CHAPTER 9

Monolayer Redox Processes

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9.1 INTRODUCTION

In the last two chapters, the phase formation and growth processes have been studied where one of the redox species remains in solution and the solid phase is formed during charge transfer. In another class of reactions, both the oxidized as well as the reduced species are confined to the solid electrode surface and the electrochemistry is mainly confined to the surface changes. These processes may be termed as surface redox processes. This can further be classified to monolayer (this chapter) and thin layer (Chapter 10) processes.

Organic compounds are found to be adsorbed on electrode surfaces when their electrochemical behaviours are investigated in aqueous solutions. These adsorbed species give rise to the so-called adsorption currents [1]. Although the quantitative features of such adsorption currents have been well established in polarographic literature [2, 3] for several decades now, such adsorption processes were considered to be a nuisance by most voltammetric investigators. However, a major revolution in the outlook emerged after it was established that such adsorbed monolayer redox species can catalyze a number of other electrochemical reactions [4]. Following this a great deal of work on such surface redox processes of monolayer as well as thin layer types is being carried out. Comprehensive reviews on such redox film electrodes and their electrocatalytic behaviour are now available [5–8]. This chapter, however, shall confine itself to the investigation of monolayer surface redox processes. Redox catalysis by such surfaces is treated in Chapter 13. Thin layer redox behaviour and redox-catalysis are treated in Chapters 10 and 14 respectively.

9.2 THE MODEL

Monolayer redox processes as a group is one of the simplest ones to treat at the phenomenological level. These processes are well described by charge transfer, adsorption effects and chemical reactions. Since the total charge transfer involved is rather small at the monolayer level, mass transfer effects need not be considered at all although methods are available to handle this situation [9]. All the three phenomena mentioned above are very similar to the concepts introduced in earlier chapters. However, there are some

subtle differentiating features which need emphasis. These concepts are outlined here.

9.2.1 SURFACE CHARGE TRANSFER

As discussed earlier in Chapter 7, the monolayer formation process may be represented as

$$M + Ox + ne \rightleftharpoons M - R \qquad 9.1$$

The surface redox process to be treated here is quite similar in form. However, both the oxidized and the reduced species are now attached to the electrode surface.

$$M - Ox + ne \rightleftharpoons M - R \qquad 9.2$$

The rate expression for surface redox process is also quite similar to the rate expression of monolayer formation process discussed in Section 7.2.

$$\frac{d\tau_R}{dt} = -\frac{d\tau_{ox}}{dt}$$

$$= k_s^o[\tau_{ox} \cdot \exp\{-\alpha nf\,(E-E_s^o)\} - \tau_R \exp\{(1-\alpha)nf(E-E_s^o)\}] \qquad 9.3$$

This expression also is based on Butler-Volmer type of relation used in monolayer formation process. However, three important differences of such surface redox processes should be noted.

In monolayer formation process, only one adsorbed species is involved and hence only one surface concentration term τ or θ which is equal to τ/τ_m will appear in the rate expression. In a surface redox process, there are two surface concentration terms M_{ox} and M_R. The total concentration of surface redox species $\tau_{ox} + \tau_R = \tau_T$ need not always correspond to the maximum concentration τ_m. However, since this assumption is usually made, one may also consciously adopt this assumption. The number of metallic sites occupied by the oxidized and reduced species may be different. In most cases this site occupancy for Ox and R is assumed to be the same. This second assumption is in fact more justified than the previous one since addition or removal of electrons alone do not change molecular size of Ox or R substantially.

Dimensional analysis of equation 9.3 easily suggests that k_s^o has

a dimension of sec^{-1}. This is in fact a simpler situation when compared with monolayer formation process where the rate constants of forward and reverse reactions have different dimensions.

The standard electrode potential of surface redox reaction E_s^o in equation 9.3 also requires some special discussion. Will E_s^o be equal to E^o, the standard electrode reaction of the same Ox/R couple in solution? The answer to this question depends on the standard free energy of adsorption of the reactants and products.

$$M + Ox \underset{\longleftarrow}{\overset{\Delta G_{ox}^o}{\longrightarrow}} M - Ox \qquad 9.4$$

$$M + R \underset{\longleftarrow}{\overset{\Delta G_R^o}{\longrightarrow}} M - R \qquad 9.5$$

E^o, E_s^o, ΔG_{Ox}^o and ΔG_R^o are related by the following expression

$$-nFE_s^o = -nFE^o + \Delta G_R^o - \Delta G_{ox}^o \qquad 9.6$$

Since $\Delta G^o = -\mathbf{R}T \ln K_p$, one gets

$$nFE_s^o = nFE^o - \mathbf{R}T \ln \frac{K_{ox}}{K_R} \qquad 9.7$$

$$E_s^o = E^o - \frac{\mathbf{R}T}{nF} \ln \frac{K_{ox}}{K_R} \qquad 9.8$$

In the literature, the equilibrium constants are commonly referred to as b_{ox}, b_R or β_{ox}, β_R [9]. However, since the adsorption processes 9.4 and 9.5 are also chemical equilibrium processes, it is worthwhile following a uniform symbol K for this process.

Now if the reduced species is more strongly adsorbed when compared with the oxidized species ($K_R \gg K_{ox}$) E_s^o would be much more positive than E_a^o and *vice versa*. Such considerations apply to monolayer formation process as well. The product adsorption ($K_R \gg K_{ox}$) leads to a prewave and the reactant adsorption ($K_{ox} \gg K_R$) leads to a postwave according to equation 9.8. In surface redox processes, however, K_{ox} and K_R are of equal magnitude. In most of monolayer redox films E_s^o was found to be equal to E^o of the redox couple as is pointed out later. In the voltammetric simulations, one assumes that E_s^o is independent of electrode potential. This means that K_{ox}/K_R is independent of potential according to equation 9.8. Experiments also substantiate this viewpoint.

