

THE MULTI-STEP CHARACTER OF ELECTRODE REACTIONS: EFFECTS OF SOLVATION, COMPLEXATION AND DOUBLE-LAYER INTERACTIONS.

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During the development of the voltammetric (relaxation) methods to study electrode kinetics, the charge transfer of many electrode reactions has been characterized in terms of the standard heterogeneous rate constant k_s and the charge transfer coefficient α . Numerous investigations have produced an overwhelming amount of data [1], from which the experienced electrochemists deduced their knowledge about the specifications of redox systems, being either notoriously slow ("irreversible") or fast ("reversible"), or of intermediate rate ("quasi-reversible"). Also it is well-known that the composition of the electrochemical system largely influences the kinetic parameters. Thus one can accelerate ("catalyse") or decelerate ("inhibit") a particular charge transfer process, e.g. through the choice of electrolyte, solvent, electrode material, surface structure, or by means of additives.

As the fundamental understanding of inhibition and catalysis is of much importance for applied electrochemistry, an impressive number of theoretical models describing charge transfer in relation to the system variables mentioned, is available to be tested by experimental results. However, in many studies dedicated to this aim, it is scarcely realized that the standard kinetic parameters k_s and α are less meaningful when the charge transfer process cannot be considered as just the simultaneous transfer of the n electrons involved in the overall reaction. Quite long ago, it

has been shown that α becomes potential-dependent if the electrons are transferred one-by-one in successive reaction steps [2,3]. Then it becomes preferable to characterize the overall reaction in terms of the potential dependent reduction rate constant $k_f(E)$ and to define an "operational transfer coefficient" α by [4,5].

$$\alpha = -\frac{nf}{RT} \frac{d \ln k_f}{dE} \quad (1)$$

In our laboratory we are able to measure $k_f(E)$ and α in a wide range of potentials by means of the powerful combination of two methods: high precision impedance voltammetry [6] and demodulation voltammetry [7]. During the last decade we collected increasing evidence that the charge transfer process of simple electrode reactions not only proceeds by successive single electron transfers, but also by "chemical reaction steps", occurring before, in between and after electron transfer. In other words, mechanisms can be established, encoded as CECEC..., CEE..., EEC..., etc. If the intermediates are unstable, the potential dependence of $k_f(E)$ is expressed by a series of exponentials of the form

$$\frac{1}{k_f(E)} = \frac{1}{k_{c,0}} + \frac{\exp(0.5fE)}{k_{s,1}} + \frac{\exp(fE)}{k_{c,1}} + \frac{\exp(1.5fE)}{k_{s,2}} + \dots \quad (2)$$

where $f = F/RT$ and E has to be referred to some reference potential (e.g. the standard potential E^0 of the overall reaction). Terms containing $k_{s,i}$ pertain to electron transfers and terms containing $k_{c,i}$ to chemical steps.

Eq. (2) shows that the relative importance of a step depends on the potential and on the relative magnitude of the individual "standard rate constant" $k_{s,i}$ or $k_{c,i}$. Also it is clear that the effect of a system variable will be the composite of its action on each individual term. Moreover, the

nature of this action can be morefold. For example, if the concentration of the inert electrolyte is varied, the result can be a change in the extent of complexation, but also a change in solvent activity, or a change of the double-layer structure.

In the present lecture results will be reported of model studies focussed on the understanding of the interactions involved in the individual steps of the mechanism of some electrode reactions. It will be discussed how the individual rate constants can be evaluated experimentally and how possible correlations with the several effects mentioned above can be investigated. A number of recently studied examples will be given, especially those where the rôle of water activity, complex formation and pH is evident. On the other hand it will be shown that studies of the type described, requiring measurements of $\ln k_f$ vs. E plots ("Tafel plots") under variation of a system parameter, are quite valuable to establish even better the type of mechanism that applies to a particular redox system in general.

References

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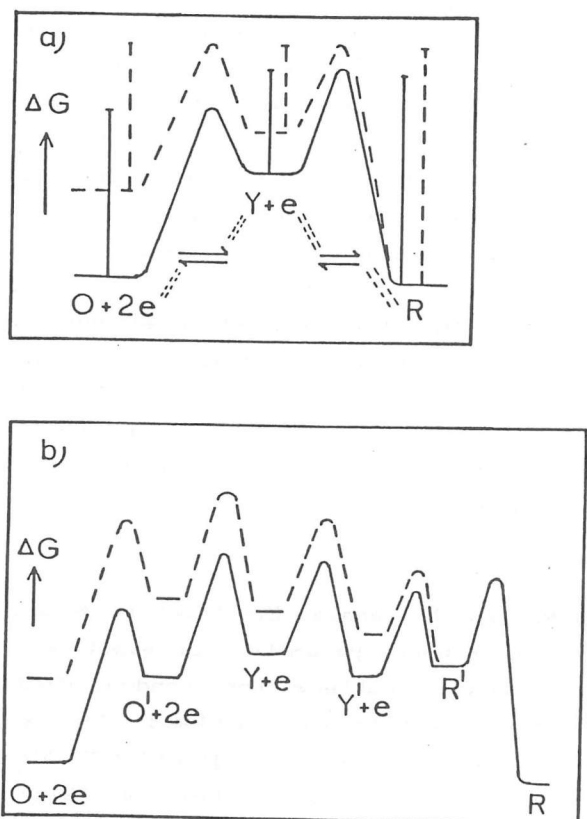


Fig. 1 Schematic representation of energy vs reaction coordinate for (a) an EE mechanism, (b) a CECEC mechanism, — at the standard potential E^0 , - - - - - at $E < E^0$.

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MEMBRANE ELECTRODES OF HERBICIDAL AND PHARMACEUTICAL INTEREST

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PVC-liquid membrane electrodes based on crown ethers will be described for diquat, paraquat and guanidinium. The crown ether systems for diquat and paraquat^{1,2} consist of dibenzo-30-crown-10 (DB30C10), bis-metaphenylene-32-crown-10 (BMP32C10), bis-metaphenylene-38-crown-12 (BMP38C12), bis-paraphenylene-34-crown-10 (BPP34C10), bis-paraphenylene-37-crown-11 (BPP37C11), and dinaphthalene-36-crown-10 (DN36C10). The data will be discussed in terms of quality of potentiometric response related to conformational phenomena of the crown ethers in their complexation with the two dications and with the related 4,4'-dipyridyl.

The crown ether system for guanidinium consists³ of dibenzo-27-crown-9. Here, as indeed with the diquat and paraquat electrodes, the optimization of solvent mediator in relation to general electrode properties and selectivity of response will be discussed.

Finally, electrodes for diquat, paraquat and 4,4'-dipyridinium based on charged or ionized complexing agents (hexafluorophosphate, anthraquinone-2-sulphonate, octylsulphate, picrate, dipicrylamine, diamine Green B, tetraphenylborate and terakis-4-chlorophenylborate) will be discussed in relation to the analogy between ion-pair extraction and ion-selective electrode function and selectivity.⁴ Some mention will be made of the charge transfer from the tetraphenylborate anion to the dications in relation to the associated electrode response.⁵

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