Electron Transfer Reactions. III. The Application of Derivative Cyclic Voltammetry for the Determination of Rate Constants and α Values for Heterogeneous Electron Transfer Processes: the Reduction of Organic Anions[†]

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The application of derivative cyclic voltammetry for the determination of standard heterogeneous electron transfer rate constants, k_s, and electrochemical transfer coefficients, α, is described. The results obtained for the frequently used model compound, 2-methyl-2-nitropropane, showed little dependence on the exact location of the potential at which voltage sweep is reversed and on small errors in the potentiostat positive feedback setting.

The approach was used for the quasi-reversible reduction of a series of aromatic carboxylate and phenolate ions in dimethyl sulfoxide. The experimental data were obtained by application of a background subtraction – fast Fourier transform procedure with differentiation carried out in the frequency domain. After correction for double layer effects the rate constants were found to decrease in the order 9-anthroate ($z = -1$) > 1-naphthoate ($z = -1$) > 3-nitrophthalate ($z = -2$) ≈ 3-nitrophenolate ($z = -1$) ≈ 2-nitrobenzoate ($z = -1$) indicating similar solvent reorganization energies for the three nitro compounds.

The values of α were found to decrease in the order 1-naphthoate (0.53) > 9-anthroate (0.48) > 2-nitrobenzoate (0.44) ≈ 3-nitrophenolate (0.43) > 3-nitrophthalate (0.34). It is suggested that the values significantly smaller than 0.5 reflect the tighter association with residual water in the product than in the reactant state.

The factors that determine the kinetics of electron exchange between an electrode and nearby molecules in solution are of central interest to electrochemists. The experimental work has benefited considerably from the development of the basic theory for electroanalytical techniques such as linear sweep voltammetry (LSV), cyclic voltammetry (CV) and AC polarography[1–7] and these techniques are now among the most frequently used for studies of electrode kinetics. Examples, taken mainly from the field of organic electrochemistry, include studies of the effects of the structure[8–14] and formal charge[15–17] of the substrate molecules, chemical reactions following the electron transfer,[18–21] the electrode material,[22–26] the solvent,[24,25,27–31] the supporting electrolyte[28,30,32–37] and the temperature.[9,13,14,17,28,35]

Although the electroanalytical techniques are well described[38–41] and their application apparently straightforward, studies of heterogeneous electron transfer are some-

times met with reservation since it is a common experience that the experimental data may be difficult to reproduce (see for example Refs. 12, 22 and 26). The origin of these difficulties may in part be traced back to non-ideal electrode behavior caused by electrode surfaces that are not smooth at the microscopic level or to adsorption of substrate, electrode products or impurities. In addition, it has been shown that the amount of residual water in non-aqueous solvents, which is extremely difficult to control, may affect the kinetic data considerably.[31]

The present popularity of LSV and CV is without doubt related to the usefulness of these techniques in studies of the kinetics and mechanisms of chemical reactions coupled to heterogeneous electron transfer, and this application has been further stimulated by the introduction of derivative cyclic voltammetry (DCV).[42] However, CV offers also the most convenient way of determining the standard rate constants, k_s, for heterogeneous electron transfer. The procedure involves measurements of the peak separation, $\Delta E_p = E_p^{ox} - E_p^{red}$, at different voltage sweep rates followed by fitting of the data to a working curve. An advantage of this approach is that ΔE_p is only moderately dependent on the value of the electrochemical transfer coefficient, α, (see

later) and for this reason the working curve calculated for example for $\alpha = 0.5$ may be used, at least, for α values in the range 0.4–0.6 without significant loss of accuracy. Further aspects of the electron transfer process, including information about α and its possible potential dependence, have been obtained by detailed analyses of the shapes of the complete LSV or CV curves.[31,34,39,40,43-54]

The ratio of the derivative current peaks, $-i'_{b,p}/i'_{f,p} = R'_1$, obtained by DCV may serve as a simple measure of the CV curve shape and this together with the improved precision offered by DCV for the determination of peak potentials suggested to us that k and α may be obtained simultaneously by measurements of both ΔE_p and R'_1 as a function of the voltage sweep rate. The approach is described in detail below and in addition we present preliminary results obtained for the reduction of a series of aromatic carboxylate and phenolate ions. The data for ΔE_p and R'_1 were obtained by application of the background subtraction – fast Fourier transform (FFT) procedure recently described.[55]

Results and discussion

The working curves. For the sake of clarity the discussion will focus only on the quasi-reversible *reduction* of **A** to **B** specified by eqns. (1)–(3), where k_{red} and k_{ox} are the heterogeneous reduction and oxidation rate contants at the potential E, and E° is the standard potential of the $\text{A}|\text{B}$ redox couple. The transposition to oxidation is straightforward.

$$\text{A} + \text{e}^- \underset{k_{ox}}{\overset{k_{red}}{\rightleftharpoons}} \text{B} \ (k_s) \tag{1}$$

$$k_{red} = k_s \exp\{-\alpha nF(E-E^\circ)/(RT)\} \tag{2}$$

$$k_{ox} = k_s \exp\{(1-\alpha)nF(E-E^\circ)/(RT)\} \tag{3}$$

The dependence of the CV peak potentials, E_p^{red} and E_p^{ox}, on the logarithm of the dimensionless rate parameter, Λ [eqn. (4)], for different values of α is shown in Fig. 1. [In eqn. (4), v is the voltage sweep rate and D is the diffusion coefficient assumed to be the same for **A** and **B**. The data in Fig. 1 were obtained by digital simulation[56] for $E_{sw}-E^\circ = -0.4$ V, where E_{sw} is the potential at which the direction of the voltage sweep is reversed. The temperature, T, was 298 K].

$$\Lambda = \frac{k_s}{\left(\dfrac{DvnF}{RT}\right)^{1/2}} \tag{4}$$

It appears from eqns. (2) and (3) that in the potential regions of the CV peaks decreasing values of α cause k_{red} to decrease and k_{ox} to increase and as a consequence both E_p^{red} and E_p^{ox} move in the negative direction. Conversely, increasing values of α cause E_p^{red} and E_p^{ox} to move in the
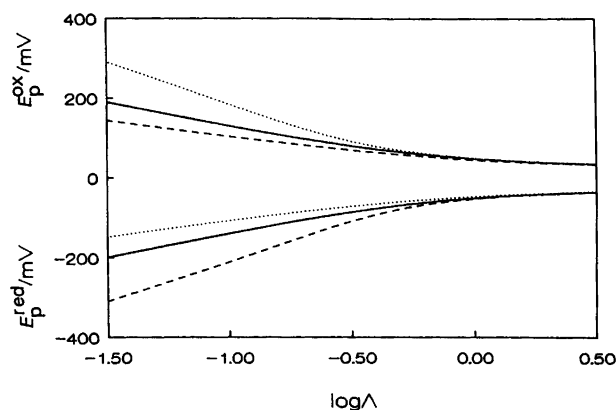

Fig. 1. Values of E_p^{red} and E_p^{ox} as a function of log Λ for $\alpha = 0.3$ (– – –), 0.5 (———) and 0.7 (·······) at $E_{sw}-E^\circ = -0.4$ V and $T = 298$ K.

positive direction. The overall result is that the effect of the magnitude of α on the peak separation, $\Delta E_p = E_p^{ox}-E_p^{red}$, is only small (Fig. 2). It is seen that ΔE_p is essentially independent of α for log $\Lambda > -0.4$, which at $v = 1$ V s^{-1}, $D = 10^{-5}$ cm^2 s^{-1} and $T = 298$ K corresponds to $k_s > 8 \times 10^{-3}$ cm s^{-1}. At log $\Lambda < -0.4$ the working curves show some dependence on α, but the slopes of the linear parts observed at log Λ less than approximately -0.7 are similar and it is obviously impossible to estimate α from ΔE_p measurements alone.

