The Effect of Heterogeneous Charge Transfer Kinetics on Electrode Measurements

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The theoretical electrode responses for potential step and linear sweep perturbations as a function of frequency are examined to determine the applicability of analyses based on Nernstian behaviour. Values for the diffusion coefficient and the heterogeneous electron transfer rate constant for a typical aromatic compound were taken to be 9×10^{-6} cm^2 s^{-1} and 0.3 cm s^{-1}. Under these conditions, non-Nernstian cyclic voltammetric response is shown to occur at voltage sweep rates as low as 1 V s^{-1}. Similarly, the assumption of reversible charge transfer is shown to be inadequate for potential step perturbation at times less than 10 ms using the parameters given above. The range of frequencies for both types of perturbation for which the reversible assumption is valid is tabulated. A useful linear equation is derived from theoretical data to relate cyclic voltammetric peak potential separations to heterogeneous charge transfer rate constants.

We have recently shown that cyclic voltammetric peak potentials for the redox reactions of organic compounds in non-aqueous solvents can be obtained to a high degree of precision using analog differentiation,[1] a technique previously described by Perone.[2] The ability to make precise potential measurements even at very high voltage sweep rates has made cyclic voltammetry a quantitative tool for the study of the kinetics of fast electrode processes.[1] The heterogeneous rate constants that we obtained for the reduction of perylene and anthracene, believed to be among the fastest existing processes,[3] are somewhat lower than previously reported.[3,4,5] Our results are more in

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accord with the recent report of Koizumi, Saji and Aoyagui[6] who, on the basis of galvanostatic double pulse measurements, question the existence of very high heterogeneous charge transfer rates. The latter workers obtained rate constants in the range of 0.3–0.6 cm s^{-1} for a number of processes which had previously been believed to have rate constants > 10 cm s^{-1} and hence out of the range of existing measurement techniques.[7]

Electrode measurements are important in the study of organic redox processes. The fact that organic chemists are beginning to find that electron transfer steps are frequently involved in organic reaction mechanisms emphasises the need for reliable kinetic methods. Thus, in view of the discussion in the previous paragraph, we have examined one of the most frequent and basic assumptions commonly made in studying the kinetics of homogeneous chemical reactions coupled to charge transfer at electrodes. The assumption is, based upon the common belief that charge transfer to organic compounds is generally rapid, that the electrode reaction is fast and the response is therefore independent of the heterogeneous charge transfer rate constant.

Cyclic voltammetry. The theory for the cyclic voltammetric response for homogeneous chemical reactions coupled to charge transfer was first developed by Nicholson and Shain[8] and that for heterogeneous charge transfer kinetics by Nicholson.[9] In cyclic voltammetry, the experimentally controlled variable is the linear potential sweep rate. Nicholson derived eqn. (1) which relates function ψ to the heterogeneous charge transfer rate constant k_s and the voltage sweep rate v, for the quasi-reversible charge transfer reaction (2). The

Table 1. Linearization of the ψ function for quasi-reversible heterogeneous electron transfer.

ψ [a]	$(\Delta E^p)/mV$ [b]	$\psi/20$	$1/(\Delta E^p - 60)$ [c]	$\psi = 24/(\Delta E^p - 60)$ [d]
20	61	1.00	1.00	24.0
7	63	0.35	0.33	8.0
6	64	0.30	0.25	6.0
5	65	0.25	0.20	4.8
4	66	0.20	0.17	4.0
3	68	0.15	0.125	3.0
2	72	0.10	0.083	2.0
1	84	0.05	0.073	1.0
0.75	92	0.0377	0.031	0.75
0.5	105	0.025	0.022	0.533
0.35	121	0.0175	0.0164	0.393
0.25	141	0.0125	0.0123	0.296
0.1	212	0.005	0.0066	0.158

[a] Data from Ref. 9. [b] Peak potential separation for a quasi-reversible system during cyclic voltammetry at 25 °C. [c] Least squares correlation; $m = 1.0065$, $c = 0.012553$, correlation coefficient $= 0.997$. [d] Calculated according to the equation given.

$$\psi = \gamma^2 k_s/(\pi D_0 nFv/RT)^{\frac{1}{2}} \qquad (1)$$

$$Ox + ne^- \rightleftarrows Red \qquad (2)$$

transfer coefficient is denoted by α and γ, the square root of the ratio of diffusion coefficients of the oxidized (D_0) and reduced (D_r) species, is generally assumed to be unity. The values of ψ calculated by Nicholson[9] for $T = 298$ K along with the corresponding peak potential separations are tabulated in the first two columns of Table 1. We have found a very good linear correlation between ψ and $(\Delta E^p - 60 \text{ mV})^{-1}$. The relationship is illustrated in the third and fourth columns of Table 1. Least squares correlation gives eqn. (3) with a correlation coefficient of 0.997. The useful range of the data in Table 1 is for ψ of 0.5 or greater, at lower values the peak separation becomes dependent upon α.

$$\psi/20 = (1.0065)(\Delta E^p - 60)^{-1} + 0.0126 \qquad (3)$$

$$\psi(6 \text{ to } 0.5) = 24/(\Delta E^p - 60) \qquad (4)$$

The fifth column in Table I shows a remarkable result. For ψ values ranging from 6 down to 0.5 eqn. (4) gives an exact linear relationship between ψ and ΔE^p, which greatly simplifies using the theoretical data in kinetic studies.

