[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Non-specific Salt Effects in Polarographic Reductions[1]

BY W. H. REINMUTH,[2] L. B. ROGERS AND L. E. I. HUMMELSTEDT

RECEIVED OCTOBER 11, 1958

A recent theory of the electron-transfer process proposed by Marcus is examined with respect to its implications in the polarographic process. A discussion is given of the effects of supporting electrolyte on electron-transfer controlled waves. Qualitative and in some cases semi-quantitative explanations are offered for the effect of medium on half-wave potentials and slopes of waves.

Introduction

Many workers have considered the influence of supporting electrolyte on electro-oxidation and reduction reactions under polarographic conditions. The causes of this influence have been described in various ways. The purpose of the present work is to point out some general trends apparent in these effects, to apply a recent theory of the electrode process to their explanation and to suggest some important implications of this treatment with particular emphasis on the interpretation of half-wave potentials and slopes of electron-transfer controlled waves.

For electrode processes in which there is only one slow electron-transfer step, the reaction can be broken down into three stages

$$\mathrm{A} \overset{(1)}{\rightleftarrows} \mathrm{X} \overset{(2)}{\rightleftarrows} \mathrm{X}^* \overset{(3)}{\rightleftarrows} \mathrm{B}$$

Species A present in the bulk of the solution arrives at the reaction site in step 1 by some mode of mass transfer. At this site it is present in the form X which may differ from A in physical or chemical form. Species X in step 2 exchanges one or more electrons with the electrode to be transformed into species X* which, because of the Frank–Condon principle, differs from X only in the number of electrons associated with it. Species X* may undergo further chemical, electrochemical, and/or physical changes and ultimately returns to the bulk of the solution in the form B.

For reactions obeying the Nernst equation, only the initial and final states need be considered. Thus, in these cases, the influence of the supporting electrolyte can be attributed to one of two causes: (Ia) specific chemical interactions in the form of complex formation,[3a] acid–base dissociation, ion-pair formation[3] and the like; (Ib) "activity" effects in which there is assumed to be no specific chemical interaction with the reactive species, A and B, but their environment in the bulk of the solution is nevertheless altered significantly.[4]

For reactions proceeding with appreciable activation overpotential, mechanisms of the types Ia and Ib can still operate; however, the actual form of the reacting species X and X* also becomes important. In these cases two more mechanisms become possible: (IIa) specific chemical interactions either possible only at the electrode surface, *e.g.*, adsorption, bridging complexes or species of such transient stability as to be unimportant in the bulk of the solution; (IIb) "activity" effects in the electrical "double layer" at the electrode surface, in particular, electrostatic repulsion from or attraction to the electrode surface.

It is apparent that in a given case any or all of these effects may be operative. For the present, we shall proceed on the assumption that they can be distinguished and consider specifically effects of the type IIb.

Theoretical

Frumkin, as early as 1936, postulated the effect of the structure of the double layer on the reduction of anions.[5] Later work by him and his co-workers was aimed at the quantitative correlation of the anomalous dip in diffusion current for several anions with the electrostatic repulsion of those anions from the electrode surface as a result of changes in the double layer with potential. Unfortunately, cases studied by these workers were ones in which, in addition to general double layer effects, ion-pair formation and complexation were also possible and, in fact, they (Frumkin, *et al.*) made no distinction between effects of type IIa and IIb above.[6a,7] Randles and Somerton[8] also found evidence for an electrostatic repulsion effect in the case of anions. Laitinen and Onstott[9] proposed a similar effect.

In later work, some doubt has been cast on these theories. Kivalo and Laitinen,[10] abandoning the theory of Laitinen and Onstott, proposed an alternative mechanism for the diffusion current "dip" phenomenon at the dropping mercury electrode (DME); the work of Popov and Geske[11] indicates that at solid electrodes oxide-film formation may play an important role. These theories consider only anion reductions.

Many authors have considered salt effects on hydrogen and oxygen evolution and reduction reactions. These reactions, because of bond or

---

(1) Presented in part before the 134th Meeting of the American Chemical Society, Chicago, September 1958.

(2) National Science Foundation Fellow 1955–1957.

(3) (a) J. J. Lingane, THIS JOURNAL, **61**, 2099 (1939); (b) H. A. Laitinen and M. W. Grieb, *ibid.*, **77**, 5201 (1955).

(4) D. D. DeFord and D. L. Anderson, *ibid.*, **72**, 3918 (1950).

(5) A. N. Frumkin, *Actualites sci. ind., Paris*, 373 (1936).

(6) See, for example, (a) A. N. Frumkin and G. M. Florianovich, *Doklady Akad. Nauk. S.S.S.R.*, **80**, 907 (1951); (b) N. V. Nikolajeva, N. S. Shapiro and A. N. Frumkin, *ibid.*, **86**, 581 (1952); (c) N. V. Nikolajeva and A. A. Grossman, *ibid.*, **95**, 108 (1954); (d) G. M. Florianovich and A. N. Frumkin, *Zhur. Fiz. Khim.*, **29**, 1887 (1955).

(7) M. A. Vorsina and A. N. Frumkin, *ibid.*, **17**, 295 (1943).

