GLOBAL ANALYSIS OF KINETIC CURRENT IN DC POLAROGRAPHY

APPLICATION TO PYRIDINE-4-ALDEHYDE REDUCTION

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ABSTRACT

We have determined theoretical relations between limiting currents and kinetic and thermodynamic parameters for complex systems which require consideration of the fact that the different electrochemical species are influenced by more than one chemical equilibrium.

These expressions were checked with the dc polarographic behaviour of 4-pyridine-aldehyde (a compound involved in several interrelated hydration and protonation equilibria which make it quite adequate as an example for the study) in an aqueous medium.

In this case, prior knowledge of the equilibrium constants allows calculation of the rate constant for the chemical reactions involved in the electrode process.

INTRODUCTION

In earlier papers [1,2] diagnostic criteria were discussed for the characterization of various mechanisms by dc polarography. It was found that 4-pyridine-aldehyde (4-Py) conforms to a global mechanism in an acid medium influenced by dimerization of the intermediate.

This work is focused on the study of the complex variation of the limiting current (sum of that of the two waves observed) over the entire pH range. Such a variation arises from the relationship between the electrode process and the different acid–base and hydration equilibria, as well as from the rate constants of these processes, which take place prior to the first transfer in an aqueous medium. Scheme 1 describes the

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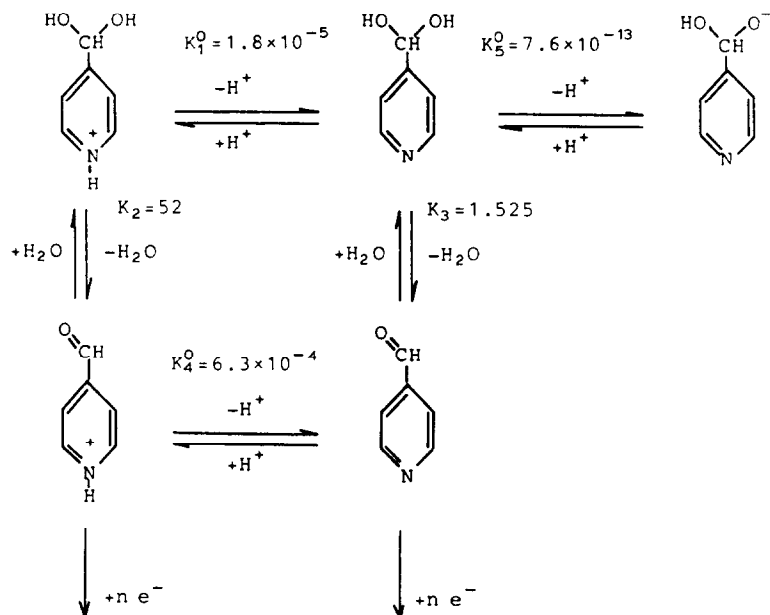
Scheme 1.

different species present in solution in a homogeneous medium, as well as the equilibrium constants for the processes involved [3,4].

Our treatment is based on a theoretical method proposed elsewhere [5] in which we will consider that the different species contributing to the mass transport are able to take part in more than one homogeneous chemical stage. In this manner, we will obtain complex functions relating kinetic and thermodynamic constants to the overall intensities of the process. The method does not allow, as a rule, the determination of the explicit influence of the different parameters, but requires the use of a curve-fitting procedure to adjust the experimental data. This procedure is simplified by a priori knowledge of the thermodynamic constants of the different equilibria occurring in solution.

Finally, this work compares the behaviour of 4-pyridine-aldehyde observed by our team with that of its three 1-methyl derivatives reported in the literature [4,6].

ANALYSIS OF THE KINETIC PROCESS

The reduction process of 4-Py (Scheme 1) can be treated as two simpler processes (see Appendix, Schemes 3 and 4). The equations corresponding to these schemes have been obtained in the Appendix (eqns. A22 and A45).

