Normalized Potential Sweep Voltammetry. V. Application to the Determination of Rate Constants of Homogeneous Chemical Reactions Coupled to Charge Transfer

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The Normalized Potential Sweep Voltammetry (NPSV) procedure has been extended to cases where the shape of the wave is dependent upon the rate of the chemical reactions coupled to charge transfer. The method is applicable to mechanisms with reaction orders greater than 1. Theoretical results were obtained for four mechanisms and the relationships between NPSV slopes and rate constants are presented in terms of 3rd order polynomial equations. Rate constants were determined for the dimerization of an anion radical and found to be in good agreement with those determined using other methods. The method is particularly valuable for fast second order reactions and is applicable for processes with rate constants of the order 10^2 greater than those that can be determined by other common measurement techniques.

Previous papers in this series [1–4] have dealt with the development and application of Normalized Potential Sweep Voltammetry (NPSV) for the study of electrode mechanisms,[1] heterogeneous charge transfer kinetics,[2,3] and the analysis of closely spaced electron transfers.[4] The work concerning electrode mechanisms[1] involved the analysis of purely kinetic waves, *i.e.* the shapes of which are independent of the rate of the reaction, the substrate concentration, and the voltage sweep rate (v). Under these conditions the shapes of the waves are dependent only on the mechanism of the reactions following charge transfer. Thus, the mechanisms of purely kinetic processes can be assigned by NPSV analysis but rate constants cannot be determined.

If we take a Nernstian electron transfer reaction (1)

$$A + e^- \rightleftharpoons B \tag{1}$$

$$2B \xrightarrow{k_1} C \tag{2}$$

followed by the irreversible second order reaction (2) and consider how changes in the magnitude of k_1 affect the shape of the linear sweep voltammetry (LSV) wave, as measured by the NPSV slope, we find that data are available for $k_1 = 0$ and for large values of k_1 (purely kinetic conditions) but not for the intermediate cases. It will be recalled that the NPSV method is a three dimensional analysis of normalized current (Z axis), theoretical electrode potential data (X axis) and experimental electrode potential data (Y axis).[1] In practice this is most often reduced to two dimensions with experimental electrode potentials linearly correlated with theoretical data for Nernstian charge transfer. Under these conditions the slope of this linear correlation, m, is equal to 1.000 for $k_1 = 0$ and to 0.69 under purely kinetic conditions. This suggests that there should be some relationship between m and k_1 in the intermediate kinetic region.

The data presented in this paper show that NPSV can be used to determine rate constants in the intermediate kinetic region. Most significantly, analysis of theoretical data revealed that the NPSV analysis is applicable to the determination of rate constants up to about 10^2 greater than those available from existing techniques such as

derivative cyclic voltammetry and double potential step chronoamperometry.

RESULTS AND DISCUSSION

Electrode Mechanisms. First order reactions of intermediate B generated in charge transfer reaction (1) give rise to NPSV slopes of greater than 0.9 for purely kinetic processes when the theoretical data are for Nernstian charge transfer.[1] Thus, this leaves a very small range, 1.0 to 0.9, for the intermediate region. Very high precision has been reported for the slopes so that analysis of first order processes is not precluded. In this study, only higher order mechanisms are considered in order to have maximum ranges of applicability. The mechanisms along with the appropriate rate equations are given in Table 1.

Theoretical Data. Theoretical LSV curves were calculated by digital simulation as presented by Feldberg.[5] In order to determine how great the resolution of the simulation must be in order to give reliable NPSV slopes, calculations were carried out on an EC mechanism at different values of the simulated sweep rate, v_{sim}, which is a direct measure of the resolution. Values of the half-peak potential, $E^{p/2}$, along with the NPSV slope are given in Table 2. The calculations are for a purely kinetic process with k/a ($a=Fv/RT$) equal to 10. The features of most interest are that m changed negligibly with a 40-fold change in v_{sim} and appears to converge to 0.935. On the other hand, $E^{p/2}$ was observed to be much more dependent upon the resolution of the simulation and did not come to a constant value as v_{sim} was decreased to 0.025. The column labeled Δ gives the difference in mV brought about by the successive changes in v_{sim}. It can be seen from the

Table 1. Electrode mechanisms and rate equations.

