

VARIATION OF THE HALF-WAVE POTENTIAL OF ORGANIC COMPOUNDS WITH pH

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INTRODUCTION

The importance of potential-pH relations in understanding and utilizing the oxidation-reduction behaviour of inorganic species has long been recognized. However, due to the fact that few organic redox systems behave reversibly, valid potentiometric data have been obtained for only a limited number of organic compounds. Where such data have been systematically gathered and analysed, the results have been fruitful as can be seen from the work of Michaelis, Clark and their collaborators.

Attempts to obtain potentiometric data on irreversible redox processes involving organic compounds led to the introduction of potential mediators and catalysis, and to the concepts of "apparent reduction potential" (Conant) and of "critical oxidation potential" (Fieser) as the energetic parameters with which to work.

The preceding work on organic systems was largely centred in the nineteen-twenties and early thirties. It is of interest that the discontinuance of large-scale potentiometric studies of organic compounds coincides with the beginning of interest in using polarography for investigating their oxidation-reduction behaviour. One need not speculate at the moment on whether a causal relation is involved. It should, nevertheless, be mentioned that the introduction of the concept of half-wave potential, $E_{1/2}$, in polarography (1935) and the recognition of its importance as an energetic parameter characterizing the electrode process and of its relation with the potentiometrically determined standard potential (E^0) doubtlessly contributed to a realization of the connection between the two techniques. In many cases, half-wave potential data on organic compounds, where they can be secured, are the only energetic data readily obtainable by electrochemical measurement. For this, and for other reasons, $E_{1/2}$ data have become of considerable interest in connection with various studies of the nature and properties of organic compounds, including the development of polarographic methods of analysis.

As in the case with E^0 -pH relations, $E_{1/2}$ -pH relations have been useful in elucidating the effect of hydrogen ion (and, in general, of proton donor species) on the redox behaviour of organic compounds, particularly in connection with the understanding of electrode processes from both mechanistic and kinetic points of view.

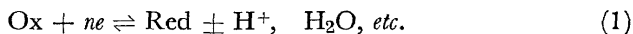
A number of excellent reviews on organic polarography have discussed the effect of pH on $E_{1/2}$, e.g., those by Müller¹, Gardner and Lyons², and

Mairanovskii³; however, none is particularly concerned with the detailed examination of the nature of $E_{1/2}$ -pH relations as is the present paper.

Rôle of hydrogen ion in an organic electrode process

Fundamentally, organic electrode reactions involve a one- or two-electron transfer, which, in the case of a reduction, results in the rupture of a bond between two atoms at the reactive centre. The resulting product is a free radical or an anion, which is frequently a carbanion; in some cases, the free radical is further reduced to an anion. The anion formed in either case usually neutralizes its charge by reaction with a Lewis acid, which in aqueous solution is typically hydrogen ion. Since bond rupture frequently necessitates the addition of protons as well as of electrons, an additional complication is correspondingly introduced into the over-all electrode process even in the reduction of neutral non-proton-releasing and -adding molecules.

The usual simplified and schematic representation of an organic electrode reaction[†],



obviously does not adequately account for the rôle of hydrogen ion in connection with both current and potential phenomena. Among the ways in which hydrogen ion may participate in the potential-determining step are the following:

(i) Reaction with the chemical system and electrons at the reaction, *e.g.*, reduction, site, the sequence of elementary acts (electron addition, protonation) being often pH-dependent.

(ii) Control of the state of reactants and/or products, *e.g.*, in acid-base equilibria involving the electroactive species (including protonation of neutral molecules) or through catalytic effects on chemical reactions involving reactants or products.

(iii) Chemical polarization of that bond in the electroactive species which is ruptured in the electrochemical process; this process may obviously be considered as part of an acid-base equilibrium, *e.g.*, in formation of a Lewis acid-base adduct.

In addition, the possible effects of pH on kinetic, steric, double layer structure and other phenomena have to be considered, in attempting to account for the rôle played by hydrogen ion in determining the potential of organic depolarizers.

Considerable effort has been expended in the derivation of equations relating the variation of the $E_{1/2}$ of organic compounds with pH. These equations have attempted to account for protonation of the electroactive species at the time of electron-transfer or preceding it, protonation of the product, other chemical reactions preceding and following electron transfer, successive proton dissociation-addition equilibria, and the relative rates of the protonation and electron transfer processes, *e.g.*, *cf.* Delahay⁴.

[†] Half-reaction or half-cell reaction equations are written as reductions, *e.g.*, $\text{Ox} + ne = \text{Red}$, with a positive potential indicating an equilibrium to the right as compared to the hydrogen ion reduction half-reaction equation. Thus, $E_{1/2}$ for the reduction of Na(I) is *ca.* -2.1 V *v.* SCE. (Potentials will generally be stated *v.* the saturated calomel electrode, SCE.)

The results of such analyses have been of varying usefulness due to the difficulties involved, the most prominent of which are the following:

(i) Uncertainties in the assumptions made in deriving the equations, *e.g.*, the definition and the thickness of the reaction layer around the electrode.

(ii) Lack of specificity in the equations themselves, *e.g.*, the experimental $E_{1/2}$ -pH relationships may be equally well represented in some cases by equations based on the proton adding either simultaneously with the electron or before it.

(iii) Uncertainties in the experimental data due not only to the error in measuring $E_{1/2}$ but also to the failure to control properly pertinent experimental conditions.

Definition of pH

The evolutionary significance of the pH concept has been described by Bates⁵, who has indicated the present uncertainty in the precise interpretation of the experimental value and has defined the conditions necessary for a fundamental interpretation. For the present discussion, it will suffice to consider pH in a purely operational sense, *e.g.*, as the experimental response of the glass electrode in aqueous media under properly standardized conditions of measurement. The effect of altering the medium by the incorporation of non-aqueous solvents is considered in the subsequent section on solvent effects.

The effective pH in the electrode-solution interfacial region may differ from that in the bulk of the solution as a result of the alteration of the distribution of charged species in the neighbourhood of the electrode surface due to the potential drop in the diffuse part of the electrical double layer. Thus, Mairanovskii³ has calculated that the pH at the electrode surface for a 0.1M solution of a 1:1 electrolyte at an electrode potential of -1.5 V *v.* SCE, may be as much as two units lower than in the bulk solution.

Reversible and irreversible processes

Our present understanding of the nature of electrode process has made the common division in the polarographic literature of electrode reactions into the two categories, "reversible" and "irreversible", unnecessary and perhaps to a certain extent erroneous. There is no fundamental difference between reversible and irreversible electrochemical reactions; the question is rather related to the magnitudes of the kinetic constants of the steps in the over-all electrode process. That is, since the physical transfer of an electron *per se* is extremely rapid, a slow electron-transfer process must be due to accompanying slow "chemical" processes, *e.g.*, alteration in molecular (or functional group) configuration preceding the physical electron transfer such as polarization due to hydrogen bonding. Thus, if the electrolytic reaction product of a reversible electrode reaction is unstable and is irreversibly transformed to another compound, the net reaction is irreversible⁶.

Reversibility is generally ascribed to electrode processes, for which, under the particular experimental situation and conditions of observation, no kinetic factor actually affects the equilibrium between electrode and solution.

As a matter of fact, whenever such kinetic factors as are capable of affecting the reversibility, *e.g.*, mass transfer or accompanying chemical processes, can be taken into account, the electrode process, or at least part of it, may still be described as reversible. Operationally, a half-reaction may be classed as "reversible", if within the error of experimental measurement, its behaviour under the experimental conditions follows the Nernst equation.

Since no reaction has an infinite rate constant, any reaction may—at least, in principle—appear to be irreversible when examined under conditions where the reaction is unable to maintain equilibrium concentrations. Furthermore, the reversibility of the electrode process depends not only on such factors as are related to the physicochemical properties of the electrode-solution system (structural properties of the depolarizer, environmental conditions, *e.g.*, pH, solvent and buffer—and nature of the electrode material), but also on the type of investigative technique used, *e.g.*, the magnitude and rate of disturbance from the equilibrium time, and the conditions of observation. A number of criteria have been proposed for polarographic reversibility, without there being unanimity of opinion regarding which are preferable or even generally applicable. Nevertheless, a few organic systems are generally considered to be polarographically reversible. (Probably the most commonly accepted criterion for polarographic reversibility is that proposed by Delahay, *i.e.*, the specific heterogeneous rate constant must exceed $2 \times 10^{-2} \text{ cm sec}^{-1}$ for typical polarographic conditions at the DME ($D = 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$; $t = 4 \text{ sec}$); *cf.* subsequent discussion of electrode kinetics.)

With these restrictions in mind, processes, which have been actually observed to behave reversibly under polarographic and voltammetric conditions, may be treated separately from irreversible processes.

Scope of the discussion

The subsequent discussion and the examples cited refer primarily to aqueous solutions or to solution media in which water predominates. Generally, the statements made and the conclusions drawn are equally valid for non-aqueous media in which the hydrogen ion may still play a rôle or in which the effect of the proton presenting itself as the hydrogen ion is replaced by some other Lewis-type acid.

It is apparent from even a superficial inspection of the literature that the polarographic behaviour of substances showing a pH-dependent $E_{1/2}$ often varies greatly in respect to both potential and current phenomena between unbuffered, poorly-buffered and well-buffered solutions. A number of investigations has been concerned with the importance of buffering and the variations in behaviour that are observed as the degree of efficiency of buffering is lessened, *e.g.*, Müller has considered some of the possible effects for reversible systems in inadequately buffered solution (pages 3218–22 of ref. 1) and Kolthoff and Orlemann⁷ have evaluated the effect of hydrogen ion production or consumption in poorly poised reversible systems. In the present study, in order to keep the problem within well-defined limits, stress will be placed on data obtained in well-buffered solution, primarily due to the difficulty of interpretation of data obtained in poorly buffered media. For example, reduction of a species by a pH-dependent process in an

inadequately buffered system may show a concentration-dependence of $E_{1/2}$ due to the varying depletion of hydrogen ion at the electrode surface with varying concentration of electroactive species, *e.g.*, pages 250–3 of ref. 8.

