulfide.

RECOMMENDATIONS

Polarography seems a very versatile and fast-moving technique for use as an analytical tool in the study of reaction kinetics. Further use of it could be very helpful in the study of the chemical equilibria and electrode reactions of the dithionous acid-sulfurous acid system. Although much work has been done on the field by other investigators, there is still much knowledge to search for.

1. A more systematic and exhaustive investigation of the anodic reaction of sodium formaldehyde sulfoxylate in basic media should be made, in order, both, to confirm the results obtained in this work and to gain new knowledge about the influence on the reaction kinetics of such other factors as temperature, mercury pressure, and formaldehyde concentration.

2. The study of the polarographic wave due to the reversible reduction of sulfur dioxide would permit an accurate determination of the electron transfer numbers as a function of pH, and lead to a more accurate knowledge of the diffusion coefficients involved.

3. A quantitative study of the reactions of this system at high acidities is needed.

4. Before further studying of sodium formaldehyde sulfoxylate is done, a procedure for its purification needs to be developed.

5. In the two runs made with 0.1 N HCl solutions of sodium formaldehyde sulfoxylate (pH=1.07), the limiting currents of the observed waves fluctuated with time. Because of the obvious gain in time, effort, and, probably, accuracy, the possibility of using the H-cell as a reaction cell for these or other kinds of reactions should be investigated.

6. The set up of the capillary and its attached mercury reservoir should be modified so as to permit the maintaining of a constant mercury head and the easy reading of such.

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TABLE 1

Diffusion current and concentration

pH=11.6 $E_{\frac{1}{2}}$=-0.36 v.vs. SCE $m^{2/3}t^{1/6}$ = 2.37 If n=2, D=0.95×10^{-5}

SFS weight (gm)	$C\times10^3$	i_d(μA)	i_d/C	I
0.0017	0.505	4.5	8.92	3.76
0.0010	0.297	2.4	8.09	3.41
0.0027	0.802	7.6	9.48	4.00
0.0035	1.04	9.2	8.84	3.73
0.0060	1.78	15.8	8.89	3.75
0.0025	0.743	6.6	8.89	3.75

ave =3.73

Reference Fig. 4

TABLE 2

Reversibility of Anodic Reaction

C=0.67×10^{-3} M SFS pH=10.75 $E_{\frac{1}{2}}$= -0.28 v. vs. SCE i_d=6.00 μA

E	i(μ A)	i_d-i	i/i_d-i
0.20	5.70	0.30	19.0
0.23	5.04	0.96	5.25
0.25	4.44	1.56	2.85
0.28	3.18	2.82	1.13
0.30	2.28	3.72	0.613
0.33	0.07	5.93	0.0118

Reference Fig. 5

TABLE 3

The observed behavior of some substances

	pH	$3 H_2O + S_2O_3^= \rightarrow SO_3^= + 4e^-$ (9)	$2 SO_3^= + Hg \rightarrow Hg(SO_3)_2^= + 2e^-$ (9)	$2 S_2O_3^= + Hg \rightarrow Hg(S_2O_3)_2^= + 2e^-$ (9)	$S_2O_4^= \rightarrow 2 SO_2 + 2e^-$ (11, 5)	$S_4O_6^= \rightarrow ?$ (19)	$SO_2 + e^- \rightarrow SO_2^-$ $SO_2 + 2e^- \rightarrow SO_2^=$ (7)	$SO_2^- + e \rightarrow SO_2^=$ (6,7)	$HCHO \rightarrow ?$
			←	$E_{\frac{1}{2}}$ vs. SCE, volts					→
SFS	6.64						-0.71	-1.20	
	5.94						-0.70	-1.10	
	5.41						-0.68	-1.20	
	5.23						-0.66	-1.20	
	5.07						-0.66		
	4.85						-0.62	-1.30	
	3.89						-0.56		
	2.98						-0.51		
	2.50						-0.50		
	1.07					-0.21	-0.48		
	1.07			-0.14		-0.21	-0.37		
$SO_3^=$	10.75		-0.03						
	5.07						-0.65		
	3.88						-0.57		
	2.98						-0.52		
	2.78						-0.49		
	1.99						-0.43		
	1.07						-0.37		
$S_2O_4^=$	6.92		0.00		-0.49		-0.66	-1.21	
	4.04						-0.55		
	1.84			-0.13		-0.29	-0.43		
$S_2O_3^=$	11.6			-0.13					
	8.0	0.14		-0.13					
	1.07			-0.11		-0.22	-0.37		
HCHO	11.6								-1.64
	10.75								-1.59
	6.92								-1.40

The numerical values in this table have been obtained in the laboratory; the mechanisms are from the references in parentheses.

