FAST TECHNIQUES IN DIRECT ELECTROCHEMISTRY AT ULTRAMICROELECTRODES: AN EASY ACCESS TO KINETICS IN THE NANOSECOND TIME-SCALE.[®]

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Abstract.

The principle of fast techniques in direct electrochemistry is presented, and the domain of their applicability is examined on the basis of classical theories. In this process two series of factors are identified which limit the method. In the one hand, ohmic drop, capacitive phenomena and coupling of diffuse and diffusion layers are intrinsic factors. They lead to built-in limitations of the time scale range of the method. These limits cannot be trepassed without the necessity of introducing severe modifications of the available theories of molecular electrochemistry. On the other hand other limitations exist which are only due to the present technology, and are therefore expected to be broken in the future.

Introduction.

The principle of *direct* electrochemical methods for the detection of transient intermediates and determination of their kinetics consists in performing a sequence of two electrochemical perturbations. A first perturbation allows to electrogenerate the desired intermediate, either at the electrode or *via* a cascade of controlled follow-up chemical reactions. At the end of this first perturbation, a second one is performed which enables the electrochemical detection of the fraction of the intermediate which has "survived" over the time, θ , elapsed during the two perturbations. Such a sequence of perturbations is required because the same physical instrument, *i.e.* the electrode, must be used in

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turn as a generator (first perturbation) and as a detector (second perturbation). The overall result is then akin to that obtained in spectroscopic methods, except for the obvious difference that the intermediate is now identified and characterized through its electrochemical "spectrum" rather than through its photochemical absorbance spectrum.

A second class of electrochemical methods, which involve a single perturbation, may also be used to determine kinetics. Yet they do not afford a direct detection of intermediates: we therefore refer to these methods as to indirect electrochemical methods. Indeed, their principle consists in opposing a rate of mass transfer from the region where the intermediate is electrogenerated, to the rate of the chemical reaction. The above functions of generating and detecting the intermediate now follow from two intrinsic properties of an electrode. For example one may adjust the electrode potential to provide the driving force which allows generation of the intermediate at the electrode surface. The transient species then diffuses away from the electrode surface, while it concomitantly reacts chemically. The ensuing competition between mass transfer and chemical reaction imposes a local concentration profile for the intermediate. Whenever the transient species is electroactive or reacts with electroactive species, this controls part or totality of the current flow at the electrode.¹ It is then easily understood that the current flowing through the electrode contains then a signature of the presence and kinetics of the intermediate, since it indirectly reflects the degree of competition between the chemical reaction and mass transfer. Thus the electrode is then at the same time the generator (potential) and the detector (current) of the intermediate. This combination is earned at the expenses of the fact that such methods (e.g. linear sweep voltammetry - LSV - , chronoamperometry, polarography, rotating disk electrode - RDE - , etc) do not allow a direct characterization of the intermediate, at least within the above "spectroscopic" sense, but merely report an indirect signature of the intermediate presence and fate.

As for direct methods, measurement of kinetics by indirect methods then consists in adjusting the characteristic time of mass transfer so that it matches the half-life of the intermediate. The rate of mass transfer is intimately related to the diffusion coefficient and to the nature and dimension of the space in which diffusion occurs. Whenever the intermediate is generated at an electrode, diffusion occurs from the electrode surface to the unperturbed bulk solution. The characteristic time of mass transfer is then simply the duration of the perturbation in transient methods (e.g. RT/Fv in LSV, duration of the potential pulse in chronoamperometry, etc), or the time required for a molecule to cross the diffusion layer in steady state methods (*i.e.* δ^2/D where δ is the thickness of the diffusion layer imposed by hydrodynamics - in RDE, polarography, etc - or by non-linear diffusion at ultramicroelectrodes).^{1a} The intermediate may also be generated within the diffusion layer by means of a redox mediator whose rôle is to carry the electron to or from the electrode.^{1b} Then the diffusion time to be considered is that required for the intermediate to cross over several molecular distances from the mediator, in order to escape the molecular diffusion layer existing around the mediator molecule. Based on the Smoluchovski equation,² this time is related to an apparent bimolecular rate constant, the so-called diffusion limit kdif, of the order of 10⁹ to 10¹⁰ M-¹s-¹ in the absence of specific interactions between the mediator and intermediate. The time scale is therefore a built-in characteristic of the method, and as a result cannot be varied significantly. Considering that most electrochemical experiments are performed in a millimolar to a ten millimolar concentration range, kdif corresponds to a nearly imposed time scale located in between ca. 1 μ s and ca. 10 ns, only slightly adjustable and mainly dictated by the viscosity of medium.