In addition, the present discussion primarily refers to the dropping mercury electrode (DME) since most of the literature involves such electrodes. Analogous results are obtained with other electrodes except for the special case where the particular reactive chemical nature of the electrode is involved, *e.g.*, occurrence of specific chemisorption. In this connection, the ability of mercury electrodes to react with some organic substances, *e.g.*, disulphides, with buffer components, *e.g.*, halogen ions, or with the solvent needs to be carefully considered.

Thirdly, the focus will be on reduction processes since these have been the ones predominantly investigated at the DME. Analogous arguments would be applicable to oxidation processes after allowance is made for the change in direction of electron transfer. It is pertinent to note that hydrogen ions will frequently be found on the same side of the half-reaction equation as electrons due to the demand for electrical balance in the reaction.

Whenever concentration terms such as those involving oxidant, reductant and hydrogen ion participants in the half-reaction



i.e., $[\text{Ox}]$, $[\text{Red}]$ and $[\text{H}^+]$, are used in equations, they refer to concentrations in the interfacial solution–electrode region. However, for convenience of discussion they will customarily be assumed to approximate—at least in the case of the reactants—the bulk concentrations of these species. Some possible dangers inherent in this assumption will be subsequently considered.

The discussion will stress three areas, which are of importance in defining the essential problem, the necessary experimental approach and some of the implications: (a) The experimentally observed patterns of $E_{1/2}$ -pH variation for reversible and irreversible systems, (b) the structural, mechanistic, kinetic and environmental factors determining such variation, and (c) the utilization of $E_{1/2}$ -pH relations for the development of analytical procedures and the correlation of half-wave potential data.

REVERSIBLE SYSTEMS: $E_{1/2}$ -pH RELATIONS

It has long been recognized that, in the case of reversible organic redox systems, the half-wave potential ($E_{1/2}$) is directly related to the potentiometrically determined standard potential (E^0) or formal potential (E_c^0) in spite of the small but appreciable net current flow under polarographic conditions. It is apparent from the well-known relations,

$$E_{1/2} = E^0 - \frac{RT}{nF} \ln \frac{D_0^{1/2} f_R}{D_R^{1/2} f_0} = E_c^0 - \frac{RT}{2nF} \ln \frac{D_0}{D_R} \quad (3)$$

in which D and f represent the diffusion and activity coefficients, respectively, of the species indicated and the other terms have their usual meaning, that the only way in which E_c^0 and $E_{1/2}$ may differ would be due to a difference

between the diffusion coefficients of the oxidized and reduced forms (*cf.* subsequent discussion of ionic strength and solvent effects). The effect of pH on $E_{1/2}$ should, therefore, be the same as that on E_c^0 , apart from a possible differential effect of pH on the magnitudes of the diffusion coefficients.

In order to account for the observed $E_{1/2}$ -pH patterns, it would be enough to explicate the E_c^0 term in equation (3) in the general form,

$$(E_c^0)_{\text{pH}} = (E_c^0)_{\text{ref.}} - \frac{RT}{nF} \ln \frac{\phi([\text{H}^+], K_{\text{ri}})}{\psi([\text{H}^+], K_{\text{oi}})} \quad (4)$$

where $(E_c^0)_{\text{pH}}$ is the formal potential at the specific pH, $(E_c^0)_{\text{ref.}}$ is that at some reference pH (usually 0), and K_{ri} and K_{oi} are the apparent equilibrium constants for the acid-base dissociation of the reduced and oxidized forms, respectively.

The following equation for $E_{1/2}$ -pH variation is then obtained from equations (3) and (4) on the assumption that the diffusion coefficients are pH-independent,

$$(E_{1/2})_{\text{pH}} = (E_{1/2})_{\text{ref.}} - \frac{RT}{nF} \ln \frac{\phi([\text{H}^+], K_{\text{ri}})}{\psi([\text{H}^+], K_{\text{oi}})} \quad (5)$$

where $(E_{1/2})_{\text{ref.}}$ is the half-wave potential at the reference pH.

Equation (5) will naturally assume particular forms according to the number and values of the constants of the acid-base equilibria involving the reduced and oxidized forms. Clark⁹ has systematically summarized the equations relating half-reaction potential and pH for various reversible systems in respect to stages of protonation for processes involving the coupling of electron transfer with proton transfer.

In general, the experimental behaviour of organic redox systems can be described by particular forms of the following equation (adapted for polarography from that given by Clark for potentiometry),

$$E_{1/2} = E_c^0 - \frac{RT}{nF} \ln \frac{[\text{H}^+]^y + K_{\text{oi}}[\text{H}^+]^{y-1} + K_{\text{oi}}K_{\text{oi2}}[\text{H}^+]^{y-2} + \dots + K_{\text{oi}}K_{\text{oi2}}\dots K_{\text{oiy}}}{[\text{H}^+]^x + K_{\text{ri}}[\text{H}^+]^{x-1} + K_{\text{ri}}K_{\text{ri2}}[\text{H}^+]^{x-2} + \dots + K_{\text{ri}}K_{\text{ri2}}\dots K_{\text{rix}}} \quad (6)$$

If the numerical values of the dissociation constants differ greatly, the graphical representation of equation (6) generally consists of straight-line portions of differing slopes, with more or less curved inflection regions. The pH of the extrapolated intersection point of two consecutive linear portions is directly related to the $\text{p}K$ of the oxidized or reduced forms, depending on the direction of variation of the slope of the linear portions. If, on passing through such an intersection point, the slope of a linear segment, defined by $-(\Delta E_{1/2}/\Delta \text{pH})$, changes to a smaller value with increasing pH, the $\text{p}K$

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pertains to the reductant; if the slope changes to a higher value, the p*K* pertains to the oxidant. The slope of each linear portion is related to the ratio of protons:electrons in that pH region.

Thus, the linear potential-pH relation obtained potentiometrically for equal concentrations of the participants in the reversible redox system, alloxan-dialuric acid, shows inflections at pH 2.83, 7.20 and 10.0, corresponding to K_1 for dialuric acid and K_1 and K_2 for alloxan, respectively¹⁰. An example of an $E_{1/2}$ -pH plot which shows an inflection at p*K* is that for the reversible system involving 4-amino-2-methyl-1-naphthol¹¹.

Based on the relatively clear-cut approach to the potentiometric potential-pH relations of organic half-reactions, a considerable number of equations on the expected $E_{1/2}$ -pH relations of organic compounds have been derived for various situations, each involving different assumptions regarding the acid-base nature of the participants in the half-reaction. In excellent reviews of organic polarography, Müller¹ has summarized the relationship of potentiometric and polarographic measurements for reversible systems with a number of interesting examples of $E_{1/2}$ -pH relations, and Gardner and Lyon² have considered in some detail such relations. In general, the equations relating $E_{1/2}$ to pH for reversible systems are, as might be expected, analogous to those summarized by Clark⁹ for potentiometric measurements of the effect of pH on reversible organic half-reactions and represent special cases of equation (6). Some of the conclusions developed are important for the light they cast on the study of the mechanisms of organic electrode processes.

For example, where the oxidant, R, is reduced in a reversible n -electron process to the reductant, R^{2-} , which is the dianion of an acid of dissociation constants K_1 and K_2 , the following equation applies if the diffusion coefficients of R and R^{2-} are assumed to be essentially the same,

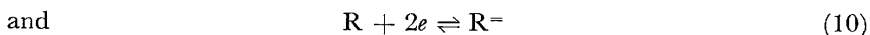
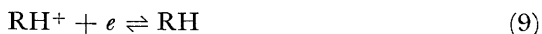
$$E_{1/2} = E_c^0 + \frac{RT}{nF} \ln ([H^+]^2 + K_1[H^+] + K_1K_2) \quad (7)$$

and $\Delta E_{1/2}/\Delta pH$ equals 0.059 V/pH unit at 25°. If, however, R is in equilibrium with a protonated form of dissociation constant K ,

$$E_{1/2} = E_c^0 - \frac{RT}{nF} \ln \frac{[H^+] + K}{K[H^+]} \quad (8)$$

It is evident in the latter case that if $[H^+] \ll K$, $\Delta E_{1/2}/\Delta pH = 0.059$; if $[H^+] \gg K$, $E_{1/2}$ is independent of pH.

Equations (7) and (8) result in the $E_{1/2}$ -pH plots shown in *Figure 1*². However, these plots are equally well represented by the analogous equations for the processes



Consequently, the $E_{1/2}$ /pH slopes do not serve to differentiate as to whether the proton is added before the electron or simultaneously with it.

Acidic dissociation removed from the electroactive site will also result

in the $E_{1/2}$ -pH curve showing inflection points for the pK values of both oxidant and reductant systems.

Clark and Cohen¹² were apparently the first to demonstrate the possibility of determining the dissociation constants of the reductant or oxidant from plots of E_c^0 against pH. Such plots are more readily obtained polaro-

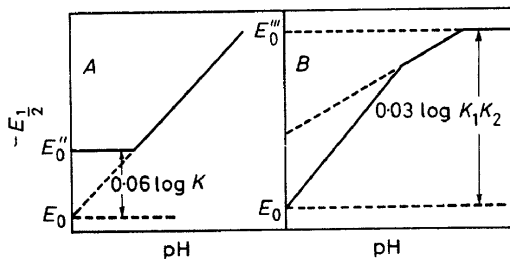


Figure 1. $E_{1/2}$ -pH relations for (A) single dissociation of oxidant ($n = 1$); and (B) double dissociation of reductant ($n = 2$). E_0'' refers to the half-reaction of equation (9) in the text; E_0''' to that of equation (10)

(By courtesy of H. J. Gardner and L. E. Lyons. *Revs. Pure Appl. Chem. (Australia)* 3, 134, 1953)

graphically than potentiometrically, since $E_{1/2}$ can be taken as equal to E_c^0 for any bulk solution concentrations of oxidant and/or reductant.

The effects of semiquinone formation on potential-pH plots and het calculation of the formation and dimerization constants of the free radical species are discussed by Clark⁹. Similar effects would be expected in reversible polarographic processes, which can proceed through two $1e$ steps and in which the product of the first electron transfer process can dimerize. Free radical formation and/or dimerization in the course of the electrochemical process can give rise to particular shapes of the polarographic (as well as of the potentiometric) curve and of the $E_{1/2}$ -pH pattern. The situation is often complicated by the fact that organic depolarizers, which give rise to more-or-less stable free radicals in the course of the electrochemical process, may be adsorbed on the electrode.

