

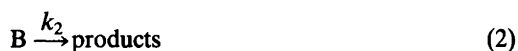
Improvement of Potential Step Methods for Electrode Mechanism Analysis. Normalization of Single Step with Double Potential Step Data

VERNON D. PARKER

Laboratory for Organic Chemistry, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway

Electrode kinetic analysis using potential step chronoamperometry was made much more effective by combining the single and double potential methods. The single step method suffers from the difficulty of normalizing data when fast processes are studied. The double step method often gives theoretical working curves for different mechanisms which are difficult to distinguish. The methods were combined by normalizing the single step current to the forward current at the pulse width where the double step normalized current ratio (R_1) is equal to 0.500. Data for the combined method are obtained in the same experiment. This combination results in a highly effective kinetic tool for mechanism analysis and the assignment of rate constants. Theoretical data are presented for 7 different electrode mechanisms. The data were obtained at fixed values of the normalized current ratio, R_1 , at 0.05 intervals ranging from 0.10 to 0.90.

Compared to cyclic voltammetry (CV), double potential step chronoamperometry (DPSC) is a somewhat "blind" method. The technique, first described in detail by Schwarz and Shain¹ involves stepping the electrode potential from a rest value where no faradaic processes occur to a value where the forward reaction (1) takes place at a diffusion controlled rate. When a chemical reaction is coupled to charge transfer, for example the first order reaction (2), this is apparent from comparing the current due to reaction (1) with the corresponding current for (3) when the potential is stepped back to the original value



where reaction (3) is diffusion controlled. Although Schwarz and Shain¹ recommended a detail analysis of the entire current time curve, this is seldom done in practice. In fact, the theoretical data which have been presented for various electrode mechanisms²⁻⁴ are invariably based on only one data set for each experiment expressed as a current ratio.

The potential-time profile for the DPSC experiment is shown in Fig. 1a. The test solution normally contains only A, solvent, and electrolyte. At the rest potential (E_1) no faradaic processes take place until after the initial potential step to E_2 where A is reduced to B at a diffusion controlled rate. The potential is stepped back to E_1 at time equal to τ , which is the potential step width. The current-time response to this electrode potential perturbation is shown in Fig. 1b. Although the detailed shape of the current-time curve is significant,¹ the data are generally analyzed using a ratio of currents, I_b/I_f where I_b for back reaction (3) is measured at time equal to 2τ and I_f for reaction (1) is measured at the instant before the potential step at time equal to τ . The ratio of the currents is then normalized to the no-reaction case, *i.e.* k_2 equal to 0, by dividing by the theoretical value for Nerstian

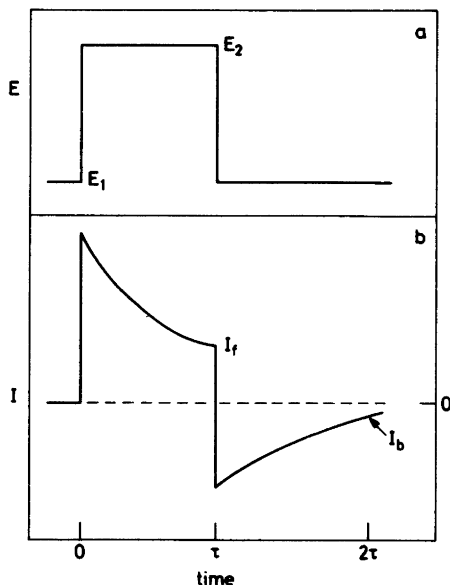


Fig. 1. The electrode potential perturbation (a) and the current response (b) during double potential step chronoamperometry.

charge transfer equal to $(1-2^{-1/2})$.¹ The normalized current ratio, R_I , can then be used to calculate rate constants by comparing with appropriate theoretical data. When only R_I are collected, irregularities in the response are usually not obvious.

Compared to DPSC, the response wave form in CV is information rich. The wave shape and the peak potential separation give immediate measures of the ideality of the response. On the other hand, CV is encumbered with problems that have no effect on the DPSC response. The two most prominent problems that must be dealt with in CV are uncompensated solution resistance and interference by heterogeneous charge transfer kinetics. These advantages inherent in the DPSC method provide considerably incentive to attempt to improve the specificity and information content of the data.