(8) J. E. B. Randles and K. W. Somerton, *Trans. Faraday Soc.*, **48**, 937 (1952).

(9) H. A. Laitinen and E. I. Onstott, THIS JOURNAL, **72**, 4565 (1950).

(10) P. Kivalo and H. A. Laitinen, *ibid.*, **77**, 5205 (1955); however, see A. N. Frumkin and N. V. Nikolajeva, *J. Chem. Phys.*, **26**, 1552 (1957).

(11) A. I. Popov and D. H. Geske, *ibid.*, **80**, 1340 (1958).

pseudo bond formation with the electrode during the course of reaction, may be different in kind from the simple electron-transfers considered in the present work since the energy of bond formation should vary with potential and double-layer structure. After completion of the present work, Breiter, Kleinerman and Delahay[12] gave an extensive review of earlier work to which the reader is referred.

Elving and co-workers[13] have demonstrated in the case of α-bromobutyric acid that, even in acid solution where the reducible species is neutral and specific chemical interactions with the electrolyte and electrode seem improbable, the constitution and concentration of the supporting electrolyte have a marked effect on the reduction process at the DME. Lothe and Rogers[14] observed similar effects in the reduction of carbon tetrachloride. They suggested that this influence was indeed associated with the structure of the double layer and qualitatively correlated shifts in the half-wave potential with the electrocapillary activity of the anions and cations of the supporting electrolyte on the anodic and cathodic sides of the electrocapillary maximum (ECM), respectively.

The influence of the double layer on a reaction can be introduced formally in several ways. We feel one of the more rewarding to be that of Marcus.[15] According to his theory, at overpotentials which are not too great, the free energy of activation for the electrode reaction process can be written as

$$\Delta F^* = {}^1/_2(w + w^* + n_\mathrm{a}F\eta + \lambda) \qquad (1)$$

where w^* and w represent the work required to bring the reducible species from the bulk of the solution to the electrode surface before and after the electron-transfer process, respectively; n_a is the number of electrons transferred, η is the overpotential equal to the difference between the applied potential E and the standard potential for the reaction $E°$, and λ the fraction of the charge separation attained in the transition state,[15b] is given by the equation

$$\lambda = {}^1/_4\, \frac{n_\mathrm{a}{}^2F^2}{N_\mathrm{o}} \left(\frac{1}{r} - \frac{1}{b}\right) \left(\frac{1}{D_\mathrm{op}} - \frac{1}{D_\mathrm{s}}\right) \qquad (2)$$

where F is the Faraday, N_o is Avagadro's number, r is the effective radius of species X, $b/2$ is the distance of the species X from the electrode surface, D_op is the square of the refractive index of the medium and D_s is its static dielectric constant.

The rate constant for the electrochemical reaction is given by[15]

$$k_\mathrm{f} = 5 \times 10^4\, p \exp(-\Delta F^*/RT) \text{ cm. sec.}^{-1} \qquad (3)$$

where p is the probability of electron-transfer during the lifetime of state X (assumed for the present discussion to be a constant).[15]

The effect of potential on the rate constant obviously enters through η in equation 1. It also enters, however, in the work terms w and w^*. The work required to transport a species from the bulk of the solution to the electrode surface can be represented approximately by the product of z, the charge of the species and ϕ_sb, the electrostatic potential difference between the reaction site and the bulk of the solution, computed in the absence of the reacting species.[15] Thus equation 3 can be rewritten in the form

$$k_\mathrm{f} = 5 \times 10^4\, p \exp\left[-\frac{1}{2RT}(n_\mathrm{a}F\eta + \lambda + 2z_\mathrm{x}F\phi_\mathrm{sb} - n_\mathrm{a}F\phi_\mathrm{sb})\right] \qquad (4)$$

The reader should note the derivation, due originally to Frumkin and recently discussed by Breiter, *et al.*,[12] which leads quantitatively to the same conclusions even though it is formally different and has an adjustable parameter in place of the factor $^1/_2$.

Koutecky[16] has formulated a theory for the polarographic process at the DME under conditions such that the rate constant for the electrochemical reaction must be considered. If conditions are such that the back electrochemical reaction can be neglected, this theory indicates that the equation for the current–potential curve can be written in the approximate form

$$E = E_{0.5} + \frac{RT}{\alpha n_\mathrm{a}F} \ln \frac{i_\mathrm{d} - i}{i} \qquad (5)$$

where i_d is the current on the diffusion plateau, i is the current at potential E, αn_a is defined by the equation

$$\frac{\alpha n_\mathrm{a}F}{RT} = \frac{\delta \ln k_\mathrm{f}}{\delta E} \qquad (6)$$

and $E_{0.5}$ is the potential at which

$$k_\mathrm{f} = KD^{1/2}/t^{1/2} \qquad (7)$$

where D is the diffusion coefficient of species A and t is the drop-time of the DME, K is a numerical constant the value of which is dependent on whether average or instantaneous current is measured.