It is seen that the time scales in which direct electrochemical methods may be used depends on the capability of electrochemists to perform *controlled* perturbations of shorter and shorter durations. The ultimate limit is given by the applicability of Fick's laws. Thus the smallest time one may envision to reach is that required for a molecule to diffuse over *ca.* several free-motion lengths,^{1b} and is therefore of the order of a tenth of a nanosecond. The upper time limit is based upon the ability to create diffusion layers which do not merge with the convective domains at the electrode surface. Under most electrochemical conditions the convection-free layer is *ca.* 50 to 100 μ m. For an average diffusion coefficient of 10⁻⁵ to 10⁻⁶ cm²s⁻¹, this corresponds to an upper time

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scale being of the order of a second. The same is obviously true for indirect methods in the absence of redox mediators.

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From what precedes one sees that, with the exception of mediated electrochemistry which is poised somewhere in the range of ca. 1 µs to 10 ns depending on the medium, direct or indirect kinetic electrochemical methods should be continuously adjustable from a time scale of ca. one second to a theoretical lower limit of ca. one tenth of a nanosecond. Up to the middle of the eighties the smallest time scales achievable were in the range of a tenth of a millisecond.³ Nowadays, thanks to the use of ultramicroelectrodes,⁴ this limit has been pushed away to the range of a few tens of nanoseconds.⁵ In the following we want to discuss how and why this considerable progress has been possible, and to examine which difficulties should be overcome to reach the ultimate limit of ca. a tenth of a nanosecond, and in this process discuss if there is any sense in trying to do it by conventional electrochemical methods.

In the following analysis we must separate limitations which are related to technology – e.g. those related to electronics, miniaturisation of electrodes, etc – since one may reasonably expect to overcome them in the future, from those related to built-in physical factors, since these are intrinsic limitations of a method.

Physical limits to short time scales in electrochemistry.

Ohmic drop results from the fact that any current, i, flowing at an electrode must be carried through a volume of solution, of electrical resistance R, surrounding the electrode.¹ On the other hand the driving force, $F \cdot \Delta E$, for an electrode reaction results from the potential difference, ΔE , existing between the electrode and the solution adjacent to it (*viz.* beyond the end of the double layer). Therefore, by applying a potential difference ΔE_{app1} to the cell, one disposes of an effective potential difference $\Delta E_{eff} = \Delta E_{app1} + iR$ usable for electrochemical purposes (note that a sign '+' is used to account for the electrochemical convention where cathodic currents are counted positive). The difficulty is that when the electrochemical perturbation takes place, the current varies and so does the difference between the effective driving force $F \cdot \Delta E_{eff}$ and that, $F \cdot \Delta E_{app1}$, applied to the cell. Up to the early eighties this difficulty was by-passed by means of electronic feedback.³ Thus potentiostats had been devised which allowed to apply to the cell a potential difference $\Delta E_{app1} = \Delta E - iR$, in order that $E_{eff} = E$. Yet, in organic media at electrodes of millimetric sizes, this could not be performed for time scales under a tenth of a millisecond, owing to the magnitude of the feedback term iR.

In the early eighties it had been realized that ultramicroelectrodes should allow to overcome easily this limit and a time scale of the order of a few microseconds could be reached at by Wightman et coll.⁶ This considerable sudden progress was due to the recognition that for a disk electrode of radius r_o , the electrode/solution electrical resistance, R, is reciprocally proportional to ro. On the other hand, the current flowing through the electrode is proportional to the electrode surface, *i.e.* to r_0^2 , and reciprocally proportional to the diffusion layer thickness, *i.e.* to $\theta^{1/2}$, where θ is the duration of the perturbation in transient methods. Thus at an electrode of radius r_0 and for a time scale θ , the ohmic drop, iR, is proportional to $r_0 \cdot \theta^{-1/2}$. This shows that in transient methods the ohmic drop decreases proportionally to the size of the electrode, which allows in turn to achieve smaller perturbation times. Use of ultramicroelectrodes, with radii of a few micrometers, instead of electrodes of millimetric sizes, has then provided a sudden gain by a factor of ca. one hundred on the time scales accessible by electrochemical methods. Pushing this approach to its limit we were able to reach a time scale of a few tens of nanoseconds,⁷ which allows to detect intermediates reacting at a rate close to the diffusion limit. This was illustrated by the reduction of pyrylium in acetonitrile: 7,8