The ratio of the derivative current peaks, R'_1, was found to be much more sensitive to variations in α as illustrated by the results shown in Fig. 3 for $E_{sw}-E^\circ = -0.4$ V. The working curves, which are given for α in the range 0.3–0.7 in increments of 0.02, separate appreciably for log $\Lambda < 0.0$ suggesting that α may be determined from measurements of R'_1 as a function of v provided the corresponding values of Λ are known, for example through ΔE_p measurements (see below).

The working curves for ΔE_p vs. log Λ are almost independent of the value of $E_{sw}-E^\circ$ as long as E_{sw} is not too
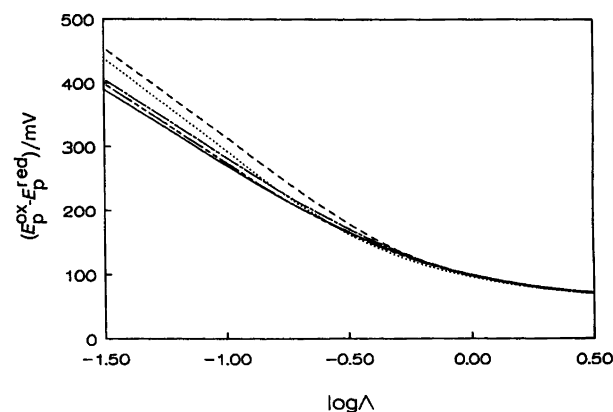

Fig. 2. Values of $E_p^{ox}-E_p^{red}$ (= ΔE_p) as a function of log Λ for $\alpha = 0.3$ (– – –), 0.4 (———), 0.5 (———), 0.6 (– – –) and 0.7 (·······) at $E_{sw}-E^\circ = -0.4$ V and $T = 298$ K.
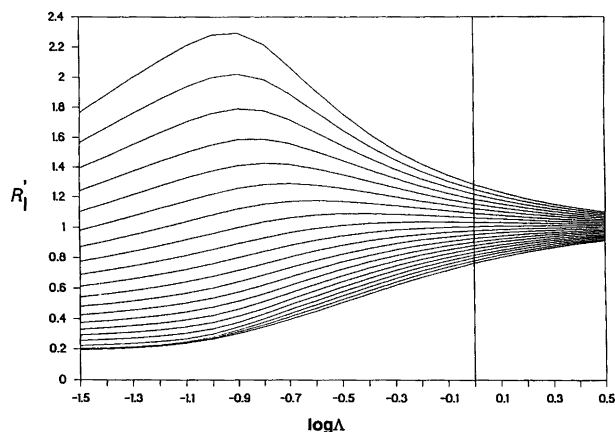
Fig. 3. The derivative current peak ratio, R'_I, as function of log Λ for α values in the range 0.3 (top)–0.7 (bottom) at $E_{sw}-E° =$ -0.4 V and $T = 298$ K. The increments in α on going from the top to the bottom are 0.02.

close to $E°$, but this is not so for the working curves for R'_I vs. log Λ, and before testing the approach on real $A|B$ systems the contours of the curves and in particular the effect of $E_{sw}-E°$ will be examined in more detail.

During CV the voltage sweep is usually initiated at a value of $E_{start}-E°$ so large that no appreciable current flows at $E = E_{start}$ and this is also assumed in the following. For a reversible (Nernstian) one-electron transfer reaction R'_I is unity for the hypothetical situation at which $E_{sw}-E° = -\infty$ corresponding to a solution containing B only when the direction of the voltage sweep is reversed. Compared with this limiting case the maximum slope observed for the oxidation peak increases as E_{sw} approaches $E°$, and since the shape of the reduction peak is left unchanged this causes R'_I to increase. However, the effect is small as seen from the pairs of $E_{sw}-E°$ and R'_I given in Table 1 and R'_I may be considered independent of E_{sw} for all practical purposes as long as $E_{sw}-E° < -0.3$ V. (It should be emphasized that values of $E_{sw}-E°$ less than approximately -0.7 V are unrealistic in most practical work and are included in Table 1 for illustration purposes only. An effect similar to that resulting from reversing the voltage sweep at potentials far away from $E°$ may be obtained by application of a potential–time program that allows the voltage to be maintained at E_{sw} for a predetermined time before the reverse sweep is initiated).

The analysis of the influence of $E_{sw}-E°$ on the CV and DCV curves for a quasi-reversible redox couple is more complicated because of the combined effects of α, Λ and $E_{sw}-E°$. Let us again as the starting point consider the hypothetical situation, $E_{sw}-E° = -\infty$. Since k_{red} depends on α and k_{ox} on $1-\alpha$, the voltammogram for $\alpha = 0.3$, for example, is superimposable with that obtained at $\alpha = 0.7$ after a 180° rotation around $E°$ in the plane defined by the voltage and current axes. Thus, for this particular pair of voltammograms we have $R'_{I(\alpha = 0.3)} = 1/R'_{I(\alpha = 0.7)}$ and similarly for other pairs for which the sum of the α values is

unity. This means that the working curves for different α values depicted as log R'_I vs. log Λ, instead of R'_I vs. log Λ, are symmetrically distributed around the line log $R'_I = 0$ corresponding to $\alpha = 0.5$. The use of finite values of $E_{sw}-E°$ results in deviations from this symmetrical distribution. This is clearly seen in Fig. 4, which shows log R'_I as a function of log Λ for $E_{sw}-E° = -0.4$ V (a), -0.5 V (b), -0.7 V (c) and -2.5 V (d), respectively. It i seen that the working curves approach the predicted symmetrical distribution around log $R'_I = 0$ with increasing distance between E_{sw} and $E°$. At values of log Λ less than approximately -0.7 the electron transfer reaction may be regarded as an irreversible process[57] and in this kinetic region the shape of the voltammogram for a given value of α, and thus the R'_I value, becomes nearly independent of Λ.[5,57] Consequently, the working curves approach straight lines of slope zero as seen in Fig. 4(d) for $E_{sw}-E° = -2.5$ V, where the effect of using a finite value of $E_{sw}-E°$ is small.