For the simplest type of reaction in which the species X does not differ from A chemically, equation 4 can be combined with equation 7 to give an expression for the half-wave potential

$$E_{0.5} = E° + \phi_\mathrm{sb}\left(1 - \frac{2z_\mathrm{x}}{n_\mathrm{a}}\right) - \frac{2RT}{n_\mathrm{a}F} \ln \frac{KD^{1/2}}{5 \times 10^4\, pt^{1/2}} - \frac{\lambda}{n_\mathrm{a}F} \qquad (8)$$

and with equation 6 to give an expression for αn_a

$$\alpha n_\mathrm{a} = n_\mathrm{a}/2 + 1/2(2z - n_\mathrm{a})(\delta\phi_\mathrm{sb}/\delta E) - 1/2F(\delta\lambda/\delta E) \qquad (9)$$

If it is assumed that $(\delta\lambda/\delta E)$ is negligible in comparison with the other terms in equation 9 and it is recognized that

$$\phi_\mathrm{sb} + \phi_\mathrm{es} = E + K \qquad (10)$$

where ϕ_es is the potential difference between the interior of the electrode and the reaction site and K is a constant dependent on the choice of reference electrode, equation 9 can be simplified to

$$\alpha n_\mathrm{a} = z_\mathrm{x} + (n_\mathrm{a}/2 - z_\mathrm{x})(\delta\phi_\mathrm{es}/\delta E) \qquad (11)$$

---

[12] M. Breiter, M. Kleinerman and P. Delahay, THIS JOURNAL, **80**, 5111 (1958).

[13] P. J. Elving, J. C. Komyathy, R. E. VanAtta, C.-S. Tang and I. Rosenthal, *Anal. Chem.*, **23**, 1218 (1951).

[14] J. J. Lothe and L. B. Rogers, *J. Electrochem. Soc.*, **101**, 258 (1954).

[15] (a) R. A. Marcus, *Can. J. Chem.*, **37**, 155 (1959); (b) R. A. Marcus, *J. Chem. Phys.*, **24**, 979 (1956).

[16] J. Koutecky, *Chem. Listy*, **47**, 323 (1953); *Coll. Czechoslav. Chem. Communs.*, **18**, 597 (1953); see also D. M. H. Kern, THIS JOURNAL, **76**, 4234 (1954).

The case in which X differs chemically from A can also be treated. However, in this case the expression for $E_{0.5}$ includes a term involving the equilibrium constant for the chemical reaction and the concentrations of the other species involved.

Even for the simple case, a number of qualitative and quantitative observations are possible concerning the effects of added salts on the half-wave potentials and slopes of electron-transfer controlled polarographic waves.

Half-wave Potentials.—Even in the absence of complexation, equation 8 indicates that salts can shift the half-wave potential by their effect on ϕ_{sb}, λ, $E°$, t and D. Effects on $E°$ would be in the form of "activity" (Ia). These and the effects on λ, t (through interfacial tension) and D (through viscosity) would presumably be small. Another effect which is not immediately apparent is that on the liquid junction potential which is included in an experimental measure of $E_{0.5}$. However, this too can be minimized by appropriate procedures. Even neglecting these effects, there remains the effect on ϕ_{sb}. In order to evaluate this factor it is necessary to know the location of the reducible species during electron transfer. Breiter, Kleinerman and Delahay have recently given a discussion of the problem.[12]

If ϕ_{sb} is assumed to be the potential difference from the inner or outer Helmholtz plane to the bulk of the solution, it becomes possible from capacitance measurements on the electrical double layer to estimate the effects of varying electrolyte composition and concentration.[17] Such estimates show that the influence of these factors should be by no means inappreciable.

Qualitatively the nature of these effects is as follows: On the anodic side of the ECM, anions form the inner layer at the electrode surface and increasing the ionic strength or changing electrolyte composition to favor greater adsorption (*e.g.*, from fluoride to chloride to iodide) makes ϕ_{sb} more negative.[17] On the cathodic side of the ECM, cations form the inner layer and increasing the ionic strength or changing the electrolyte composition to favor greater adsorption (*e.g.*, from sodium or potassium to tetraalkylammonium) makes ϕ_{sb} more positive. Further, the effect becomes greater at potentials farther removed from the ECM and, at the potential of the ECM, no effect is observed.[18]

Equation 8 then predicts that on the anodic side of the ECM changes in electrolyte described above will produce cathodic shifts if $2z_x/n_a < 1$, no shift if $2z_x/n_a = 1$, and anodic shifts if $2z_x/n_a > 1$. On the cathodic side of ECM the opposite is true. Vivid support for this contention can be found in the work of Elving and co-workers[13] on the effect of ionic strength in the reduction of α-bromobutyric acid. In this case $z_x = 0$, so that $2z_x/n_a < 1$. The observed experimental effects are precisely those predicted by equation 8. That the constitution as well as the concentration of the electrolyte is important, is also apparent from the work of these authors. This effect, however, is much more apparent in the results obtained by Lothe and Rogers for the reduction of carbon tetrachloride.[14] Here, where z is almost undoubtedly zero and n_a is again probably one, the correlation between electrocapillary activity of anions and cations and the halfwave potentials is again exactly that predicted from equation 8.