The radical formed upon reduction of a pyrylium cation undergoes a fast dimerization which results in chemically irreversible voltammo-

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Figure 1. Background substracted voltammograms of 2,6-diphenylpyrylium perchlorate, 10 mM, in acetonitrile, 0.1 M NBu4BF4 at a platinum disk ultramicroelectrode (Ø 10µm) at 20°C. Scan rates: (a) 250, (b) 200, (c) 150, (d) 100 and (e) 75 kV.s⁻¹.

grams for scan rates under 10 000 Vs⁻¹. Using ultramicroelectrodes of 5 μ m radius and cyclic voltammetry up to scan rates of 250 000 Vs⁻¹ we were able to detect the transient pyrylium radical⁷ formed in eqn.1 (see Figure 1) and to estimate its dimerization rate constant at 2.5 $\cdot 10^9$ M⁻¹s⁻¹, *i.e.* in close agreement with a value of 1.2 $\cdot 10^9$ M⁻¹s⁻¹ reported previously on the basis of flash photolysis.⁹ Note that such rate constants correspond to a half-life of *ca.* 20 to 50 ns for the pyrylium radical under the conditions (10 mM solutions) used in this study.

On the basis of these results, one may think of decreasing even more the electrode sizes to reach shorter and shorter time scales. However there is a built-in limitation to the process. Indeed, in order to achieve transient experiments at an electrode of radius ro, the diffusion layer must be smaller than the radius of the electrode, to avoid significant contribution from edge diffusion.^{4,10} This imply that θ , the duration of the perturbation, must be much less than r_0^2/D . It follows that θ and r_0 cannot be varied independently, and thus that one cannot completely eliminate ohmic drop by decreasing the size of electrodes. Nevertheless an optimum ohmic drop can be reached by selecting adequately the radius of the electrode for a given time scale. Figure 2a illustrates this point for the cyclic voltammetry of anthracene, 10 mM, in acetonitrile, 0.6 M NBu₄BF₄ at a gold electrode. Imposing that the ohmic drop due to the Faradaic current is less than 15 mV,^f leads to the condition in eqn.2, where r_{o} is in μm and v in Vs⁻¹ (note that θ = RT/Fv):

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 $\log(r_{o}) \leq -\frac{1}{2} \cdot \log(v) + 2.55$ (2)

This condition is represented by the region located below line (i) in Figure 2a. Edge diffusion contributions can be evaluated from the general solution of cyclic voltammetry at a disk electrode.¹⁰ For the example considered, considering $D = 10^{-5} \text{cm}^2 \text{s}^{-1}$, it is then shown that in order that edge diffusion introduces an error less than 15 mV on the peak potential, one must have:

$$\log(r_{o}) \ge -\frac{1}{2} \cdot \log(v) + 1.05 \tag{3}$$

which is represented by the region above line (ii) on Figure 2a. Yet such a limit corresponds to an error of *ca*. 70% on the current peak value. Whenever current peaks are of interest for mechanism diagnosis, one must then impose a more severe condition than that in eqn.3. Considering for example a 10% precision on the current peak

f: The limit of 15 mV is taken arbitrarily since it corresponds to ca. one fourth of the half-width of one electron Nernstian cyclic voltammograms.^{1c} For one electron irreversible voltammograms, *i.e.* a situation more relevant here, this limit corresponds to ca. one sixth of the half-width of voltammograms for $a = 0.5.1^{c}$