As previously noted, there are a limited number of organic redox systems showing polarographic reversibility, *e.g.*, the quinone-hydroquinone system, the analogous *p*-phenylenediamines, and the nitrosobenzene-phenylhydroxylamine system. Investigation of the $E_{1/2}$ -pH relations for such systems has been important, because the knowledge thus obtained of the fundamental implications of hydrogen ion in the organic electrode process has helped in understanding the effect of pH in irreversible processes.

Experimentally, in spite of the limited number of examples for which polarographic and potentiometric potential-pH data are in satisfactory agreement, there seems to be no doubt that the effect of pH is basically the same in both cases. Whenever a disagreement has been observed, investigators have generally been able to account for it on the basis, *e.g.*, of chemical or adsorption phenomena or of a differential effect on diffusion coefficients. However, the utmost caution should be used in applying the equations derived for reversible systems to irreversible ones, since misleading deductions, *e.g.*, concerning the number of protons involved in the half-reaction, may result.

The many pitfalls possible in an overly naïve interpretation of potential-pH curves are delightfully and instructively described by Clark⁹, whose book cannot be too highly recommended to anyone interested in $E_{1/2}$ -pH relations or, for that matter, to anyone interested in a critical approach to experimental data.

IRREVERSIBLE SYSTEMS: $E_{1/2}$ -pH RELATIONS

Most organic electrochemical reactions, similar to most organic reactions in homogeneous solution, are irreversible inasmuch as chemical and electrochemical rate phenomena often predominate over thermodynamic effects. Consequently, the potential for an irreversible half-reaction is a function not only of the effective concentrations of the reactants (including hydrogen ion, when it is a primary reactant) but also of the kinetics of the electrochemical—as well as perhaps of the chemical—reactions involved, of such secondary processes as adsorption of reactant or product on the electrode surface, and, naturally, of experimental conditions which affect the preceding. Although the causes of irreversibility are varied, they must be regarded as particular effects of the general scheme of an organic electrode process. The most important phenomenon is frequently the apparent rate of the electron transfer process (*cf.* subsequent discussion of electrochemical kinetics).

Before considering the most important factors controlling the variation of $E_{1/2}$ with pH, the experimentally observed types of variation will be discussed.

Observed patterns of $E_{1/2}$ -pH variation

The variation of $E_{1/2}$ with pH for organic systems undergoing reversible oxidation-reduction under polarographic conditions, is, as already discussed, essentially analogous to that revealed by potentiometric studies. Reasons for the more complex variation seen in the case of irreversible electrode processes have been indicated.

pH-Independent potentials

Several types of organic electrochemical processes show pH-independent half-wave potentials, *e.g.*, reduction of the carbon-carbon double bond in phenyl-substituted ethenes^{13, 14}. Normally, after the effects due to change in the general state of the molecule with varying pH are removed, the electrochemical fission of carbon-halogen bonds, where the halogen is chloride, bromine or iodine, is a pH-independent process, *e.g.*, as in the 2-halo esters^{15, 16}. The slight pH-dependency of C-Cl bond fission in appreciable acidity¹⁷ and the variation of $E_{1/2}$ with pH for C-F bond fission below¹⁸ pH 6 serve to indicate a general way in which hydrogen ion concentration may affect the $E_{1/2}$, bridging the transition from pH-independence to strong dependency.

The case of the phenyl-substituted olefins, which are generally accepted to show pH-independence of $E_{1/2}$ over the limited pH range in which these compounds can be investigated, raises the important question of how extensive a pH range needs be studied before a comprehensive statement concerning the pH independence of $E_{1/2}$ can be made. Generally, because of the

prior reduction of hydrogen ion in acidic media, difficultly reducible systems cannot be studied in such media where the effect of proton activity on the electrode reaction would be most readily observed. Consequently, the experimental evidence is actually only that the reduction is independent of pH within the pH region, for which the bond fission is observable and which is characterized by very low hydrogen ion activity.

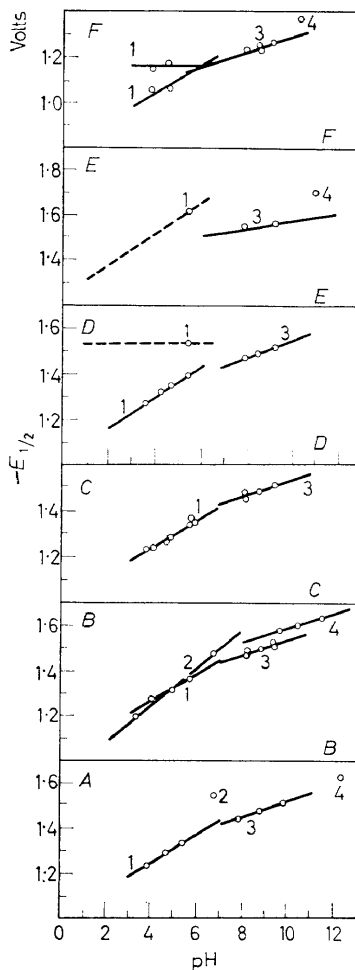


Figure 2. Variation of $E_{1/2}$ with pH for the electrochemical reduction of ketones: A, acetophenone; B, propiophenone; C, n-butyrophenone; D, isobutyrophenone; E, pivalophenone; and F, benzophenone. Numbers refer to the buffer systems: 1, acetate; 2, citrate; 3, ammonia; 4, phosphate

(From reference 19, courtesy of the *Journal of the American Chemical Society*)

The difficulty of deciding whether a given polarographic wave is pH-independent is well illustrated by the second wave observed for the reduction of the ketone carbonyl group in acidic media, which the present author in company with others has reported to be pH-independent¹⁹, e.g., Figure 2.

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However, a very careful reinvestigation²⁰ of this wave for benzophenone revealed a slight pH-dependence (Figure 3), which, when observed in the past, has been assumed to be due to experimental error, since the $E_{1/2}$ for an irreversible polarographic wave can seldom be reproduced to better than ± 10 mV. It is easy to see how this factor, when combined with observation over a limited pH range, might lead to error.

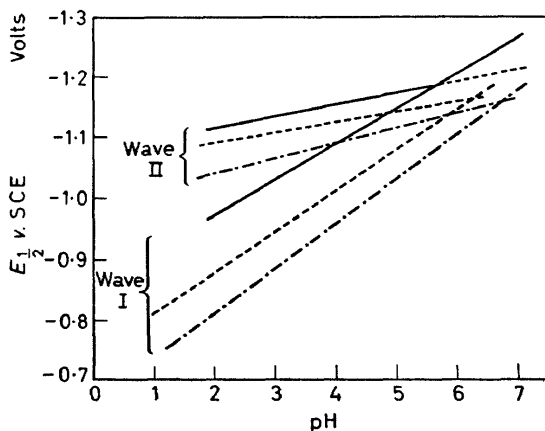


Figure 3. Variation of $E_{1/2}$ with pH for benzophenone (solid line, 38% EtOH; short dash line, 19% EtOH) and *p*-bromobenzophenone (long dash line, 19% EtOH)

(From reference 20, courtesy of the *Journal of Physical Chemistry*)

pH-Dependent potentials

The more important types of patterns observed when $E_{1/2}$ does vary with pH, are discussed in the following sections.

(i) *Linear variation*— $E_{1/2}$ for the first stage of ketone reduction in acidic medium (the reduction of carbonyl group to the free radical) varies linearly with pH^{14, 20}, e.g., wave I of Figures 2 and 3. $E_{1/2}$ for the first wave of the polyene aldehydes also varies linearly with pH with a slope of -0.06 V per pH unit²¹.

Such linear variation is equivalent to a Nernst-type of relationship, in which the potential depends on a term, which is the product of a constant and the logarithm of the hydrogen ion activity. Presumably, it should then be possible from the slope of the linear relation to determine the stoichiometric rôle of hydrogen ion in the controlling process.

Unfortunately, such calculations, which are not infrequently encountered in the literature, are somewhat questionable when an irreversible system is involved. For a reversible system, the slope of the $E_{1/2}$ -pH plot at 25°C equals $0.0591 m/n$, where m is the number of hydrogen ions participating in the half-reaction involving the transfer of n electrons; n is usually readily determined. In the case of an irreversible system, the slope involves the term $m/\alpha n$, (cf. subsequent discussion), where the value of α is most commonly unknown even when n can be assumed to be 1 or 2. Although the latter slope is generally given in the literature as $0.0591 m/\alpha n$, it is evident from Meites' considerations²² that the numerical term should be 0.0542 if maximum currents are measured.

(ii) *Sigmoidal variation*—An S-shaped variation of $E_{1/2}$ with pH may indicate a linear variation of the potential with hydrogen ion activity. Such a relationship would not be due, in general, to the hydrogen ion activity affecting the potential through a Nernst-type relationship but through a relationship which depends upon some other type of mass action effect.

Such sigmoidal variations are seen in a variety of organic electrochemical processes, *e.g.*, reduction of the aliphatic nitro group to either hydroxylamine or amine²³⁻²⁵ and fission of the C-Br bond in the 2-bromo acids^{26, 27}, *e.g.*, Figures 4 (where straight lines have been drawn simply as a matter of convenience) and 5. Examples of such variations and possible causes for them will be subsequently discussed.

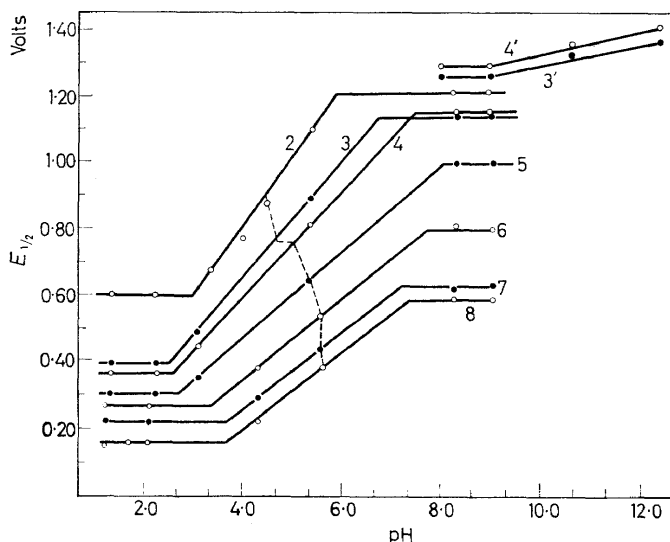


Figure 4. Variation of $E_{1/2}$ with pH for the 2-bromo-*n*-alkanoic acids; the numbers indicate the number of carbons in the parent acid; the dotted tie-line joins the midpoints of the S-shaped curves

(From reference 27, courtesy of the *Journal of the Electrochemical Society*)

(iii) *Other patterns*—Other types of $E_{1/2}$ -pH patterns, in addition to the two mentioned, have been observed. At least some of these are due to the fact that only part of the sigmoidal relation curve may be attainable within the usable range of pH. In extreme cases only a linear section of the rising portion or of either horizontal portion may be observed; such a situation might lead to an erroneous interpretation of the rôle of hydrogen ion in the half-reaction under consideration.