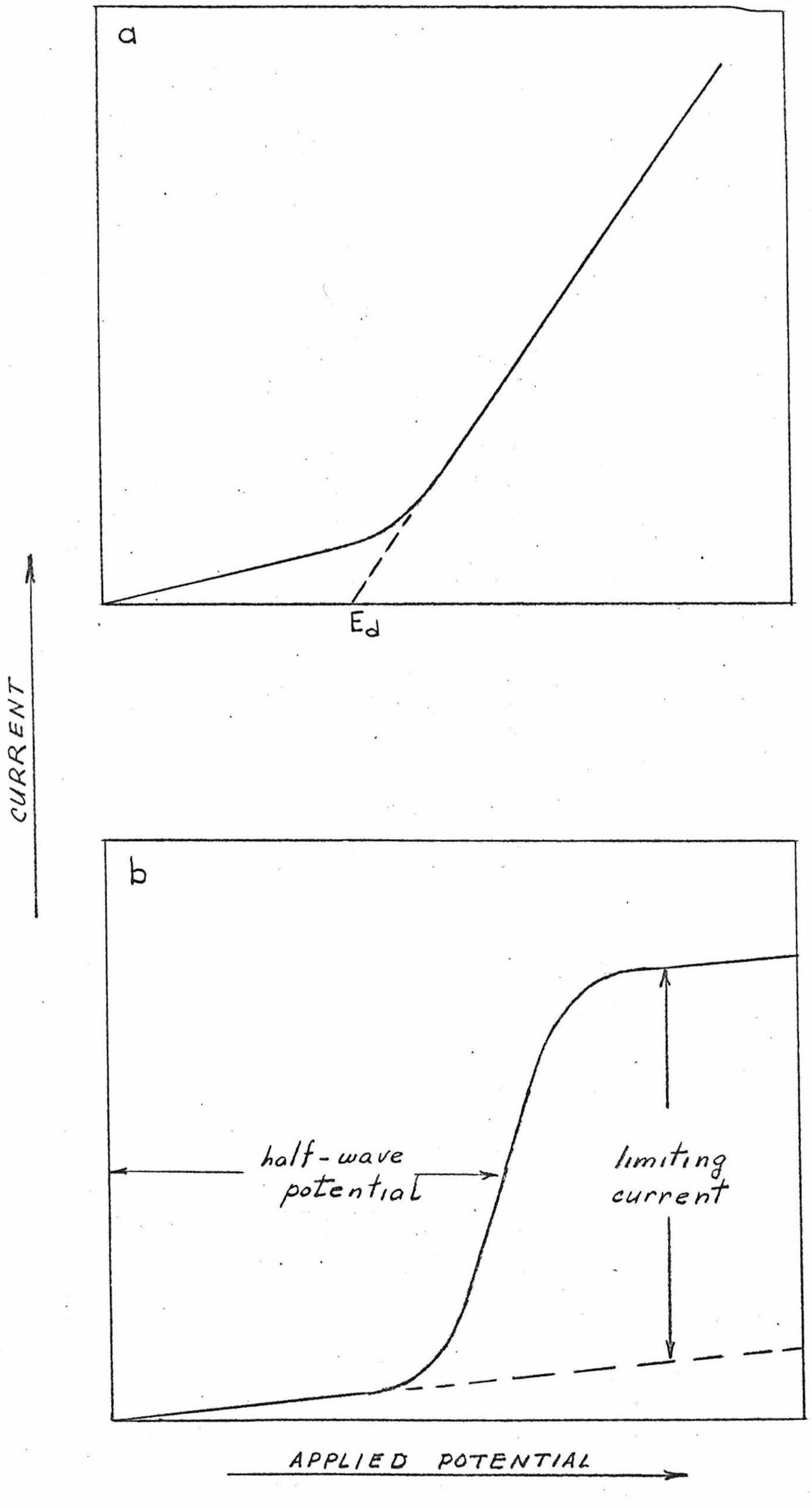
a
E$_d$
CURRENT
b
half-wave potential
limiting current
APPLIED POTENTIAL