Further, these authors showed that the shift of $E_{0.5}$ with iodide concentration exactly paralleled the shift of the ECM with the same factor. Equation 8 predicts that $E_{0.5}$ should vary directly with ϕ_{sb} under such circumstances. Devanathan has suggested the same variation of E_{ECM} with ϕ_{sb}.[19]

These cases, in which $2z_x/n_a$ is zero, can be contrasted with the effect of supporting electrolyte on the reduction of *p*-dinitrobenzene. In acid solution the reduction of this compound is *p*H dependent, indicating that the species X has one or more hydrogen ions associated with it and is thus positively charged. The quantity $(1 - 2z_x/n_a)$ is then much smaller than for the halogen reductions and in fact may even be negative. Under conditions in which the half-wave potential of carbon tetrachloride reduction was shifted markedly to cathodic potentials by the addition of electrocapillary-active thiocyanate, Hummelstedt and Rogers[18] have observed that the nitro reduction shows little, if any, effect. Recently, Breiter, Kleinerman and Delahay[12] discussed the reduction of nitromethane and of iodate and explained the observed salt effects in terms similar to those given here. While we agree in principle with their calculations, we differ with their conclusions. These authors assumed the reducible species to be neutral in the case of nitromethane and thence concluded that reduction took place at the inner Helmholtz plane. However, it is well known that the rate of this reaction is decreased by increasing *p*H.[20] From this fact that it can be concluded that either the reactive species gains a positive charge prior to the rate-determining electron-transfer or that the kinetics are more complicated than those treated theoretically. We favor the former view but in any event the conclusions are suspect.

The effect of electrolytes on half-wave potentials of irreversible waves obviously has important implications with respect to the meaning which can be assigned to these potentials. Many authors have attempted to correlate half-wave potentials for organic reductions with Hammett's sigma values or other parameters which might be expected to be related to reactivity. Delahay and co-workers[21] have repeatedly suggested the dangers inherent in this procedure. From the discussion above, the explicit nature of these dangers becomes apparent. For such a comparison to be valid, the gross mechanism of reaction must be the same for each of the species compared, *i.e.*, the chemical and physical

---

(17) (a) D. C. Grahame, *Chem. Revs.*, **41**, 451 (1947); (b) R. Parsons, Chapter 3 in "Modern Aspects of Electrochemistry," edited by J. O'M. Bockris, Butterworths, London, 1954.

(18) L. E. I. Hummelstedt and L. B. Rogers, *J. Electrochem. Soc.*, **106**, 248 (1959).

(19) M. A. V. Devanathan, *Trans. Faraday Soc.*, **50**, 373 (1954).

(20) M. J. Astle, Thesis, Purdue University, 1941; F. Petru, *Coll. Czechoslov. Chem. Communs.*, **12**, 620 (1947).

(21) (a) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954; (b) T. Berzins and P. Delahay, THIS JOURNAL, **75**, 5716 (1953); (c) P. Delahay and C. C. Mattax, *ibid.*, **76**, 5314 (1954).

differences between A and X must be the same for all. This is necessary but not sufficient, for, in addition, the work terms for the species must be directly comparable. Such will be the case when they are negligible, *i.e.*, $2z_x/n_a = 1$ or $E_{0.5}$ is in the ECM region, or when they are the same for all members of the series, *i.e.*, the trivial case in which $E_{0.5}$ is nearly the same for all members. Unless one of these conditions holds, *the half-wave potentials for each member of the series must be corrected for the work terms before valid comparison can be made.*

Delahay and Mattax[21] attempted to make such a correction in the reduction of iodate by comparing for different media not the half-wave potentials for reaction in these media, but rate constants calculated from the half-wave potentials and extrapolated back to the ECM's. They thought by comparing rate constants at the ECM where $\phi_{sb} = 0$ they could correct for any possible influence of the double layer. This method of correction is wholely inadequate, however, for two reasons. Firstly, any extrapolation of rate constants from one potential to another by assuming constant αn_a is suspect because of the nature of αn_a (*vide infra*). Even conceding that such an extrapolation is possible, the "correction" is not a correction at all. The position of the ECM in the media in which Delahay and Mattax worked was determined primarily by the nature of the anion of the supporting electrolyte[17]; whereas, in the potential region in which they worked, the characteristics of the double layer are determined entirely (except for the case of iodide) by the nature of the cation. Consequently, these workers "corrected" for an effect which was not operative in their experiments. Recently Breiter, Kleinerman and Delahay have offered a different interpretation.[12]

A possible example of the effect of ignoring the work term in making half-wave–σ correlations can be seen in the work of Strier and Cavagnol.[22] The ρ value calculated by these workers for the reduction of several quinoxalines varies in the fashion −0.07, −0.06, −0.04, −0.05, −0.05 at the potentials −0.35, −0.5, −0.65, −0.75, and −0.90, respectively, corresponding to a range of *p*H of two to ten. This systematic change of ρ with potential closely parallels the expected change of work term with potential in the same region.

In addition to its theoretical implications, the effect of inert electrolytes on the half-wave potentials of irreversible reductions has important consequences for the analyst. By suitable adjustment of the electrolyte composition, waves can be shifted along the potential axis and interferences minimized or eliminated. Thus, some corticosteroids, which in acetate buffers are difficult to determine because their waves are drawn out and merge with that for solvent decomposition, can be determined readily if tetrabutylammonium salts are added to the solution.[23] The effect is not due to increased overpotential for background discharge but results from an anodic shift and a steepening of the slope of the steroid wave. Interestingly, addition of calcium ion under similar conditions causes no such shift. Similarly, Elofson[24] found that the presence of tetraalkylammonium salts was essential to the satisfactory polarographic determination of cycloöctatetraene. The wave of chloroform, from the work of Lothe and Rogers,[14] can also be improved by the same technique.