Other terms in equation 9.3 have their usual meaning. α is the transfer coefficient and $f = F/RT$. With the assumption that

$\tau_{ox} + \tau_R = \tau_m$ one gets $\theta_{ox} + \theta_R = 1$. and so $\theta_R = 1 - \theta_o$. With this assumption equation 9.3 may be rewritten in a simplified form

$$\frac{-d\theta_{ox}}{dt} = k_s^o \; [\theta_{ox}. \exp \{- \alpha nf (E - E_s^o \} - (1 - \theta_{ox}) \exp \{(1-\alpha) nf (E - E_s^o)\}] \quad 9.9$$

It may be noticed that in this form, the mathematical expression is exactly similar to the one used for Langmuir adsorption case of monolayer formation process (Section 7.2). The current is also given by an equation similar to the one employed earlier.

$$i = - nFA \; \tau_m. \frac{d\theta_{ox}}{dt} \quad 9.10$$

Because of this similarity in form, as observed later most of the expressions derived for monolayer formation can be used for monolayer surface redox processes as well (Section 9.3.1).

9.2.2 LATERAL INTERACTIONS

In the monolayer formation processes, the effect of lateral interaction was also investigated between adsorbed species and the resultant Frumkin isotherm. However, in these processes only one type of adsorbed species is involved and hence only one type of lateral interaction term g. A negative g value corresponds to attractive interaction (Section 7.2).

In the surface redox process, there are two types of adsorbed species $M - Ox$ and $M - R$. Hence one has to consider three components of lateral interactions even under reversible charge transfer conditions; the interactions between Ox and Ox, R and R and the cross interactions between Ox and R. When charge transfer kinetics is considered, two more interactions between Ox and activated complex as well as R and activated complex must also be considered. The mathematics for handling all these interactions should certainly be more involved and probably no analytical method for evaluating all these parameters from voltammetric experiments would be developed in the near future.

Comprehensive discussions on the interaction parameters and their relationship with the overall charge transfer rate are available [9, 10]. In a simple fashion, it may be stated that both the forward and reverse reaction 9.2 would be affected by θ_{ox} and θ_R factors.

Hence at least four new parameters should be introduced into equation 9.9 which are valid for charge transfer in the absence of lateral interaction. Hence the rate expression for charge transfer with lateral interactions may be written as

$$\frac{-d\theta_{ox}}{dt} = k_s^o [\theta_{ox} \exp \{-\alpha nf(E - E_s^o) + (2\beta\theta_{ox} + 2\nu\theta_R)\} - \theta_R \exp \{(1-\alpha) nf(E - E_s^o) + (2\lambda\theta_R + 2\mu\theta_{ox})\}] \quad 9.11$$

In the presence of lateral interactions, in addition to usual parameters, the charge transfer rate is also affected by β, ν, λ and μ. With such a large number of parameters to be evaluated, numerical solutions are the only possibility under most situations. It has, however, been found that the general shape of voltammetric response depends on two new parameters derived from them.

$$\nu G = \lambda - \nu - \mu + \beta \quad 9.12$$

$$\delta = \lambda - \nu + \mu - \beta \quad 9.13$$

The overall current response in the presence of lateral interaction is again obtained using equation 9.10.

9.2.3 SURFACE HETEROGENEITY

The charge transfer rate expressions presented above apply only to the situations in which the electrode surface free energy is uniform throughout and remains constant. In most solid electrodes, this condition will not hold. The surface would show heterogeneity effects. It is generally assumed that the surface free energy uniformly changes with the change in surface coverage. The charge transfer rate expression would again be similar to the rate expressions developed for monolayer formation (Section 7.2). The lateral interaction term g will now refer to the coefficient of surface free energy variation. Secondly, g will only take a positive value as the surface free energy cannot increase with surface coverage. In a heterogeneous surface the adsorption sites whose surface free energy is high will always be occupied first.

In most experimental situations, the lateral interaction effects and surface heterogeneity effects would be simultaneously operative. It is seldom possible to isolate both these effects. Interestingly, an

attractive interaction between adsorbed species and decreasing surface free energy effects would counteract each other. It is widely believed that this mutual cancelling effect is responsible for the observation of adsorption processes obeying simple (Langmuir) adsorption isotherm in most occasions.

9.2.4 CHEMICAL REACTIONS

In Section 9.2 so far, only one phenomenon was discussed: the surface charge transfer, although some typical modifications were considered. In surface redox process, only one more phenomenon should be considered at the monolayer level; the chemical reactions associated with charge transfer.

The chemical reaction may be very fast such as acid-base reactions at the electrode surface.

$$M - O_x + H^+ = M - O_xH^+ \qquad 9.14$$

These reactions are described by their equilibrium constants such as K_a, K_b, and stability constants of complexes. The methods for handling these chemical equilibrium properties have been comprehensively discussed earlier (Section 3.2). The same methods apply here as well. However, the equilibrium parameters of surface chemical reactions need not be the same as those of solution phase ones. Substantial evidence exists, for example, to show that the acid-dissociation constant (pK_a) in solution is different from the acid dissociation constant of the same acid adsorbed on the electrode surface ($pK_{\hat{a}}$) [11]. However at the modelling level, no changes are involved.

The chemical reactions may be much slower and the kinetics of the reaction may also influence charge transfer. A slow chemical reaction 9.15 may in fact follow reaction 9.2.

$$M - R \xrightarrow{k_c} M - Z \qquad 9.15$$

The methods for handling such slow chemical reactions also follow the methods described for solution phase reactions earlier (Section 5.2). Again, one must remember that the rate of a surface chemical reaction may be different from that of the same reaction in solution. Some examples are considered later.