FIG. 1

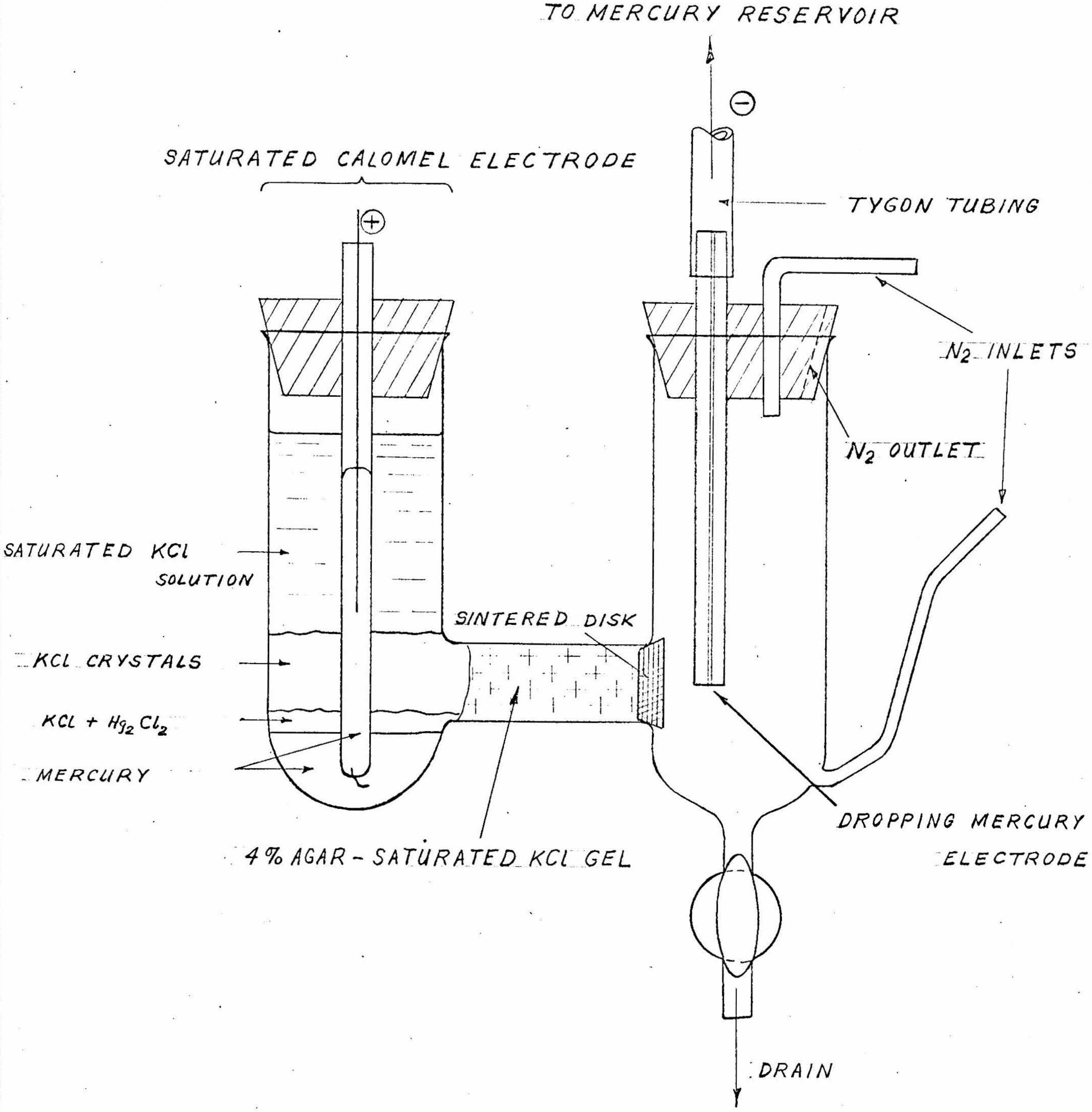

FIG. 2 DIAGRAM OF CELL

