Acta Chemica Scandinavica B 37 (1983) 597–601

The Quantitative Comparison of Experimental to Theoretical Electrode Mechanism Data Using Normalized Working Curves

VERNON D. PARKER

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

The theoretical working curve is a plot of dimensionless observables on one axis and dimensionless variables on the other and is used for the comparison of experimental with theoretical electrode measurement data during electrode mechanism studies. This comparison is highly subjective and gives no quantitative measure of the correspondence of experimental and theoretical data. A method is described to remedy this situation. Theoretical and experimental values of variables (V) necessary for the observable (O) to be equal to fixed values are related by eqn. (i),

$$\ln (V_{exp}y) = m \ln (V_{theory}) + c \qquad \text{(i)}$$

where m and c are the slope and intercept and y is a constant. Providing that the experimental and theoretical data correspond to the same process and y is properly chosen, m will be unity. The analysis provides a quantitative measure of the fit of experimental data to the working curve. Normalized theoretical data for double potential step chronoamperometry (DPSC) and derivative cyclic voltammetry (DCV) analysis of several electrode mechanisms are presented. The method is demonstrated using experimental data for the dimerization of 9-diazofluorene anion radical in acetonitrile.

The most common way to relate experimental electrode measurements to the theoretical values for a particular electrode mechanism is to use a theoretical working curve. The theoretical working curve is a plot of some dimensionless observable such as the peak current ratio in cyclic voltammetry on one axis and the variables, in dimensionless form, on the other axis. The quantities that must be taken into account on the variable axis are evident from the units of the kinetic constants of the rate law for the process. For example, if the theoretical data correspond to a first order reaction of the primary intermediate (B) according to reactions (1) and (2), the unit of k_2 is s^{-1} or for the second order reaction (3), the units of k_3 are $M^{-1}\ s^{-1}$.

$$A \pm e^- \rightleftarrows B \qquad (1)$$

$$B \xrightarrow{k_2} C \qquad (2)$$

$$2B \xrightarrow{k_3} D \qquad (3)$$

In the first case, it is necessary that the other variable, such as the reciprocal of a ($=Fv/RT$), v is the voltage sweep rate, in cyclic voltammetry be expressed in s so that the units cancel. For the second order reaction (3) a dimensionless set of variables is obtained by the product of k_3, the electrochemical variable in s and the substrate concentration (C_A) in M.

Kinetic constants are estimated by finding the theoretical value of the variable corresponding to the experimental value of the observable. An undesirable feature of this procedure is that there is usually some question as to how well the experimental data fit the theoretical working curve. When data are presented in figures the deviations of the experimental data from the theoretical data are only evident when they are quite large. It is most often impossible for the reader of a paper making use of working curves

0302-4369/83 $02.50

to evaluate the reliability of the conclusions based on the data. It is the purpose of this paper to present a quantitative method for the comparison of experimental and theoretical electrochemical data related to electrode mechanisms. The method is similar to the procedure used for normalized potential sweep voltammetry.[1-4]

RESULTS AND DISCUSSION

The method is illustrated by the three dimensional plot in the figure. The observable (O) is represented as the z axis, the theoretical variables (V_{theory}) on the x axis and the experimental variables ($V_{exp}y$) on the y axis. Providing that the experimental and the theoretical data correspond to the same process and the constant y is properly chosen, the projection of the curve onto the x–y plane will define a straight line of unit slope and zero intercept. The value of y can be determined from linear regression relationship (4) by adjusting the scale so that $c=0$.

$$\ln(V_{exp}y) = m \ln(V_{theory}) + c \quad (4)$$

This can be done as a mechanism test by assuming the data at some arbitrary point correspond to that mechanism. That point is conveniently a value of 0.500 of the normalized observable such as the ratio of the derivative peaks during DCV (R'_I) or the normalized current ratio ($R_I=(1-2^{-1/2})i_b/i_f$) durring DPSC. In order to carry out the analysis both theoretical and experimental data must be obtained at the same values of the observable. Preferably, the data represent an as wide as possible range of O.