The use of these expressions is rather complex, though it can be simplified by making some considerations [5]. However, the peculiarities of our system make the application of any simplification inadvisable; in fact, $K_3 = 1.525$ [3] and thus neither k_3 nor k_{-3} may be neglected with respect to each other.
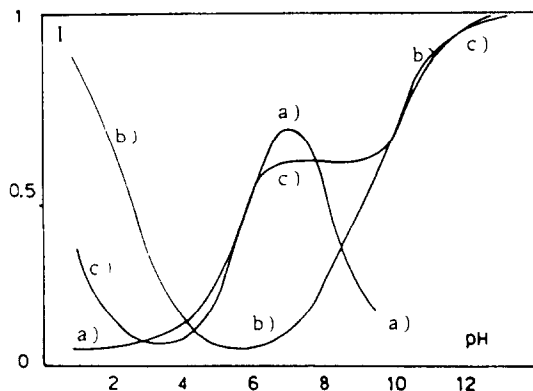
Fig. 1. Theoretical examples of the variation of I vs. pH according to eqn. (A22). (a) $K_1^{\circ} = 10^{-7}$, $k_1 = 1$ s^{-1}, $K_2 = 100$, $k_2 = [0.02 + 10^8(OH^-)]$ s^{-1}, $K_3 = 30$, $k_3 = [0.02 + 10^8(H^+)]$ s^{-1}. (b) $K_1^{\circ} = 10^{-8}$, $k_1 = 1$ s^{-1}, $K_2 = 100$, $k_2 = [0.02 + 10^3(H^+)]$ s^{-1}, $K_3 = 4.5$, $k_3 = [0.1 + 10^4(OH^-)]$ s^{-1}. (c) $K_1^{\circ} = 10^{-6}$, $k_1 = 1$, $K_2 = 100$, $k_2 = [0.02 + 10(H^+) + 10^8(OH^-)]$ s^{-1}, $K_3 = 1$, $k_3 = [0.05 + 10^3(OH^-)]$ s^{-1}.

In Fig. 1 some theoretical examples of the application of eqn. (A22) are illustrated. In the caption of the figure the different values of the rate and equilibrium constants used to obtain each curve are given. As can be seen, the assumption of acid–base catalysis in the hydration processes, as well as the specific values of all the constants involved in calculating each curve, may lead to the existence of current maxima or minima according to the pH.

This behaviour was also observed in the reduction of various α-substituted aldehydes [7] and tricarbonyl compounds such as alloxan [8].

Figure 2 shows some theoretical examples of the application of eqn. (A45), which corresponds to the reaction sequence sketched in Scheme 4. This scheme can be applied to the case in which species A_2 may undergo two competitive processes, one towards A_3 (through dehydration) and the other towards A_5 (via the dissociation of an H^+ ion), as well as to the situation in which species A_5 undergoes a two-fold reaction to yield the electroactive species A_3 [5]. In the example illustrated in Fig. 2, we have taken into account the possible competitive processes (dehydration and dissociation of an H^+ ion) which species A_2 may undergo.

Moreover, we took $K_3 = 1,525$ and $K_5^{\circ} = 10^{-12.12}$, which correspond to the equilibrium constants of the dehydration and protonation of pyridine-4-aldehyde [3,4]. In addition, we assumed that $K_5 = K_5^{\circ}(OH^-)/K_w$, $k_5 = k_5^{\circ}(OH^-) = 30(OH^-)$ s^{-1} and $k_3 = k_3^{\circ} + k_3^{OH}(OH^-) = [0.55 + k_3^{OH}(OH^-)]$ s^{-1}, where the k_3° and k_5° values chosen are the same as those found for 4-Py in the following section. Finally, k_3^{OH} was given the values 0 (a), 10^2 (b), 10^4 (c), 10^6 (d) (see Fig. 2).