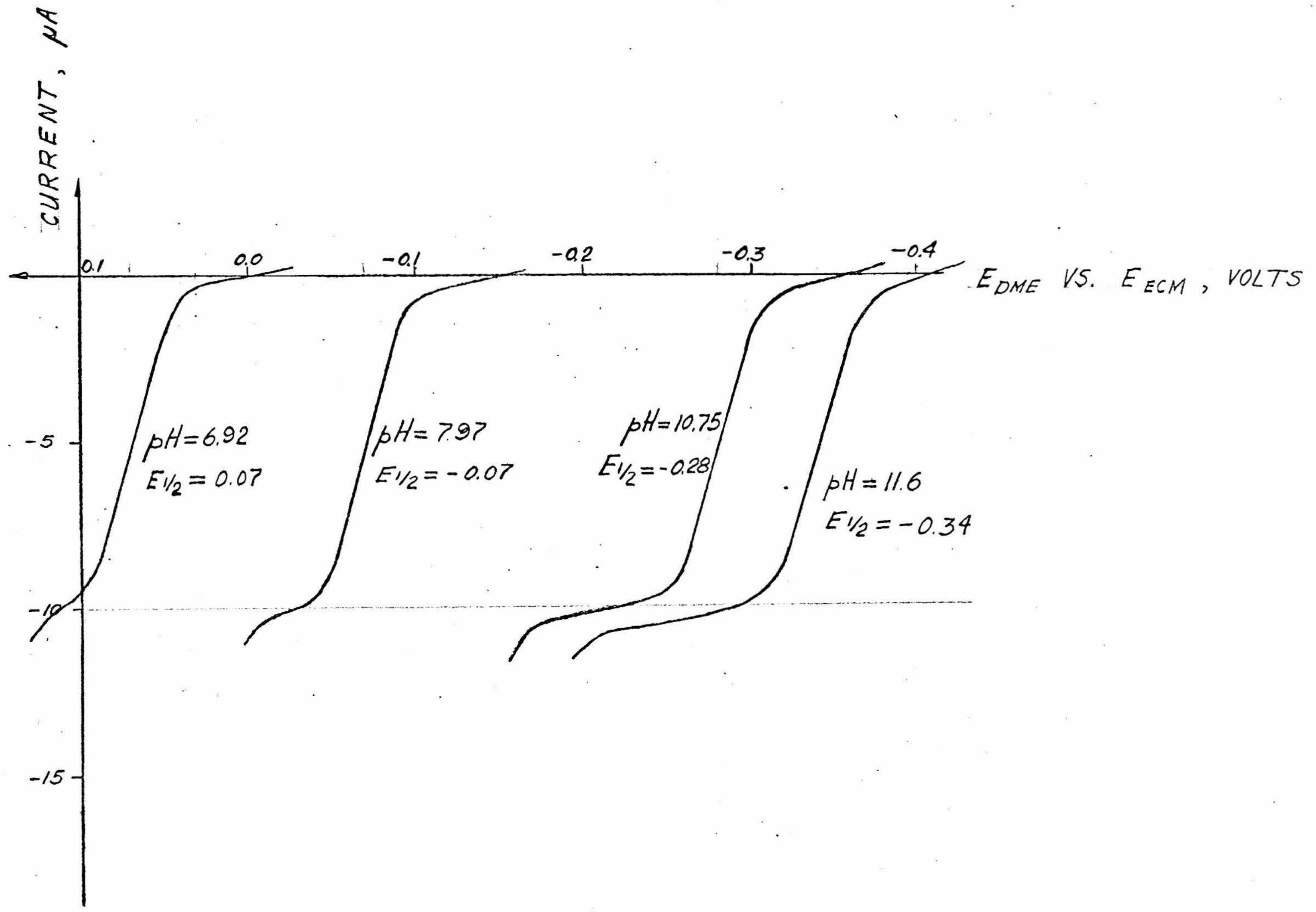

FIG. 3 pH DEPENDENCE OF $E_{1/2}$ FOR SFS IN BASIC MEDIA