Slopes of Polarographic Waves.—Many authors have suggested that the slope of the log $(i_d - i)/i$ plot for a polarographic wave is a valid criterion as to its obedience to the Nernst equation. Some have gone so far as to suggest that slopes which were non-Nernstian provided a valid measure of the "degree of reversibility." Equation 11, however, suggests that this type of interpretation is questionable. The slope of an electron-transfer controlled wave is determined simply by the relative magnitudes of z_x, n_a and $\delta\phi_{es}/\delta E$.

The equation suggests further that it should be possible to correlate αn_a with the position of the reduction wave relative to the ECM and with the composition of the electrolyte. Qualitatively $(\delta\phi_{es}/\delta E)$ is a minimum near the ECM and rises roughly parabolically on either side at distances not too far removed. The steepness of the rise is dictated by the electrocapillary activity of the ions of the electrolyte, being steepest for species such as iodide and tetraalkylammonium ions which are most strongly adsorbed. Roughly, the form of this variation parallels that of the differential capacitance of the double layer.

In the simplest case of a species for which $z = 0$, the curve of αn_a *versus* potential would be expected to have this same parabolic shape. Unfortunately, experimental verification of this prediction is not a simple matter. Any particular polarographic wave gives only one measure of αn_a (essentially an average value over the rising portion of the wave which approximates the value at the half-wave potential), so that in order to obtain αn_a over a range of potentials, it is necessary to shift the half-wave potential over the same range. It is obvious that any procedure which shifts the half-wave potential could affect αn_a by means other than simple alteration of ϕ_{es}. Nevertheless, two sets of experimental evidence will be offered.

Lothe and Rogers[14] observed that the half-wave potential for carbon tetrachloride reduction shifts markedly to cathodic potentials on lowering the dielectric constant. One might expect that this shift reflects merely the decreased stability of the intermediate CCl_4^- relative to CCl_4 in a medium of lower dielectric constant rather than a change in mechanism. If so, since $z_x = 0$, the behavior should be that described above. Figure 1 shows the experimental data of Lothe and Rogers. Of course, the ECM changes somewhat with solvent composition and there is uncertainty as to the liquid junction potential but the essential features are present. On the anodic side of the ECM, the anion determines αn_a, on the cathodic side the cation is important, and a minimum is observed in the vicinity of the ECM. Unfortunately, no data are available on $\delta\phi_{es}/\delta E$ in these mixed solvents to allow quantitative comparison with theory.

---

(22) M. P. Strier and J. C. Cavagnol, THIS JOURNAL, **80**, 1565 (1958).

(23) B. M. Mitzner, private communication, 1958.

(24) R. M. Elofson, *Anal. Chem.*, **21**, 917 (1949).

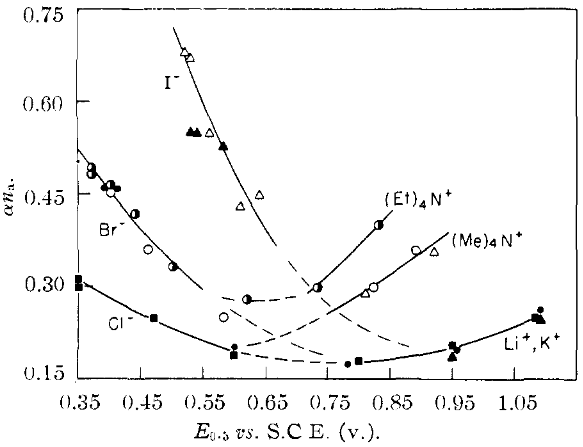

Fig. 1.—Variation of αn_a with $E_{0.5}$ for carbon tetrachloride in ethanol–water mixtures. Data of Lothe and Rogers: circle, bromide; open circle, tetramethylammonium; square, chloride; dark square, lithium or potassium; triangle, iodide; cross-hatch, tetraethylammonium.

Rosenthal, Albright and Elving[25] studied the reduction of the C_3 to C_8 α-bromoalkanoic acids. They observed that the half-wave potentials had a sigmoidal *p*H dependence which can probably be ascribed to reduction of the undissociated acid at low *p*H and of some other species at high *p*H with transition between the two in the intermediate range. One might expect that the mechanism for the reaction would not change from that in strong acid until attainment of relatively high *p*H. If so, since $z_x = 0$, αn_a would again be expected to vary in parabolic fashion. The data of Elving and co-workers are plotted in Fig. 2. Again, there are unfortunately no data available on $\delta\phi_{es}/\delta E$ in the buffers chosen by these workers. However, for purposes of comparison, since n_a is probably unity for this system, $0.5(\delta\phi_{es}/\delta E)$ for 0.3 *M* sodium chloride[17] is plotted (triangles) in Fig. 2. The correspondence of the αn_a data with this curve is amazingly close.