For cases b, c and d, which involve basic catalysis, $k_3 > k_5$ at any pH value, whereas, on account of the values of K_3 and K_5°, $K_5 > K_3$ above pH 12.3. This fact
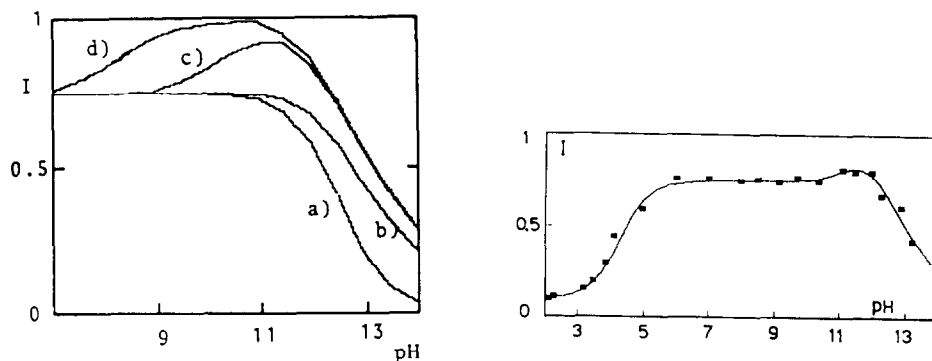
Fig. 2. Theoretical examples of the variation of I as a function of the pH according to eqn. (A45). $K_3 = 1.525$, $K_s^o = 10^{-12\,12}$, $k_3 = [0.55 + k_3^{OH}(OH^-)]$ s^{-1}, $k_5 = 30(OH^-)$ s^{-1}. With $k_3^{OH} = 0$ (a), 10^2 (b), 10^4 (c) and 10^6 (d).

Fig. 3. Variation of the limiting current ($I = i_k/I_D^o$) with the pH for 4-Py (squares). Under the working conditions, $i_D = 6.59$ μA. The fine line represents the application of eqn. (A22) between pH 2 and 7 and eqn. (A45) between pH 7 and 14. $K_1^o = 10^{-4.74}$, $K_2 = 52$, $K_3 = 1.525$, $K_s^o = 10^{-12\,12}$, $k_1 = 1$, $k_2 = 0.04$, $k_3 = [0.55 + 75(OH^-)]$ s^{-1} and $k_5 = 30(OH^-)$ s^{-1}.

(i.e. the dual influence, kinetic and thermodynamic, relating the current to the pH) accounts for the occurrence of maxima in the plot of I vs. pH.

EXPERIMENTAL

The materials and the method used herein have been described in detail elsewhere [1].

RESULTS AND DISCUSSION

Figure 3 shows the variation of the limiting current as a function of the pH (squares). The process is never fully governed by diffusion. An estimate of the diffusion current can be made from the i–t curves [1,2] since the slope of the plot of ln i vs. ln t is directly related to the ratio i_k/i_D.

The method employed was developed with the aid of the Koutecký equation [9], which was applied assuming the occurrence of a single kinetic step prior to the transfer. However, the t-dependence of the limiting current in eqns. (A2) and (A45) is similar, under steady-state conditions, to that of the Koutecký equation [9]. In fact, under steady-state conditions ($\lambda_i t \geqslant 3$) [5]

$$F(\lambda_i) \cong 1.349(\lambda_i t)^{1/2} \tag{1}$$

Hence, eqns. (A22) and (A45) can be rewritten as

$$I/(1 - I) = F(k_i, K_1)t^{1/2} \tag{2}$$

where $F(k_1, K_2)$ are the function analysed in eqns. (A22) and (A45). Thus,

$$(\partial \ln I/\partial \ln t) = (1 - I)/2 \tag{3}$$

or

$$(\partial \ln i_k/\partial \ln t) = \tfrac{1}{6} + \tfrac{1}{2}\left(1 - \frac{i_k}{i_D}\right) \tag{4}$$