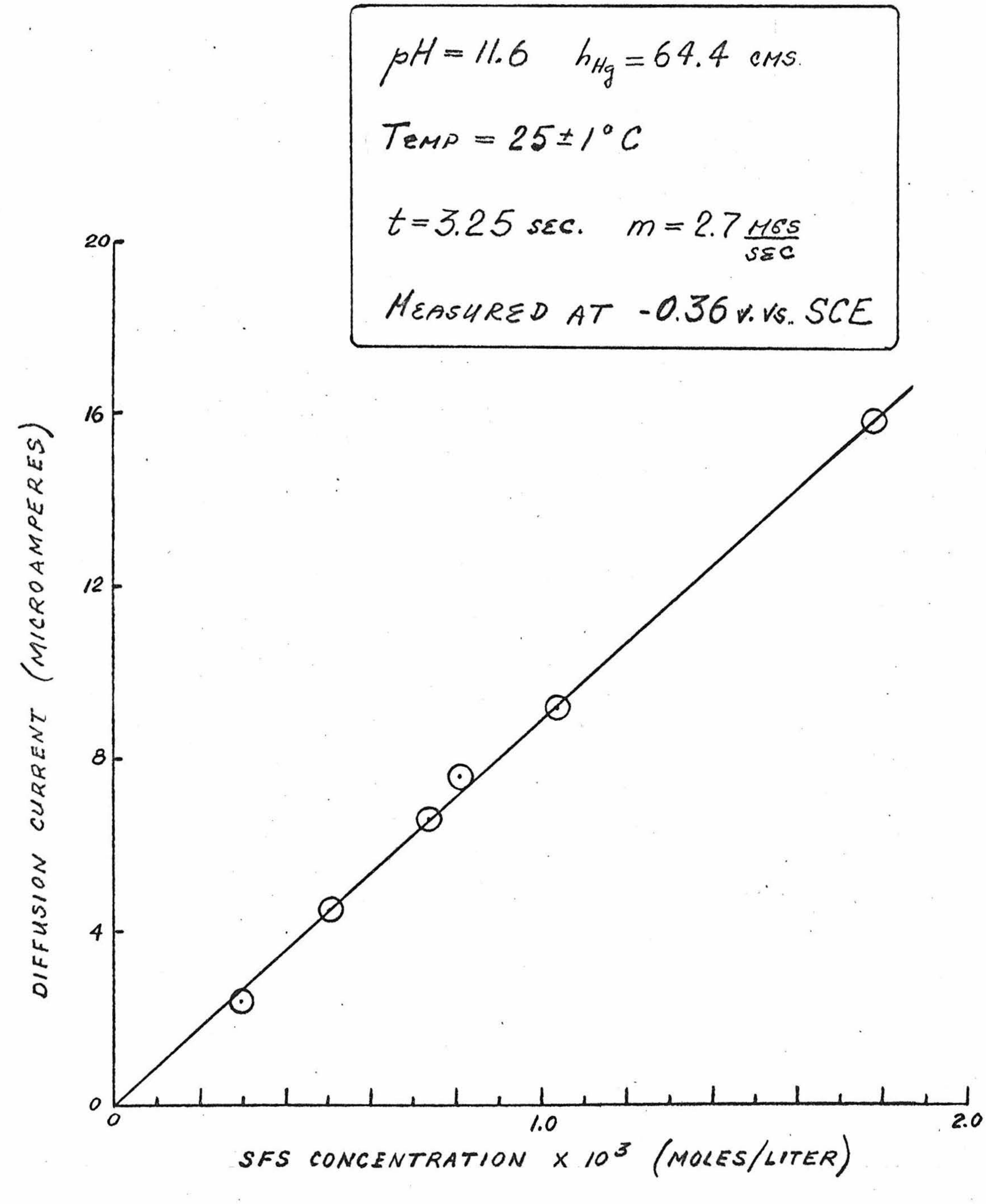

FIG. 4. DIFFUSION CURRENT VS. SFS CONCENTRATION