Figure 2. Domain where direct electrochemical methods may be applied without severe distortions due to cell resistance (below lines i and iii) and cell capacitance (below line iii) or to edge diffusion (above lines ii or ii'). Lines i, ii and iii correspond to the limit for an error of 15 mV on the peak potential in cyclic voltammetry. Line ii' corresponds to a limit of 10% accuracy on the current peak. The locations of the different boundaries are shown for a solution of anthracene, 10 mM, in acetonitrile, 0.6 M NBu4BF4, at a gold electrode of radius ro. (a) Effect of edge diffusion and ohmic drop due to Faradaic current only. (b) Effect of edge diffusion (10% on current peak), ohmic drop due to Faradaic and capacitive currents and cell time constant. (c) Modification of the limits i and iii in (b) when using on-line resistance compensation with $\beta = 0.90$ and 0.99 (see text). In (b,c) the vertical line iv, corresponds to the limit of classical theories (vide infra).

yields:

$\log(r_{o}) \ge -\frac{1}{2} \cdot \log(v) + 1.80$

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(4)

represented by the domain above line (ii') on Figure 2a. It ensues that depending of the type of variable of interest (*i.e.* current or potential), the point representing the system must be located in the region between lines (i) and (ii), or between lines (i) and (ii') on Figure 2a. A displacement of the system on a line parallel to these boundaries corresponds to a constant distortion by ohmic drop and edge effects.

In the foregoing analysis we have taken into account only the Faradaic current. However when v is increased, *i.e.* θ decreased, capacitive current which varies proportionally to v, tends to overwhelm the Faradaic contribution proportional to v^{1/2}. At high scan rates ohmic drop then arises mainly from the capacitive component of the voltammogram and the region limited by line (i) must be replaced by that below line (iii) of eqn.:

$$\log(r_0) \le -\log(v) + 5.50$$
 (5)

This more severe condition establishes that the domain of constant distortion by ohmic drop and edge diffusion is in fact limited, as represented in Figure 2b. In other words one cannot expect to have access to shorter and shorter time scales simply by decreasing the electrode size.

Time constant of the electrochemical cell. The time constant of an electrochemical cell is given by $\tau = R \cdot C_d$, where R is the resistance of the cell as defined above and C_d the capacitance of the double layer at the electrode/solution interface, proportional to the electrode surface area.^{1c} It then follows that τ is proportional to ro, the radius of the electrode. For an electrochemical perturbation not to be significantly distorted by the existence of the cell time constant, one must have $(\tau/\theta) \ll 1$, *i.e.* one must minimize the product $r_0 \cdot \theta^{-1}$, *i.e.* $r_0 \cdot v$ in cyclic voltammetry. The distortion of a voltammogram by the first order filter formed by the cell capacitance and resistance, can be estimated.¹¹ For the system considered above, *i.e.* anthracene in acetonitrile, it ensues that a shift less than by

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15 mV of the peak potential is observed provided that:

$$\log(r_0) \le -\log(v) + 5.55$$
 (6)

This new boundary condition is identical to that in eqn.5. Therefore the domain represented in Figure 2b corresponds to the region were the experimental system must be located so that errors less than 15 mV on peak potential and 10% on current peak can be achieved (*sed vide infra*).

Combined use of ultramicroelectrodes and compensation of the cell resistance by electronic positive feedback.

Satisfying the constraints due to ohmic drop, time constant and negligible edge diffusion, imposes that the system must be located in the domain limited by lines i, ii' and iii in Figure 2b. This suffices to demonstrate that even if the use of smaller and smaller electrodes has proven successful in by-passing the limits of time scale at which electrochemistry was poised in the early eighties (i.e. ca. 0.1 ms), this approach alone cannot be expected to lead to any significant improvement of the present limit of ca. 10-100 ns. To break this limit one must find a way of extending the domain in Figure 2b toward shorter time scales. One may think of suppressing the limit ii' by using recessed electrodes. Indeed, at a recessed electrode edge effects are necessarily negligible, because lateral diffusion is suppressed by the shaft above the electrode. However, the electrical resistance of the cell is now increased by that due to the shaft, of a length necessarily larger than $I = (D\theta)^{1/2}$. Since the resistance of a solution tube of radius ro and length 1 varies as 1.ro-2, it is understood that no significant progress may be found in this direction. We therefore need to consider that the limit ii' in Figure 2a or b is a physical limit which cannot be by-passed. Let us examine now if one can extend the domain in Figure 2b by pushing up the limits due to ohmic drop (i) and time constant (iii).