No.	Mechanism	Rate Equation
1	$A+e^- \rightleftharpoons B$ $2B \xrightarrow{k_1} products$	Rate$=k_1 C_B{}^2$
2	$A+e^- \rightleftharpoons B$ $B+A \overset{K_2}{\rightleftharpoons} C_2$ $C_2+B \xrightarrow{k_2} P_2+A$	Rate$=k_2 K_2 C_A C_B{}^2$
3	$A+e^- \rightleftharpoons B$ $B+A \xrightarrow{k_3} C3$ $C_3+B \xrightarrow{fast} P_3+A$	Rate$=k_3 C_A C_B$
4	$A+e^- \rightleftharpoons B$ $B \overset{K_4}{\rightleftharpoons} C4$ $C4+B \xrightarrow{k_4} P_4+A$	Rate$=k_4 K_4 C_B{}^2$

Δ values that a factor of 2 decrease in v_{sim} brings about approximately a factor of 2 decrease in Δ which suggests that $E^{p/2}$ converges to a value of very close to 58.35. This suggests that the simulations give reliable NPSV data as long as v_{sim} is less than 1 and that an error no more than about 0.1 mV will be involved in the $E^{p/2}$ values when v_{sim} is 0.05 mV/step. All theoretical data reported in the remainder of this paper refer to calculations in which v_{sim} was equal to 0.05 mV/step.

Results of the Calculations. The data obtained for mechanisms (1) to (4) are summarized in Tables 3 to 6. In the intermediate kinetic region, with the exception of mechanism (3), the NPSV slopes measured with the normalized current I_N

Table 2. Test for convergence in the simulations of the EC mechanism.[a]

v_{sim}/(mV/step)	k_{sim}	$E^{p/2}$/mV	Δ/mV	N[b]
1.00	0.3893	60.48		0.933
0.50	0.3893/2	59.38	1.10	0.934
0.25	0.3893/4	58.86	0.52	0.934
0.10	0.03893	58.56	0.32	0.935
0.05	0.03893/2	58.46	0.10	0.935
0.025	0.03893/4	58.41	0.05	0.935

[a] For reaction with a normalized rate constant, $k(Fv/RT)^{-1}$, equal to 10.0. [b] The NPSV slope with I_N ranging from 0.20 to 0.80.

Table 3. Theoretical LSV data for the second order dimerization mechanism.[a]

log kC/a^b	$E^{p/2}$ ^{c}/mV	$m(1)$ ^{d}	$m(2)$ ^{d}	$m(1)-m(2)$ ^{d}
2.408	66.09	0.663	0.678	−0.015
2.107	60.19	0.686	0.684	0.002
1.806	54.40	0.699	0.691	0.008
1.505	48.80	0.707	0.702	0.005
1.204	43.46	0.746	0.719	0.027
0.903	38.59	0.786	0.746	0.040
0.602	34.44	0.837	0.785	0.052
0.301	31.29	0.891	0.835	0.056
0.000	29.32	0.936	0.889	0.047
−0.301	28.35	0.966	0.935	0.031
−0.602	28.00	0.984	0.965	0.019

[a] Digital simulation with a resolution of 0.05 mV/time step assuming a temperature of 298.1 K. [b] Dimensionless rate constant for the mechanism as indicated in Table 1. [c] The half-peak potential. [d] The NPSV slopes with I_N ranging from 0.20 to 0.50 [m(1)] and from 0.50 to 0.80 [m(2)].

Table 4. Theoretical LSV data for the third order Radical-Substrate Coupling mechanism.[a]

log kC/a^b	$E^{p/2}$ ^{c}/mV	$m(1)$	$m(2)$	$m(1)-m(2)$
3.010	78.59	0.697	0.745	0.048
2.709	72.44	0.703	0.749	0.046
2.408	66.42	0.709	0.753	0.044
2.107	60.53	0.717	0.756	0.039
1.806	54.76	0.729	0.762	0.033
1.505	49.20	0.747	0.770	0.023
1.204	43.94	0.774	0.784	0.010
0.903	39.17	0.812	0.806	−0.006
0.602	35.17	0.859	0.840	−0.019
0.301	32.16	0.905	0.879	−0.026
0.000	30.21	0.943	0.919	−0.024
−0.301	29.11	0.969	0.952	−0.017
−0.602	28.57	0.984	0.974	−0.010

[a] See Table 3 for definitions.

Table 5. Theoretical LSV data for the second order Radical-Substrate Coupling mechanism.[a]

log kC/a	$E^{p/2}$	$m(1)$	$m(2)$	$m(1)-m(2)$
1.806	92.09	1.005	1.011	−0.006
1.505	82.51	1.008	1.015	−0.007
1.204	73.36	1.007	1.021	−0.014
0.903	64.57	1.013	1.029	−0.016
0.602	56.23	0.999	0.998	0.001
0.301	48.60	0.999	0.996	0.003
0.000	42.02	0.999	0.998	0.001
−0.301	36.84	1.001	1.001	0.000
−0.602	33.19	1.003	1.006	−0.003

[a] See Table 3 for definitions.