In some cases, the observed $E_{1/2}$ -pH pattern is obviously a composite one, *e.g.*, that for fumaric acid (Figure 6) seems to consist of a linear relation which then changes into a sigmoid one, probably as a result of the change in nature of the electroactive species (pK_a values for fumaric acid are 3.0 and 4.4).

An example of the difficulty of deciding whether a given $E_{1/2}$ -pH relation is an S-shaped curve, a group of intersecting lines or a combination thereof,

VARIATION OF $E_{1/2}$ OF ORGANIC COMPOUNDS WITH pH

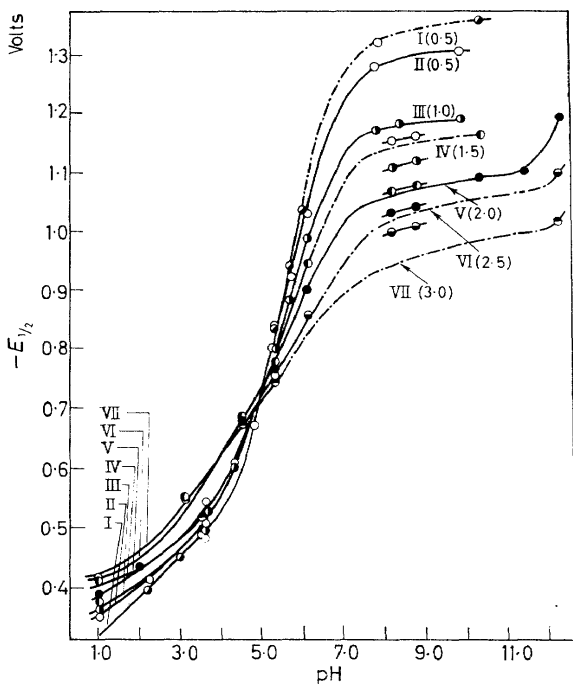


Figure 5. Variation of $E_{1/2}$ with pH for 2-bromobutyric acid; arabic numbers in parenthesis indicate ionic strength

(From reference 26, courtesy of *Analytical Chemistry*)

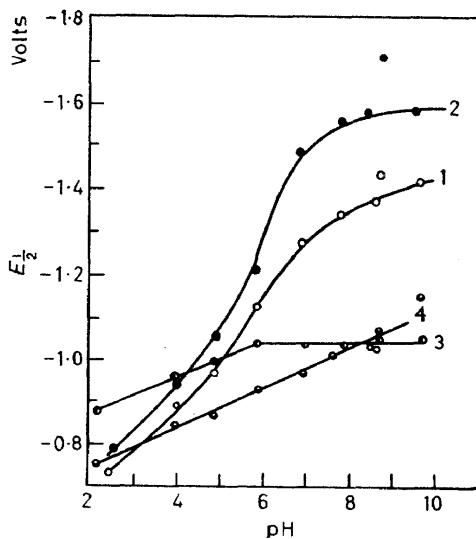


Figure 6. Variation of $E_{1/2}$ with pH: 1, maleic acid; 2, fumaric acid; 3, diethyl maleate; 4, diethyl fumarate

(From reference 28, courtesy of the *Journal of the American Chemical Society*)

is evident from the plots of the data for the diethyl esters of maleic and fumaric acids reported by the present author in two studies published six years apart^{28, 29} (Figures 6 and 7).

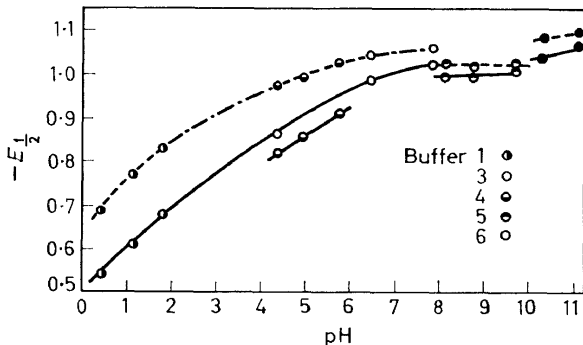


Figure 7. Variation of $E_{1/2}$ with pH: solid line, diethyl fumarate; broken line, diethyl maleate (From reference 29, courtesy of the *Journal of the American Chemical Society*)

FACTORS DETERMINING VARIATION OF $E_{1/2}$ WITH pH

Participation of hydrogen ion in the essential step of the reaction

The fundamental cause of variation of $E_{1/2}$ with pH would be the participation of hydrogen ion in the essential potential-determining step.

For example, in some reductions the order of addition is H^+ , e , e , H^+ with the first electron adding essentially simultaneously with the first proton. However, the possibility exists in many reductions, *e.g.*, those of carbonyl and nitro groups, that the participation of hydrogen ion in the potential-determining step is due to a preprotonation of the organic species R to form the (generally more readily reducible) species RH^+ . Such surface preprotonation is favoured when the electroactive centre in the organic molecule contains an electronegative atom such as nitrogen, oxygen or sulphur having an available lone pair of electrons and when the medium contains an appreciable proton activity as in acidic solution. Resulting formation of a hydrogen bond would tend to polarize the bond connecting the electronegative atom to its neighbour.

A question may be raised as to the ability to distinguish the preprotonation process from one in which the proton participates by simultaneously polarizing the bond to be broken as the latter bond is distorted when the organic species comes into the field of the electrode (*e.g.*, references 18, 19, 30). One obvious instance of the existence of the preprotonation phenomenon is in the case of kinetic-controlled currents, where the protonated form is more readily reduced than the non-protonated form and waves for the two forms may simultaneously appear; this situation will be subsequently discussed.

Variation in nature of species with pH

Reactant

An important cause of the observed variation of $E_{1/2}$ with pH for organic compounds is a change in the nature of the electroactive reactant due to

solution equilibria involving hydrogen ion and the species considered to be present, *e.g.*, that originally added. Since such behaviour may be superimposed on the participation of hydrogen ion in the potential-controlling step, two situations have to be considered: (a) the electrode process is intrinsically independent of pH, but a variation of $E_{1/2}$ with pH is observed due to variation in the nature of the electroactive species, and (b) a variation in the nature of the electroactive species with pH is superimposed upon an intrinsically pH-dependent electrode process.

(i) *pH-Independent $E_{1/2}$* —An example of the first type is seen in the reduction of the C—Br bond in the 2-bromo acids^{26, 27, 31, 32}, which exhibit a sigmoidal variation of $E_{1/2}$ with pH (Figures 4 and 5). The essential pH-independence of the C—Br bond fission can be verified by examining the behaviour of acid, anion and corresponding ester^{16, 33, 34}. $E_{1/2}$ of the ester is independent of pH and slightly more positive than that of its parent acid. In acidic solution of the acid there is a pH-invariant region of $E_{1/2}$ corresponding to reduction of the undissociated acid; in more alkaline solution, there is another pH-invariant region where the anion is being reduced at a much more negative potential. In the intermediate region, where both acid and anion are present in appreciable relative concentration, $E_{1/2}$ varies with pH.

Such a variation cannot be explained in terms of the classical pattern observed in the potentiometry of reversible redox systems or in the polarography of a compound such as pyruvic acid³⁵ where the difference in ease of reduction of acid and anion forms results in the appearance of two waves in the intermediate pH region, one due to acid and the other more negative wave due to anion. The relative heights of the waves at any one pH do not always correspond to the equilibrium concentrations of acid and anion due to the fact that, as the more easily reducible acid is being reduced, some of the anion present is converted to the acid form, resulting in the acid wave being greater than that corresponding to the equilibrium concentration of acid at the pH concerned and the anion wave being correspondingly less. It is possible that, if the rates of the dissociation-association process were very slow compared to the electrode reaction rates, the relative wave heights would indicate the equilibrium concentrations of acid and anion.

It is perhaps due to a similar conflict in rate processes that the midpoint of the sigmoidal variation of $E_{1/2}$ with pH for an acid for which only a single wave is observed occurs at a pH, which is somewhat greater than the pK_a value.

(ii) *pH-Dependent $E_{1/2}$* —Reduction of the isomeric maleic and fumaric acids involves an acid-anion equilibrium superimposed on a pH-dependent process^{28, 32}. The difference in the two effects can be qualitatively seen by comparing the variation of $E_{1/2}$ with pH for the acids and their esters (Figure 6). Although apparently satisfactory equations have been derived for the variation of the current heights with pH, the S-shaped relationships between pH and $E_{1/2}$ have not yet been entirely adequately explained.

The possible complications can be seen by considering the reversible case, where both oxidant and reductant are polyprotic species. Thus, in the reduction of a dibasic unsaturated acid to the corresponding saturated acid,



$E_{1/2}$ for a reversible system can be expressed as follows, assuming equal diffusion coefficients for the acid species,

$$E_{1/2} = E_c^0 + \frac{RT}{F} \ln (H^+) + \frac{RT}{2F} \ln \frac{(H^+)^2 + K_{r1}(H^+) + K_{r1}K_{r2}}{(H^+)^2 + K_{o1}(H^+) + K_{o1}K_{o2}} \quad (12)$$

where the subscripts "o" and "r" designate the dissociation constants of the unsaturated and saturated acids, respectively.