9.3 THE METHOD

9.3.1 SURFACE CHARGE TRANSFER

Surface charge transfer without lateral interactions is one of the simplest cases for voltammetric investigations. By substituting $E = E_i + vt$ in equation 9.9 and substituting it in equation 9.10, straightaway the current-potential response may be obtained [12]. Since these two equations are very similar to the ones used in monolayer formation processes, the current-potential responses also would be identical to the figures presented in Section 7.3.1. In fact, one can straightaway use Table 7.1 to evaluate the equilibrium and rate parameters. However, in surface redox processes, E_a^o should be read as E_s^o and k_a^o should be read as k_s^o. In spite of such a close relationship, the voltammetric responses for surface redox processes have been separately and independently developed in several papers [3, 12–16].

The theoretically simulated voltammetric response (the points) and the corresponding experimental voltammogram (the line) of adsorbed benzo-c-cinoline on Hg electrode are presented in Fig 9. 1.a. The voltammogram is very symmetric in the cathodic as well as anodic sweep. The E_{pc} is equal to E_{pa}. The half peak width is $90.6/n$ mV. All the diagnostic criteria presented in Table 7.1 are found to be obeyed. The exact fit between the theoretical and experimental voltammograms are noteworthy.

The voltammetric behaviour of trans 4-4′ dipyridyl 1-2 ethylene is a typical example of irreversible surface redox process [3], as presented in Fig. 9.1.b. The rising portion of the voltammogram and the falling portion of the voltammogram are not symmetric with each other. The peak potential now shifts with sweep rate. The peak current as well as half peak width expressions are also different (Table 7.1). The perfect coincidence between experimental and simulated voltammograms is again noticed.

Although equations in Table 7.1 can be used to evaluate k_s^o an easier and more straight forward method would be to use the $\Delta E_p = E_{p,a} - E_{ps,c}$ value as a measure of the rate constant [16]. The ΔE_p value is only a function of η, α and Λ_s defined by equation 9.16.

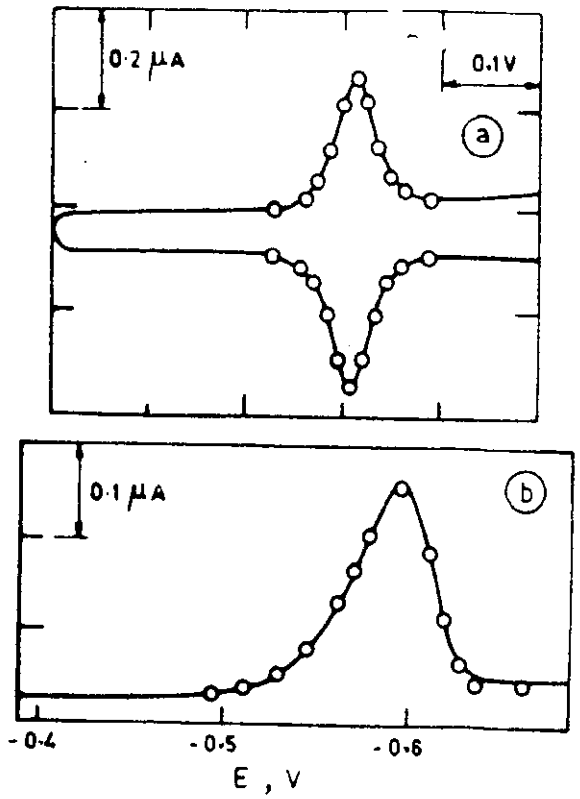

Fig. 9.1 Experimental (lines) and simulated (points) voltammograms of surface redox processes on Hg electrode. (a) reversible redox behaviour of benzo-c-cinnoline in alkaline water-ethanol mixture with pH = 11.0 (b) irreversible reduction of trans 4-4′ dipyridyl-1-2 ethylene in 0.05 M H_2SO_4.
[From E Laviron, J Electroanal Chem 52 (1974) 355]

$$\Lambda_s = \frac{k_s^o}{nfv} \qquad 9.16$$

If n and αn values are obtained using Table 7.1, the value of Λ_s and hence k_s^o can be obtained using Fig. 9.2. In most of the single-step surface processes, α value is likely to be around 0.5. For this specific case, one may also use Table 9.1 for obtaining Λ_s^{-1} value from experimentally observed $n\Delta E_p$ values. From Λ_s value calculation of k_s using equation 9.16 is quite straightforward [16].

One should however remember that ΔE_p as well as E_p shifts can be caused by iR drop in the solution [9]. Proper compensation efforts should hence be made before evaluating the rate parameters (Chapter 2).

Surface redox processes may also involve multistep electron transfer. Consider a multistep process represented by equation 9.17.

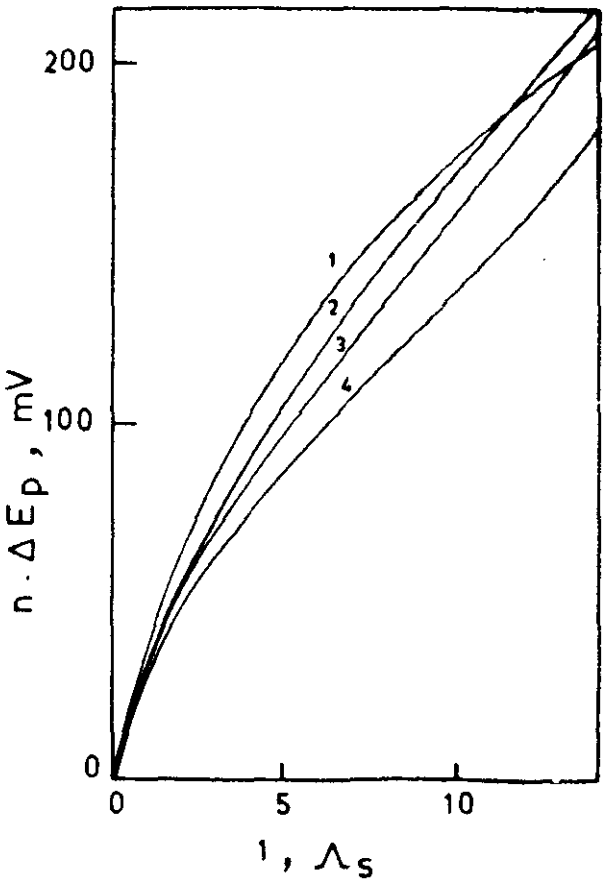

Fig. 9.2 Variation of ΔE_p value with $1/\Lambda_s$ value for surface charge transfer without lateral interactions. (1) $\alpha = 0.5$., (2) $\alpha = 0.8$, (3) $\alpha = 0.85$, and (4) $\alpha = 0.9$.
[From E Laviron, J Elecrtoanal Chem 101(1979) 19].