It is of interest that the working curves at $E_{sw}-E° = -0.4$ V [Fig. 4(a)] and $\alpha \geq 0.66$ are almost indistinguishable for log $\Lambda < -1.1$ indicating that R'_I is nearly independent of α in this region. The effect is less pronounced at $E_{sw}-E° = -0.5$ V [Fig. 4(b)] and vanishes completely for $E_{sw}-E° \leq -0.7$ V [Figs. 4(c) and 4(d)]. The origin of this phenomenon is understood most easily by inspection of the three pairs of CV and DCV curves shown in Fig. 5 for $\alpha = 0.7$, $E_{sw}-E° = -0.5$ V and log $\Lambda = 0.0$ (a), -1.0 (b) and -2.0 (c), respectively. The current observed during the back sweep at potentials close to E_{sw} is determined mainly by the rate of diffusion of A to the electrode and for log $\Lambda = 0.0$ [Fig. 5(a)] the reduction current continues to flow until $E-E°$ is close to -50 mV, where the current–voltage curve passes the zero line and the reoxidation of B to A becomes the predominant process. This sudden change in the direction of the current flow reflects the net result of a rapidly decreasing value of k_{red} and a rapidly increasing value of k_{ox} in this potential region. For log $\Lambda = -2.0$ [Fig. 5(c)], the current due to reduction of A still decreases rapidly when E approaches $E°$, but because of the small Λ value appreciable oxidation current for B is not observed until $E-E°$ is larger than approximately 150 mV. As a result of this, large

Table 1. The effect of the switch potential, $E_{sw}-E°$, on the derivative current peak ratio, R'_I, for a reversible one-electron transfer reaction.

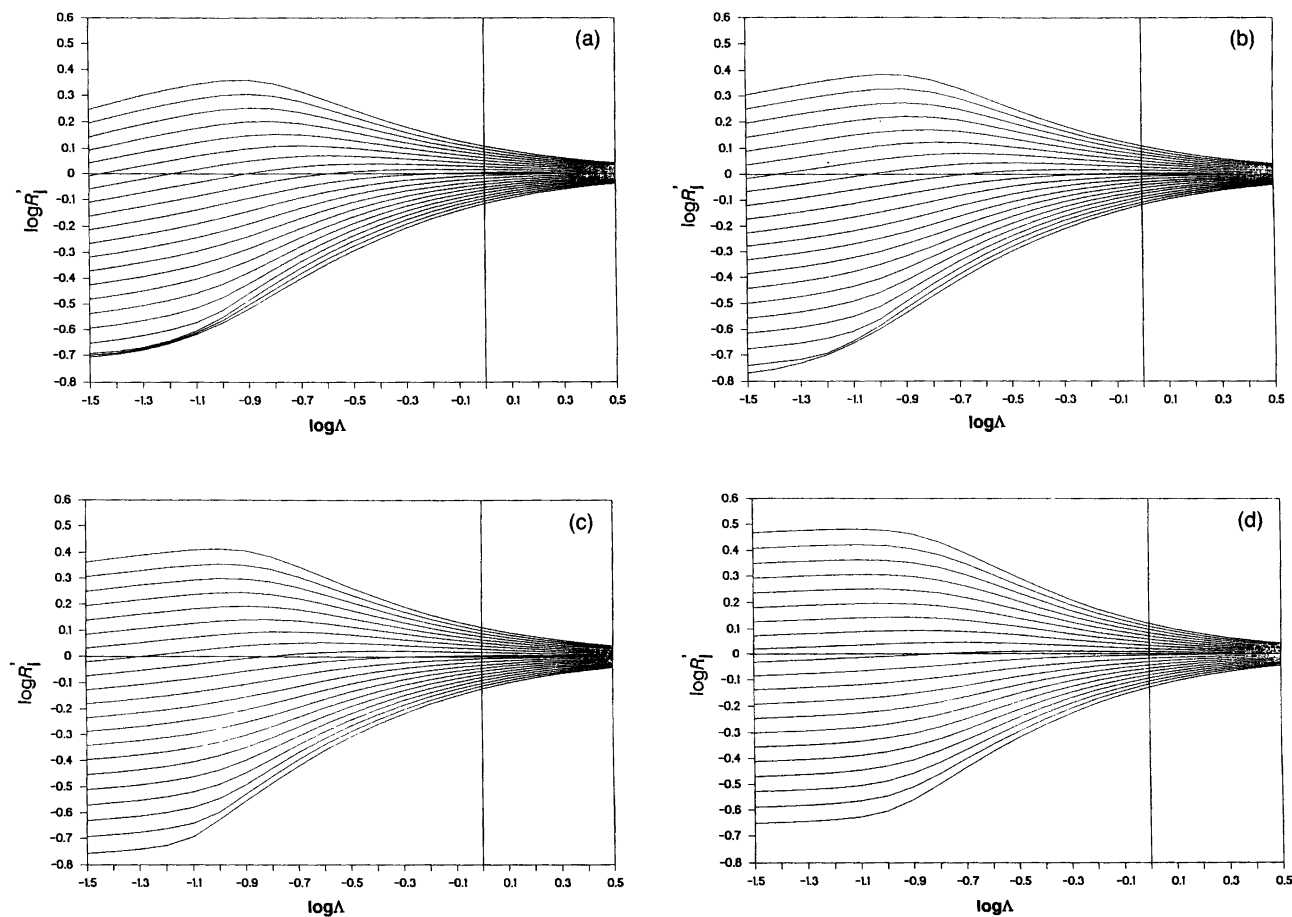| $(E_{sw}-E°)/V$	$R'_I{}^a$
-0.1	1.112
-0.2	1.034
-0.3	1.018
-0.4	1.011
-0.5	1.008
-0.7	1.005
-1.5	1.002
-2.5	1.001

[a] Data obtained by digital simulation.

Fig. 4. Values of log R_i' as function of log Λ for α values in the range 0.3 (top)–0.7 (bottom) at $T = 298$ K and $E_{sw}-E° = -0.4$ V (a), -0.5 V (b), -0.7 V (c) and -2.5 V (d). The increments in α on going from the top to the bottom are 0.02.

current changes are observed *twice* during the back sweep and two derivative current peaks instead of one are observed in the DCV curve [Fig. 5(c)]. In the transition between these extremes, here illustrated by log $\Lambda = -1$, the current–voltage curve is nearly linear in the potential range to $E°$ [Fig. 5(b)], which results in DCV curves that are almost flat in this region. Which part of the DCV signal that is the larger during the back sweep is a delicate balance between the magnitudes of α, Λ and $E_{sw}-E°$. At $E_{sw}-E° = -0.4$ V it turns out that for α values larger than approximately 0.66 the first part of the CV curve, that corresponding to the decreasing reduction rate of A, is steeper than the second part corresponding to reoxidation of B. In addition the steepness of the first part, and hence R_i', is essentially independent of α and the overall result is that the DCV working curves tend to merge as seen in Figs. 4(a) and 4(b). Since the steepness of the first part of the curve decreases with increasing distance between $E°$ and E_{sw} and eventually becomes smaller than the steepness of the second part which is less sensitive to the value of E_{sw}, the conditions for measuring the α dependence of R_i' are reestablished. On the other hand, the problem is accentuated as expected when E_{sw} approaches $E°$ and it was found that measure-

ments at $E_{sw}-E° = -0.3$ V, for example, could only be carried out in the kinetic region down to log $\Lambda = -2$ for $\alpha < 0.52$.