Assuming that $\partial \ln i_D/\partial \ln t = 1/6$, eqn. (4) is identical to that obtained previously (see eqn. 14 in ref. 1) using the Koutecký equation for the kinetic current. The diffusion current thus calculated [1,2] was $i_D = 6.59$ μA. All the current values in Fig. 3 are referred to this value.
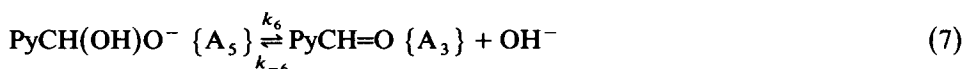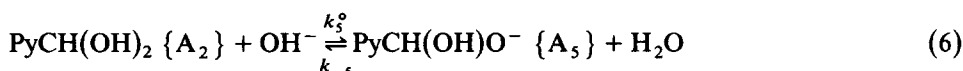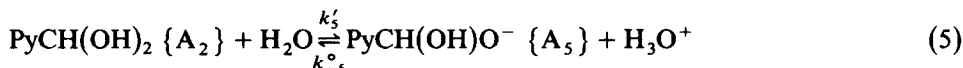
The plot of I vs. pH shows five distinct zones. In the first (below pH 2.5), the limiting current is constant and approximately equal to 0.09. In the second (pH 2.5–6), I changes with the pH in the pattern of a dissociation curve. In the third, I is again constant and approximately equal to 0.76. Between pH 10.5 and 12, the current increases slightly ($I \cong 0.82$), which results in an increase of about 0.4 μA in the limiting current. Finally, above pH 12, the current decreases to the value $I = 0.41$ at pH 13.3. However, the variation of I with the pH suggests that the current continues to decrease with increasing pH.

The increase in the current between pH 2.5 and 6 is due to the influence of the first pK of the hydrated form of 4-Py ($K^{\circ} = 10^{-4.74}$). Therefore, Scheme 3 and eqn. (A22) are adequate for the analysis of the current in this pH region.

In fact, the fine line in Fig. 3 illustrates the application of eqn. (A22) to the pH range 2–7. It was plotted taking $K_1^{\circ} = 10^{-4.75}$, $K_2 = 52$, $K_3 = 1.523$, $K_1 = K_1^{\circ}/(H^+)$ and choosing those k_1, k_2 and k_3 values which provide the best agreement between the experimental results and the predictions of eqn. (A22). The best fit is obtained when $k_2 = 0.04$ s^{-1} and $k_3 = 0.55$ s^{-1} are used. The I values obtained from eqn. (A22) are virtually independent of the particular k_1 chosen (provided that $k_1 < 10^3$). Below pH 2.5, the current is a function of k_2 and K_2 only — which allows the former to be determined — whereas above pH 6 it is a function of k_3 and K_3 — therefore allowing the determination of k_3. The virtual k_1-independence of I is a peculiar feature of the system considered rather than a general characteristic. This arises because I is much smaller below pH 2 than above pH 6. In addition, the species prevailing in solution above pH 6 is A_2, and both $k_{-1} = k_{-1}^{\circ}(H^+)$ and k_4 are rather small compared with k_3 at these pH values, all of which indicates that A_2 will react via A_3 — on account of the values of K_3, the concentration of A_3 will be quite high — rather than via A_1. Consequently, the current at any pH value will be roughly proportional to the concentration of A_2 in solution, which implies that the inflection point in the plot of I vs. pH (about pH 4.4) must be related to the first pK of pyridine-4-aldehyde (4.74). The divergence between the two values can be accounted for theoretically on the basis of the drop time used and eqn. (A22) (see Fig. 3). However, only under conditions similar to those involved in our system can the variation of I as a function of pH be used to obtain the pK of a given substance.

Above pH 10, the behaviour of the system can be justified — as we have done — on account of the competition between the dehydration and the dissociation of an H^+ ion (Fig. 3). When the processes involved can be considered irreversible and the rate constants are large enough, methods such as that used by Savéant and co-workers [10,11] allow the competition between the two reactions to be readily shown. As our system does not meet these requirements, we are led to use a treatment which has already been applied by our team in a previous paper [5].