Since most experimentally studied systems involve irreversible processes with more complicated mechanisms than that indicated by equation (11) and with possibly appreciable rates of dissociation and association, it has not been frequently possible to derive equations of the type of equation (12), which will successfully describe the observed variation of $E_{1/2}$ with pH. However, the polarographic data do tend to show changes at pH values near, if not exactly at, pK values (*cf.* subsequent discussion of the reduction of maleic and fumaric acids in the section on analytical procedures).

(iii) *Miscellaneous*—Frequently, the change in the manner of dependence of $E_{1/2}$ on pH indicates the participation over a pH range of species protonated to different extents, *e.g.*, positively charged protonated acid form, uncharged acid form, and negatively charged conjugate base (*cf.* subsequent discussion of the effect of ionic strength).

Hydrogen bonding involving the electroactive species (intramolecular or with a solution species) will generally facilitate a reduction where the bond to be broken is that of the atom to which the proton bonds, since such bonding tends to weaken the bond to be severed, *e.g.*, reduction of the carbonyl group¹⁹. In some cases, hydrogen bonding may make the reduction more difficult through its effect on the electron density at the electroactive site, *e.g.*, *ref.* 36.

Product

A change in the nature of the product produced with varying pH may affect the $E_{1/2}$ because the nature of the activated complex, which helps determine the electrode potential, would differ as well as the final product. Several such cases will be briefly described to illustrate the types of phenomena observed.

A classical example is that of the nitrophenols³⁷. In acidic solution, the *ortho*, *meta* and *para* isomers are each reduced in an over-all $6e$ process to the corresponding aminophenol. In alkaline solution, the *meta* and *para* isomers are similarly reduced, but the *ortho* isomer is reduced in a $4e$ process to the hydroxylamine. The latter change is due to there being opportunity for hydrogen bonding in the *ortho* isomer between the oxygen and hydrogen atoms of the phenolic and partially reduced nitro groups, which serves to stabilize the product at the hydroxylamine stage; further reduction would probably not be observed until a potential is reached which is not obtainable in the background electrolytes used.

A more drastic alteration in product, as pH is varied, occurs with the aromatic *N*-nitrosohydroxylamines (cupferron and its analogues). In acidic solution, these compounds are reduced to the hydrazine by a $6e$ process³⁸.

In alkaline solution, the product is the corresponding hydrocarbon, resulting from a $5e$ process.

Another type of alteration of product with pH is observed in reduction of the *meso* and *racemic* α, α' -dibromosuccinic acids, which involves electrochemical fission of one C—Br bond *via* a $2e$ process to produce an anion, which neutralizes its charge by internal electronic rearrangement and expulsion of the adjacent bromine atom as bromide ion to produce an olefinic bond^{29, 39}. Throughout the pH range, the *meso* acid produces only fumaric acid; the *racemic* acid, however, produces maleic acid in varying amount in the pH range where the dibromosuccinic acid exists as a mono-anion. Production of a *cis* product is presumably due to intramolecular hydrogen bonding between the adjacent carboxyl and anionic carboxylate groups stabilizing the molecule in a *cis* position during electroreduction.

Since irreversibility may be caused or emphasized by kinetic processes following the electron transfer process, *e.g.*, due to instability or reactivity of the product first produced, the effect of pH on such processes may need to be considered in special situations.

Effect of species behaviour

In addition to alteration in the identity of reactant or product with changing pH, other properties of the species involved may significantly affect the observed potential. These properties may in themselves show a pH-dependence.

(i) *Adsorption effects*—The effect of differences in adsorbability of reactant and product on the electrode in splitting a normal polarographic wave to produce a prewave (product preferentially adsorbed) or a postwave (reactant preferentially adsorbed) has been extensively discussed. Relatively less attention has been given to the possible effect of a difference in adsorbability of the acid and anion forms of the electroactive species. *A priori*, one would expect a neutral undissociated acid to be more readily adsorbed than its negatively charged anion except on the positive side of the electrocapillary maximum; such a situation would be likely to affect the variation of $E_{1/2}$ with pH. The effect would be marked if the surface-active nature of the species changed appreciably with pH.

The change in the slope of the nitromethane wave (with consequent shift in $E_{1/2}$) as pH changes has been related to the extent of adsorption of the nitromethane species and its preprotonation^{3, 40}.

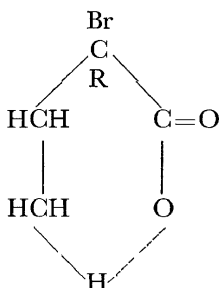
The change in the structure of the double layer and thus the potential associated with the latter as solution composition is changed, as subsequently discussed, is intimately connected with such adsorbability phenomena, *e.g.*, *cf.* the study of the adsorbability of organic bases and their ions by Conway and Barradas⁴¹.

(ii) *Steric effects*—Reference has been made to the steric change in the products formed in reduction of the α, α' -dibromosuccinic acids.

The effects of steric hindrance relative to the closeness of approach of the electroactive site in the molecule to the electrode in increasing the required potential, has been frequently considered. However, it is usually difficult to separate the steric factor from changes in electron density at the

electroactive site due to substitution. The effect of pH on such a situation has generally not been evaluated.

An interesting type of steric effect on the $E_{1/2}$ -pH relationship is that due to formation of a ring structure by intramolecular hydrogen bonding³⁶. In reduction of the C—Br bond in 2-bromo alkanic acids, the branched-chain acids are more easily reduced in the acidic region than their straight-chain isomers; in the alkaline region, acids having ethyl or larger groups on the same carbon as the halogen have more negative $E_{1/2}$ values than expected. The latter phenomenon apparently arises from the tendency towards stable ring formation in compounds having chains of at least six members with terminal atoms differing in electronegativity:

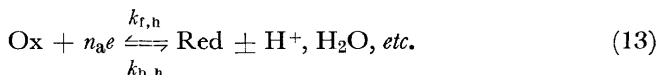


This structure, which can be written as a resonance hybrid, and the resulting behaviour are in accord with Newman's concept of 6-number.

Effect of pH on electrochemical kinetics

Analysis of the possible ways in which pH may affect the factors controlling the kinetics of the essential electrochemical reaction, reveals additional mechanisms for the variation of $E_{1/2}$ with pH.

On the basis of the kinetics of the prototype electrode reaction



where n_a is the number of electrons involved in the rate-determining step, *i.e.*, formation of the activated complex, and $k_{f,h}$ and $k_{b,h}$ represent the heterogeneous rate constants for the forward and backward reactions, respectively, the half-wave potential for reduction at the DME can be defined in terms of absolute rate theory as

$$E_{1/2} = \frac{RT}{\alpha n_a F} \ln \frac{k_{f,h} t^{1/2}}{\lambda D_0^{1/2}} \quad (14)$$

where $k_{f,h}^0$ is the rate constant for the forward reaction at the selected reference potential (usually 0 *v.* NHE), α is the transfer coefficient, *i.e.*, the fraction of the applied potential effective in forming the activated complex, t is the electrode drop-time and λ is a constant, which equals 0.76 at the $E_{1/2}$. Equation (14) is strictly applicable only if the over-all electron-transfer process involves a single slow step and the backward reaction can be neglected (generally the case when $k_{f,h}$ is less than about 10^{-5} cm sec⁻¹).

VARIATION OF $E_{1/2}$ OF ORGANIC COMPOUNDS WITH pH

It is evident from equation (14) that, if correction is made for the variation in drop-time, hydrogen ion concentration variation can affect the $E_{1/2}$ of an organic compound by affecting one or more of four parameters: (a) the transfer coefficient, (b) the number of electrons involved in the rate-determining step, (c) the rate constant for the latter, and (d) the diffusion coefficient of the electroactive species or of the diffusing species which produces the latter.

Of these parameters, it seems rather doubtful that n_a , which should be 1 or 2, would be affected by pH except insofar as pH changes the nature of an equilibrium composition involving the reactant and thereby causes n_a to pass from 1e to 2e or the reverse.

Hydrogen ion may affect the transfer coefficient through its participation in the formation of the activated complex for the potential-determining step. The transfer coefficient, which may obviously only vary from 0 to 1, is generally between 0.3 to 0.7.

The magnitude of the diffusion coefficient may be pronouncedly dependent upon pH. Actually, though, D for many, if not most, organic compounds encountered is in the relatively restricted range of $(0.7 \text{ to } 1.2) \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$. This range of variation corresponds to *ca.* 63 mV at 25° for $\alpha = 0.5$ and $n_a = 1$; the magnitude of this rather extreme shift must be compared with the probable error of 10 mV in the measurement of $E_{1/2}$ for an irreversible polarographic wave.

If t and D are assumed to be relatively unchanged by a small change in pH, differentiation of equation (14) with respect to pH gives

$$\frac{d(E_{1/2})}{d(\text{pH})} = \frac{RT}{\alpha n_a F} \frac{d(\ln k_{f,h}^0)}{d(\text{pH})} \quad (15)$$

Since the heterogeneous rate constant is a *quasi* first-order rate constant which includes effects due to variation in concentration of all species entering into the actual rate law, except for that of the nominal reactant, it may vary with pH if the latter affects such species.

Where the rôle of hydrogen ion participation in the electrode reaction is summarized through its effect on the heterogeneous rate constant, the logarithm of the rate constant would be expected to vary with pH identically to $E_{1/2}$ after necessary correction for variation in the other parameters of equations (14) and (15). Conversely, differences in the two pH relations could serve to evaluate other processes, which may be operative in causing $E_{1/2}$ to change with changing pH. Unfortunately, heterogeneous rate constants k_a are available for only a very few organic compounds. In the case of nitro methane, for example, the sigmoidal variation of the logarithm of the rate constant with pH is generally similar to the corresponding variation of $E_{1/2}$ with pH although there is a noticeable difference in slope (Figure 8)⁴⁰.

It is generally not possible to evaluate the exact magnitudes of the effects of pH variation on the terms of equation (14) and, correspondingly, on the variation of $E_{1/2}$; however, qualitative deductions can occasionally be made. In any case, variation in hydrogen ion concentration will affect all or several of these terms, but in varying magnitude. In this connection, Delahay and

Vielstich⁴² have shown how erroneous interpretation may result from the use of inadequately buffered solutions in electrochemical kinetics.