$$Ox \underset{}{\overset{+e}{\rightleftharpoons}} P \overset{+e}{\rightleftharpoons} R \qquad 9.17$$

The voltammetric response of this system under reversible charge transfer conditions will depend on the following disproportionation equilibria

$$2P \rightleftharpoons Ox + R \qquad 9.18$$

whose disproportionation rate constant would be given by

$$K_D = \frac{\tau_P^2}{\tau_{ox} \cdot \tau_R} \qquad 9.19$$

The voltammetric response of this system as a function of various

Table 9.1

Relation between peak separation ΔE_p and rate parameter Λ_s for single step surface redox process when $\alpha = 0.5$

$n.\Delta E_p$ (mV)	Λ_s^{-1}	$n.\Delta E_p$ (mV)	Λ_s^{-1}
18.8	0.5	130	6.0
27	0.75	142.4	7.0
34.8	1	153.8	8.0
48.8	1.5	164.0	9.0
61.2	2.0	173.4	10.0
72.2	2.5	182.0	11.0
82.4	3.0	190.0	12.0
91.8	3.5	197.6	13
100.6	4.0	204.6	14
116.2	5.0		

K_D values are presented in Fig. 9.3. When K_D value is very small, the intermediate is unstable, and hence it is reduced at the formation potential itself resulting in a single voltammetric peak. As K_D value increases, the adsorption of P leads to its formation at much earlier potential (product adsorption-positive shift of first peak). Since it is stable as an adsorbed entity, its further reduction to R takes place only at much more negative potentials [17].

9.3.2 LATERAL INTERACTIONS AND SURFACE HETEROGENEITY

The correct voltammetric response in the presence of lateral interactions is correctly described by equations 9.10 and 9.11. However,

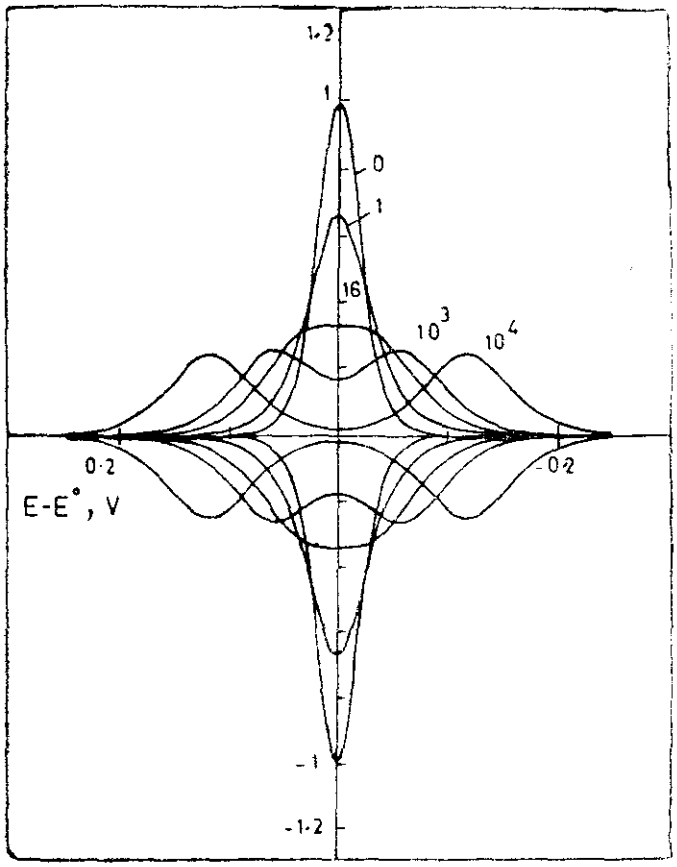

Fig. 9.3. Cyclic voltammograms for a two-step reversible charge transfer process. The value of $K = \tau_p^2/\tau_{ox}.\tau_R$ is shown on each curve. [From V Plichon and E Laviron, J Electroanal Chem 71 (1976) 143]

since a large number of parameters namely k_s^o, α, β, γ, λ and τ control the overall voltammetric response, it is quite difficult to obtain simple analytical expressions for ΔE_p, i_p etc. which can be used to evaluate these parameters. However, by selecting appropriate values for the parameters mentioned above, one can obtain a variety of voltammetric responses [18-21]. For example, Fig. 9.4 shows a voltammetric response when the reduction process is associated with the overall attractive interaction (half peak width less than $90/n$ mV) whereas the oxidation process is associated with the overall repulsive interaction (half peak width greater than $90/n$ mV). Voltammetric responses for different νG and S values represented by equations 9.12 and 9.13 may be found in the literature [21]. In a recent work [22] an attempt has been made to narrow down the number of interaction parameters to two experimentally measurable units.

However, more work is needed for a comprehensive understanding of the different types of lateral interactions involved.

In this context, it is still useful to consider the sum total result of all the lateral interactions using just one lateral reaction term g introduced in Section 7.3.1. The mathematical model then becomes exactly identical to the Frumkin isotherm condition treated in that section. Tables 7.2 and 7.3 can then be used to evaluate all the thermodynamic and kinetic parameters involved. Evaluation of g value under reversible charge transfer condition has been treated several times by several workers [23, 24]. Two aspects must however be remembered. First of all the experimental g value which is a direct measure of $\Delta E_{1/2}/n$ value is actually a net result of all types of interactions between $O_x - O_x$, $O_x - R$ and $R - R$ nearest neighbours. Secondly, the interaction parameter for a reduction process may be quite different from the interaction parameter for the oxidation process since the individual constituents of interaction parameters for both these processes can be different as noticed in Fig. 9.4. This is in contrast to the same g value for anodic as well as cathodic processes.

