

# Electrode Mechanism Analysis by Linear Sweep Voltammetry.

## IV.\* The Practical Aspects

VERNON D. PARKER

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

The sweep rate range for the quantitative measurement of linear sweep voltammetry (LSV) peak potentials was extended downward by an order of magnitude to  $10 \text{ mV s}^{-1}$ . Using the analog derivative of the response, standard deviations in  $E^p$  of the order of  $\pm 0.2 \text{ mV}$  were observed in the mM concentration range and about  $\pm 0.5 \text{ mV}$  at a concentration of  $0.25 \text{ mM}$ . The protonation of anthracene anion radical by phenol in DMF was used as a model reaction to demonstrate the validity of results using the low sweep rates. The sweep rate dependence,  $dE^p/d \log v$ , was examined over three ranges of  $v$ ;  $100$  to  $1000 \text{ mV s}^{-1}$ ,  $10$  to  $100 \text{ mV s}^{-1}$  and  $10$  to  $1000 \text{ mV s}^{-1}$ . The value of  $dE^p/d \log v$  was found to be nearly independent of which range of  $v$  analyzed. The effect of measurement error on LSV slopes is discussed. Measurement procedures are recommended and the problems associated with the rate of heterogeneous charge transfer are discussed.

In the previous paper in this series,<sup>1</sup> equations were established which relate the linear sweep voltammetry (LSV) slopes to the reaction orders of the species involved in an electrode process. Thus, it is no longer necessary to resort to numerical methods to calculate the LSV response. The simple equations also make it possible to conduct mechanism analyses on both complex and competing reaction schemes which either cannot be or have not been treated theoretically. The procedure for analyzing a mechanism is to first derive the rate expression (1) where A is the

$$\text{Rate} = k_{\text{app}} C_A^a C_B^b C_I^i C_X^x \quad (1)$$

substrate, B the electrode generated intermediate, I a species formed during the reaction that participates further and X is an additional reactant. The LSV response expected for the process can then be derived from eqns. (2)–(4).

$$dE^p/d \log v = [1/(b+1)]RT/nF \quad (2)$$

$$-dE^p/d \log C_A = [(a+b+i-1)/(b+1)]RT/nF \quad (3)$$

$$dE^p/d \log C_X = [x/(b+1)]RT/nF \quad (4)$$

As is evident from the discussion above, the simple equations for the response reduce the theoretical aspects of LSV to a very usable form. There are a number of practical aspects, such as the measurement procedure, the necessary precision, the available sweep rate range and the influence of heterogeneous charge transfer kinetics on the results which have not been paid adequate attention to in the past. Our development of derivative cyclic voltammetry (DCV) into a quantitative kinetic method has provided a way to conduct measurements that is 10–50 times more precise than has been used in LSV measurements in the past.<sup>2</sup> Although this measurement technique has already been used in the other papers in this series,<sup>1,3,4</sup> the sweep rate range where the measurements are applicable has not been defined, the practical aspects of the measurements have not been clearly described, and the effect of heterogeneous charge transfer kinetics has not been clarified. These aspects of LSV mechanism analysis are discussed in this paper.

\* For part III see Ref. 1.

Table 1. Calibration of the linear sweep voltammetry measurement procedure on the reversible reduction of anthracene.<sup>a</sup>

$v/\text{mV s}^{-1}$	$\text{mV/point}^b$	$-E_{sw}/\text{mV}^c$	$-E^p/\text{mV}^d$	Correction/ $\text{mV}^e$
10	0.2022	602.0	411.4(0.3)	-0.3
100	0.2028	602.4	411.1(0.2)	0.0
200	0.2030	602.1	409.8(0.2)	+1.3
400	0.2032	602.1	410.1(0.2)	+1.0
1000	0.2033	602.2	411.4(0.2)	-0.3)

<sup>a</sup> At a mercury electrode in DMF containing  $\text{Bu}_4\text{NBF}_4$  (0.1 M) at 22 °C. <sup>b</sup> Determined by the initialization procedure described in Ref. 2 and refers to the time axis on the digital oscilloscope. <sup>c</sup> The peak on the triangular wave-form used to drive the potentiostat. The value is arbitrary and used in the initialization to test for consistency. <sup>d</sup> The peak potential for the reduction of anthracene measured by analog differentiation. Potentiostat bias of  $-1.900\text{ V vs. Ag/Ag}^+$  in acetonitrile. <sup>e</sup> The error in the peak potential relative to that measured at  $100\text{ mV s}^{-1}$ .