In this paper a simple means of greatly increasing the information content of DPSC data is presented. The method simply involves incorporation of the data that would be obtained in the single step chronoamperometry experiment with the DPSC R_I data. Single step chronoamperometry is used to a limited extent. The principal

disadvantage of the method is the difficulty of normalizing the data since currents rather than current ratios are measured. To properly normalize the current it is necessary to measure them at times short enough that any follow-up chemical reactions do not affect the current. This is very often impossible for practical reasons. This problem can be circumvented by taking some other reference instead of the no-reaction case as a standard. The method developed here involves normalizing the chronoamperometric current to the value where R_I for the process in question is equal to 0.500. Theoretical data for the seven most commonly discussed electrode mechanisms are presented for the combined single-double step method and the advantages are pointed out.

RESULTS AND DISCUSSION

The Method. The data that are used in the analysis are the values of I_f and I_b as defined in Fig. 1b. From these, R_I is obtained as is customary.²⁻⁴ Values of I_f and R_I are retained for analysis. The pulse width, τ , is varied at narrow intervals so that sufficient data are obtained with R_I ranging from 0.900 to 0.100. For direct comparison with theoretical data, discussed in the following section, it is desirable to have R_I at 0.050 intervals in this range. This is readily accomplished by adjusting the variable, τ , so that values of R_I very close on either side of those desired, *i.e.* 0.900, 0.850, 0.800, *etc.*, are obtained. The pertinent values of τ are then available by interpolation using relationship (4) in which the slope m is evaluated from the

$$\ln \tau = m \ln R_I \quad (4)$$

the data points on either side of the one desired. The \ln - \ln interpolation, as observed in similar cases,⁵ is much more accurate than a simple linear interpolation. The error that is involved in the interpolation is less than experimental error in the measurement of I_f and I_b . A similar interpolation is then used to obtain I_f when R_I are 0.900, 0.850, ..., 0.150, and 0.100.

Once the complete set of τ and I_f has been gathered, the data are normalized by division by the corresponding value for the case where $R_I=0.500$. The normalized values can then be compared directly with the corresponding theo-

Table 1. Description of electrode mechanism and simulation parameter.

No.	Symbols ^a	Mechanism ^b	Rate	Digital (C _A) _{t+1}	Simulations (C _B) _{t+1}
1	eC	$B \xrightarrow{k} P$	kC_B	(C _A) _t	(C _B) _t -rate
2	eCe _h	$B \xrightarrow{k} C$ $C+B \rightarrow A+P$	kC_B	(C _A) _t +rate	(C _B) _t -2 rate
3	ecE _h	$B \xrightleftharpoons{K} C$ $C+B \xrightarrow{k} A+P$	kKC_B^2	(C _A) _t +rate	(C _B) _t -2 rate
4	eC(dim)	$2 B \xrightarrow{k} P$	kC_B^2	(C _A) _t	(C _B) _t -2 rate
5	RS-2	$B+A \xrightarrow{k} C$ $C+B \rightarrow A+P$	$kC_A C_B$	(C _A) _t	(C _B) _t -2 rate
6	RS-3	$B+A \xrightleftharpoons{K} C$ $C+B \xrightarrow{k} A+P$	$kKC_A C_B^2$	(C _A) _t	(C _B) _t -2 rate
7	ee _h C (disp)	$2 B \xrightleftharpoons{K} C+A$ $C \xrightarrow{k} P$	kKC_B^2/C_A	(C _A) _t +rate	(C _B) _t -2 rate
8	eE _h c ^c	$2 B \xrightarrow{k} C+A$ $C \xrightarrow{\text{fast}} P$	kC_B^2	(C _A) _t +rate	(C _B) _t -2 rate

^a The symbols e and c have the usual meaning and capital letters are used to indicate rate determining steps while the subscript h is used for homogeneous electron transfers. RS-2 and RS-3 refer to versions of the radical-substrate coupling mechanism. ^b All mechanisms are preceded by; $A \pm e^- \rightarrow B$. ^c The simulation for this mechanism is identical to that for 3.

retical values. The normalized I_t vs. τ data, if desired, can be plotted to give the response curve equivalent to that obtained by single step chronoamperometry.