Table 6. Theoretical LSV data for the second order, electron transfer rate limiting mechanism.[a]

log kCa	$E^{p/2}$/mV	$m(1)$	$m(2)$	$m(1)-m(2)$
2.408	54.72	0.686	0.695	−0.009
2.107	48.86	0.697	0.707	−0.010
1.806	43.15	0.711	0.720	−0.009
1.505	37.64	0.730	0.739	−0.009
1.204	32.43	0.759	0.762	−0.003
0.903	27.72	0.812	0.796	0.016
0.602	23.88	0.857	0.844	0.013
0.301	21.44	0.921	0.908	0.013
0.000	20.90	0.975	0.975	0.000
−0.301	22.16	1.003	1.018	−0.018

[a] See Table 3 for definitions.

($I_N=I/I^p$) ranging from 0.20 to 0.80 showed some deviation from linearity. For this reason, overlapping slopes m_1 ($I_N=0.20$ to 0.50) and m_2 ($I_N=0.50$ to 0.80) were calculated. For mechanisms (1), (2) and (4) theoretical working curves, either m_2 or $E^{p/2}$ vs. the appropriate rate constant normalized both for sweep rate and substrate concentration, were plotted. The curves for mechanism (1), which would commonly involve the dimerization of B, are shown in Figs. 1 and 3. In Fig. 2, Δm the difference in the two overlapping slopes is plotted vs. the normalized rate constant. The solid lines in Figs. 1 and 3 were obtained by fitting to third order polynomial equations (3) where x refers to the

$$y=A+Bx+Cx^2+Dx^3 \tag{3}$$

normalized rate constant and y to either m_2 or $E^{p/2}$. In all cases the best fit was obtained by dividing the data in two overlapping portions. In the case of Fig. 1, the point with coordinates (0.602, 0.786) was part of both segments of the line. The coefficients for eqn. (3) for the three mechanisms are listed in Table 7.

It is interesting to note that the shape of the LSV wave for mechanism (3) which corresponds to the coupling of the electrode generated intermediate with substrate is very nearly independent of the rate of the homogeneous reaction. In this case m_1 and m_2 are practically identical and
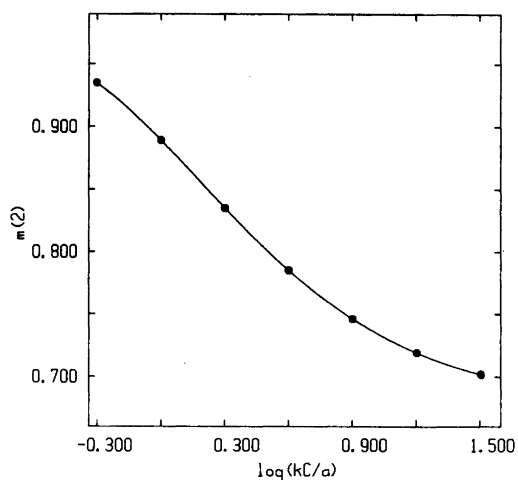

Fig. 1. Theoretical working curve for the determination of rate constants using NPSV data for irreversible dimerization.
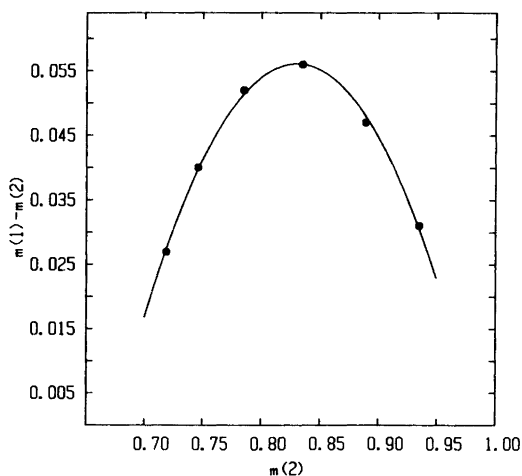

Fig. 2. The difference in NPSV slopes m_1 and m_2 as a function of normalized rate constant for irreversible dimerization.

Fig. 3. Theoretical working curve for the effect of the normalized rate constant on the half-peak potential for irreversible dimerization.

very close to unity. This mechanism differs from the others in that it is first order in B while all the others are for reactions second order in B. Thus, it appears that the reaction order in the electrode generated intermediate is the factor most responsible for the shape of LSV waves for Nernstian charge transfer coupled to homogeneous chemical reactions.

Experimental Demonstration of the Method. The dimerization of the anion radical of *p*-methylbenzylidenemalononitrile (MBM) was chosen as a model reaction to demonstrate the determination of rate constants by NPSV. The kinetics of the reaction have previously been investigated by derivative cyclic voltammetry,[6] LSV[6,7] and Convolution Potential Sweep Voltammetry.[8] The products of the reaction have

been determined[9,10] to be cyclic dimers as tautomeric mixtures as in the related structures *1* and *2*.