## RESULTS

*The measurement procedure.* The measurements described in this paper were all made by analog differentiation of the response. If instrumentation for differentiation is not available, the alternative of measuring  $E^{p/2}$  as recently described<sup>5</sup> gives comparable results. The procedures described here apply equally well to the latter method.

It is first necessary to determine very accurately the values of the sweep rates used in the LSV analysis. The data in Table 1 were obtained using a digital oscilloscope interfaced to a desk computer. The values given in the first column are the settings on the sweep generator. The data in the second column give the observed  $\text{mV/point}$  obtained by linear regressions analysis of the output from the sweep generator as described earlier.<sup>2</sup> Had the sweep rate settings been correct, the  $\text{mV/point}$  value would have been 0.2000 in all cases. The data show that there is a 1.5% error in the calibration of the sweep generator. Since the error is essentially independent of the sweep rate, no error is introduced in the LSV slopes if the calibrated values are used directly. However, if the 1.5% error had been random, potentials measured at 300 mV from the start potential would be in error by as much as  $\pm 4.5\text{ mV}$ . Obviously, errors of this magnitude cannot be tolerated in the LSV analysis. The third column gives the value of the switching potential on the triangular wave form which is also obtained by the initialization procedure.<sup>2</sup> The latter value is only needed for cyclic experiments.

The values in the fourth column of Table 1 give the reduction potentials of anthracene (1.00 mM) in DMF containing  $\text{Bu}_4\text{NBF}_4$  (0.1 M) at a mercury electrode at 22 °C. The purpose of these

measurements is to test the entire measurement procedure on a Nernstian charge transfer where no follow-up kinetics are involved. The correct peak potential should be independent of the sweep rate under these conditions. The values are found to vary slightly and the deviations from the value measured at  $100\text{ mV s}^{-1}$  are given in the last column. The numbers in parentheses after the potentials are the standard deviations in five replicates. The errors listed in the last column are due to a number of factors including the sweep rate error, any non-linearity in the amplifier used for the differentiation, and possible non-ideality in the electrode process. The fact that no trend is observed in the error over the 100-fold change in sweep rate makes it unlikely that non-ideality contributes to the error. Also, the values do not correspond to those in the  $\text{mV/point}$  column which indicates that the sweep rate is not the principal cause of the deviations. Thus, it is most likely that non-linearity of the amplifier is a major cause of the deviations. In any case, the deviations are small and can be applied as correction factors to experimental potentials measured in kinetic systems. On the other hand, if sweep rates of 10, 100 and  $1000\text{ mV s}^{-1}$  are used for an analysis the observed value of  $dE^p/d\log v$  would be exactly the same whether the corrections are applied or not.

The procedure described in the previous paragraphs for determining the voltage sweep rate and then testing the instrumentation on a reversible system gives a very good indication of the level of precision which can be attained in experimental systems.

*The sweep rate range.* The lower limit of  $v$  for the use of LSV for mechanism analysis has been stated

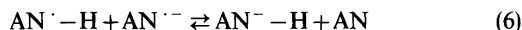
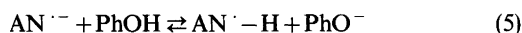
Table 2. Verification of the validity of linear sweep voltammetry slopes at low sweep rate.<sup>a</sup>

Range of measurements of $dE^p/d \log v/mV s^{-1}$	$dE^p/d \log v/mV$ per decade						
	[PhOH]/10 mM and [AN]/mM				[PhOH]/100 mM and [AN]/mM		
	0.25	0.50	1.00	2.00	0.50	1.00	2.00
100 to 1000	22.4	21.9	20.3	18.5	24.8	25.2	25.5
10 to 1000	21.9	23.2	21.0	19.7	22.5	25.7	25.6
10, 100 and 1000	22.0	23.2	20.9	19.6	22.9	25.9	25.8
$-(E_{1000}^p - E_{100}^p)$	22.2	22.0	20.1	18.5	24.7	25.6	25.2
$-(E_{100}^p - E_{10}^p)$	21.8	24.3	21.7	20.7	21.1	26.5	26.4
$-\frac{1}{2}(E_{1000}^p - E_{10}^p)$	22.0	23.2	20.9	19.6	22.9	25.9	25.8

<sup>a</sup> Measurements made by derivative LSV on DMF solutions of anthracene containing phenol and  $Bu_4NBF_4$  (0.1 M) at a mercury electrode at 22 °C.

to be of the order of  $100 mV s^{-1}$ .<sup>6</sup> It is not clear what the basis for this conclusion was but the LSV wave is affected at low sweep rates by undesirable factors such as convective mass transport, electrode edge effects, and deviations from planarity. However, it is clear from the data in Table 1 that reliable peak potentials for the reversible reduction of anthracene in DMF can be obtained at sweep rates as low as  $10 mV s^{-1}$ . No attempts were made to go to even lower sweep rates because of the limitations of the amplifier used in the differentiation of the response. It is conceivable that if sufficient experimental care is taken this range could be extended downward to about  $1 mV s^{-1}$ .