Acquisition of the Theoretical Data. It has recently been pointed out that approximate working curve fitting procedures for electrode mechanism analysis can be avoided by the direct comparison of theoretical and experimental values of variables necessary to obtain particular values of the observable.⁶ For DPSC, the variable is τ and the observable is R_I . A complete set of theoretical data for an electrode mechanism using this analysis consists of theoretical values of $k\tau$ or $kC_A^n\tau$, where C_A is the substrate concentration and n is an integer, for R_I ranging from 0.100 to 0.900 at 0.05 intervals.

The theoretical data were obtained by digital simulation⁷ for the seven mechanisms listed in Table 1. The rate equations for the electrode

mechanisms are given along with the appropriate finite difference equations used in the simulations.

The procedure for obtaining the theoretical data at the fixed R_I values was as follows. For each mechanism calculations were carried out over a wide range of k . The data were interpolated to the desired R_I using relationship (5) which is approximately followed

$$\ln R_I = m \ln k\tau \quad (5)$$

over small data intervals. The calculations were all carried out with a simulation concentration of unity so that (5) was applicable to all mechanisms. This procedure gave estimates of $k\tau$ at each of the appropriate R_I values in the range 0.100 to 0.900. Calculations were then carried out using this set of 17 $k\tau$ values. This resulted in a new set of data on which interpolation rela-

Table 2. Theoretical double and single step chronoamperometric data for mechanism 1, eC.

R_I	$k\tau$	τ_N	I_N^a
0.900	0.0627	0.153	1.000
0.850	0.0964	0.235	1.000
0.800	0.1321	0.321	1.000
0.750	0.1702	0.414	1.000
0.700	0.2110	0.514	1.000
0.650	0.2549	0.620	1.000
0.600	0.3024	0.736	1.000
0.550	0.3541	0.862	1.000

0.500	0.4109	1.000	1.000

0.450	0.4739	1.153	1.000
0.400	0.5446	1.325	1.000
0.350	0.6249	1.521	1.000
0.300	0.7181	1.748	1.000
0.250	0.8288	2.017	1.000
0.200	0.9651	2.349	1.000
0.150	1.1423	2.780	1.000
0.100	1.2947	3.394	1.000

$$^a I_N = I(\tau)\tau^{1/2}/I(\tau \text{ when } R_I=0.500) \tau^{1/2} (R_I=500).$$

Table 3. Theoretical double and single step chronoamperometric data for mechanism 2, eC_e_h.

R_I	$k\tau$	τ_N	I_N
0.900	0.0262	0.1479	0.885
0.850	?	?	?
0.800	0.0552	0.312	0.910
0.750	0.0717	0.405	0.922
0.700	0.0893	0.504	0.936
0.650	0.1084	0.612	0.951
0.600	0.1291	0.729	0.966
0.550	0.1520	0.847	0.982

0.500	0.1772	1.000	1.000

0.450	0.2055	1.160	1.018
0.400	0.2375	1.340	1.039
0.350	0.2742	1.547	1.062
0.300	0.3172	1.790	1.087
0.250	0.3690	2.082	1.116
0.200	0.4334	2.446	1.149
0.150	0.5184	2.926	1.189
0.100	0.6413	3.619	1.240

Table 4. Theoretical double and single step chronoamperometric data for mechanism 3, eC_e_h.

R_I	$k\tau C_A$	τ_N	I_N
0.900	0.0639	0.113	0.818
0.850	0.1009	0.178	0.837
0.800	0.1425	0.251	0.856
0.750	0.1896	0.334	0.878
0.700	0.2434	0.429	0.898
0.650	0.3055	0.538	0.922
0.600	0.3781	0.666	0.946
0.550	0.4640	0.818	0.972

0.500	0.5675	1.000	1.000

0.450	0.6945	1.229	1.030
0.400	0.8542	1.505	1.063
0.350	1.061	1.870	1.098
0.300	1.341	2.363	1.136
0.250	1.738	3.063	1.178
0.200	2.345	4.132	1.224
0.150	3.383	5.961	1.274
0.100	5.539	9.760	1.332

Table 5. Theoretical double and single step chronoamperometric data for mechanism 4, eC(dim).