The data presented so far were obtained under the tacit assumption that α is independent of the potential. However, electron transfer theory[58-60] predicts that α may vary with potential and by linking the definition of α to the Tafel slope[61,62] we have the following equations for α and $d\alpha/dE$, where λ is the reorganization energy.

$$\alpha = \tfrac{1}{2} + F(E-E°)/(2\lambda) \tag{5}$$

$$d\alpha/dE = F/(2\lambda) \tag{6}$$

During digital simulation, which is based on the Butler–Volmer equations (2) and (3), the value of α at a given potential, E, can then be calculated from eqn. (7),[34,62] where α_0 is the transfer coefficient at $E = E°$.

$$\alpha = \alpha_0 + \tfrac{1}{2}(d\alpha/dE)(E-E°) \tag{7}$$

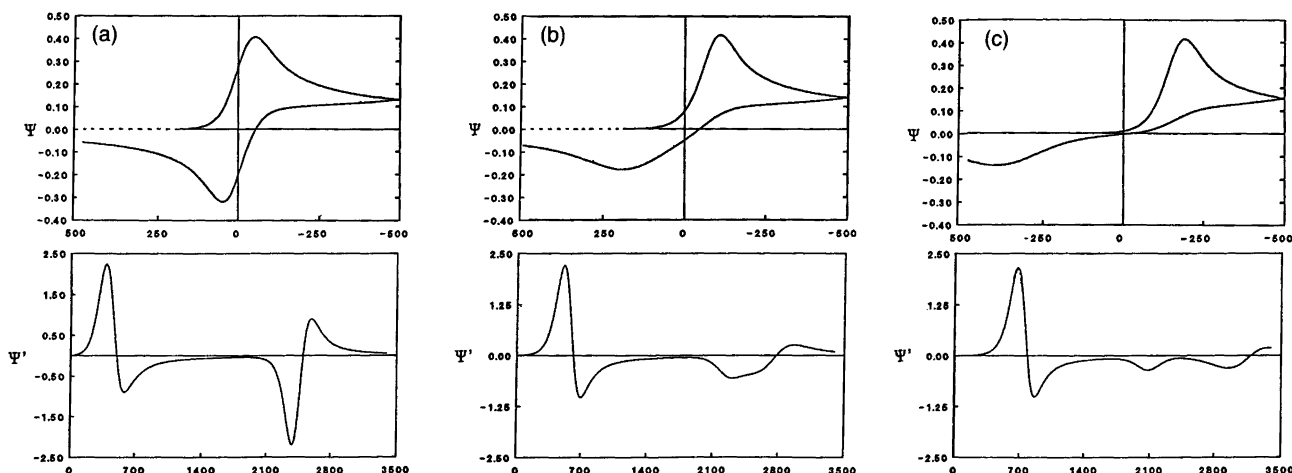Results, which seem to indicate a potential dependent transfer coefficient, have been obtained for 2-methyl-2-

Fig. 5. Simulated CV (top) and DCV (bottom) response curves for $\alpha = 0.7$ and $E_{start}-E^\circ = 0.2$ V, $E_{sw}-E^\circ = -0.5$ V and $E_{final}-E^\circ = 0.5$ V at $T = 298$ K. The values of log Λ are 0.0 (a), -1.0 (b) and -2.0 (c), respectively. The time scale for the DCV curves is defined by arbitrary units corresponding to a potential change of 0.5 mV with E_{sw} located at $\tau = 1400$.

nitropropane,[31,34,47,48,53] nitromesitylene and nitrodurene,[48,53,63] phthalonitrile and terephthalonitrile,[53,63] benzaldehyde,[53] and p-diacetylbenzene.[53,63] The reported values of $d\alpha/dE$ are typically in the range 0.3–0.7 V^{-1}. However, the results of a recent study[54] suggest that α for the reduction of 2-methyl-2-nitropropane does not depend on the potential, which has cast some doubt on the validity of the earlier conclusion.

The effect of a potential dependent transfer coefficient on the DCV working curves was briefly examined for $d\alpha/dE = 0.5$ V^{-1}. The results for $E_{sw}-E^\circ = -0.5$ V are shown in Fig. 6 and comparison of these working curves with those obtained for the same switch potential, but at $d\alpha/dE = 0$ [Fig. 4(b)], shows that there is essentially no difference between the two sets of curves as long as log Λ > -0.9. At log Λ < -0.9 the deviations are still small if α is close to 0.5 and values of $d\alpha/dE \neq 0$ are not likely to be detected in practical experiments. However, for α values outside the range $0.4 < \alpha < 0.6$ the working curves deviate appreciably and at least a semi-quantitative estimate of $d\alpha/dE$ may be obtained.

Before reporting the results of the experimental work the problem of presetting $E_{sw}-E^\circ$ for a system with an unknown E° will be discussed briefly. We have found with experience that it is generally possible to adjust $E_{sw}-E^\circ$ within an error limit of $\pm$ 40 mV and if α is not too far away from 0.5 the error is usually less than $\pm$ 20 mV. A series of simulations (Fig. 7) showed that the effect of errors of this magnitude is only small. For $E_{sw}-E^\circ = -0.4$ V it is found that the error in log $R_I^\prime$ caused by an uncertainty in $E_{sw}-E^\circ$ as large as $\pm$ 40 mV amounts to less than 6% and if the uncertainty can be reduced to $\pm$ 20 mV the error is less than 3%. The corresponding error in α amounts to less than 0.005, which is clearly smaller than the error introduced by other factors.
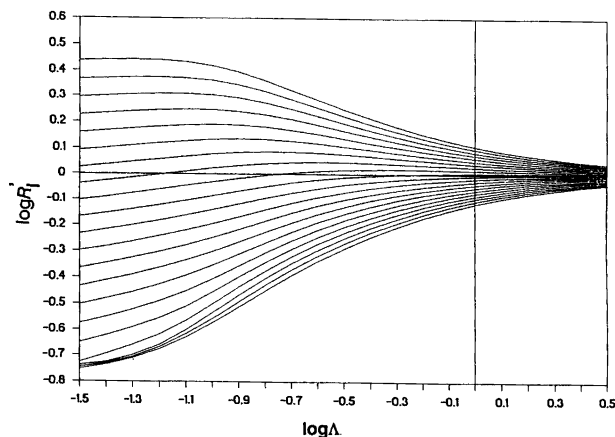