The data are summarized in Table 8. The reaction was studied both in the absence and presence of acetic acid. The role of acetic acid is to protonate the dimer dianions formed in the dimerization of MBM$^-$ and the acid does not enter into the rate law.[6] It has been found that the kinetic results are better reproducible in the presence of HOAc. The overall results of the five sets of analyses is a rate constant equal to $4.84(\pm 7\ \%)\times 10^5\ M^{-1}s^{-1}$. The results from the previous study (6) were less consistent. Rate constants ranging from 2.8 to $6.8\times 10^5\ M^{-1}s^{-1}$ were reported under comparable conditions (Table 8 in Ref. 6) and were dependent upon the substrate concentration.

The data in Table 8 encompass *v* from 0.20 to 20 V/s with m_2 values ranging from 0.704 to 0.926, respectively. Thus, nearly the entire range of m_2 available for analysis was used in the determination of the rate constant.

Table 7. Parameters for the third order polynomial equations for the theoretical working curves.

Mechanism	$m(2)$ Range	A^b	B^b	C^b	D^b
1	0.702–0.785	0.9070	−0.2580	−0.991	−0.0122
1	0.785–0.935	0.8890	−0.1728	−0.0441	−0.0733
2	0.762–0.840	0.9543	−0.2518	0.1135	−0.0183
2	0.840–0.952	0.9190	−0.1257	−0.0386	0.0489
4	0.707–0.796	0.9766	−0.2820	0.1052	−0.0153
4	0.796–0.975	0.9750	−0.2132	−0.0552	0.0795

^{a} The mechanisms are defined in Table 1. ^{b} Parameters for the equation, $y=A+B\,x+C\,x^2+D\,x^3$, where $y=m(2)$ and x the logarithm of the appropriate dimensionless rate constant.

Table 8. Evaluation of rate constants for the dimerization of methylbenzylidenemalononitrile anion radical in DMF.[a]

[MBM]/mM	[HOAc]/mM	v/Vs^{-1}	$m(2)$	$10^{-5}\ k/M^{-1}s^{-1}$
0.50	0	0.20	0.704(2)	4.46
0.50	0	0.50	0.721(2)	5.99
0.50	0	1.00	0.751(1)	5.74
				5.40+0.8
1.00	0	20.0	0.926(8)	4.66
1.00	0	10.0	0.871(14)	4.98
1.00	0	5.00	0.830(5)	4.23
				4.62+0.4
0.50	22	10.0	0.911(9)	5.87
0.50	22	5.00	0.883(4)	4.29
0.50	22	2.00	0.816(2)	4.07
0.50	22	1.00	0.760(2)	4.77
				4.75+0.8
1.00	22	10.0	0.869(6)	5.16
1.00	22	5.00	0.822(6)	4.69
1.00	22	2.00	0.757(5)	5.11
1.00	22	1.00	0.731(1)	4.44
				4.85+0.3
1.50	22	10.0	0.840(8)	4.97
1.50	22	5.00	0.797(8)	4.42
1.50	22	5.00	0.801(11)	4.17
1.50	22	2.00	0.742(6)	4.60
1.50	22	2.00	0.744(6)	4.39
1.50	22	2.00	0.740(7)	4.81
				4.56±0.3

[a] At 293 K in the presence of Bu_4NBF_4 (0.1 M) and water (0.278 M).

CONCLUSIONS

The rate constants for homogeneous reactions coupled to charge transfer are readily determined by NPSV analysis providing that the reaction order in primary intermediate is greater than one and that the rate constant is in the applicable range. For mechanism (1) this range corresponds to (k_1C/a) from 0.5 to 64. If the substrate concentration (C) can be varied from 0.1 to 10 mM and v from 0.1 to 300 V/s the applicable range is from 2×10^2 to 7.5×10^9 $M^{-1}s^{-1}$. This involves a considerable extension in range for rapid reactions as compared to derivative cyclic voltammetry or double potential step chronoamperometry. This is evident from considering the theoretical data for mechanism (1). In derivative cyclic voltammetry the rate constants are most often evaluated at a peak ratio of 0.50 which in this case corresponds to (k_1C/a) equal to 0.4.

Under these conditions m_2 is equal 1.00, *i.e.* the shape of the wave is still that for Nernstian charge transfer. NPSV can be used to evaluate reactions with rates about 160 times as great. Thus, it appears that NPSV studies of reaction rates can compliment those using other techniques.

EXPERIMENTAL

The instrumentation was the same as that described in previous work from this laboratory.[11] The collection and treatment of the data have been described.[1] The adjustment of the IR compensation circuit of the potentiostat was accomplished by the NPSV method described in detail in an earlier paper.[3] The substrate (MBM) was the same as used earlier.[6]

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