The deviations of m and c from unity and zero are numerical measures of the fidelity of the fit of the experimental to the theoretical data. The most effective way to test for linearity in the data is to divide the data into two equal segments of V_{theory} and then carry out three correlations; one on each data segment (m_1 and m_2) and one encompassing all of the data (m_T). The required data fit is $m_1=m_2=m_T=$unity. Any deviations from this relationship must be accounted for before assigning a mechanism to an electrode process.

Electrode mechanisms. Four different mechanisms will be considered and are listed below.

I. First order EC.

$$B \xrightarrow{k_I} \text{products} \quad (5)$$

II. First order ECE (or ECE_h).

$$B \xrightarrow{k_{II}} C \text{ (rate determining)} \quad (6)$$

$$C \pm e^- \rightarrow D \text{ (fast)} \quad (7)$$

$$C + B \rightarrow D + A \text{ (fast)} \quad (8)$$

III. Second order ion radical-substrate.

$$B + A \xrightarrow{k_{III}} B-A \text{ (rate determining)} \quad (9)$$

$$B-A \pm e^- \rightarrow \text{dimer (fast)} \quad (10)$$

IV. Second order dimerization.

$$2B \xrightarrow{k_{VI}} \text{dimer} \quad (11)$$

The working curve variables (V_{theory}) for the mechanisms are summarized both for DPSC and DCV in Table 1 along with the V_{exp} and the significance of y.

Theoretical data for all mechanisms are tabulated in Tables 2 and 3 for DPSC and DCV,

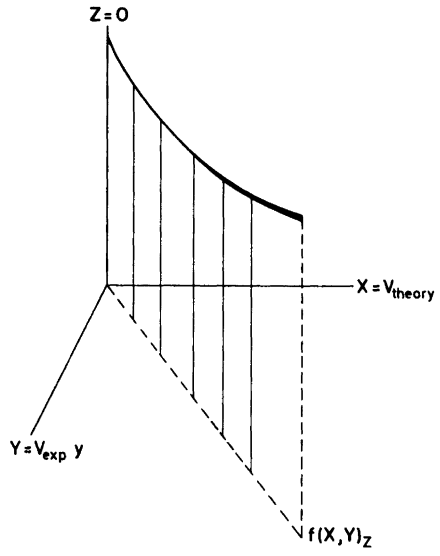

Fig. 1. Representation of the normalized working curve.

Table 1. Working curve parameters for electrode mechanisms.

Mechanism	Technique	V_{theory}	V_{exp}	y
I	DPSC	$k_I\tau$	τ	k_I
I	DCV	k_I/a	a^{-1}	k_I
II	DPSC	$k_{II}\tau$	τ	k_{II}
II	DCV	k_{II}/a	a^{-1}	k_{II}
III	DPSC	$k_{III}C_a\tau$	$C_A\tau$	k_{III}
III	DCV	$k_{III}C_A/a$	C_A/a	k_{III}
IV	DPSC	$k_{IV}C_A\tau$	$C_A\tau$	k_{IV}
IV	DCV	$k_{IV}C_A/a$	C_A/a	k_{IV}

respectively. In the case of DCV, a working curve is necessary for each value of $E_{sw}-E_{rev}$ which is the difference in switching and reversible potentials. The values given are for $E_{sw}-E_{rev}$ equal to 300 mV for mechanisms II–IV and 200 mV for mechanism I. Very nearly linear relationships have been reported for DCV mechanism analysis for all mechanisms but the first order EC so that the full working curve is not generally necessary.[5] The theoretical data used to construct

Table 2. Double potential step chronoamperometric theoretical data for normalized analysis.

R_I	$k\tau$(I)[a]	$k\tau$(II)[a]	$kC_A\tau$(III)[a]	$kC_A\tau$(IV)[a]
0.90	0.058	0.035	0.095	0.083
0.85	0.093	0.057	0.14	0.13
0.80	0.12	0.079	0.20	0.20
0.75	0.16	0.11	0.26	0.26
0.70	0.21	0.13	0.33	0.35
0.65	0.25	0.16	0.40	0.43
0.60	0.30	0.20	0.49	0.54
0.55	0.35	0.23	0.58	0.66
0.50	0.405	0.272	0.678	0.830
0.45	0.47	0.32	0.80	1.03
0.40	0.53	0.37	0.94	1.26
0.35	0.61	0.43	1.10	1.58
0.30	0.71	0.50	1.30	2.07
0.25	0.81	0.58	1.53	2.67
0.20	0.95	0.70	1.85	3.69
0.15	1.12	0.84	2.22	5.55
0.10	1.37	1.05	2.88	9.16
0.05	1.83	1.45	4.04	21.6

[a] The Roman numerals refer to the number of the mechanism in the text.