This can be achieved theoretically by combining the use of ultramicroelectrodes to that of electronic on-line compensation of the cell resistance.¹² Indeed, positive feedback amounts to introduce a negative resistance, $-R_{comp}$, in the cell electrical circuit, so that

the effective cell resistance is now given by $R_{cell} = (R - R_{comp})$, where R is the "physical" resistance considered in the previous sections. To avoid electronic unstabilities, only a fraction, $\beta < 1$, of the cell resistance may be compensated, so that $R_{cell} = R \cdot (1 - \beta)$. Not taking into account any limitation due to electronics (*vide infra*), this shows that the ohmic drop, iRcell, and time constant, $\tau = R_{cell}C_d$ may then be reduced by a factor (1- β). This results in an upward translation of the limits i and iii in Figure 2b by a constant equal to log(1- β). This is represented in Figure 2c for two values of β , corresponding to 90% and 99% compensation.

Obviously this requires that the electronic instrumentation used for resistance compensation does not introduce any limitation due to bandpass, unstabilities, *etc.* Yet, as explained above this does not constitute a physical limitation of the method *per se*, but is a technological limit which hopefully may be overcome in the future. Let us nevertheless examine the limitations due to the present technology.



Figure 3. Cyclic voltammetry of anthracene, 10 mM, in acetonitrile 0.1 M NBu4BF4 at a gold disk ultramicroelectrode (ro 8.5 μ m) with ($\beta \approx 1$) and without ($\beta = 0$) on-line ohmic drop electronic compensation. Scan rates: (a) 9, (b) 18, (c) 37, (d) 56, (e) 75 and (f) 94 kV.s⁻¹. 20°C.

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Table 1: Rate constants for the deprotonation of alkyl benzene cation radicals by a series of pyridine bases, in acetonitrile at 20°C:

Ar-CH₃·+ + py \longrightarrow py-H+ + Ar-CH₂·

Pyridine / Substituent	ArCH3ª	k (M ⁻¹ s ^{−1})	
		Cyclic voltammetry ^b	Laser picosecond ^c
2,6-Me ₂	HMB d ₁₈ -HMB	1.1.10 ⁷ 2.9.10 ⁶	2.1.10 ⁷ 7.5.10 ⁶
	PMB	3.6.107	4.0.107
	DUR	1.1.108	5.8.107
2,4,6-Me3	HMB	2.5.107	3.5.107

a: HMB: Hexamethylbenzene, PMB: pentamethylbenzene, DUR: durene. b: From reference 13. c: From reference 14.

Several approaches are feasible which depend on the type of cell configuration adopted. We have established that with current technology and classical circuitry ohmic drop at ultramicroelectrodes could be compensated up to scan rates of 100 000 Vs⁻¹ in cyclic voltammetry ($\theta \approx 250$ ns, $\delta E^{p} \leq 15$ mV) in a three electrode configuration.¹² An example of the validity of this approach is shown on Figure 3 by the comparison between uncompensated and ohmic drop compensated cyclic voltammograms of anthracene. From this series of compensated voltammograms an heterogeneous rate constant of 3.8 ± 0.4 cm.s⁻¹ was determined,¹² in agreement with the value previously reported by Savéant *et* coll. on the basis of sophisticated deconvolution procedures applied to uncompensated voltammograms.¹⁵

Using the same potentiostat and scan rates in the range of $50\ 000\ Vs^{-1}$, we were also able to measure a series of rate constants for the deprotonation of methylbenzene cation radicals by pyridine bases.^{13,16} These rates are compared in Table 1 to those previously determined by laser picosecond spectroscopy.¹⁴ The comparison of the two sets of values clearly establishes the validity of the electrochemical approach, as compared to more sophisticated spectros-

copic techniques.

As reported later by Savéant *et* coll., ohmic drop may be compensated up to scan rates above 200 000 Vs⁻¹, provided that a two electrode configuration is adopted, and current amplifiers are used instead of potential amplifiers.¹⁷ Yet this gain is made at the expenses of precision on absolute potentials, owing to the two electrode configuration, and corresponds also to a considerable decrease of the signal-to-noise ratio. We are presently developing a new concept of potentiostat, able to perform ohmic drop compensation up to scan rates of 400 000 Vs⁻¹ ($\delta E^p \leq 15$ mV) in a three electrode mode and with a signal-to-noise ratio akin to that shown in Figure 3.