The data in Table 2 summarize an extensive series of experiments on the protonation of anthracene anion radical by phenol in DMF. The mechanism of this reaction has recently been found to be complex, consisting of reactions (5) to (7).<sup>7</sup> Under certain



conditions the apparent kinetics appear to only reflect forward step (5)<sup>8,2</sup> but generally the reaction order in  $AN^{\cdot-}$  is greater than one reflecting the contribution of step (6) as well.<sup>7</sup> The feature of interest in the context of this paper is the effect on  $dE^p/d \log v$  of extending the range of  $v$  down to  $10 mV s^{-1}$ . A detailed discussion of the mechanism can be found elsewhere.<sup>7</sup>

Experiments were conducted on solutions containing phenol, 10 mM and 100 mM, with

anthracene concentrations varying from 0.25 to 2.00 mM, (Table 2). The sweep rates used were the same as in Table 1. The average standard deviation of the six different values of  $dE^p/d \log v$  obtained in each column of data was found to be  $\pm 0.7 mV$  and only one value was greater than 1.0 mV. The average difference between  $-(E_{1000}^p - E_{100}^p)$  and  $-(E_{100}^p - E_{10}^p)$ , where the subscripts refer to the sweep rate, was found to be 1.7 mV. There is no trend in these data and the higher standard deviation in this case seems to be a reflection of the fact that only 2 potentials are used in each of the slopes. Further evidence for this is that if the values at each phenol concentration are averaged,  $-(E_{1000}^p - E_{100}^p)$  is smaller than  $-(E_{100}^p - E_{10}^p)$  at [PhOH] equal to 10 mM but the opposite was found when [PhOH] was 100 mM.

*The effect of heterogeneous charge transfer kinetics on LSV peak potentials.* A linear equation has recently been presented for the relationship between cyclic voltammetric peak potential separations and  $k_s$ , the heterogeneous rate constant.<sup>9</sup> Similarly, eqn. (8) gives the relationship between the peak potential during LSV and that for a Nernstian charge transfer ( $E^p - E_{rev}^p$ ) as a function of the dimensionless heterogeneous rate constant ( $\Lambda$ ) defined by eqn. (9) where  $D$  is the diffusion coefficient of the substrate. The success of eqn. (8) in predicting  $E^p - E_{rev}^p$  is shown in Table 3. The second column gives results of numerical calculations<sup>6</sup> using the method developed by Matsuda and Ayabe<sup>10</sup> for  $E^p - E_{rev}^p$  for various values of  $\Lambda$ . \* The third column gives the values calculated using (8) and the numbers in

\* Eqn. (8), as well as the calculations, is valid for the case where the transfer coefficient,  $\alpha$ , is equal to 0.5.

Table 3. Comparison of peak potentials calculated with a linear equation to those calculated by a numerical method.<sup>a</sup>

$\Lambda^b$	$(E^p - 28.5)/\text{mV}^c$	$(\ln 10)(RT/nF) / (0.40625)\Lambda^{-1}/\text{mV}^d$
31.62	0.69	0.76(0.07)
19.95	1.15	1.20(0.05)
12.59	1.90	1.91(0.01)
7.94	3.05	3.02(0.03)
5.01	4.90	4.79(0.11)
3.16	7.73	7.59(0.14)
2.00	12.06	12.03(0.03)
1.26	18.61	19.06(0.45)

<sup>a</sup> Calculated according to eqn. (8) as described in the text.

<sup>b</sup> Dimensionless rate constant defined in eqn. (9).

<sup>c</sup> Calculated according to (8). The numbers in parenthesis give the difference in values obtained by the linear equation and the numerical method.

$$E^p - E_{\text{rev}}^p = (\ln 10) (RT/nF) (2^{-1} - 2^{-3} + 2^{-5}) \Lambda^{-1} \quad (8)$$

$$\Lambda = k_s (DF/RT)^{-1/2} v^{-1/2} \quad (9)$$

parentheses give the differences between the values calculated by the two methods. The differences are nearly negligible and it is safe to conclude that in the range of  $\Lambda$  encompassed by the data in Table 3, eqn. (8) is valid.