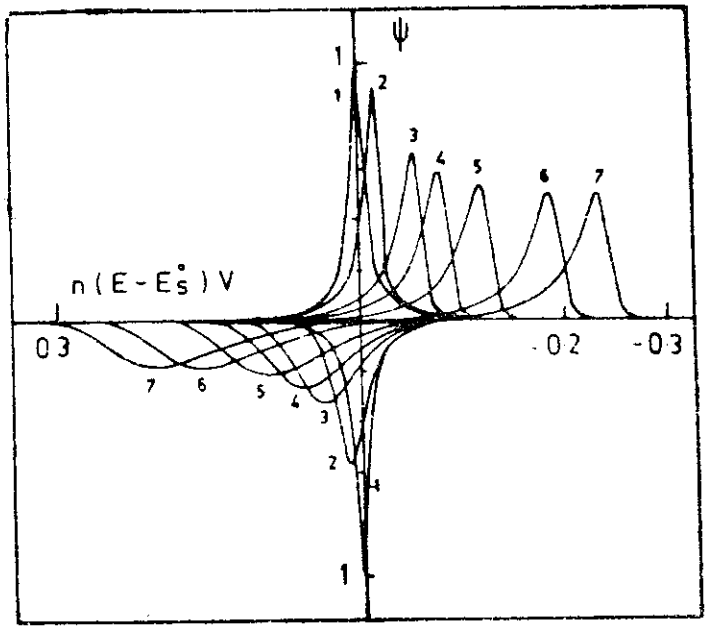

Fig. 9.4 Voltammetric response for surface charge transfer with lateral interactions. $\beta\theta_T = -0.75$; $\gamma\theta_T = 0.75$; $\lambda\theta_T = \tau\theta_T = 0$; $\alpha = 0.5$;Λ_s; (1) α (2) 3 (3) 0.5 (4) 0.25 (5) 0.1 (6) 0.025 (7) 0.01.

[From E Laviron and L Roullier, J Electroanal Chem 115 (1980) 65]

Tables 7.2 and 7.3 may also be used to evaluate the surface heterogeneity effects if it is assumed that lateral interactions are absent and surface free energy linearly decreases with surface coverage. The g value will always be positive in this case and the half peak width will always be greater than $90/n$ mV.

Another explanation is also offered for $\Delta E_{1/2}$ values greater than $90/n$ mV. It is assumed that due to high concentrations and interactions of densely packed redox couples on the electrode surface the E_s^o value of the same redox couple may vary slightly for different fractions of redox couples [25]. In this model, the single voltammetric peak is assumed to be a superposition of different closely spaced peaks. Although this possibility cannot be ruled out, there is practically no way of establishing this type of assumption.

9.3.3 CHEMICAL REACTIONS

In the surface charge transfer one can generate radicals, radical ions and unstable complexes that can undergo further chemical reactions. The methods for handling such reactions are just the same as developed for the solution phase reactions described in Chapter 5. In the rate expressions such as equation 9.9 one can directly incorporate the change of concentration due to chemical reactions.

Consider the simple EC reaction scheme as an example.

$$M - Ox + ne \rightleftharpoons M - R \qquad 9.2$$

$$M - R \xrightarrow{k_c} M - Z \qquad 9.15$$

If the charge transfer is very fast, the voltammetric response will depend on k_c and the sweep rate or a dimensionless parameter relating the two.

$$\lambda_c = \frac{k_c}{nfv} \qquad 9.20$$

The voltammetric responses for different λ_c values are presented in Fig. 9.5. Just as in solution phase chemical kinetics (Section 5.3), if the chemical reaction is very fast (large λ_c), the voltammetric peak appears at more positive potential when compared with E_s^o. From such E_p shifts and i_p variations with λ_c, one can actively evaluate the rate parameters of such chemical reactions [26].

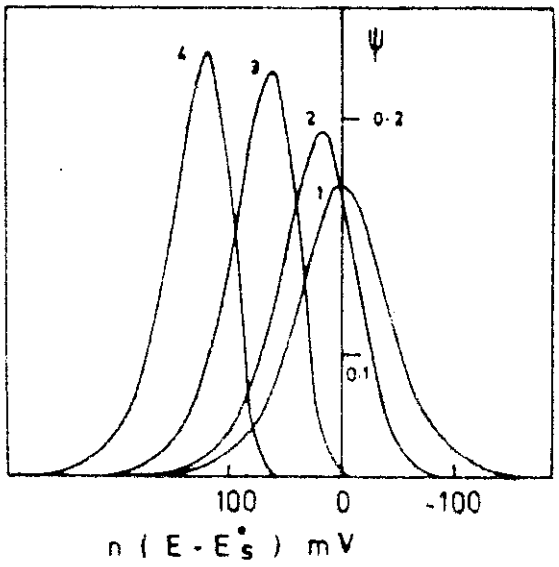

Fig. 9.5 Linear sweep voltammetric response for EC reaction mechanism as a function of chemical reaction rate parameter λ_c (1) 0, (2) 1, (3) 10 and (4) 100.
[From E Laviron, J Electroanal Chem 35 (1972) 333]

Similar voltammetric methods for analyzing second order *EC* reaction [27], dimerization reaction at the electrode surface [28], *ECE* reaction sequence [29] and redox catalysis [30] have been worked out. Apart from redox catalysis, these reaction schemes have not been widely used in voltammetric studies of surface processes. Hence, the original literature may be consulted if required. The surface redox catalysis is treated later in some detail (Chapter 13).