Rusling and Zuman [4] propose a scheme providing a qualitative explanation for the behaviour of 1-methyl derivatives which is apparently different from that proposed by the authors (see Scheme 4). Such a scheme, using the original terminology (our own appears in brackets) can be summarized as

$$PyCH(OH)_2 \ \{A_2\} + H_2O \underset{k^o_{-5}}{\overset{k'_5}{\rightleftharpoons}} PyCH(OH)O^- \ \{A_5\} + H_3O^+ \tag{5}$$

$$PyCH(OH)_2 \ \{A_2\} + OH^- \underset{k_{-5}}{\overset{k^o_5}{\rightleftharpoons}} PyCH(OH)O^- \ \{A_5\} + H_2O \tag{6}$$

$$PyCH(OH)O^- \ \{A_5\} \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} PyCH{=}O \ \{A_3\} + OH^- \tag{7}$$

$$PyCH{=}O \ \{A_3\} + n \ e^- \rightarrow \tag{8}$$

Stages (5) and (6) correspond to the protolytic and hydrolytic schemes for the dissociation of an H^+ ion from species A_2 to form the anion A_5. The treatment of these authors [4,6] is based on the selection of a rate-determining step (rds) and the application of the Koutecký equation to it in order to account for the behaviour of the kinetic current as a function of the pH.

The scheme considered by our team is partly equivalent (see Scheme 4) if we take into account that the sum of stages (6) and (7) is

$$PyCH(OH)_2 \ \{A_2\} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} PyCH{=}O \ \{A_3\} + H_2O \tag{9}$$
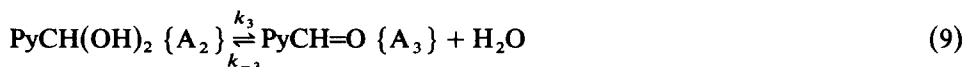
namely, the direct dehydration of A_2. Our assumption that this stage is subject to base catalysis is equivalent to considering the implicit occurrence of the two elementary steps (6) and (7), in which the equilibrium is displaced towards those sides in which OH^- have been consumed, as is logical at very basic pHs.

The above scheme is worth commenting on. First, these authors assume [4] that stage (7) attains equilibrium rapidly at any pH value — which may be difficult to account for at very high pHs — and that either step (5) or (6) is a very slow stage. If these assumptions were strictly true, as A_5 is the species which prevails in solution at high pHs, the current at very high concentrations of OH^- ions whould reach the value of the diffusion current. However, this is the case for neither 1-methyl derivatives nor 4-pyridine-aldehyde, for which the current is always kinetic in nature and attains its maximum at a plateau and even decreases for 4-Py. This must be the result of two competitive stages, which implies that it is impossible to apply the

Koutecký equation and that the approximation of the rds is inadequate under these conditions — this is a proven fact for 4-Py, since $K_3 = 1.525$ and hence neither k_3 nor k_{-3} may be neglected with respect to each other.

Finally, in our treatment we have assumed that, strictly, state (7) is very slow or even does not occur at all. This may not be applicable to the behaviour of other compounds such as 1-methyl derivatives. This hypothesis is based on the fact that the limiting current decreases sharply above pH 12, which can be expressed mathematically with the aid of the inequality $k_3 \gg k_6 \cong 0$. However, we do not exclude the possibility that the calculated k_3 may correspond to an apparent value to which k_6 contributes to some degree. It is absolutely impossible to determine these two constants individually.