Table 3. Derivative cyclic voltammetric theoretical data for normalized analysis.

R'_I	k/a(I)[a]	k/a(II)[b]	kC_A/a(III)[b]	kC_A/a(IV)[b]
0.85	0.025	0.0152		
0.80	0.034	0.022		0.020
0.75	0.044	0.030	0.045	0.027
0.70	0.056	0.038	0.060	0.037
0.65	0.069	0.052	0.077	0.049
0.60	0.085	0.066	0.097	0.065
0.55	0.103	0.085	0.122	0.088
0.50	0.124	0.111	0.157	0.120
0.45	0.153	0.148	0.20	0.168
0.40	0.193	0.21	0.27	0.25
0.35	0.262	0.30	0.39	0.38
0.30	0.382	0.48	0.59	0.62
0.25	0.664	0.85	0.99	1.12

[a] For $E_{switch}-E_{rev}$ equal to 200 mV. [b] For $E_{switch}-E_{rev}$ equal to 300 mV.

Table 2 are those reported by Childs [6] and those for Table 3 were obtained by Ahlberg in connection with the analysis given in Ref. 5. For both DPSC and DCV relationship (12) was used to interpolate between the available theoretical values of the observable.

$$\ln O = m \ln V_{theory} + c \qquad (12)$$

This linear relationship holds over a very large range of the theoretical data for DCV[5] and over shorter intervals for the DPSC theoretical data. In no case is error introduced in the theoretical values due to inapplicability of (12).

The use of the normalized working curves is illustrated using DCV and experimental data obtained for the dimerization of 9-diazofluorene anion radical [7] in acetonitrile. The data are correlated with theoretical data for mechanism IV and the data are gathered in Table 4. Where possible, four different substrate concentrations were used. Some indication as to how well the experimental data correspond to the theoretical data can be obtained by noting the degree of deviations in y. The standard deviations at each R'_I value are no greater than ±10 % of y. Results from linear regression analysis of the data are summarized in Table 5. Some deviations from unity are observed in the slopes m. However, the

Table 4. Derivative cyclic voltammetry working curve data for the dimerization of 9-diazofluorene anion radical.

R'_I	$k_{IV}C_A/a$	C_A/mM	v/V s^{-1}	10^7 (C_A/a)	$10^{-5}y$/M^{-1}s^{-1}	
0.70	0.037	0.25	32.9	1.92	1.93	
0.65	0.049	0.25	27.2	2.32	2.11	
0.60	0.065	0.25	21.6	2.92	2.23	
0.55	0.088	0.25	16.2	3.90	2.26	2.13(0.18)
0.55	0.088	0.50	28.7	4.40	2.00	
0.50	0.120	0.25	11.9	5.30	2.26	2.34(0.09)
0.50	0.120	0.50	24.5	5.15	2.33	
0.50	0.120	0.75	38.4	4.93	2.43	
0.45	0.168	0.25	8.62	7.32	2.30	2.39(0.09)
0.45	0.168	0.50	18.1	6.67	2.41	
0.45	0.168	0.75	27.8	6.81	2.47	
0.45	0.168	1.00	33.2	7.60	2.21	
0.40	0.25	0.25	6.05	10.4	2.40	2.49(0.10)
0.40	0.25	0.50	12.5	10.1	2.48	
0.40	0.25	0.75	20.0	9.46	2.64	
0.40	0.25	1.00	24.7	10.2	2.45	
0.35	0.38	0.25	4.00	15.8	2.41	2.46(0.10)
0.35	0.38	0.50	8.26	15.3	2.48	
0.35	0.38	0.75	12.9	14.7	2.59	
0.35	0.38	1.00	15.7	16.1	2.36	
0.30	0.62	0.25	2.08	30.3	2.05	2.29(0.22)
0.30	0.62	0.50	4.91	25.7	2.41	
0.30	0.62	0.75	7.70	24.6	2.52	
0.30	0.62	1.00	8.82	28.6	2.17	
0.25	1.12	0.50	2.57	49.1	2.28	2.25(0.09)
0.25	1.12	0.75	4.00	47.3	2.37	
0.25	1.12	1.00	4.92	51.3	2.18	
					2.32(0.17)	