Organic electrode processes are often coupled with acid-base equilibria and both the acidic and basic form of the organic species may be electroactive as represented by the following reaction scheme. As represented here, the charge transfer rate constant k_s^o for the acidic and basic species may also be different.

$$\begin{array}{ccc} A & \overset{k^o_{s,2}}{\rightleftharpoons} & A^{\cdot-} \\ \Big\uparrow\Big\downarrow pK_{a,1} & & \Big\uparrow\Big\downarrow pK_{a,2} \\ AH^{+} & \overset{k^o_{s,1}}{\rightleftharpoons} & AH \end{array} \qquad 9.21$$

The apparent charge transfer rate constant measured for such system would naturally depend on the pH of the medium. The voltammetric response for such situations have been worked out [31]. This method has further been extended to $2e$, $2H^+$ scheme involving nine members [32]. As is seen later, this method has not found widespread usage.

9.4 THE PROCESS

9.4.1 MONOLAYER REDOX FILMS

As mentioned earlier (Section 9.1), for a very long time, monolayer redox films were not intentionally produced on electrode surfaces. Some organic compounds got adsorbed on electrode surfaces and gave rise to the adsorption prewaves or postwaves. However, from 1973 onwards an extensive collection of experimental work on the synthesis and characterization of monolayer redox films have emerged. These works have been comprehensively reviewed in the literature [5-9]. Hence we shall only outline the types of works that are being carried out in this field.

At least three different methods are now adopted for the synthesis of monolayer redox films on electrode surfaces. The classical method of irreversible adsorption of organic compounds on electrodes surfaces is still employed. The first chemically modified electrode [4] itself was formed by irreversible adsorption of alkenyl side chain on Pt elctrodes. A great variety of molecules were later attached to electrode surfaces by this method [33-35] on Pt, metal oxides as well as carbon electrodes.

In a second method the molecule containing the electroactive group is directly attached to the electrode surface using covalent bonding between the molecular species and the surface functional groups such as M—OH and MO groups on metal oxides and —C—OH, —C=O and —COOH groups on carbon electrodes. Silanes, cyanuryl chlorides. acid chlorides and a variety of functional groups on the molecular species were used for the covalent bonding [36, 37]. The synthetic aspects have been completely reviewed elsewhere [8].

A third method is to covalently attach a molecular species containing a ligand species which need not necessarily be electroactive.

— CN, $-NH_2$ or pyridyl group, for example, can thus be covalently linked. This electrode can now form stable surface redox complexes with a variety of inorganic ionic species [38, 39]. In this approach, the same surface modification reaction can be employed to generate different surface redox electrodes.

Using all the three methods mentioned above, a great variety of inorganic, organic and organometallic redox couples such as ferrocenes [40, 41], ruthenium complexes [42, 43], cobalt complexes [44], benzenediamines [45], naphthaquinones [46], viologens [47] and cytochrome-c species [48] have been attached to electrode surfaces and their redox behaviours have been investigated [5–8]. A complete monolayer film in most cases correspond to 1×10^{-10} Moles/cm^2 as measured by integrating the area under the voltammetric peak. The total charge in the cathodic as well as anodic sweep in cyclic voltammetric experiments were the same, suggesting that most of the redox couples are chemically reversible. The E_s^o values measured on such surface redox processes are also very close to the E^o values of the same redox couple in solution under identical experimental conditions [8]. More details on surface modified electrodes may be obtained from the literature [5–8].

Apart from the tailor-made redox electrodes mentioned above, there may be electrode surfaces with the inherent presence of redox couples. Carbon electrode surfaces, for example, contain reducible and oxidizable surface functional groups [49, 50]. The cyclic voltammograms of glassy carbon in NaOH medium presented in Fig. 9.6, for example, shows the presence of a number of redox couples on the surface [50]. There is as yet very little understanding of the nature of the surface functional groups and their catalytic effects. Metal oxide electrodes may also exhibit similar redox behaviour, but most of the metal-oxide surfaces may not be of monolayer type being discussed here.

9.4.2 LATERAL INTERACTIONS

In general, only those redox couples that show very fast charge transfer kinetics are employed in the preparation of surface redox films. Hence most of these redox films exhibit reversible charge transfer behaviour. The $E_{p,a}$ and $E_{p,c}$ for example are very close to each other on most occasions. However, since the surface cov-

erage on most occasions corresponds to a compact monolayer, the surface concentration is much higher than the concentration levels employed in the solution phase reactions. This gives rise to a high level of attractive or repulsive interactions. The half peak width is usually employed to estimate the overall interaction effect [23–25]. Table 7.3 for example can be used to directly measure the g parameter as discussed earlier (Section 9.3.2).