R_I	$k\tau C_A$	τ_N	I_N
0.900	0.0910	0.106	1.000
0.850	0.1447	0.168	1.000
0.800	0.2056	0.239	1.000
0.750	0.2754	0.320	1.000
0.700	0.3561	0.414	1.000
0.650	0.4505	0.562	1.000
0.600	0.5621	0.654	1.000
0.550	0.6960	0.810	1.000

0.500	0.8594	1.000	1.000

0.450	1.063	1.237	1.000
0.400	1.323	1.539	1.000
0.350	1.665	1.937	1.000
0.300	2.133	2.482	1.000
0.250	2.811	3.271	1.000
0.200	3.865	4.497	1.000
0.150	5.706	6.640	1.000
0.100	9.602	11.17	1.000

Table 6. Theoretical double and single step chronoamperometric data for mechanism 5, S-2.

R_1	$k\tau C_A$	τ_N	I_N
0.900	0.0500	0.148	1.000
0.850	0.0767	0.228	1.000
0.800	0.1055	0.313	1.000
0.750	0.1365	0.405	1.000
0.700	0.1697	0.504	1.000
0.650	0.2061	0.612	1.000
0.600	0.2454	0.729	1.000
0.550	0.2890	0.858	1.000

0.500	0.3368	1.000	1.000

0.450	0.3908	1.160	1.000
0.400	0.4515	1.341	1.000
0.350	0.5216	1.549	1.000
0.300	0.6039	1.793	1.000
0.250	0.7026	2.079	1.000
0.200	0.8267	2.455	1.000
0.150	0.9896	2.938	1.000
0.100	1.2300	3.652	1.000

Table 7. Theoretical double and single step chronoamperometric data for mechanism 6, RS-3.

R_1	$k\tau C_A^2$	τ_N	I_N
0.900	0.1989	0.106	1.000
0.850	0.3173	0.168	1.000
0.800	0.4511	0.239	1.000
0.750	0.6046	0.320	1.000
0.700	0.7828	0.414	1.000
0.650	0.9900	0.524	1.000
0.600	1.235	0.654	1.000
0.550	1.520	0.810	1.000

0.500	1.889	1.000	1.000

0.450	2.336	1.237	1.000
0.400	2.907	1.539	1.000
0.350	3.657	1.936	1.000
0.300	4.684	2.450	1.000
0.250	6.168	3.265	1.000
0.200	8.476	4.630	1.000
0.150	12.50	6.617	1.000
0.100	21.01	11.12	1.000

tionship (5) was again applied. The third round of calculations invariably resulted in R_1 no further removed from the desired values than 0.0003.

Table 8. Theoretical double and single step chronoamperometric data for mechanism 7, $e_e C$.

R_1	$k\tau$	τ_N	I_N
0.900	0.00930	0.0812	0.747
0.850	0.01521	0.133	0.774
0.800	0.02225	0.194	0.801
0.750	0.03074	0.269	0.830
0.700	0.04104	0.358	0.862
0.650	0.05364	0.469	0.894
0.600	0.06935	0.606	0.928
0.550	0.08913	0.778	0.964

0.500	0.1145	1.000	1.000

0.450	0.1476	1.289	1.038
0.400	0.1915	1.673	1.078
0.350	0.2521	2.202	1.118
0.300	0.3386	2.957	1.160
0.250	0.4684	4.091	1.201
0.200	0.6778	5.920	1.241
0.150	1.054	9.205	1.282
0.100	1.870	16.33	1.320