A simple test for conditions where cyclic voltammetric response is expected to exhibit reversible

behaviour is to calculate ψ values. At ψ equal to 20 or greater, the cyclic voltammogram is expected to be experimentally indistinguishable from that calculated assuming Nernstian behaviour. Typical values of diffusion coefficients for aromatic compounds in non-aqueous solvents fall in the range from 10^{-6} to 10^{-5} cm^2 s^{-1}. Taking a value of 9×10^{-6} cm^2 s^{-1} for D and 0.3 for k_s as an example, we find from (1) that reversible behaviour is expected only for very low voltage sweep rates. Even at voltage sweep rates as low as 1 V s^{-1}, the response is expected to be experimentally distinguishable from the reversible case. Values of ψ as a function of v for the example taken are summarized in Table 2.

Potential step chronoamperometry. In order to analyze this case for the onset of non-Nernstian

Table 2. The dependence of the ψ function on voltage sweep rate for a typical quasi-reversible electron transfer.[a]

$v/V \ s^{-1}$	ψ/mV^{-1} [a]
1000	0.29
100	0.90
10	2.86
1	9.04
0.1	28.6

[a] Calculated from eqn. (1) assuming D_0 equal to 9×10^{-6} cm^2 s^{-1} and k_s equal to 0.3 cm s^{-1}.

Table 3. The relationship between frequency, heterogeneous rate constant and quasi-reversible response during potential step perturbation.

p/s^{-1} [a]	$k_\mathrm{f}/\mathrm{cm\ s}^{-1}$	$(D_\mathrm{o}^{\frac{1}{2}}/k_\mathrm{f})p/\mathrm{s}^{-\frac{1}{2}}$	$p^{\frac{1}{2}}/\mathrm{s}^{-\frac{1}{2}}$
10^6	300	10	10^3
10^6	30	10^2	10^3
10^6	3	10^3	10^3
10^6	0.3	10^4	10^3
10^4	30	1	10^2
10^4	3	10	10^2
10^4	0.3	10^2	10^2
10^2	3	0.1	10
10^2	0.3	1	10
10^2	0.03	10	10

[a] As defined in eqns. (5) and (6). Calculations assume a value of $D_\mathrm{o}^{\frac{1}{2}}$ equal to 3×10^{-3} cm s$^{-\frac{1}{2}}$.

behaviour we can consider the Laplace transform of the diffusion-kinetic expression derived for the case of an irreversible charge transfer following a potential step perturbation.[10] The expression, given in eqn. (5), reduces to the reversible case (6) when k_f, the rate constant for charge transfer as in (2) neglecting the backward step, is large. The term p has

$$nFAC_\mathrm{o}^\mathrm{b}D_\mathrm{o}^{\frac{1}{2}}/I = p^{\frac{1}{2}} + (D_\mathrm{o}^{\frac{1}{2}}/k_\mathrm{f})p \qquad (5)$$

$$nFAC_\mathrm{o}^\mathrm{b}D_\mathrm{o}^{\frac{1}{2}} = Ip^{\frac{1}{2}} \qquad (6)$$

units of frequency (s^{-1}),* A is the electrode area and I is the instantaneous current. If deviations from reversible response greater than 1 % are detectable, conditions where the second term on the right hand side of (5) is 0.01 $p^{\frac{1}{2}}$ or greater define the limit of applicability of the reversible charge transfer eqn. (6). Table 3 shows the relationship between the terms as a function of p and k_f. The data show that the second term on the right hand side of (5) is expected to be significant even when the rate constant is extremely large, $k_\mathrm{s} \sim 300$ cm s^{-1}, on the microsecond time scale. For the case where the heterogeneous rate constant is equal to 0.3 cm s^{-1} the second term predominates when p is equal to 10^6 s^{-1}. At frequencies of 10^4 and 10^2 s^{-1} deviation from Nernstian behaviour is predicted for rate constants equal to 30 and 3.0 cm s^{-1}, respectively.

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* Eqns. (5) and (6) are written in the Laplace plane where p is the Laplace variable and is equal to $2\pi f(-1)^{\frac{1}{2}}$ for a sine wave where f is the frequency.

Conclusions. It is quite obvious that kinetic analysis using the assumption of reversible electron transfer can lead to erroneous results in studies of organic electrode processes where few electrode reactions will have rate constants in excess of 1 cm s^{-1}. Linear potential sweep voltammetry and potential dependent chronoamperometry, both of which involve making measurements at potentials lower than the reversible value can be expected to be especially sensitive to charge transfer effects. The effect can be mimimized during potential step experiments by stepping to potentials very much greater than the reversible potential when this is possible since the heterogeneous rate constant increases by a factor of about 10 for a 120 mV change in potential. This problem has been considered by others.[11,12] Since the thorough study by Nadjo and Savéant[12] assumed a measurement precision of ± 2 mV the conclusions must be modified somewhat when the precision can be improved by an order of magnitude as we have recently found.[1] Also, application of the common assumption that aromatic compounds behave as Nernstian systems even at very high voltage sweep rates[13,14] should be discontinued.

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