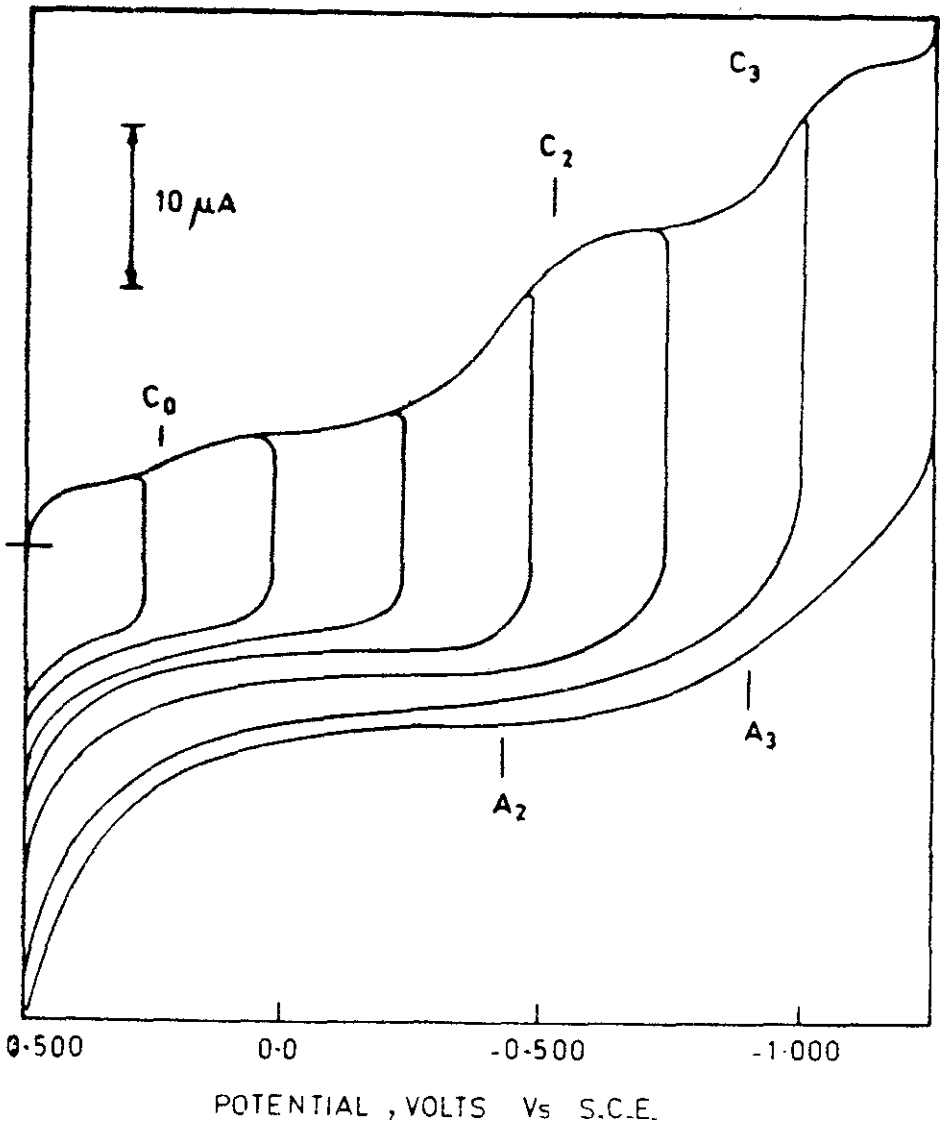

Fig. 9.6 Voltammetric behaviour of glassy carbon electrode in 1.0 M NaOH solution. Sweep rate 160 mV/sec.
[From M Noel and PN Anantharaman, Surface and Coatings Technol 28 (1986) 161]

A typical cyclic voltammogram showing lateral interaction effects is presented in Fig. 9.7.a. It may be noticed that the cathodic peak

is much sharper than the anodic peak due to different levels of contributions from β, r, λ and μ parameters in equation 9.11. The theoretically simulated voltammograms using equation 9.11 are presented in Fig. 9.7.b. The exact similarity between the two figures is an indication of accuracy levels achieved in the monolayer surface redox processes [21].

On Hg electrode where surface heterogeneity effects are absent, as in Fig. 9.7, it may be asserted with confidence that the voltammetric half peak width characteristics discussed above are due to lateral interaction effects. Most chemically modified electrodes are solid electrodes and hence in these cases there is no way of distinguishing between repulsive lateral interaction effect from surface heterogeneity effects.

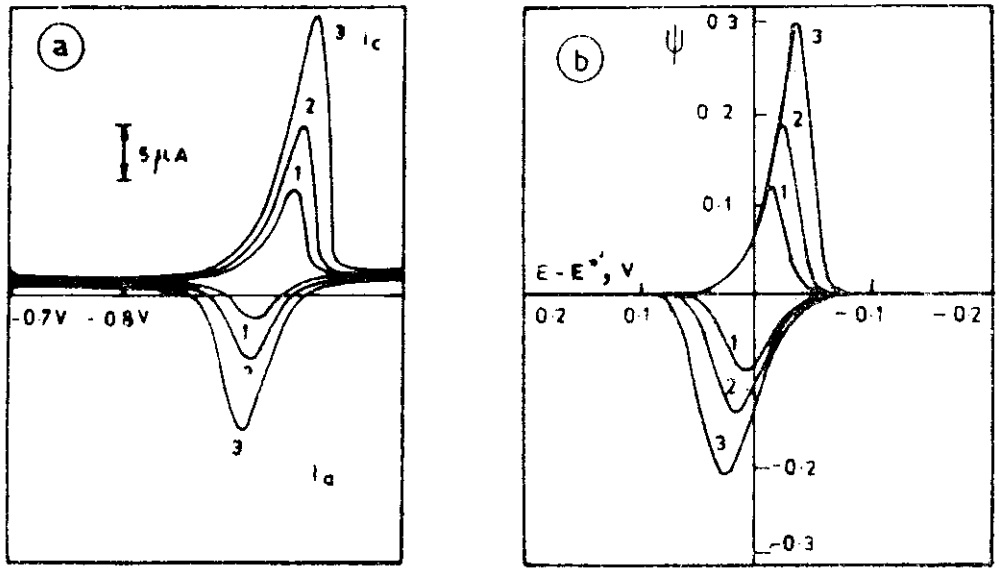

Fig. 9.7 (A) voltammograms of benzo-c-cinnoline in 0.1 M KNO_3 at 298K of pH = 12.8. Sweep rates in Volt. sec^{-1}. (1) 0.5, (2) 1 and (3) 2.

(B) Calculated voltammograms for the same conditions with $\eta = 2$; $\alpha = 0.5$; $\beta\theta_T = -1.95$; $\gamma\theta_T = -1.25$; $\lambda\theta_T = -1.4$; Λ_s (1) 16.2, (2) 8.1, (3) 4.05.