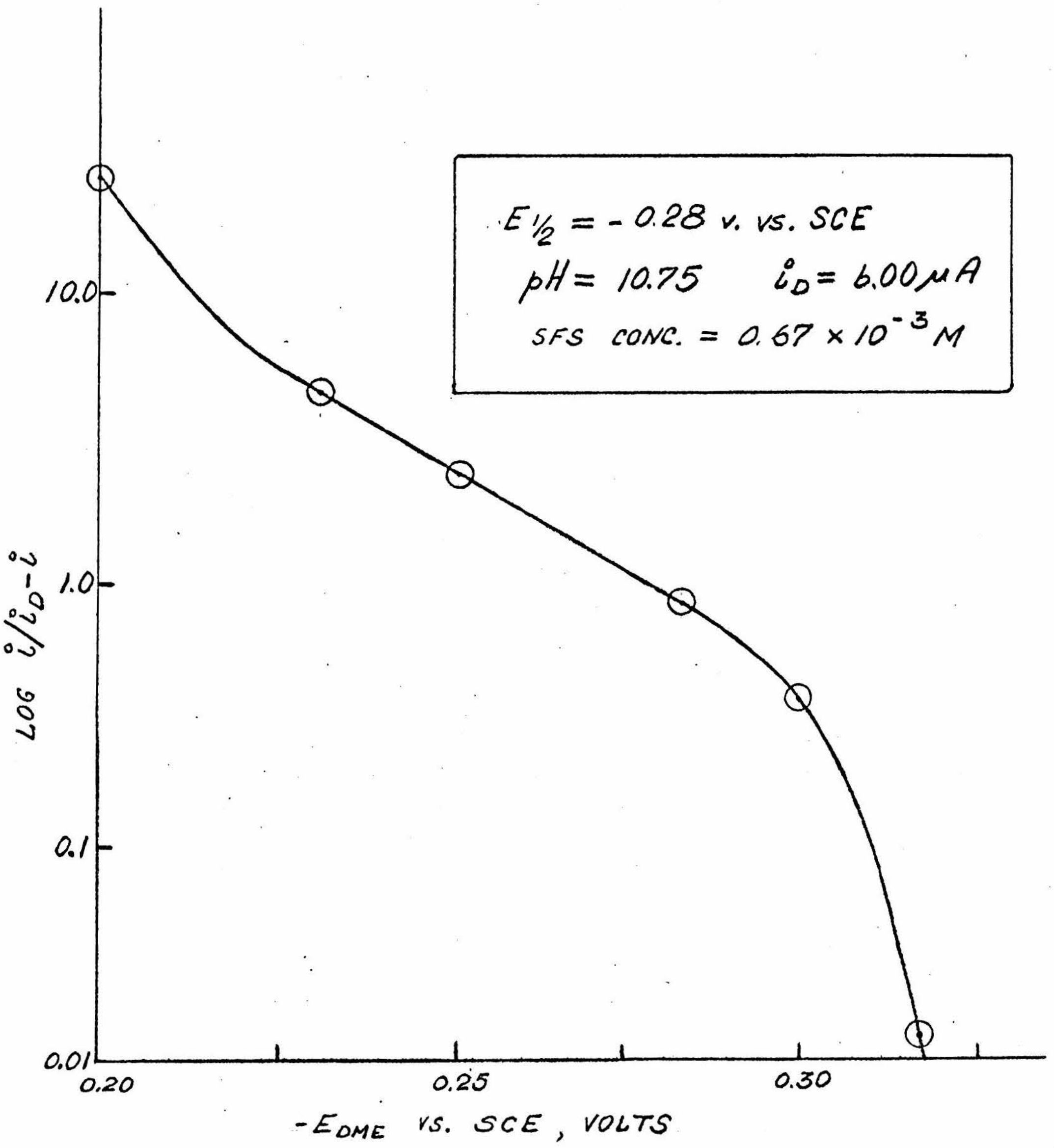

FIG 5. LOG i/i_D-i VERSUS ELECTRODE