The fine line in Fig. 3 illustrates the application (between pH 7 and 14) of eqn. (A45) (see Scheme 4, in which we have assumed that the dissociation of an H^+ ion from species A_2 takes place via the hydrolytic route, eqn. 6). Thus, asssuming the effect of base catalysis on $k_3 = k_3^\circ + k_3^{OH}(OH^-)$ and taking into account that $K_5 = K_5^\circ(OH^-)/K_w$ and $k_5 = k_5^\circ(OH^-)$, the best fit of the curves (Fig. 3) to the experimental data is found for $k_3^\circ = 0.55$ s^{-1}, $k_3^{OH} = 750$ s^{-1} M^{-1} and $k_5^\circ = 30$ s^{-1} M^{-1}, the approximate error in k_3^{OH} and k_5° being 40%, i.e. larger than that in the previous case since in this case both rate constants must be determined simultaneously as there is no pH region in which the process is influenced by only one of them, therefore allowing the individual determination of both.
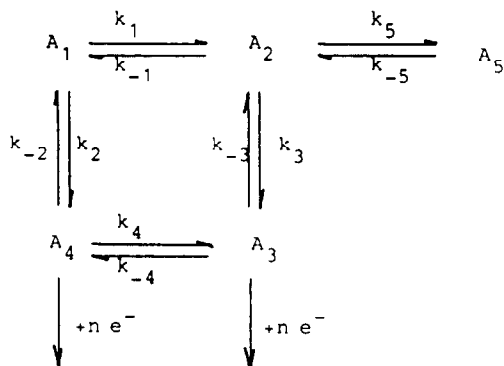
We believe that the behaviour of 4-pyridine-aldehyde can be attributed to a base-catalysed dehydration [12–14] in competition with the dissociation of an H^+ ion from the hydrated form. This assumption accounts for our experimental results, as well as for the behaviour of 1-methyl derivatives reported in the literature [6], although in the latter case we may not assess the influence of stage (7), which has not been considered in our treatment, on the behaviour of these compounds.

The mechanism of electrode processes occurring in a basic medium will be the subject of future work.

APPENDIX

Consider the reaction scheme depicted in Scheme 2, which, except for appropriate changes in terminology, is equivalent to Scheme 1. The assignment of the different species to the symbol which denotes them is easily accomplished by comparing the two schemes.

In the above scheme, we have defined $K_1 = k_1/k_{-1}$, $K_4 = k_4/k_{-4}$ and $K_5 = k_5/k_{-5}$, which correspond to the three acid–base equilibria involved in the system. These three constants are apparent and are defined as $K_1 = K_1^\circ/(H^+)$, $K_4 = K_4^\circ/(H^+)$ and $K_5 = K_5^\circ/(H^+)$. Therefore, k_{-1} and k_{-4} are also apparent rate constants, defined as $k_{-1} = k_{-1}^\circ(H^+)$ and $k_{-4} = k_{-4}^\circ(H^+)$, whereas on account of the value of K_5° $(10^{-12.12})$, k_5 and k_{-5} will be apparent rate constants depending on the protolytic or hydrolytic nature of the H^+ ion dissociation, as will be seen below.

$$A_1 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_2 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} A_5$$

$$k_{-2} \big\updownarrow k_2 \qquad k_{-3} \big\updownarrow k_3$$

$$A_4 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} A_3$$

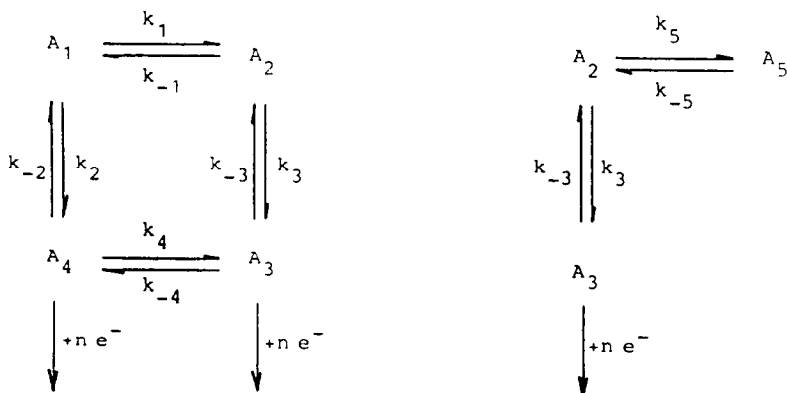$$\downarrow +n\ e^- \qquad \downarrow +n\ e^-$$

Scheme 2.