[From E Laviron and L Roullier, J Electroanal Chem 115 (1980) 65]

9.4.3 CHARGE TRANSFER KINETICS

As mentioned earlier (Section 9.3.1), for a reversible charge transfer the voltammogram must be symmetric on X axis and $\Delta E_p = E_{p,a} - E_{p,c}$ should be zero. In most monolayer surface redox pro-

cesses, however, a small drift ΔE_p value of 5–20 mV is found at slow sweep rates [51]. The cause for such a shift is not clear [8, 51]. However, such shifts are sweep-rate independent. Additional ΔE_p shifts that depend on sweep rates according to Fig. 9.2 are noticed at high sweep rates. They are certainly related to charge transfer kinetics.

The surface charge transfer kinetics itself is receiving some attention only in recent times [52, 53]. From simple comparison of frequency and free energy factors [53] it was predicted that k_s^o value should be about 10^6 times the value of k_h^o of the same reaction in solution. This assumption has been found to be correct in the case of some fast redox couples [52–54]. In all these cases the k_s^o

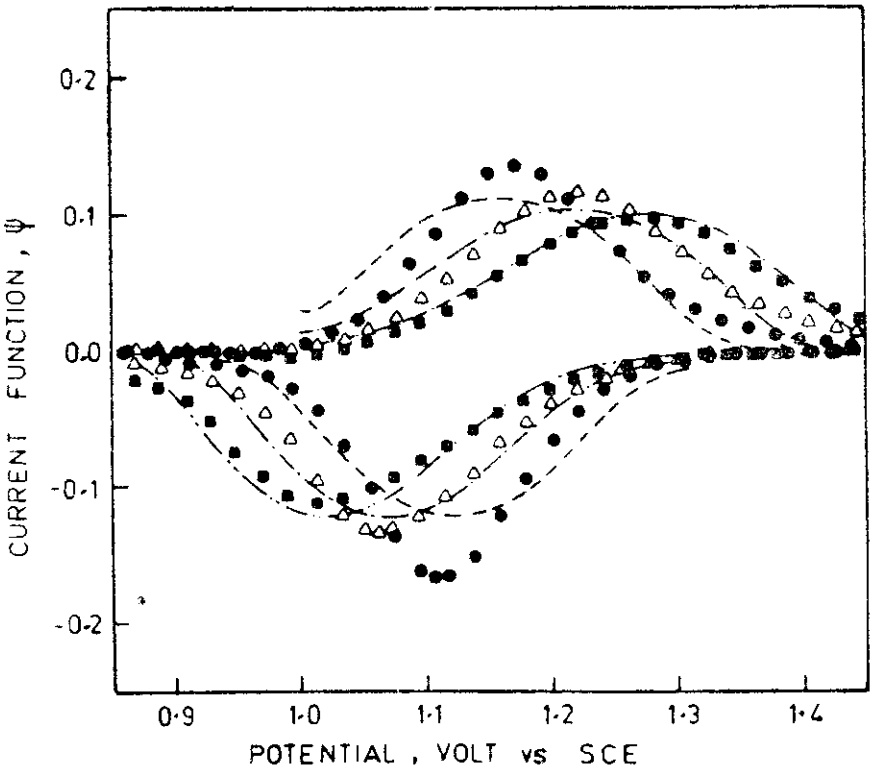

Fig. 9·8 Experimental (points) and simulated voltammetric response of Ru (II)/(III) polypyridine complex coated on SnO_2 electrodes. Sweep rates in Volt. sec^{-1}, $\alpha_c - 0.54$; $\alpha_a = 0.44$; $\lambda - \mu + \beta - \gamma = +2.15$; $\lambda - \mu - \beta + r = 0.05$; $k_s^o = 7.2$ sec^{-1}; Sweep rate in Volt. sec^{-1} (●) 10.28 (△) 50.86 (■) 143.6

[H Daifuku, K Aoki, K Tokuda and H Matsuda, J Electroanal Chem 183 (1985) 1]

value is found to be greater than 3×10^3 sec^{-1} which is the limit of the measurement technique employed. Some slower charge transfer rate constants have been reported [55]. This may be due to uncompensated solution resistance as this *IR* drop can also produce similar ΔE_p shifts at higher sweep rates [56].

But some recent investigations under controlled conditions with proper *IR* compensation does indicate [22] that k_s^o value around 100 sec^{-1} is not uncommon. The broad coincidence between experimental and theoretical CV curves (Fig. 9.8) lends strong support to this veiw. The difference in the activation entropy factors in heterogeneous and surface charge transfer processes must be responsible for the relative slowing down of surface electron transfer. Some recent investigations on comparatively slower electron transfer processes, indeed substantiate this view [56a–58].

9.4.4 CHEMICAL KINETICS

The models as well as the methods for studying chemical reactions associated with surface charge transfer have been developed very well as described in Section 9.3.3. However, these have not found much application. The only *EC* reaction investigated on electrode surface using voltammetric method seems to be benzidine rearrangement [59]. The dimerization followed by surface charge transfer of mercuro-organic compounds has also been investigated [60]. In both these cases, surface chemical reaction rate is found to be quite different from solution phase chemical reaction kinetics. This method thus offers a very good scope for investigating the surface effects of some simple chemical reactions.

9 5 ANALYTICAL APPLICATIONS AND SCOPE

Monolayer redox processes are certainly one of the simplest processes at the modelling level. But the concentrations and current levels involved are very low and the practice of synthesizing a reproducible surface and completely characterizing its redox behaviour still remains to be a challenging problem in electrochemistry. The greatest impetus for the continuous efforts in this direction of course is its probable application in electrocatalysis (Chapter 13). A number of redox couples can show different colours in the oxidized and reduced states. Such materials may be used in electrochromic

devices [61]. In electroanalysis, the electroactive materials may be covalently bonded or irreversibly adsorbed on the electrode surface from the solution to be analysed, and the voltammetric response may be evaluated in a separate pure electrolyte solution [62, 63]. Very low concentration levels up to 10^{-7} M samples have been estimated in this way using linear sweep as well as differential pulse voltammetry. Being a newly developing research area, one would certainly hope that more fundamental and applied research work will continue in this exciting field.

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