Meites²² has described an interesting application of the information derivable from equation (15). $E_{1/2}$ of the anodic wave resulting from the oxidation of hydrazine between pH 10 and 15.5 changes by -0.0628 V per

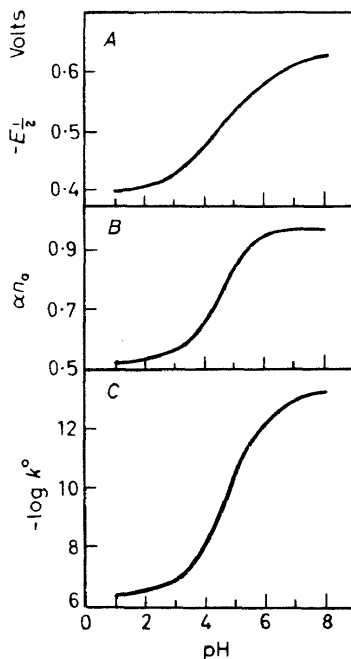


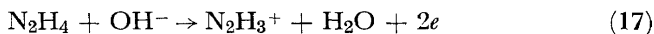
Figure 8. Variation of $E_{1/2}$, αn_a and $\log k^0$ with pH for nitromethane

(From reference 40, courtesy of the Collection of Czechoslovak Chemical Communications)

pH unit; αn_a , calculated from the slope of the wave, is 0.89 and n_a is assumed to be 2. Therefore, $\Delta \log k_{f,h}^0 / \Delta \text{pH} = 0.95$. Since, as mentioned, the variation of $k_{f,h}^0$ with pH arises from its being a *quasi* first-order rate constant, which includes the effect of variation of any species that enters into the rate equation, one can calculate p to be -1 in the equation,

$$k_{f,h}^0 = (\text{H}^+)^p K_{f,h}^0 \quad (16)$$

where $K_{f,h}^0$ is the heterogeneous rate constant, independent of pH effects, and p is the necessary integral number of hydrogen ions consumed in the rate-determining step (or in fast processes preceding that step). Therefore, the rate-determining step giving rise to the wave must be



or a reaction kinetically indistinguishable from it.

Among the most common of kinetic-controlled polarographic currents are those due to the transformation as a result of proton transfer of a species

non-electroactive under the experimental conditions to one which is electroactive. The effect of the kinetics of such chemical processes upon the over-all kinetics of the electrode process has been theoretically examined by several investigators and the resulting effect on $E_{1/2}$ (and hence on the $E_{1/2}$ -pH relation) discussed⁴³.

Effect of solution composition

Changes in the solution composition other than that of pH can have pronounced effects on the observed $E_{1/2}$ -pH relation for a given organic compound. The most important items involved are probably the nature of the solvent, the specific identity of buffer system and other background components, and the ionic strength; these factors must be carefully controlled in experimental studies of the variation of $E_{1/2}$ with pH.

For example, part of the effect on $E_{1/2}$ normally associated with the variation of ionic strength may be due to variation in the double layer structure as a result of changes in concentration and nature of the buffer system components and other electrolytes present (*cf.* discussion of salt effects). The disengagement of the various phenomena involved is obligatory in attempting to elucidate the effect of pH *per se* upon $E_{1/2}$.

Solvent

In the case of reversible redox systems, the effect of solvent is apparently the same for both potentiometric and polarographic conditions after correction for changes in diffusion coefficients, reference electrodes, liquid junction potentials and iR drop.

There is frequently a question as to even the relative validity of the pH values reported for aqueous-organic or non-aqueous media, in which pH is generally that measured by the glass electrode-aqueous saturated calomel electrode pair; Bates has indicated the problems involved⁵. The work of Bates and others^{44, 45} in establishing pH scales for aqueous-organic or non-aqueous solvents should ameliorate this situation.

Possible effects of a change in solvent nature on the $E_{1/2}$ -pH relation are often partially obscured by the failure to resolve the various effects in addition to the changes in activity coefficients due to change in dielectric constant and in diffusion coefficients due to change in viscosity, *e.g.*, $E_{1/2}$ for an electron-transfer process, such as a reduction, in which the charge on the reduced form is greater than that on the oxidized form, would decrease in absolute magnitude with increasing solvent dielectric constant (the charge may be positive or negative).

A minor effect except in poorly buffered media would be the possible interaction of the electroactive species with a proton-donating solvent as pH was varied. In attempting to interpret $E_{1/2}$ -pH behaviour on variation of solvent and ionic strength, all acid-base equilibria possible in the interface must be considered as well as such obvious effects as those due to liquid junction potentials.

In solvents of low proton availability, the electron-transfer process *per se* can presumably be observed more-or-less independently of protonation processes, thus enabling the rôle of protonation to be elucidated by

comparison with experiments in solvents of increasing proton availability. Given and Peover⁴⁶, and Grodzka and Elving¹⁴ have summarized the theoretical and experimental aspects in terms of the behaviour and mechanisms involved.

For example, the reduction of benzophenone in the basic aprotic solvent, pyridine, is generally similar to that in strongly alkaline aqueous solution, where the relative lack of hydrogen ion results in the ketone being reduced in a $1e$ process to an anion free radical, which, being more difficultly reducible than the neutral free radical, dimerizes to a dianion in preference to being further reduced⁴⁷.

Buffer components

Specific effects may arise from interaction of the reactant with the components of the buffer systems used to regulate pH. Such interaction may vary from obvious chemical reaction involving condensation of a carbonyl compound with ammonia of an ammonia buffer to form an imine to more subtle interaction, which may affect the nature of the activated complex in the electrode reaction.

Many commonly used buffer systems such as those based on phosphate and borate have been reported to interact in one way or another with various types of organic electroactive species as indicated by unexpected $E_{1/2}$ shifts.

Such effects are of primary interest in connection with the variation of $E_{1/2}$ with pH because of the necessity of using a series of different buffer systems to cover the normal pH range and of the concomitant necessity of disengaging shifts primarily due to pH from those due to buffer component nature. Even the use of one buffer system, such as the McIlvaine system, over a considerable pH range may involve uncertainty due to the variation in the relative amounts of the undissociated, monoanionic and dianionic forms of the polyprotic acids upon which the buffer is based.

The type of difficulty that may be encountered is illustrated by the behaviour of trichloroacetic acid, which above pH 3 gives two well-defined waves at low ionic strength for the fission of the first C—Cl bond; these waves gradually merge as the ionic strength is increased due to $E_{1/2}$ for the first wave becoming linearly more negative and $E_{1/2}$ for the second becoming linearly more positive¹⁵. These effects can be explained on the basis of the trichloroacetate anion existing in two reducible forms, one of which is due to interaction with a buffer component.

In another example of buffer component effect, maleic acid gives two waves in supposedly nonreactive 0.1M acetate buffer at pH 5.9; these waves gradually merge with increasing acetate concentration until at 1M acetate there is only a single wave²⁸. The effects due to ionic strength or buffer capacity on the merging of the two waves are negligible compared to those due to the increase in acetate concentration.

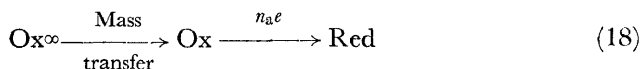
In connection with any consideration of buffer components, mention should be made of the possible variation in pH at the electrode interface from the bulk pH due to the kinetics of dissociation of the acidic buffer component in an otherwise adequately buffered solution, *e.g.*, behaviour observed with bicarbonate buffers⁴⁸. While this effect is apt to be negligible

in ordinary polarography, it might be significant with rapid scanning technics.

Non-specific salt effects and double layer structure

A number of theoretical treatments of the influence of the structure of the electrical double layer, as determined by so-called non-specific salt effects, on electrochemical reactions have recently appeared, some of which have not yet been rigorously tested experimentally. It is of value, however, to consider the conclusions reached in two typical analyses as an indication of the probable effect of the double layer structure.

In the general case of an irreversible electrochemical reaction (backward reaction neglected)⁴⁹,



(Ox^∞ indicates bulk species; Ox indicates species being reduced),

$$E_{1/2} = E^0 + \phi_{sb} \left(1 - \frac{2z}{n_a} \right) - \frac{2RT}{n_a F} \ln \frac{KD_0^{1/2}}{5 \times 10^{-4} p t^{1/2}} - \frac{\lambda}{n_a F} \quad (19)$$

where ϕ_{sb} is the electrostatic potential difference between reaction site and bulk solution (computed in absence of reacting species), z the charge on Ox , p the probability of electron-transfer during the lifetime of Ox , λ the fraction of the charge separation attained in the transition state, and K a constant dependent on the choice of reference electrode. The dependence of αn_a on the double layer is indicated in the following equation:

$$\alpha n_a = n_a/2 + \frac{1}{2}(2z - n_a)(\delta\phi_{sb}/\delta E) - \frac{1}{2}F(\delta\lambda/\delta E) \quad (20)$$

Thus, $E_{1/2}$ depends on ϕ_{sb} and αn_a upon $\delta\phi_{sb}/\delta E$. On the negative side of the electrocapillary maximum, increasing the ionic strength or changing the electrolyte composition to favour greater adsorption makes ϕ_{sb} more positive, and consequently $E_{1/2}$ more negative if $2z/n_a$ is greater than 1.

The effect of double layer structure and of the adsorption of electrode reaction participants upon the polarographic waves observed in the reduction of organic compounds has been ably reviewed by Mairanovskii³. The variation of $E_{1/2}$ for irreversible pH-independent waves with double layer structure can be expressed on the basis of the theory of slow discharge as

$$E_{1/2} \cong k(\Delta\psi_1)[(\alpha n_a - z)/\alpha n_a] \quad (21)$$

where k is a proportionality constant, z the charge on the electroactive species and ψ_1 the potential drop in the diffuse part of the double layer. Consequently, $E_{1/2}$ for a non-charged species will vary only with the effective potential difference, $\Delta\psi_1$. Furthermore, since the product αn_a is generally less than 1, $E_{1/2}$ for reduction of a cationic species will become more negative and $E_{1/2}$ for reduction of an anion will become more positive as ψ_1 decreases with increasing ionic strength. These deductions are in accord with the variation with ionic strength of $E_{1/2}$ of 2-bromobutyric acid (Figure 9), which is considered in the next section.

To sum up, it is probably not too much to say that a significant fraction of the observed $E_{1/2}$ shifts, when pH is altered, are—at least to some extent—the result of alteration of the structure of the electrical double layer, as reflected in variation of the potential difference, ϕ_{sb} or ψ . Unfortunately, direct determination of this potential gradient is a complicated matter.