Table 5. Correlation parameters for the dimerization reaction.

Slope	R'_I	m [a]	r [b]	(s/Y_{mean})100/% [c]
m_1	0.70–0.45	0.89(3.4 %)	0.994	2.3
m_2	0.40–0.25	1.07(2.6 %)	0.996	8.1
m_T	0.70–0.25	0.97(1.6 %)	0.997	5.3

[a] From eqn. (4) and the data in Table 4. The error was calculated according to Ref. 12. [b] Linear regression correlation coefficient. [c] The standard deviation about the regression divided by the mean value of Y expressed in percent.

only significant deviation occurs in m_1. There are two likely reasons for the deviation. The first is that the rate of charge transfer may be interfering at the higher sweep rates necessary for high R'_I and secondly the data for the highest R'_I values are all from the lowest substrate concentrations which were necessary to limit the rate of the reaction. The R'_I data for the lowest C_A are expected to be in greater error than that for the higher concentrations.

Since there are plausible reasons for the deviations of m from the theoretical values, it can

be concluded that the experimental data for the dimerization of 9-diazofluorene anion radical correspond reasonably well to the theoretical data for the second order dimerization mechanism (IV). The slope m_T calculated for mechanism III is 1.19 with a standard deviation of 0.016 and is therefore significantly different from unity.

It has recently been emphasized that theoretical working curves may not be unique for a particular electrode mechanism.[8] Other drawbacks to the use of the theoretical working curve were also pointed out and an alternative method, using reaction orders without calculations, has been presented.[9] If the theoretical working curves are to be used in electrode mechanism determination it is surely highly desirable that some indication be given of how well the experimental and theoretical data correspond. The method presented here provides a quantitative comparison of experimental to theoretical data for electrode mechanisms.

EXPERIMENTAL

The instrumentation, electrodes, cells and data handling procedures were those described earlier.[10] Reagent grade acetonitrile containing Bu_4NBF_4 (0.1 M) was passed through a column containing neutral alumina before use. 9-Diazofluorene was that used in earlier work.[7] Derivative cyclic voltammetry experiments were carried out as previously described.[11]

REFERENCES

1. Aalstad, B. and Parker, V. D. *J. Electroanal. Chem. 122* (1981) 183.
2. Aalstad, B., Ahlberg, E. and Parker, V. D. *J. Electroanal. Chem. 122* (1981) 195.
3. Aalstad, B. and Parker, V. D. *J. Electroanal. Chem. 133* (1982) 33.
4. Aalstad, B. and Parker, V. D. *J. Electroanal. Chem. 136* (1982) 251.
5. Ahlberg, E. and Parker, V. D. *Acta Chem. Scand. B 35* (1981) 117.
6. Childs, W. V., Maloy, J. T., Keszthelyi, C. P. and Bard, A. J. *J. Electrochem. Soc. 118* (1971) 874.
7. Parker, V. D. and Bethell, D. *Acta Chem. Scand. B 35* (1981) 691.
8. Parker, V. D. *Acta Chem. Scand. B 35* (1981) 123.
9. Parker, V. D. *Acta Chem. Scand. B 35* (1981) 233.
10. Ahlberg, E. and Parker, V. D. *Acta Chem. Scand. B 34* (1980) 97.
11. Ahlberg, E. and Parker, V. D. *J. Electroanal. Chem. 121* (1981) 73.
12. Davies, O. L. and Goldsmith, P. L. *Statistical Methods in Research and Production,* Imperial Chemical Ind., 1972, Chapter 7.

Received October 15, 1982.