Coupling between diffusion layer and diffuse layer at scan rates above a few hundred of kilovolts per second.

The above limitations due to cell resistance and cell capacitance have been identified since the early days of electrochemical kinetics. We have shown above that the use of ultramicroelectrodes, together with electronic feedback, has allowed to master these phenomena so that virtually undistorted voltammograms can be recorded at scan rates of a few hundred of kilovolts per second. Expected improvement of electronics, and possible resort to deconvolution procedures, give the feeling that scan rates exceeding several megavolts per second ($\theta \approx 10$ ns) could be used in a next future, and that still usable kinetic information could be extracted from voltammograms recorded at a few tens megavolts per second ($\theta \approx 1$ ns). We wish to show in the following that unfortunately this is not achievable because of another built-in limitation of the method.

Classical theories of electrochemistry, *e.g.* that of cyclic voltammetry,¹⁸ suppose that the concentration profiles of the reactants, intermediates and products are mainly controlled by pure diffusion and kinetics. This amounts to consider that the size of the double layer, δ_{d1} , is a vanishingly small fraction of the diffusion layer, δ_{d1f} , *i.e.* that δ_{d1f} . Under these conditions, the effects due to the electrical potential variations in the double layer are taken into account via a simple correction of the electrode boundary condition, *viz.* the Frumkin correction.¹⁹ However such a situation is

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clearly not met when the diffusion layers are made shorter and shorter i.e. when the scan rates are made larger and larger. Within the classical theory of cyclic voltammetry, the forward peak of a cyclic voltammogram recorded at a scan rate v, corresponds to a diffusion layer of the order of $(DRT/Fv)^{1/2}$. Thus, at room temperature and for an average diffusion coefficient of ca. $5 \cdot 10^{-5}$ cm²s⁻¹, $\delta_{dif^{\approx}} 3.5 \cdot v^{-1/2}$, when v is expressed in V.s⁻¹ and δ in µm. Therefore at e.g. v \approx 1 to 2M V.s⁻¹,²⁰ the diffusion layer at the forward peak is of the order of 20 to 35 Å, that is comparable to the thickness of the diffuse layer under usual electrochemical conditions in organic solvents.^{1c} The transport equations in the two layers, i.e. the diffuse layer and the diffusion layer, obviously cannot be theoretically separated under such circumstances.

This is a clear evidence that the classical theories for cyclic voltammetry are no more valid as such scan rates. In the following we want to discuss the effects predicted on cyclic voltammograms due to the intimate coupling between the two layers. This is presented here for a single electron transfer reduction mechanism of a neutral molecule (n = 1, $z_a = 0$, $z_b = -1$), i.e. for a case corresponding to usual conditions found in organic electrochemistry:

 $A^{Za} + ne \iff B^{Zb=Za-n}$ (E⁰, k⁰t, a) (7)

whereas reference 21 gives a general analysis for the cases corresponding to any value of z_a and z_b (n = z_a-z_b). Also, the analysis presented in this text considers only the limiting situation of a fast electron transfer (see reference 21 for a treatment of quasi-reversible and slow electron transfer). Although this limiting situation is clearly not realistic for the scan rates considered in this study, owing to the exceedingly high values of k^{0}_{t} it would require, we want to present it here, for the purpose of demonstrating that the main effects predicted hereafter originate from concentration profile distortions and are not related only to electron transfer kinetics, as *e.g.* in the case of the Frumkin correction.