Fig. 6. Values of log $R_I^\prime$ as function of log Λ for $d\alpha/dE = 0.5$ V^{-1} and α_0 values in the range 0.3 (top)–0.7 (bottom) at $E_{sw}-E^\circ = -0.5$ V and $T = 298$ K. The increments in α_0 on going from the top to the bottom are 0.02.
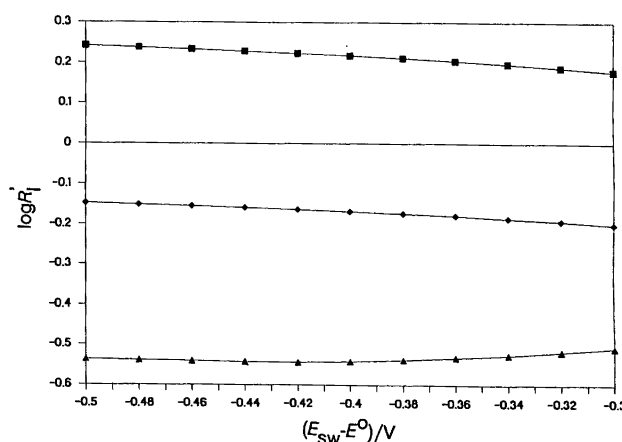

Fig. 7. The effect of the switch potential, E_{sw}, on log $R_I^\prime$ at log Λ = -1 and $d\alpha/dE = 0$ V^{-1} for $\alpha = 0.35$ (■), $\alpha = 0.5$ (◆) and $\alpha = 0.65$ (▲); $T = 298$ K.

The experimental work. The procedure was applied for the reduction of 2-methyl-2-nitropropane and a series of aromatic carboxylate and phenolate ions in dimethyl sulfoxide (DMSO) containing 0.1 M Bu$_4$NPF$_6$ as the supporting electrolyte. The values of k_s and α were determined by a two-step iteration procedure from data obtained by means of the background subtraction – FFT procedure recently described.[55] First the experimental data for ΔE_p were plotted against $-\frac{1}{2}$log v and by matching these data with the working curve (Fig. 2) a preliminary value of Λ linking the two scales on the *X*-axes was obtained. This value of Λ was then used for a first crude determination of α from the log R'_1 vs. $-\frac{1}{2}$log v data and the working curve corresponding to the applied value of $E_{sw}-E°$ (Fig. 4). Once α is known approximately a more accurate match of the two horizontal scales may be obtained by using the appropriate ΔE_p working curve after which α is redetermined. We never found it necessary to use more than these two iterations. The precision in α in practical experiments was estimated to be $\pm$ 0.02.

The reduction of 2-methyl-2-nitropropane. 2-Methyl-2-nitropropane, which has served as a model compound in earlier work,[10,31,34,47,48,53,54] was used to test for the effect of errors in the $E_{sw}-E°$ and the potentiostat positive feedback setting. Only v > 2 V s^{-1} were used because of the slow decomposition of the anion radical to the 2-methyl-2-propyl radical and nitrite ion.[64] The results are summarized in Tables 2–4.

The effect of $E_{sw}-E°$ on the value of R'_1 is seen in Table 2.

Table 2. The effect of the switch potential, $E_{sw}-E°$, on the derivative current peak ratio, R'_1, for the quasi-reversible one-electron reduction of 2-methyl-2-nitropropane.[a]

$(E_{sw}-E°)/V$	R'_1[a]
−0.30	0.626
−0.32	0.644
−0.34	0.653
−0.36	0.679
−0.38	0.686
−0.40	0.698
−0.42	0.716
−0.44	0.717
−0.46	0.735
−0.48	0.737
−0.50	0.760

[a] In DMSO containing Bu$_4$NPF$_6$ (0.1 M) at a mercury film electrode; v = 10 V s^{-1}, $C°_{substrate}$ = 1.0 mM and T = 296 K. Because of the changing values of $E_{sw}-E°$ the application of the background subtraction – FFT procedure was inconvenient for these measurements and instead differentiation without background subtraction was accomplished by means of a PAR Model 189 selective amplifier using a frequency-to-voltage sweep rate ratio equal to 500 V^{-1}. The potentiostat positive feedback resistor was set at 90 % of the oscillation value detected by the overload indicator of the PAR model 276 current-to-voltage converter.

Table 3. The effect of the potentiostat positive feedback setting on ΔE_p and R'_1 for the reduction of 2-methyl-2-nitropropane in DMSO.[a]

Feedback setting[b]	ΔE_p/mV	R'_1
99	337	0.724
95	339	0.731
90	340	0.724
85	339	0.731
80	340	0.733
75	342	0.727
70	343	0.725

[a] In solvent containing Bu$_4$NPF$_6$ (0.1 M); $C°_{substrate}$ = 1.0 mM; T = 296 K; v = 10 V s^{-1}; $E_{sw}-E°$ = −0.4 V. The measurements were carried out using a mercury film electrode by application of the background subtraction – FFT procedure[55] including differentiation in the frequency domain. [b] As percentages of the oscillation value detected by the overload indicator of a PAR model 276 current-to-voltage converter.

Table 4. Derivative cyclic voltammetry data for the reduction of 2-methyl-2-nitropropane.[a]

v/V s^{-1}	$E_{sw}-E°$ = −0.4 V		$E_{sw}-E°$ = −0.5 V	
	ΔE_p/mV	R'_1	ΔE_p/mV	R'_1
100	484	0.568	478	0.613
50	438	0.619	433	0.700
20	377	0.675	376	0.723
10	339	0.724	334	0.756
5	297	0.761	297	0.789
2	249	0.793	246	0.805
k_s/cm s^{-1}	3.1×10^{-3}		3.1×10^{-3}	
α	0.44		0.46	

[a] In DMSO containing Bu$_4$NPF$_6$ (0.1 M); $C°_{substrate}$ = 1.0 mM; T = 295 K. The measurements were carried out using a mercury film electrode by application of the background subtraction – FFT procedure[55] including differentiation in the frequency domain. The potentiostat positive feedback resistor was set at 90 % of the oscillation value. The value of D was taken as 7×10^{-6} cm^2 s^{-1}.[31]

The data show that a change in $E_{sw}-E°$ of $\pm$ 40 mV gives rise to a 2–5 % change in R'_1 in good agreement with the predictions resulting from digital simulation.

The data in Table 3 show that R'_1 shows only slight dependence on the potentiostat positive feedback setting. This is a well-known benefit of the DCV technique[65] related to the fact that $i'_{f,p}$ and $i'_{b,p}$ are both affected similarly by inadequate feedback adjustment and therefore any error introduced this way partly cancels by taking the ratio $-i'_{b,p}/i'_{f,p} = R'_1$. We consider the lack of sensitivity towards the positive feedback setting and the improved baseline handling the two major advantages offered by the present DCV technique compared with procedures based on fits of theoretical data to the entire CV curves.