The linear equation (8) can be used to define the upper limit of sweep rates advisable to use in LSV studies in order to avoid interference from charge transfer kinetics. Nadjo and Savéant<sup>6</sup> have pointed out that Evans<sup>11</sup> overestimated the effect of heterogeneous charge transfer kinetics as a result of

Table 4. Errors in peak potentials introduced by slow heterogeneous charge transfer.<sup>a</sup>

$v/V \text{ s}^{-1}$	$(E^p - 28.5)/\text{mV}$ at $k_s/\text{cm s}^{-1}$				
	0.01	0.03	0.10	0.30	1.00
100	— <sup>b</sup>	— <sup>b</sup>	43.4 <sup>b</sup>	15.0	4.3
10	— <sup>b</sup>	45.7 <sup>b</sup>	13.7	4.6	1.4
1	43.4 <sup>b</sup>	14.5	4.3	1.5	0.4
$10^{-1}$	13.7	4.6	1.4	0.5	0.1
$10^{-2}$	4.3	1.5	0.4	0.2	0.0
$10^{-3}$	1.4	0.5	0.1	0.1	0.0

<sup>a</sup> Calculated according to eqn. (8) with  $T=298 \text{ K}$ ,  $D=10^5 \text{ cm}^2 \text{ s}^{-1}$  and  $\alpha=0.5$ . <sup>b</sup> The linear equation is only valid for  $E^p - E_{\text{rev}}$  up to about 20 mV.

his simulations but since their results<sup>6</sup> are based on a precision on  $\pm 2 \text{ mV}$  and were not supported by any experimental data, it is conceivable that their conclusions must be modified somewhat. The data in Table 4 illustrate the shift in the peak potential from the reversible value as a consequence of quasi-reversible charge transfer at various voltage sweep rates for the case where there is no follow-up reaction involved. This can serve as a guide to determine what sweep rate range is applicable for processes involving homogeneous kinetics following charge transfer. If  $k_s$  is equal to  $1.0 \text{ cm s}^{-1}$ , assuming that  $T=298 \text{ K}$  and  $D$  is  $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , voltage sweep rates as high as  $10 \text{ V s}^{-1}$  can be used without introducing any serious complication from heterogeneous charge transfer. On the other hand if  $k_s$  is equal to  $0.1 \text{ cm s}^{-1}$ , the sweep rate must be restricted to values equal to or less than about  $100 \text{ mV s}^{-1}$ . The extreme case given in Table 4,  $k_s$  equal to  $0.01$ , indicates that when charge transfer is this slow, the sweep rate must be even lower than  $10 \text{ mV s}^{-1}$  in order to obtain meaningful LSV slopes.

On the basis of the discussion in the previous paragraph, it appears reasonable to recommend that  $v$  always be kept to values lower than  $1 \text{ V s}^{-1}$  when the rate of charge transfer is unknown since in most cases  $k_s$  will be less than  $1 \text{ cm s}^{-1}$ .

## DISCUSSION

The necessity of achieving a high degree of precision in peak potential measurements is evident from the data summarized in Table 5. If the error in peak potentials is equal to  $\pm 0.2 \text{ mV}$ , the error expected in the LSV slopes from this source is only  $\pm 1.3 \text{ mV}$  even if  $v$  is varied by only a factor of 2. If  $v$  is varied by a factor of  $10^2$ , the error in the LSV slope

Table 5. The effect of error in peak potentials on LSV slopes.

$v_{\text{high}}/v_{\text{low}}^a$	Error in LSV slope/mV at $E^p$ error/mV			
	$\pm 0.2$	$\pm 0.5$	$\pm 2.0$	$\pm 5.0$
2	1.3	3.3	13.2	33.2
4	0.7	1.7	6.6	16.6
10	0.4	1.0	4.0	10.0
100	0.2	0.5	2.0	5.0

<sup>a</sup> The ratio of the extremes in sweep rate used in the analysis.

becomes the same as the error in the peak potentials. The common values of the LSV slopes expected for simple mechanisms of electrode processes are 14.8, 19.7, 29.6 and 39.4 mV/decade at 298 K. Since the greatest difference between any two of these numbers is slightly less than 10 mV, an experimental slope falling half-way between any of these numbers could not be distinguished from the theoretical values under any circumstances if the error in peak potentials was  $\pm 5.0$  mV. The latter is the most commonly quoted experimental error for peak potentials. This indicates that an LSV mechanism analysis cannot be made with this sort of precision. In the case where the experimental error in peak potentials is  $\pm 2.0$  mV as indicated by Nadjo and Savéant,<sup>6</sup> it is necessary to vary  $v$  by a factor of  $10^2$  and still there can be doubt about mechanism assignment based on this analysis. There clearly is no problem if the precision can be improved to  $\pm 0.5$  mV. The data in Table 1 indicate that the precision attained in the peak potential measurements is about  $\pm 0.2$ . During the measurements summarized in Table 2, it was found that the precision in peak potentials was  $\pm 0.5$  mV when the substrate concentration was 0.25 mM and  $\pm 0.2$  at 1.00 mM. Thus, the efforts that we have made in improving LSV precision<sup>2,5</sup> represent a necessity for meaningful mechanism analysis rather than trivial extensions.