POTENTIAL

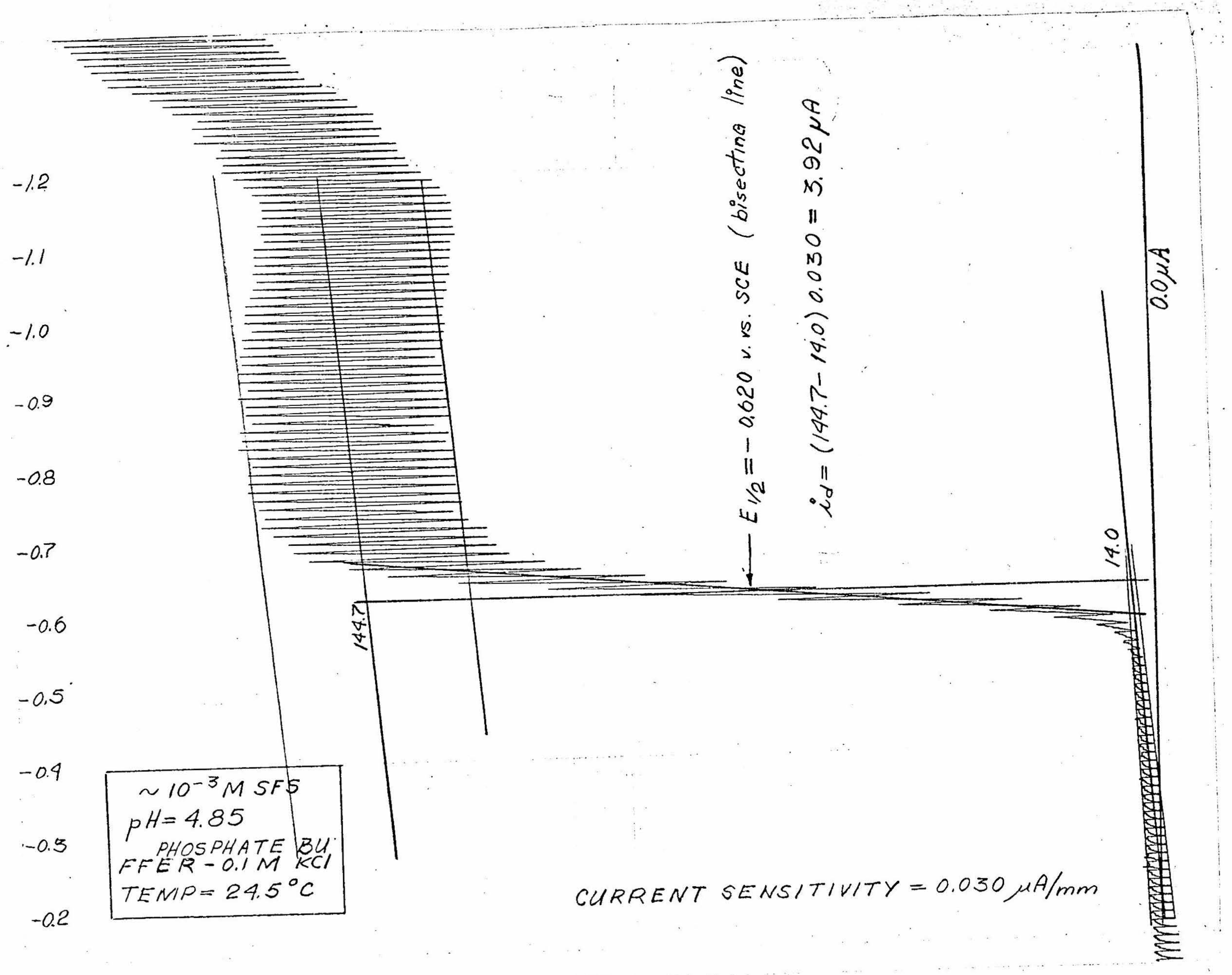

FIG. 6 TYPICAL RECORDED WAVE