If the theory is correct, the agreement in Fig. 2 is good evidence that one electron is involved in the rate-determining step and thus that the reduction proceeds through a free-radical intermediate. That the change in αn_a is more directly related to change in $E_{0.5}$ than to change in *p*H becomes evident on comparison of Figs. 2 and 3. The plot of αn_a *versus* *p*H shows quite random behavior, while that *versus* potential (allowing for changes in medium) has a more systematic form.

A number of interesting conclusions can be drawn from the predictions of equation 11. By extrapolation of the data of Fig. 2, it would seem that at more anodic potentials αn_a would become very large and the slope of the log $(i_d - i)/i$ plot might even *exceed* the value predicted by the Nernst equation. Thus Elving, Rosenthal and Kramer[26] observed that at *p*H 3.7 the αn_a values for reduction of tri-, di- and monobromoacetic acids with half-wave potentials at −0.08, −0.21 and −0.79 volts *versus* SCE, respectively, were 2.4, 1.1 and 0.43, respectively. These workers suggested that the steep slope for tribromo reduction might imply obedience to the Nernst equation. In view of the consistently irreversible character of other halo-compound reductions, however, it might be more plausible to suggest that the steepness of slope in this case is merely a consequence of the double-layer structure in the potential region in which the reduction occurs.

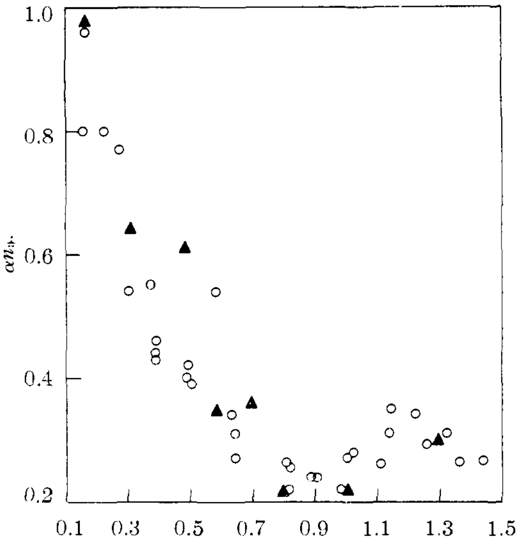

Fig. 2.—Variation of αn_a with $E_{0.5}$ for C_3-C_8 α-bromo-*n* alkanoic acids: ○, experimental (Rosenthal, Albright and Elving)[21]; ▲, theoretical (Grahame).[17]

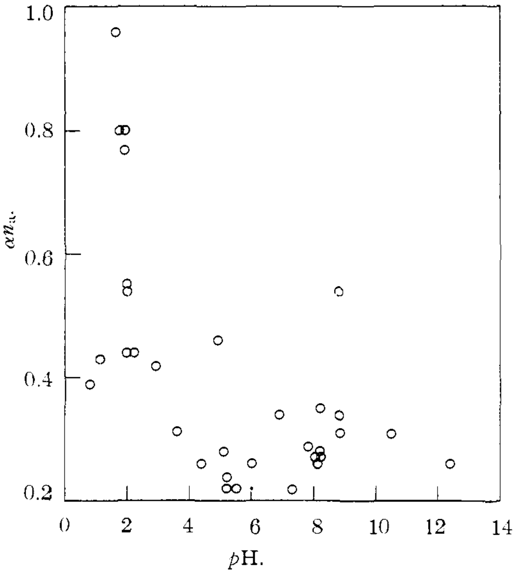

Fig. 3.—Variation of αn_a with *p*H for C_3-C_8 α-bromo-*n*-alkanoic acids. Data of Rosenthal, Albright and Elving.[21]

The foregoing results indicate that wave slope is a questionable criterion for polarographic reversibility. If the slope appears to be non-Nernstian, then complicating factors are involved, but the inverse is not necessarily true. It would seem much safer to use variation of half-wave potential with drop-time,[27] variation of current

---

(25) I. Rosenthal, C. H. Albright and P. J. Elving, *J. Electrochem. Soc.*, **99**, 227 (1952).

(26) P. J. Elving, I. Rosenthal and M. K. Kramer, THIS JOURNAL, **73**, 1717 (1951).

(27) E. F. Orlemann and I. M. Kolthoff, *ibid.*, **64**, 1970 (1942).

with mercury height on the rising portion of the wave[14,28] or, where possible, superposition of half-wave potentials of anodic and cathodic waves.

In this light, it is also interesting to speculate as to whether transfer coefficients determined by oscillographic techniques are directly comparable to those obtained in conventional polarographic experiments since, in the former case, the measurements are often made in times comparable to those required for the establishment of the double layer. Indeed, Gerischer[29] and Berzins and Delahay[29b] found transfer coefficients for cadmium ion reduction of approximately 0.2 while Bauer and Elving's[29c] values were in the range 0.37 to 0.47. All of these values were determined by methods in which this factor might be important.

Some Limitations and Complications.—Thus far we have considered cases which are more or less explicable in terms of equations 8 and 11. It might be well to point out, however, some cases to which these equations are not directly applicable or in which complicating factors are present.

Firstly, the theory of Marcus applies only to cases in which there is electron-transfer between electrode and species. Cases in which there is ion transfer across the interface are not considered, although it is obvious that salt effects based on the same principles would be expected to occur.