The theoretical data are reported in Tables 2–8. We can take mechanism 1, the simple first order eC case, as an example and examine the theoretical data. The first column gives the R_1 rounded off to 3 decimals. The second column gives the $k\tau$ corresponding to the R_1 values. The third column labeled τ_N gives the range of experimental τ , normalized to that at R_1 equal to 0.500, corresponding to R_1 ranging from 0.100 to 0.900. The last column gives the appropriate single step chronoamperometry data, I_N . This consists of the current at the end of the first potential step, *i.e.* the forward current used in calculating R_1 , normalized by dividing by the value at R_1 equal 0.500 and multiplying by $\tau^{1/2}$. In other words, the last column corresponds to the normalized chronoamperometric working curve for the eC mechanism. It should be noted that the combination of the single step with the double step data does not require any new data that isn't used in the analysis of the double step data in the first place. The fact that I_N is unity for all R_1 for this mechanism is a reflection of the fact that the chemical step following the charge transfer has no effect on the flow of electrons since the e step is taking place at a diffusion controlled rate.

Table 9. A comparison of the theoretical chronoamperometric data for electrode mechanisms.

Mechanism	n^a	$\tau_N(\text{range})$	$I_N(\text{range})$
1, eC	0	0.153 to 3.394	1.000
2, eCe _h	0	0.148 to 3.619	0.885 to 1.240
3, ecE _h	1	0.113 to 9.760	0.818 to 1.332
4, eC(dim)	1	0.106 to 11.17	1.000
5, RS-2	1	0.148 to 3.652	1.000
6, RS-3	2	0.106 to 11.12	1.000
7, ee _h C(dis)	0	0.081 to 16.33	0.747 to 1.320
8, eE _h c(dis)	1	same as ecE _h	same as ecE _h

^a The exponent of C_A on the theoretical working curve X axis, i.e. $kC_A^n\tau$.

The limiting features of the data for all of the mechanisms are gathered in Table 9. A comparison of this data allows one to determine the ease with which the mechanisms are distinguished by the combined single step-double step analysis. Mechanisms 1, 2 and 5 are virtually indistinguishable from the range of τ_N . However 2 distinguishes from 1 and 5 on the basis of I_N leaving 1 and 5 which differ in reaction order and hence the exponent n of the theoretical working curve X axis, $kC_A^n\tau$. Similarly, mechanisms 3, 4 and 6 do not differ greatly in the range of τ_N . In this case it is 3 that has the unique range of I_N leaving once again 4 and 6 to be distinguished by the reaction order. Mechanism 7 is readily distinguished by the values of τ_N and I_N .

Conclusions. The theoretical data presented in Tables 2–8 are complete for all of the common simple electrode mechanisms for reactions following one electron transfer at the electrode. There are other cases involving the transfer of 2 e⁻ but these are rare and have not been implicated in experimental electrode mechanism studies.

What is unique with these data in comparison with other theoretical DPSC working curve data that have been presented,²⁻⁴ for example by Bard and co-workers,² is that data for the single step experiment are incorporated. Another useful feature of the data is that they can be, and should be, used in non-graphical form. Thus each experimental data point can be compared directly with the theoretical value and expressed as a standard deviation. Thus, the fidelity of the correspondence of experimental and theoretical data is readily expressed in quantitative terms.

The discussion of the data comparison in Table

9 makes it clear that the combined single step-double step analysis is highly effective in distinguishing between mechanistic possibilities. Providing that the experimental data are ideal and that the mechanism is one of those for which calculations have been carried out, mechanism assignment can be expected to be reliable using this method.

The data in Tables 2–8 also provide the limiting case data for complex and competing mechanisms which undergo a transition from one limiting case to another as the substrate concentration is changed. A procedure for determining rate constants and mechanisms in these cases using only the limiting case theoretical data has been presented.⁸

It must be kept in mind that the electrode response for an experimental system is not always ideal. Thus the situation frequently arises that the data do not fit any known theoretical data. Sometimes these problems are due to heterogeneous phenomena such as adsorption of products or intermediates on the electrode surface. In cases such as this the experimental data cannot be expected to fit the theoretical data which do not take into account the complications. It is often possible to make meaningful mechanism assignments even in these cases by the direct determination of reaction orders from the experimental data using the "Reaction Order Approach" which has recently been described in detail.⁸

Digital Simulation. The finite difference method was that of Feldberg.⁷ The resolution of the simulations was the same in all cases and consisted of 500 iterations for each potential step and assumed diffusion controlled charge transfer.

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