The results from the determination of k_s and α at two

different settings of $E_{sw}-E°$ are summarized in Table 4 and it is seen that within the experimental error the same value, 3.1×10^{-3} cm s^{-1}, for k_s is observed. This is approximately one order of magnitude smaller than that reported by Corrigan and Evans for the same solvent.[31] The difference most likely reflects the application of different supporting electrolytes, Et_4NClO_4 in the work by Corrigan and Evans and Bu_4NPF_6 in the present work (see Ref. 34 for a similar effect of the same magnitude). The average value of α, 0.45, compares favourably with earlier results, which all fall in the range 0.42–0.51.[10,31,48,54] In contrast with k_s, α depends only marginally on the nature of the solvent and the supporting electrolyte.

The reduction of aromatic carboxylate and phenolate ions.
We have recently observed[66] that the voltammetric reduction of the carboxylate ions obtained by deprotonation of 1-naphthoic acid and 9-anthroic acid proceeds as quasi-reversible one-electron transfers in DMSO and it was found that the corresponding dianion radicals are stable on the time scale of slow sweep voltammetry. Since little is known about the effect of charge on the reduction of organic compounds it was decided to carry out a more extensive series of measurements for the reduction of aromatic carboxylates and phenolates. The preliminary results for typical substrates are reported below.

The fit of the experimental data to the working curves were, in general, good as seen in Fig. 8 for the 3-nitrophenolate anion and the 3-nitrophthalate dianion, although minor deviations, presumably caused by follow-up reactions, were occasionally observed at low-voltage sweep rates. The results are summarized in Tables 5 and 6. The diffusion coefficients necessary for the conversion of Λ into k_s were determined as follows. First the peak currents, i_p, were measured at the same working electrode at $v = 10$ V s^{-1} for 1 mM solutions of all the substrates including 2-methyl-2-nitropropane for which D is known.[31] From the data for 2-methyl-2-nitropropane and the definition of the
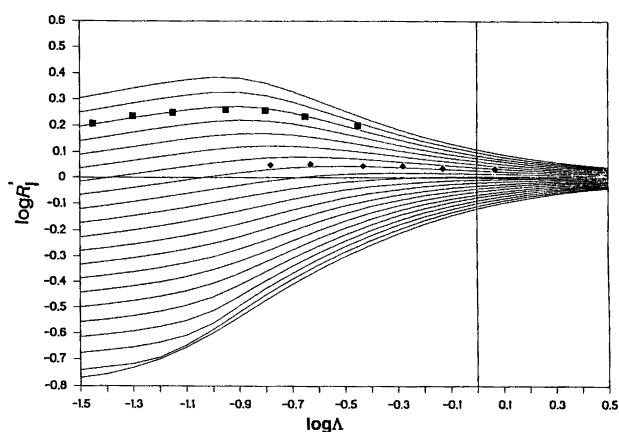

Fig. 8. Experimental values of log R_i' for the voltammetric reduction of 3-nitrophenolate (◆) and 3-nitrophthalate (■) fitted to the working curves shown in Fig. 4(b).

peak current function, Ψ_p [eqn. (8)], the constant, $c = nFAC_A°[nF/(RT)]^{1/2}v^{1/2}$, containing the unknown electrode area, A, was determined. The value of Ψ_p required for this purpose was calculated by digital simulation using the experimental data for Λ and α.

$$\Psi_p = \frac{i_p}{nFAC_A°D^{1/2}[nF/(RT)]^{1/2}v^{1/2}} = \frac{i_p}{cD^{1/2}} \tag{8}$$

Similarly, Ψ_p was calculated for the anions and the successive introduction of these values in eqn. (8) together with c and the appropriate i_p provided the values of D given in Table 6.

The kinetics of electrode reactions are strongly affected by the structure of the electrochemical double layer and when the pre-electrode site is located within the diffuse

Table 5. Values of ΔE_p and R_i' for the reduction of 1-naphthoate ($z = -1$), 9-anthroate ($z = -1$), 2-nitrobenzoate ($z = -1$), 3-nitrophenolate ($z = -1$) and 3-nitrophthalate ($z = -2$) in DMSO.[a]

v/V s^{-1}	1-Naphthoate		9-Anthroate		2-Nitrobenzoate		3-Nitrophenolate		3-Nitrophthalate	
	ΔE_p/mV	R_i'	ΔE_p/mV	R_i'	ΔE_p/mV	R_i'	ΔE_p/mV	R_i'	ΔE_p/mV	R_i'
100	319	0.510	128	0.975			227	1.121		
50	271	0.578	110	1.001	165	1.103	190	1.129		
20	219	0.684	94	1.003	132	1.106	151	1.112	449	1.612
10	184	0.746	84	1.041	113	1.101	127	1.111	402	1.727
5	156	0.818			99	1.107	108	1.088	352	1.783
2					87	1.091	94	1.082	299	1.823
1					80	1.080			260	1.812
0.5									224	1.715

[a]Measurements were carried out by application of the background subtraction – FFT procedure[55] in solvent containing Bu_4NPF_6 (0.1 M) at $T = 296$ K and $E_{sw}-E° = -0.5$ V except for 1-naphthoate for which $E_{sw}-E°$ was -0.3 V. The positive feedback resistor was adjusted to 90 % of the oscillation value.

Table 6. Experimental data for the voltammetric reduction of 1-naphthoate ($z = -1$), 9-anthroate ($z = -1$), 2-nitrobenzoate ($z = -1$), 3-nitrophenolate ($z = -1$) and 3-nitrophthalate ($z = -2$) in DMSO.[a]

Substrate	$E_p{}^b$	Λ^c	α	$i_p{}^d$	$\Psi_p{}^e$	D/cm^2 s^{-1}	k_s/cm s^{-1}	$-\Phi_2$/mV	k_s^{corr}/cm s^{-1}
1-naphthoate	−2.57	0.23	0.53	567	0.376	7×10^{-6}	1.2×10^{-2}	110	8.80
9-anthroate	−2.08	1.59	0.48	526	0.416	5×10^{-6}	2.2×10^{-1}	99	68.7
2-nitrobenzoate	−1.36	0.68	0.44	388	0.383	3×10^{-6}	2.3×10^{-2}	74	1.50
3-nitrophenolate	−1.43	0.53	0.43	420	0.370	4×10^{-6}	2.1×10^{-2}	77	1.57
3-nitrophthalate	−1.67	0.049	0.34	190	0.291	1.3×10^{-6}	1.1×10^{-3}	80	1.69