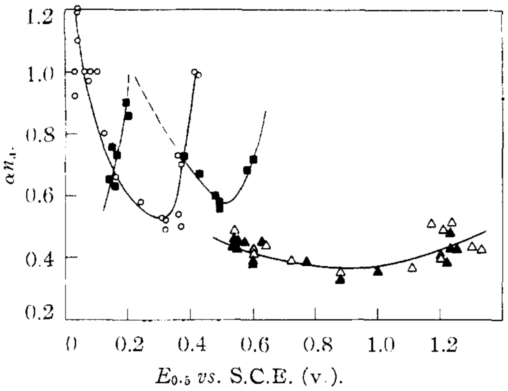

Fig. 4.—Variation of αn_a with $E_{0.5}$ for various α-haloalkanoic acids, data of Elving, Rosenthal and Kramer.[26]: O, dibromoacetic; ■, iodoacetic; △, bromoacetic; ▲, dibromoacetic (second wave).

Secondly, we have assumed that there is only one slow electrochemical step in the reduction process. Qualitatively, the same phenomena would occur in more complicated reactions, but quantitative interpretation would be much more difficult.

Thirdly, by invoking Koutecky's theory of the polarographic process, the equations have been limited to cases in which diffusion is the sole mode of mass transfer and the electrode is an expanding sphere. Extension to other cases in which the Nernst diffusion-layer treatment of Fick's laws of diffusion are valid is trivial. Even cases in which the limiting process is a kinetic one would be expected to show qualitatively the same salt effects.

Fourthly, the presence in the solution of such surface-active agents as gelatin would materially affect the characteristics of the double layer and the influence of salts upon polarographic waves.

Fifthly, cases in which the reaction process is complicated by a change in mechanism or a possible chemical reaction between reactants and products must be viewed with suspicion. A specific example of this type of complication is pertinent here. One might expect that, since organo-halogen reductions are all similar in character, the same arguments applied to the α-bromo acid reductions (*vide supra*) would hold in the case of iodoacetic acid and the αn_a, *versus* $E_{0.5}$ curve would be similar to that of Fig. 2. However, Elving, Rosenthal and Kramer[26] give the values shown in Fig. 4 for the reduction of iodoacetic acid at varying *p*H. Within a limited potential range (-0.2 to -0.5 volt) the variation in slope with half-wave potential shows the same behavior for the bromo and iodo acids except that in the iodo case the curve seems displaced to more cathodic potentials. In this region the previous explanation is still valid with the complication that iodide, a strongly electrocapillary ion, is produced in the reduction. This fact accounts for the cathodic shift. To account for the drastic drop in αn_a in the region less cathodic that -0.2 volt one must again consider the iodide formed in the reaction. In this region, especially near the foot of the wave, the iodide formed in the reduction can react with mercury. This would tend to draw out the wave and produce a marked decrease in the apparent αn_a.[30]

The rise in αn_a at -0.4 volt is not so easily explained. A similar phenomenon is shown by dibromoacetic acid (Fig. 4) except that the rise occurs at even less cathodic potentials. The data are again those of Elving and co-workers.[26] The drastic rise is evidently associated with some change in mechanism and can be closely correlated with the change of the species in bulk solution from acid to anion form. However, equation 11 indicates that if the actual reducible species became an anion, αn_a would be expected to decrease rather than increase. Possibilities which suggest themselves are: a change in gross mechanism; a change in the relative rates of the two electrochemical steps of the reaction, *i.e.*, first and second electron additions; or reaction of intermediates, which become longer lived at higher *p*H, with one another or the incoming reducible species.

Another possibility is that the reaction site is changing. We have assumed the potential ϕ_{sb} to be the potential difference between the inner Holmholtz plane and the electrode surface. However, *a priori* there is no reason to presume that the reaction cannot take place at some other place or, indeed, at a position which varies with potential and with the structure of the double layer.

Conclusions

An explanation has been offered for some salt effects in polarographic reductions. It is apparent that more data must be amassed before this explanation can be accepted as generally valid.

---

[28] K. B. Oldham, P. Kivalo and H. A. Laitinen, This Journal, **75**, 4148 (1953).

[29] (a) H. Gerischer, *Z. Elektrochem.*, **57**, 604 (1953); (b) T. Berzins and P. Delahay, This Journal, **77**, 6448 (1955); (c) H. H. Bauer and P. J. Elving, *Anal. Chem.*, **30**, 341 (1958).

[30] I. M. Kolthoff and C. S. Miller, This Journal, **63**, 1405 (1941).

However, a number of tentative conclusions can be reached. The slopes and half-wave potentials of electron-transfer controlled polarographic waves are markedly affected by electrolyte concentration and constitution in a manner which suggests strongly that the double-layer structure at the electrode surface is an important factor in these reactions. Interpretations of data which do not take this influence into account are strongly suspect.

Acknowledgments.—The authors are indebted to Professor R. A. Marcus for stimulating discussions and the opportunity to view his manuscript prior to publication. The authors wish to thank Professor D. C. Grahame for providing a Russian translation. This work was supported in part by the Atomic Energy Commission under Contract AT(30-1)-905.