In the diffuse layer the species A and B diffuse and simultaneously migrate in the electrical potential.²² Therefore the classical



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Figure 4. Normalized concentration profiles for the reaction in eqn.7, compared to the variations of the normalized electrical potential $(\emptyset_N = \emptyset/\emptyset_2)$. $y = (x-x_2) \cdot \underline{K}$, where \underline{K} is the reciprocal Debye length, x the distance from the electrode and x_2 the abscissa of the OHP. Scan rate: (a) 10³, (b) 10⁵, (c) 10⁷, (d) 10⁹, (e) 10¹¹ and (f) 10¹³ Vs⁻¹. These profiles are determined under conditions featuring those of the reduction of anthracene in acetonitrile, 0.1 M NBu4BF4 at 20°C. (See reference 21).

equations of pure diffusion cannot apply and a general second Fick's law including migration must be used.²¹ Figure 4 presents the results of such a treatment in terms of the normalized concentration profiles for A and B in the diffuse layer, for different scan rates. It is seen that at moderate scan rates ($v < 10^5 Vs^{-1}$), the concentrations of A and B at the end of the diffuse layer are almost identical to what is considered in classical theories (viz. [A] ≈ 0 and [B] $\approx C^{0}$, where C⁰ is the bulk concentration of A). However above 105 Vs-1 severe discrepancies appear, with respect to classical theories, owing to an increasing coupling between the two layers when scan rate increases. These distortions of the concentration profiles result in severe modifications of the voltammograms with respect to the predictions of classical theories. This is illustrated by the voltammograms in Figure 5a. It is seen from this Figure that the forward peak is less affected than the reverse one. This is easily understood since in the example of Figure 5a, A is a neutral molecule, thus its concentration

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Figure 5. Distortions of a Nernstian voltammogram ($z_a=0$, n=1) as a function of the scan rate (a), the supporting electrolyte concentration C_s (b) and potential of zero charge. (a): v = 10^5 , 10^6 and $10^7 Vs^{-1}$; $C_s = 0.1 M$; $F(E_{pzc}-E^0)/RT = 10$. (b): $C_{s.} =$ 0.5, 0.1 and 0.05 M; $v = 10^6 Vs^{-1}$; $F(E_{pzc}-E^0)/RT = -10$. (c) $F(E_{pzc}-E^0)/RT = 10$, 30 and 50; $v = 10^5 Vs^{-1}$; $C_s = 0.1 M$. Other conditions feature anthracene in acetonitrile. In each set the less distorted voltammogram corresponds to classical theories (i.e. to $v \longrightarrow 0$; $C_s \longrightarrow \infty$; $F(E_{pzc}-E^0)/RT \longrightarrow 0$. For each series, distortion increases following the order of variation of each parameter given above. $V = -F(E-E^0)/RT$.

profile is less affected than that of B which is an anionic species. Since these deviations are related to the effect of the electrical field in the diffuse layer, any experimental parameter which affects the diffuse layer results in a distortion of the voltammogram for scan rates above 10⁵ Vs⁻¹, as illustrated in Figures 5b,c.

The results in Figure 5 were determined with parameters featuring the reduction of anthracene in acetonitrile, except for the rate constant of heterogeneous electron transfer which was supposed infinite (*vide supra*). Therefore they demonstrate that classical theories cannot be used for the extraction of kinetic information from voltammograms recorded at scan rates exceeding a few hundred kilovolts *per* second.

This introduces an additional intrinsic limit to be considered in Figure 2c. Obviously more sophisticated theories (as the one²¹ whose results are presented here) may be used so that data obtained beyond this limit can be used. However this will be done at the expenses of severe difficulties in the data treatment and will require a correct description of the diffuse layer in organic conditions. Moreover, the ensuing kinetics will be difficult to rationalize owing to the fact that they occur in a region where an intense and variable electrical field operates. One may even question the true significance of a constant rate constant under such conditions; indeed, a description in terms of local microscopic rate constants varying as a function of the field strength, *i.e.* of the distance from the electrode, seems more appropriate than classical macroscopic rate constants.

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References.