[a]In solvent containing Bu$_4$NPF$_6$ (0.1 M) at $T = 296$ K; $C^\circ_{substrate} = 1.0$ mM. [b]In V vs. and Ag/Ag$^+$ reference electrode. [c]At v = 10 V s^{-1}. [d]Peak current in an arbitrary unit. [e]Current function calculated by digital simulation by application of the values of Λ and α given in the table.

double layer the measured values of k_s must be corrected for the potential drop in this region. The correction, eqn. (9), that results from the Gouy–Chapman–Stern–Frumkin (GCSF) treatment of double layer effects assumes the electron transfer to take place at the outer Helmholtz plane (oHp).[67–69]

$$k_s^{corr} = k_s \exp\{(z - \alpha n)F\Phi_2/(RT)\} \qquad (9)$$

The value of the potential at the oHp, Φ_2, in solvents such as acetonitrile (MeCN), N,N-dimethylformamide (DMF) and DMSO in the presence of 0.1 M Bu$_4$N$^+$ ion is typically in the range −70 to −150 mV for values of E between −1 and −2 V vs. SCE[9,12,15,16,24,35] corresponding to values of the exponential term between 5 and 20 for neutral substrates ($z = 0$, $\alpha = 0.5$, $n = 1$ and $T = 298$ K). For anions ($z = -1$) and dianions ($z = -2$) the exponential term in eqn. (9) may take enormous values. For example, for $\Phi_2 = -100$ mV, $\alpha = 0.5$, $n = 1$ and $T = 298$ K the corrections amount to 3.4×10^2 for $z = -1$ and 1.7×10^4 for $z = -2$. Thus, considering the crudeness of the model it is obvious that extreme care should be taken in the interpretation of k_s^{corr} values and the conclusion from several studies[12,16,33–35] is that the simple GCSF treatment is often inadequate for the description of electron transfer under the conditions typically used in studies of organic compounds. In spite of the anticipated difficulties, an attempt was nevertheless made to correct the values of k_s for the anions in the manner just described. The values of Φ_2 were determined by an AC technique described in the Experimental section and are listed in Table 6 together with the resulting values of k_s^{corr}.

When the values of the electron transfer rate constants for the monocarboxylates are compared, it is seen that k_s^{corr} for 9-anthroate is approximately eight times larger than k_s^{corr} for 1-naphthoate, which again is approximately six times larger than k_s^{corr} for 2-nitrobenzoate. Assuming that all three-electron transfer reactions are of the outer-sphere type this is equivalent to an increasing value of the solvent reorganization energy, which may reflect a progressively increased charge localization at the oxygen atom(s) in the resulting dianion radicals on passing from the reduction of

9-anthroate to 2-nitrobenzoate.* Further work on the solvation of these species is now in progress.[71]

The values of k_s^{corr} and α obtained for 2-nitrobenzoate and 3-nitrophenolate are indentical to within experimental error and in addition it is seen that E_p differ by only 70 mV. Thus, it appears that both the nature and the ring position of the group formally carrying the negative charge has only a minor effect on the electrochemical behavior of anions of this type, which considering their structural similarity may not be surprising. More striking is that k_s^{corr} for the 3-nitrophthalate dianion is very close to that found for the two other nitrobenzene derivatives. This may indicate that the solvent reorganization energy associated with the reduction of 3-nitrophthalate is of the same magnitude as that for the two monoanions and that the much smaller value of k_s observed for 3-nitrophthalate is essentially caused by double layer effects.

Although α is important in determining the nature of the transition state for electrochemical reactions, it does not easily lend itself to chemical interpretation. However, the results for the five compounds included in this study indicate trends that should be pointed out. The values of α fall into three different categories, the first including 1-naphthoate and 9-anthroate for which α is close to 0.5. The α values of the second category, which includes 2-nitrobenzoate, $\alpha = 0.44$, and 3-nitrophenolate, $\alpha = 0.43$, are both significantly smaller than 0.5 and identical to within experimental error. An even smaller α value, 0.34, was found for the third category which is defined only by the dianion, 3-nitrophthalate. According to the Marcus theory,[58] α can

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* A referee pointed out that a discussion of the magnitudes of k_s^{corr} (and α) including only solvation reorganization terms, λ_0, may be too limited. For the nitro compounds in particular it was suggested that the inner reorganization terms, λ_i, are not necessarily negligible and that further information on this problem may be gained through semiempirical or ab initio calculations.

Although it is common to treat the electrochemical reduction of substituted aromatic compounds as outer-sphere processes, we have now initiated a series of geometry and force-constant calculations using the AM1 method, which we used recently for other purposes.[70] Hückel molecular orbital calculations have been applied earlier to estimate λ_i for the electrochemical reduction of 1,4-diazines[13] and quinones.[14] (See Ref. 11 for a short discussion of the approach).

be written as eqn. (10), where ΔG_r° is the free energy of reaction at the reaction site, λ is the reorganization energy, and w_r and w_p are work terms given by eqns. (11) and (12), in which z and z' are the charges of the reactant and the product, respectively. For a simple one-electron reduction ($z' = z - 1$) at $\Delta G_r^\circ = 0$, eqn. (10) reduces to eqn. (13), which is of the same form as eqn. (5).

$$\alpha = \frac{1}{2} + \frac{\Delta G_r^\circ + w_p - w_r}{2\lambda} \tag{10}$$

$$w_r = zF\Phi_2 \tag{11}$$

$$w_p = z'F\Phi_2 \tag{12}$$

$$\alpha = \frac{1}{2} - \frac{F\Phi_2}{2\lambda} \tag{13}$$

Thus, it follows that α should always be larger than 0.5. However, the values of α reported[9,12,15,18,24,27,31,33–35,48,53,54,63] for typical organic substances appear to be almost equally distributed in two groups with $\alpha \geq 0.5$ and $\alpha < 0.5$. It is of interest to notice that $\alpha \geq 0.5$ is frequently observed for planar aromatic compounds giving rise to anion radicals in which the additional electron is fairly evenly distributed, whereas $\alpha < 0.5$ has been observed, for example, for the reduction of nitro or carbonyl compounds the anion radicals of which are characterized by a high degree of charge localization at the oxygen atom(s). Our preliminary results appear to be in agreement with this general trend. For example, we find that α for the reduction of 1-naphthoate and 9-anthroate are both very close to 0.5 and in this respect these two compounds are similar to most extended aromatic systems. Similarly, the α values found for the two nitrobenzene derivatives are close to those observed for many neutral nitro compounds. It has been suggested[48,53] that the 'too' low values of α observed for the reduction of for example aromatic nitro compounds may reflect different solvation modes for the reactant and the product states in particular as far as solvation by residual water is concerned. The argument was based on the expectation that water is bound more tightly to the product anion radical because of the negative charge, which in the harmonic approximation corresponds to a parabola narrower than that for the neutral starting material. This idea is supported by the fact that anion radicals derived from aromatic nitro and carbonyl compounds are known to form hydrogen-bond complexes with water in MeCN, DMF and DMSO[70] with equilibrium constants, K, in the range 1–25 M^{-1}, whereas K for the anion radicals derived from aromatic hydrocarbons are too small to be detected by voltammetric methods. In the present study preferential solvation by water may play an even more important role since the water concentrations in our solutions are higher than usual for aprotic solvents owing to the *in situ* preparation of the carboxylate and phenolate ions from the corresponding

acids and aqueous Bu_4NOH (see the Experimental section). The water concentration in the experiments involving the monoanions was typically 0.02–0.03 M and for the dianion approximately twice as high.