The LSV mechanism analysis is only applicable to purely kinetic waves which implies that there is no interference by charge transfer kinetics and that the reactions following charge transfer are sufficiently rapid that the peak potential varies linearly with the sweep rate. A very simple analysis has recently been presented which can be used to determine whether or not the process fulfills the criteria for a purely kinetic wave.<sup>5</sup> The analysis involves using a very nearly linear portion of the LSV voltammogram and when the current is normalized to the peak current,  $dE/dI_N$  ( $I_N = I/I^p$ ), the slope in the linear region gives an indication of the mechanism. Typical values of the linear current potential (LCP) slopes are 68.9 mV for the simple EC mechanism, 68.9 mV for the ECE<sub>n</sub> mechanism<sup>4</sup> and 53.2 mV for the EC dimerization mechanism.

Another valuable test to make in connection with the LSV mechanism analysis involves the DCV peak ratio.<sup>2</sup> If the overall reaction is reversible, at low sweep rates the peak potential during LSV can be a reflection of both the forward and reverse kinetics. When this is the case, the linear relationships will

not hold. When this situation is suspected, analysis of the DCV peak ratios as a function of the sweep rate can be used to verify the reversible nature of the reactions. The telltale observation in this case is that  $R'_p$ , the DCV peak ratio, decreases with decreasing sweep rates as expected but does not reach the value expected for a purely kinetic process and instead goes through a minimum before beginning to increase with further decreases in  $v$ . Reversibility in the overall reactions has been demonstrated by this analysis in two different cases, the reversible dimerization of substituted anthracene anion radicals<sup>12</sup> and the hydrodimerization of diethyl fumarate in proton-poor media.<sup>13</sup>

In conclusion, I would like to emphasize that LSV mechanism analysis is a very powerful tool for the study of reactions coupled to charge transfer at electrodes. It has been the purpose of this series of papers to demonstrate to the physical organic chemists interested in the study of such reactions that both the theoretical relationships and the experimental techniques are readily acquired and set into practice. It is hoped that the results presented in this paper will serve as a practical guide to those initiating LSV studies.

## EXPERIMENTAL

The instrumentation, electrodes, cells and data handling procedures as well as solvent and electrolyte purification procedures were the same as described recently.<sup>2,14</sup> In order to avoid any disturbance from mechanical vibrations, the support for the cell was placed on a stone plate which was supported by an inflated automobile tire inner tube.

## REFERENCES

1. Parker, V. D. *Acta Chem. Scand. B* 35 (1981) 259.
2. Ahlberg, E. and Parker, V. D. *J. Electroanal. Chem.* 121 (1981) 57, 73.
3. Parker, V. D. *Acta Chem. Scand. B* 34 (1980) 534.
4. Ahlberg, E. and Parker, V. D. *Acta Chem. Scand. B* 35 (1981) 117.
5. Aalstad, B. and Parker, V. D. *J. Electroanal. Chem.* 112 (1980) 163.
6. Nadjo, L. and Savéant, J. M. *J. Electroanal. Chem.* 48 (1973) 113.
7. Parker, V. D. *Acta Chem. Scand. B* 35 (1981) 349.
8. Amatore, C. and Savéant, J. M. *J. Electroanal. Chem.* 107 (1980) 353.

9. Ahlberg, E. and Parker, V. D. *Acta Chem. Scand. B* 34 (1980) 71.
10. Matsuda, H. and Ayabe, Y. *Z. Electrochem.* 59 (1955) 494.
11. Evans, D. H. *J. Phys. Chem.* 76 (1972) 1160.
12. Hammerich, O. and Parker, V. D. *Acta Chem. Scand. B* 35 (1981) 341.
13. Parker, V. D. *Acta Chem. Scand. B* 35 (1981) 279.
14. Ahlberg, E. and Parker, V. D. *Acta Chem. Scand. B* 34 (1980) 97.

Received February 12, 1981.