CAMBRIDGE 39, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

A Potentiometric Study of 2-Substituted Benzimidazole Ligands[1]

BY T. J. LANE, C.S.C. AND JOHN M. DALY[2]

RECEIVED OCTOBER 29, 1958

The dissociation constants for several 2-substituted benzimidazole ligands have been determined in 50% v./v. dioxane-water. The stability constants of the ligands with various metals are reported. Thermodynamic result for 2-benzimidazoleacetic acid and for 2-benzimidazolepropionic acid agrees with crystal field treatment by George.[16]

As part of a program investigating effect of donor groups, ring size and steric effects on stabilities of chelate compounds several 2-substituted benzimidazole ligands have been prepared and their metal complexes have been investigated by potentiometric methods. The compounds studied in this work are shown in Fig. 1.

Experimental

Preparation of Reagents.—2-Benzimidazolecarboxylic acid,[3] 2-methylhydroxybenzimidazole,[3] 2-benzimidazoleacetic acid[3] and 2-benzimidazolepropionic acid[4] were prepared from known methods in the literature.

The standardization procedure for sodium hydroxide and perchloric acid is the same as that described by Freiser, Charles and Johnston.[5] Carbide and Carbon Co. technical 1,4-dioxane was purified according to method of Vogel[6] (final m.p. 11.65°). Stock solutions of approximately 0.01 *M* metal ion were prepared from reagent grade perchlorates (G. F. Smith Co.) and standardized by either electrodeposition (Cu(II), Co(II), Pb(II)), precipitation with dimethylglyoxime (Ni(II)) or precipitation as the 8-hydroxyquinolate (Mn(II) and Zn(II)).[7]

Apparatus and Procedure.—The titration apparatus consisted of a silvered water jacketed Pyrex vessel fitted with a leucite top through which holes were bored to accommodate microburets, thermometer, inlet and outlet tubes for Lamp nitrogen and the external glass-saturated calomel electrode pair. The system was thermostatically controlled to maintain the desired temperatures. Rapid mixing was effected by a magnetic stirrer. A Beckman Model G *p*H meter was standardized with Beckman buffer solutions (*p*H 4, 7, 10). The titration procedure is essentially the same as that described by Calvin and Wilson.[8]

The pK_{NH^+}, pK_{COOH} and pK_{OH} values were calculated by assuming that the *pK* of the protonated nitrogen is equal to the *p*H at the mid-point of the neutralization curve of the ligand and that the same is true of pK_{OH} and pK_{COOH} values. Stability constants of the chelates were calculated from equations developed by Freiser.[5] $\Delta H°$ values were determined from plots of $\ln K_n$ *vs.* $1/T$ for 2-benzimidazoleacetic acid and 2-benzimidazolepropionic acid.

Results and Discussion

As seen in Table I, the most basic ligand, as expected, is 2-hydroxymethylbenzimidazole. A gradual increase in basicity among the acids occurs with increasing distance between the basic nitrogen and the carboxylate group. This effect, also noted in amino acids,[9] is expected when an inductive group is further from the reaction center. The rather low basicity of 2-benzimidazolecarboxylic acid is explained by conjugation between the carboxylate group and the pyridine nitrogen.

TABLE I

ACID DISSOCIATION CONSTANTS IN 50% DIOXANE AT 25°

	pK_{NH^+}	pK_{COOH}
2-Hydroxymethylbenzimidazole	4.90	12.70[a]
2-Benzimidazolecarboxylic acid	3.04	6.48
2-Benzimidazoleacetic acid	4.14	7.20
2-Benzimidazolepropionic acid	4.72	6.52

[a] pK_{OH} in case of 2-hydroxymethylbenzimidazole.

The pK_{COOH} value of benzimidazoleacetic acid compared to that of benzimidazolecarboxylic acid shows the expected decrease in acid strength because of the shielding effect of the methyl group between the carboxylate group and the nitrogen of the ring. The surprising increase in the acidity of benzimidazolepropionic acid may be explained by its ability to form an intramolecular lactam.[10] In such a structure, ionization could take place easier and the acid dissociation constants as listed in Table I are the expected values.

Stability Constants.—Data for the determination of stability constants for all the ligands with all the metals could not be obtained because formation of the system occurred at low *p*H value or at *p*H value above the hydrolysis *p*H of metal ion used. As

---

[1] Presented in part before the Division of Physical and Inorganic Chemistry, 133rd National Meeting of the American Chemical Society held in San Francisco, California, April, 1958.

[2] From a dissertation presented by John M. Daly in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1958.

[3] R. A. Copeland, THIS JOURNAL, **65**, 1072 (1943).

[4] M. A. Phillips, *J. Chem. Soc.*, 2393 (1928).

[5] H. Freiser, R. G. Charles and W. D. Johnston, THIS JOURNAL, **74**, 1383 (1952).

[6] A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1951, p. 175.

[7] F. J. Welcher, "Organic Analytical Reagents," D. Van Nostrand Co., New York, N. Y., 1947, p. 263.

[8] M. Calvin and K. W. Wilson, THIS JOURNAL, **67**, 2003 (1945).

[9] E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 576.

[10] K. Hoffman, "Imidazole and its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1953, p. 315.