For 1-naphthoate and 9-anthroate α is very close to 0.5 which leads to the conclusion that the solvation modes for the carboxylate ion and the resulting dianion radical are similar. For each of the three nitrobenzene derivatives α is significantly lower than 0.5 and from eqn. (14),[72] which in the harmonic approximation describes the relation between α and the oscillator frequencies, ω_r and ω_p, in the reactant and product states, it is seen that $\alpha = 0.43$–0.44 would correspond to a value of the ratio ω_r/ω_p of approximately 0.6 decreasing to approximately 0.3 for $\alpha = 0.34$. However,

$$\alpha = \frac{\omega_r^{1/2}}{\omega_r^{1/2} + \omega_p^{1/2}} \tag{14}$$

these calculations should only be taken as a rough indication of the frequency changes associated with the electron transfer reactions. In particular for the reduction the 3-nitrophthalate to the trianion radical we may have reached the limit of the harmonic approximation and a more rigorous description of solvent reorganization, taking into account anharmonicity effects, is probably required. Further studies along these lines are now in progress and the effect of water on k_s and α for organic mono- and di-anions is under investigation.

As mentioned earlier the voltammetric technique described in this paper is only likely to reflect values of $d\alpha/dE \neq 0$ as long as α is not too close to 0.5 and 3-nitrophthalate would then be the most likely candidate for which a potential-dependent α value might be observed. However, if the parabola representing the product state is narrower than that for the reactant state as discussed above, that is for $\omega_r < \omega_p$, the value of $d\alpha/dE$ will decrease relative to the situation in which $\omega_r = \omega_p$. An attempt to fit the data for 3-nitrophthalate to the working curves for $d\alpha/dE = 0.5$ V^{-1}
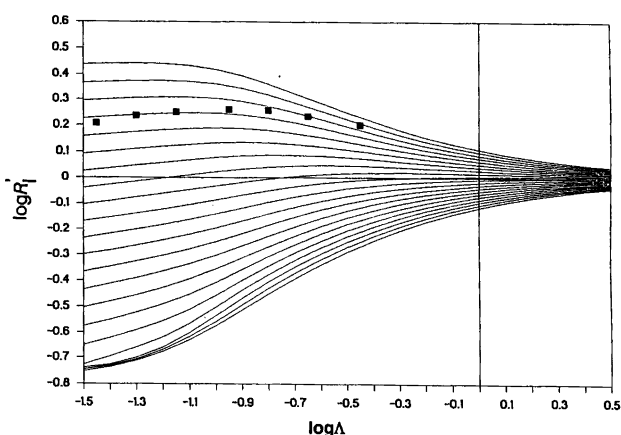

Fig. 9. Experimental values of log R_i' for the voltammetric reduction of 3-nitrophthalate fitted to the working curves shown in Fig. 6.

is shown in Fig. 9. It is seen that the experimental points cross two of the working curves and the fit is clearly of lower quality than that shown in Fig. 8 for $d\alpha/E = 0$. Thus, we conclude that $d\alpha/dE$ for the reduction of 3-nitrophtha- late under the present conditions is considerably less than $0.5 \ V^{-1}$, if at all different from zero.

Experimental

Chemicals. The chemicals were reagent grade and used as received. The supporting electrolyte, Bu_4NPF_6, was made from Bu_4NHSO_4 and HPF_6 by a procedure analogous to that described earlier for Bu_4NBF_4.[73] The solvent, DMSO (Fluka, *purum*), containing the supporting electrolyte (0.1 M) was passed through activated neutral alumina (Woelm W200) before use. The carboxylate and phenolate solutions for voltammetry were prepared directly in the electrochem- ical cell containing the solvent – supporting electrolyte system by mixing 0.01 mmol of the corresponding acid with a slight excess (20 %) of Bu_4NOH (Fluka, *purum*, 40 % in water). The water concentrations in the resulting solutions were 0.02–0.03 M for the monoanions and 0.04–0.06 M for the dianion.

Instrumentation and measurement procedures. The electro- chemical instrumentation, the cell and the mercury work- ing electrodes were as described previously.[55] The measure- ments of ΔE_p and R'_1 were carried out by application of the background subtraction – FFT procedure[55] in the following way. First, the background current for a nitrogen-saturated blank solution in the potential range of interest was re- corded and the average of four such base lines were stored in the computer. After introduction of the substrate, vol- tammetric measurements were carried out in the same po- tential range and again the average of four voltammograms was stored. This was followed by (i) background substrac- tion, (ii) noise filtration and differentiation in the fre- quency domain and (iii) back transformation to the time domain. The values of ΔE_p were obtained from the zero- crossings of the DCV curve.

Data for the differential capacity, C_d, were obtained by measuring the in-phase, i_1, and out-of-phase, i_2, compo- nents of the AC admittance of the mercury film electrode – DMSO/Bu_4NPF_6 solution interface[74] using a 10 mV peak- to-peak sine wave with a frequency of 1 kHz superimposed a 10 mV s^{-1} voltage ramp. The values of i_1 and i_2 were determined by means of a PAR model 5206 two phase lock-in amplifier and C_d was calculated from eqn. (15), where ω_{AC} is the angular frequency and V the amplitude of the sine wave; A is the electrode area.

$$C_d = (i_1^2 + i_2^2)/(\omega_{AC}AVi_2) \tag{15}$$

The value of A was determined by measuring i_p for the voltammetric reduction of anthracene in a fashion similar to that described above for 2-methyl-2-nitropropane using the value, 0.4463, of Φ_p for a reversible redox couple.[40] The

value of D for anthracene in DMSO was taken as 4.4×10^{-6} $cm^2 \ s^{-1}$.[24] The potential of zero charge in the absence of specific adsorption[35,75] is -0.314 V vs. NCE[76] correspond- ing to -0.53 V vs. the Ag/Ag^+ reference electrode used in this study.

Digital simulations. Digital simulations for $T = 298$ K were carried out using the explicit formulation of the diffusion problem described by Feldberg.[56] Differentiation was ac- complished by application of the five point Savitzky–Golay procedure.[77] The spike observed in the DCV curve when the direction of the voltage sweep was changed close to the reduction peak was minimized by avoiding differentiation at the switch potential and right after. The simulations were carried out on an IBM Model 6151/115 desk computer equipped with an Advanced Floating Point Accelerator or a MEGA 80386/80387 personal computer. The simulation accuracy was 0.5 mV/time step.

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