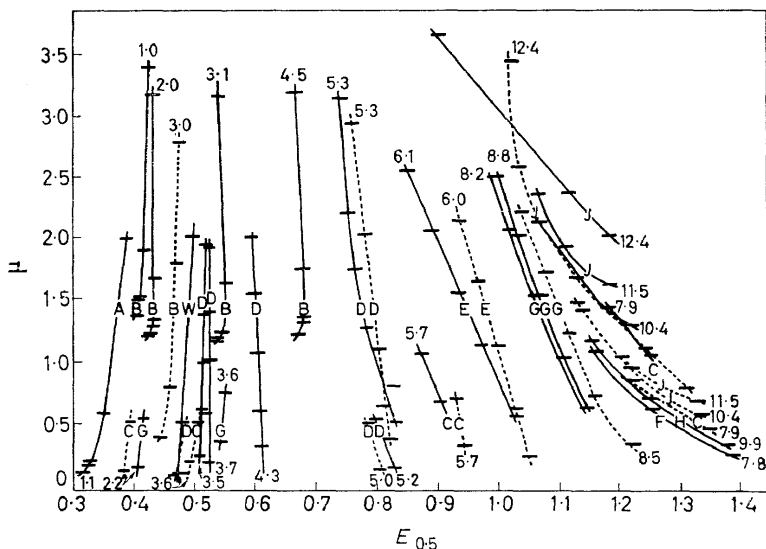


Figure 9. Variation of $E_{1/2}$ of 2-bromobutyric acid with ionic strength, pH, buffer nature, and buffer component concentration; letters refer to buffer types; numbers refer to pH; solid lines in any particular set indicate higher concentration of principal buffer component than in results connected by dashed line

(From reference 26, courtesy of *Analytical Chemistry*)

An excellent experimental study of the effect of varying the nature of the cation and anion of the background electrolyte and of solvent on the electrical double layer and therefore on the polarographic behaviour is that of Lothe and Rogers⁵⁰ on carbon tetrachloride.

Ionic strength

The most immediate manner in which variation in ionic strength can affect $E_{1/2}$ —at least in the case of a reversible system—is evident from the equation relating $E_{1/2}$ to standard potential,

$$E_{1/2} = E^0 - \frac{RT}{nF} \ln \frac{f_R}{f_0} - \frac{RT}{2nF} \ln \frac{D_0}{D_R} \quad (22)$$

Any variation in the ratios of the activity and diffusion coefficients of the participants in the half-reaction will be mirrored in the $E_{1/2}$. The effect of ionic strength on activity coefficients is expressed by the Debye-Hückel relation; its effect on diffusion coefficients is more complex, *e.g.*, alteration of solvation of species, change of solution viscosity, *etc.*

The observed effect of ionic strength on the variation of $E_{1/2}$ with pH can

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be useful in interpreting the nature of the species involved in the electrode process. The concept has developed that changes in ionic strength affect $E_{1/2}$ only when the reactant is charged, *e.g.*, due to acid-anion dissociation or to protonation. Actually, ionic strength variation seems to have little effect on the $E_{1/2}$ of pH-independent processes; any variation that is observed, may be due to changes in diffusion coefficients.

In the case of pH-dependent processes, ionic strength may profoundly affect the variation of $E_{1/2}$ with pH, *e.g.*, *Figure 9* on the fission of the C—Br bond in α -bromobutyric acid²⁶ whose pK_a is about 3. In the more acidic region where the acid may exist as a protonated species, increasing ionic strength makes the reduction somewhat more difficult, perhaps as a result of decreasing the coulombic attraction between the electrode regarded as an electron sink and the positively charged species. In the intermediate region where the effective reactant is the uncharged acid, changing ionic strength does not affect the $E_{1/2}$. In the pH region where the effective species is the anion, increasing ionic strength makes reduction pronouncedly less difficult, probably as a result of decreasing the repulsive forces between electrode and anion. The analytical implication of the reversal of the manner of variation of $E_{1/2}$ with ionic strength is the presence of a "cross-over" region as shown in *Figure 5* where re-plotting of the data of *Figure 9* emphasizes that $E_{1/2}$ is relatively independent of variation in ionic strength around pH 4.8 and that, consequently, 2-bromobutyric acid is generally best determined at this pH. It is likely that other polarographically reducible acids and acid-forming species show similar pH regions where $E_{1/2}$ is independent of ionic strength.

The use of constant ionic strength buffers is to be highly recommended as minimizing extraneous effects when examining the effect of pH on $E_{1/2}$. Unfortunately, the desirability, if not necessity, of this practice has frequently been overlooked, especially in the older literature. Data on such buffer systems are available⁵¹⁻⁵².

UTILIZATION OF $E_{1/2}$ -pH RELATIONS IN THE DEVELOPMENT OF ANALYTICAL PROCEDURES

One of the principal factors in the successful analysis of mixtures is adequate resolution of the measurement responses of the different components as a result of control of the experimental conditions under which the measurements are made. Consequently, one of the important requirements in developing a method in organic analysis is the thorough investigation of the effects of experimental variables upon the response of the species being measured; this is particularly true when physicochemical methods are used to analyse mixtures of related compounds.

In the polarographic analysis of mixtures of organic compounds, the significant factor is generally the pattern of variation of their half-wave potentials as the composition of the test solution is altered; pH is usually the most critical experimental variable in this respect. In fact, the variation of the $E_{1/2}$ of organic compounds with pH is as useful a device for securing analytically selective measurement as is the addition of complex-forming reagents in inorganic analysis. This can be simply illustrated by the case of

the isomeric *cis-trans* acids, maleic and fumaric. The early literature is quite contradictory as to whether or not it is possible to analyse polarographically mixtures of the two acids⁵³. A systematic study of their behaviour revealed two reasons for the conflicting reports, one related to the behaviour of the acids and the other to an artefact of measurement; recognition of these two factors led to simple and satisfactory procedures for analysing mixtures of the acids^{32, 53}.

The fundamental difficulty was the failure to recognize the pattern in the variation of $E_{1/2}$ of the acids with pH (*Figure 6*)²⁸. In the acid region the potentials are much too close together to permit resolution of the waves, which can, however, be readily resolved in alkaline solution. The accentuation of the difference in $E_{1/2}$ beginning at pH 6 is probably connected with the chelated structure possible only in maleic acid in the pH region where existence of the monoanionic species is expected.

Since certain explained—as well as of yet unexplained—apparently anomalous effects in the variation in the polarographic behaviour of maleic and fumaric acids with pH constitute a potential source of error in analysis, it is worthwhile reviewing the $E_{1/2}$ -pH relations of these acids and the interpretations suggested as an example of $E_{1/2}$ -pH phenomena which may be typically encountered with organic compounds, which are irreversibly reduced at the DME, and of the need for further research on $E_{1/2}$ -pH relationships. Frequent reference has been made in the present paper to the behaviour of these acids; the literature on them is summarized in refs. 1, 28, 32 and 53-55.

The maleate-fumerate system

The general behaviour of the acids over the pH range (*Figures 10 and 11*) is qualitatively the same and is attributable to the operations of (a) the acid-anion equilibria involving a dibasic acid and (b) the two S-shaped relations between pH and $E_{1/2}$ for the two acid-anion systems of such an acid³². There are pH-invariant regions in the $E_{1/2}$ -pH relation corresponding to the regions where substantially only undissociated acid, single charged anion, and double charged anion exist with regions of increasing (in a negative sense) $E_{1/2}$ between these plateaus. The magnitude and location of these flats are determined by the relative K_a values, and the relative rates of association-dissociation and of electron transfer. The split wave phenomena observed near pH 6 are due to the rates of acid-anion interconversion being slow enough to permit the waves of both acid and corresponding but more difficultly reducible anion to be simultaneously observed. The theory of this type of kinetic-controlled current has been frequently discussed^{35, 43, 56, 57}. If pK_a of the dibasic acid is close to the pH region where separate waves appear for undissociated acid and monoanion, the dissociation of the latter to give the double charged anion must be taken into account, because the rate of formation of undissociated acid depends on the concentration of the singly charged anion which is diminished by dissociation.

With maleic acid, it may be assumed, as previously discussed, that the pH-dependence found with the ester^{28, 58} is due only to pH effects on the actual bond reduction and that these bond pH effects are the same in the

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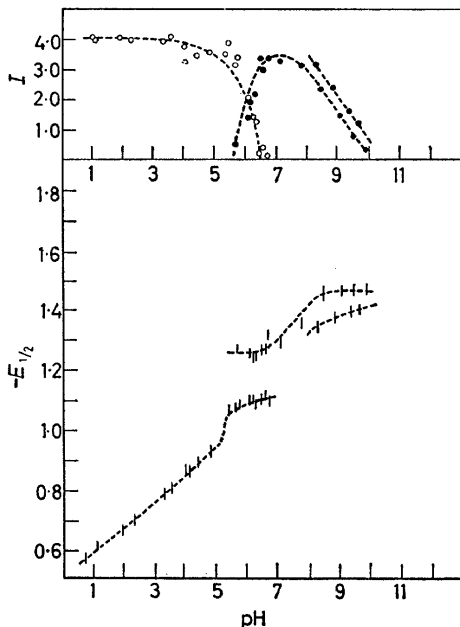


Figure 10. Maleic acid: Variation of $E_{1/2}$ and I ($i_d/cm^2/3t^{1/6}$) with pH at 25° and ionic strength of 1.0M; lines represent $E_{1/2}$; circles and crosses represent I values for first and second waves, respectively

(From reference 32, courtesy of Analytical Chemistry)

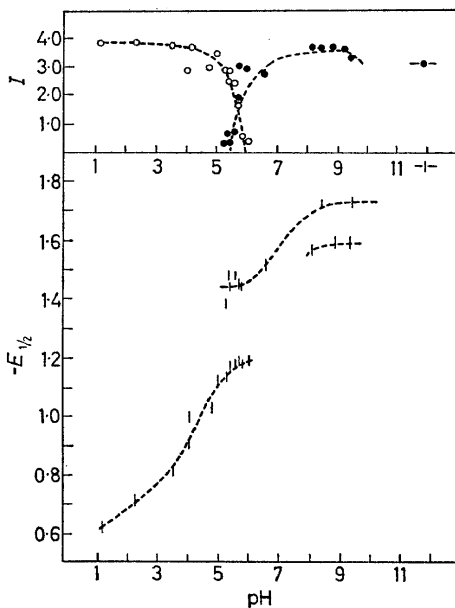


Figure 11. Fumaric acid: Variation of $E_{1/2}$ and I ($i_d/cm^2/3t^{1/6}$) with pH at 25° and ionic strength of 1.0M; lines represent $E_{1/2}$; circles and crosses represent I values for first and second waves, respectively

(From reference 32, courtesy of Analytical Chemistry)

acid. Therefore, to obtain the pH effects due to acid-anion kinetics the pH effects found with the corresponding ester, *i.e.*, $E_{1/2}$ *v.* pH slopes (not actual $E_{1/2}$ values)—may be subtracted from those found with the acids. The curve thus obtained differs qualitatively from *Figure 10* only in being essentially pH-independent below pH 2.8 because $E_{1/2}$ of diethyl maleate is pH-independent above pH 6 and the slope of its $E_{1/2}$ -pH plot is equal to that for maleic acid between pH 0.7 and 3.