- (a) C. Amatore, in Organic Electrochemistry, H. Lund and M. Baaizer, Eds., M. Dekker, New York, 1991. 3rd edition, chap. 2, pp.11-119. (b) C.P. Andrieux, J.M. Savéant, in Investigations of Rates and Mechanisms, C. Bernasconi, Ed., Wiley, New York, 1986. Vol.6, 4/E, Part 2, pp.305-390. (c) A.J. Bard, L.R. Faulkner, Electrochemical Methods, Wiley, New York, 1980.
- 2. M. Smoluchovski, Phys. Z., 1916, 17, 557; ibid. 585.
- 3. J.M. Savéant, D. Tessier, J. Electroanal. Chem., 1977, 77, 225.
- For a documented review on ultramicroelectrodes, see: R.M. Wightman, D.O. Wipf, in *Electroanalytical Chemistry*, A.J. Bard, Ed., Dekker, New York, 1989. Vol.15, pp.267-353.
- For reviews, see (a) R.M. Wightman, D.O. Wipf, Acc. Chem. Res., 1990, 23, 64. (b) C.P. Andrieux, P. Hapiot, J.M. Savéant, Chem. Rev., 1990, 90, 723.
- 6. J.O. Howell, W.G. Kuhr, R.E. Ensman, R.M. Wightman, J. Electroanal. Chem., 1986, 209, 77.
- 7. C. Amatore, A. Jutand, F. Pflüger, J. Electroanal. Chem., 1987, 218, 361.
- 8. C. Amatore, A. Jutand, F. Pflüger, C. Jallabert, H. Strzelecka,

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- M. Weber, Tetrahedron Lett., 1989, 30, 1383.
- 9. H. Kawata, Y. Suzuki, F. Niizuma, Tetrahedron Lett., 1986, 26, 4489.
- (a) K. Aoki, K. Akimoto, K. Tokuda, H. Matsuda, J. Osteryoung, J. Electroanal. Chem., 1984, 171, 219. (b) A.C. Michael, R.M. Wightman, C.A. Amatore, J. Electroanal. Chem., 1989, 267, 33.
- 11. D.O. Wipf, E.W. Kristensen, M.R. Deakin, R.M. Wightman, *Anal. Chem.*, 1988, *60*, 306.
- 12. C. Amatore, C. Lefrou, F. Pflüger, J. Electroanal. Chem., 1989, 270, 43.
- 13. C. Amatore, C. Lefrou, to be submitted to J. Electroanal. Chem.
- 14. J.M. Masnovi, S. Sankararaman, J.K. Kochi, J. Am. Chem. Soc., 1989, 111, 2263.
- 15. C.P. Andrieux, D. Garreau, P. Hapiot, J.M. Savéant, J. Electroanal. Chem., 1988, 248, 447.
- 16. C.J. Schlesener, C. Amatore, J.K. Kochi, *J. Phys. Chem.*, 1986, 90, 3747.
- 17. D. Garreau, P. Hapiot, J.M. Savéant, J. Electroanal. Chem., 1990, 289, 73.
- 18. See e.g. theoretical results presented in references 1b,c.
- 19. See e.g. P. Delahay, in Double Layer and Electrode Kinetics, Interscience, New York, 1965. pp.153-167, p.199.
- 20. D. Garreau, P. Hapiot, J.M. Savéant, J. Electroanal. Chem., 1989, 272, 1.
- C. Amatore, C. Lefrou, J. Electroanal. Chem., 1990, 296, 335.
 Reference 19, pp.33-52.

TWO CENTURIES OF BIOELECTROCHEMISTRY: SINCE LUIGI GALVANI UP TO NOW.*

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As the very father of Bioelectrochemistry Luigi Galvani must be considered. He was physician professor of anatomy at the Archiginnasio (ancient name of the University of Bologna). His first publication with the latin title "De Viribus Electricitatis in Motu Musculari Commentarius" (Note on the influence of Electricity on Muscular Motion) appeared in 1791, while the experiments were carried out 5 years before in 1786 observing the muscle contraction in the legs of a dead frog pending on the banister of the balcon when touching its nerves with a pair of scissors during a storm.

This discovery was followed by a long polemics with the physicist Alessandro-Volta, and by a tentative, more correct interpretation by Johan Wilhelm Ritter.

After this somewhat dramatic start a period of silence followed, during which few scientists were concerned with (really) bioelectrochemical research. Worthwhile to be mentioned are Leonor Michaelis (born 1875; physician, who investigated redox reaction involving ionic species occurring in living bodies); David Keilin (born 1887, chemist, who investigated redox processes in respiratory chain); René Bernard Wurmser (born 1890, chemist, who introduced potentiometric technique in biological research); and more recently two Nobel Prices: Albert Szent Giorgy (born 1893, who introduced semiconductor theory): and Ilia Prigogine (born 1917, who developed the treatment of biological phenomena using then thermodynamics of non reversible processes).

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