The situation is similar for diethyl fumarate, except that instead of a completely pH-independent region above pH 5, there is a region with a relatively small pH-dependence, *i.e.*, 0.025 V per pH unit as compared to 0.14 V at lower pH, which decreases with increasing pH, *e.g.*, 0.015 V at pH 8, and may be responsible for the fact that in the region where both acid and anion waves exist, these appear to have a slight pH-dependence in contradistinction to the maleic acid system.

Equations relating $E_{1/2}$ to pH

The general trend in explaining the $E_{1/2}$ -pH relations of maleic and fumaric acids has followed Herasymenko^{59, 60} and Vopicka⁶¹, which Kolthoff and Lingane⁸ have summarized. Herasymenko's development starts with the equation,

$$E = - \frac{RT}{2F} \ln \frac{iK}{[R_0][H^{2+}]} \quad (23)$$

where i is the current flowing at applied potential E , K is a constant (subsequently defined), and $[R_0]$ and $[H^+]$ are the concentrations of undissociated acid and hydrogen ion at the electrode surface. The significance of equation (23) and the assumptions inherent in it are best realized by examining the derivation⁶² of a similar but more general formula, which assumes as the most probable reduction scheme,



with the potential of the whole system determined by the perfectly mobile equilibrium assumed to exist for the first reaction. This leads to

$$E = - \frac{RT}{2F} \ln \frac{iK}{K'[R_0][H^+]^2} \quad (26)$$

where K is the ratio of the "solution tensions" of the two forms of hydrogen of equation (24) and K' is the rate constant for reaction (25) in units such that it will directly give i .

Equation (26) is similar to Herasymenko's starting point. His main contribution was to assume that only the undissociated acid is reduced and to develop the pH-dependency of that form; he assumed the dissociation equilibrium of the acid at the electrode to be instantaneous. The final equation obtained, which is the one currently used, is

$$E = \frac{2RT}{F} \ln [H^+] - \frac{RT}{2F} \ln ([H^+]^2 + K_1[H^+] + K_1K_2) + K^{11} \quad (27)$$

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where K_1 and K_2 are the first and second dissociation constants of the acid, and K^{11} is implied to be $E_{1/2} + (RT/2F) \ln [(i_d - i)/i]$. Herasymenko⁵⁹ calculated $E_{1/2}$ for maleic and fumaric acids up to pH 9, using Vopicka's⁶¹ experimental $E_{1/2}$ value of -0.58 V for the two acids at pH 0 (actually, in 1N hydrochloric acid).

Significance of Herasymenko's equation

Extrapolation of the data of ref. 32, from which *Figures 10* and *11* are taken, to pH 0 gives $E_{1/2}$ values for maleic and fumaric acids of -0.51 and -0.53 V, respectively. Use of these in equation (27) gives values close in absolute amount to experimental results³² over pH ranges of 0 to 5 and 0 to 4, respectively. However, this agreement has little significance with respect to clarifying the behaviour of the acids and testing the assumptions upon which equation (27) was derived. For example, Herasymenko's calculated values predict maleic to be more difficultly reducible than fumaric near pH 1.5 to 5; use in equation (27) of the $E_{1/2}$ values at pH 0 from *Figures 10* and *11* still gives a calculated crossover at pH 4, which would require that maleic be more difficultly reducible than fumaric. Experimentally, this is not the case, cf. *Figure 6*. From pH 0 to 4, $E_{1/2}$ of the acids differ by 20 mV with fumaric always being more difficultly reducible; as pH increases, the difference is accentuated. Barring steric effects, the *cis* acid is expected to be more readily reduced than the *trans*. Furthermore, over the pH region in which the calculated and experimental values agree, the plots of $E_{1/2}$ v. pH are essentially straight lines; as soon as the experimental values differ from linearity, the agreement fails.

This lack of agreement is ascribed⁸ to the small concentration of undissociated acid at higher pH and possible direct reduction of anions. However, the latter is to be associated only with the second wave³². The important factor is not the equilibrium concentration of undissociated acid at the electrode, but rather the rate at which equilibrium is attained.

The derivation of equation (27) assumes instantaneous attainment of dissociation equilibrium, which is contradicted by the existence of separate acid-anion waves. Since $E_{1/2}$ becomes more negative as (R_0) in equation (23) decreases, the decrease in rate of equilibrium attainment should result in a sharper increase of $E_{1/2}$ with pH than is called for by the equilibrium concentration³². Such behaviour can then partially explain the fact that in the region just before separate anion and acid waves appear, Herasymenko's equation gives values that are more positive than the experimental ones. It does not explain, however, why $E_{1/2}$ does not vary with pH in the region where the two waves coexist.

A more fundamental consideration is the fact that assumption of the reduction mechanism⁶² of equations (24) and (25) is not a prerequisite for obtaining equation (26), from which Herasymenko derived his equation. We may assume, for example, that maleic acid, R, reversibly adds two electrons to give R_2 , which step determines the electrode potential. Then, R_2 , which may be assumed to be stabilized by adsorption on the electrode and loose combination of the free electrons with the mercury, reacts irreversibly with hydrogen ions at the electrode surface to give the final product RH_2 . (The difficulties here are certainly no greater than those involved in

assuming the presence of nascent hydrogen.) By proper substitution, an equation identical to (26) emerges. Thus, the basic issues concerning the mechanism of reduction and the potential-determining step remain unexplained, even if the equation did fit the data, which, except for the trivial case where the data give a straight line, it does not.

The purpose of the foregoing analysis is not to belittle the value of the equations used to fit the data, but to emphasize that the problem is still practically unsolved. The method of reasoning backwards from equations that fit the data to mechanisms consistent with the equations is basically unfruitful. The mechanism should be elucidated by investigation, *e.g.*, of such factors as the steric course of the reaction, the effects of solvent and ionic strength, and the effect of substituents. Once the mechanism is clarified, it will then be necessary to introduce the effects of the recombination rate of anion to form undissociated acid instead of using purely equilibrium concentrations as was done originally.

CONSEQUENCES OF $E_{1/2}$ -pH RELATIONS ON $E_{1/2}$ CORRELATIONS

Because the half-wave potential of organic compounds is probably the most readily measured electrochemical energetic parameter of such compounds, considerable attention has been given to the search for consistent relationships between it and structural and other characteristics, such as absorption maxima. Generally, none of the various relationships developed has been widely applied. However, specific areas of good agreement between the observed behaviour of a series of related compounds and a particular correlating equation are well known, especially in connection with the Hammett-Taft equation, as indicated in the many able studies of Zuman, *e.g.*, refs. 63 to 66.

The different factors determining the manner in which $E_{1/2}$ varies with pH need to be more seriously considered in connection with such proposed correlations than has been done in the past. One major reason for this need is the widespread use made in such correlations of "normalized" half-wave potential values based on extrapolation of the experimental data to pH = 0. It is often not clear as to the extent to which the experimental $E_{1/2}$ -pH relation is sufficiently well defined at lower pH to allow geometrically valid extrapolation, and as to the varying extent of protonation of the compounds being compared in the region below pH 2, where the hydrogen ion population begins to exceed by a factor of 100 or more the population of electroactive species. The consequences of extrapolation can be unwittingly disastrous if the actual $E_{1/2}$ -pH relation is an S-shaped curve with the pH 0 value being on the lower horizontal portion and the experimental range involving only the slanting linear portion.

The preceding discussion has made evident the necessity of considering not only pH but also ionic strength and the nature and concentration of buffer components and of so-called "indifferent electrolytes", which may affect the double layer structure, when attempting to correlate $E_{1/2}$ for irreversible polarographic waves with structure, with other experimental data or with calculated parameters. The disengagement of effects due to

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variation in other experimental conditions is obviously essential in correctly elucidating the correlation of $E_{1/2}$ even for a specified pH.

SUMMARY

Various possible causes for the observed variation in the half-wave potentials of organic compounds with pH have been considered. It has not been possible within a limited space to develop in detail the explicit physical and theoretical bases for the observed variations. Rather, emphasis has been placed on indicating the principal factors which seem to be involved.

It has also not been possible to do more than merely to indicate the utility and limitations of the use of $E_{1/2}$ -pH curves in the study of organic electrode processes, e.g., in the development of specific analytical methods, in the derivation of information concerning the numbers of electrons and of protons participating in the electrode reaction from the slope of the curve, and, in general, as one of the most important diagnostic tests for the elucidation of organic electrode mechanisms. It has also not been possible to generalize concerning the organic structures, which show different types of pH-dependence.

It is hoped that the present discussion will stimulate the development of more detailed investigations and explanations for some of the observed $E_{1/2}$ -pH behaviour patterns, as well as a comprehensive theoretical statement as to the causes of the variations of $E_{1/2}$ with pH, which would be especially applicable to the irreversible electrode processes characteristic of most organic electro-reductions and electro-oxidations. Typical of the areas, which merit further investigation, is that of the dependence of $E_{1/2}$ on Lewis acid concentration in non-aqueous media.

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General discussion pertinent to many of the experimental generalizations made and theoretical relations cited will be found in references 1 to 4, 9, 30, 67 and 68.

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