Scheme 2 also involves $K_2 = k_{-2}/k_2$ and $K_3 = k_{-3}/k_3$, which correspond to the two hydration equilibria; these may be subject to general acid–base catalysis, and thus the different rate constants are apparent constants, e.g. $k_3 = k_3^\circ + k_3^H(H^+) + k_3^{OH}(OH^-)$.

Our treatment will include the following approximations:

(1) Our analysis will deal only with the obtainment of the current sum of the reduction processes undergone by A_3 and A_4. The reason for this is that the difference between these two species lies in the protonation of a group which is not directly involved in the transfer; therefore, their reduction potentials will be very close, thus rendering it impossible to discriminate between both processes experimentally.

$$A_1 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_2 \qquad A_2 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} A_5$$

$$k_{-2} \big\updownarrow k_2 \qquad k_{-3} \big\updownarrow k_3 \qquad k_{-3} \big\updownarrow k_3$$

$$A_4 \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} A_3 \qquad A_3$$

$$\downarrow +n\ e^- \qquad \downarrow +n\ e^- \qquad \downarrow +n\ e^-$$

Scheme 3.

(2) The concentrations of A_3 and A_4 at the electrode will be assumed to be nil, which is equivalent to stating that both processes will be in their limiting zone.

(3) As $K_1 \gg K_5$, i.e. the two pKs corresponding to the hydrated form are sufficiently distant, the treatment will be simplified by considering that, at acid and neutral pHs, the process is represented by the reaction sequence depicted in Scheme 3.

At basic pHs, the concentration of species A_1 and A_4 can be neglected, and thus the process is described by the further simplified Scheme 4.

(4) The mutual conversion of A_3 and A_4 will not be taken into account since it does not affect the value of the limiting current in any case.

Treatment of Scheme 3

Taking into account the assumptions made above and that

$$c^\circ = \sum_{i=1}^{5} c_{A_i} \tag{A1}$$

$$a_i = c_{A_i}/c^\circ \tag{A2}$$

we may express the equations of mass transport by a suitable linear combination of the concentrations [5]:

$$\nabla \psi_i = -\lambda_i \psi_i \qquad \text{for } i = 1,2,3 \tag{A3}$$

$$\nabla \psi_4 = 0 \tag{A4}$$

$$\nabla = \frac{\partial}{\partial t} - D \frac{\partial^2}{\partial x^2} - \frac{2x}{3t} \frac{\partial}{\partial x} \tag{A5}$$

where we have assumed all the species to have the same diffusion coefficient, D, and where

$$\psi_i = \sum_{j=1}^{4} r_{ij} a_j \qquad \text{for } i = 1,2,3 \tag{A6}$$

$$\psi_4 = a_1 + a_2 + a_3 + a_4 \tag{A7}$$

λ_i denoting the three roots of the determinant

$$\begin{vmatrix} \lambda - k_1 - k_2 & k_{-1} & 0 & k_{-2} \\ k_1 & \lambda - k_3 - k_{-1} & k_{-3} & 0 \\ 0 & k_3 & \lambda - k_{-3} & 0 \\ k_2 & 0 & 0 & \lambda - k_{-2} \end{vmatrix} = 0 \tag{A8}$$

By taking $r_{i3} = 1$ [5], we obtain

$$r_{i1} = \frac{\{k_3 + k_{-1} - \lambda_i\}\{k_{-3} - \lambda_i\}}{k_{-1}k_{-3}} - \frac{k_{-3}}{k_{-1}} \tag{A9}$$

$$r_{i2} = \{k_{-3} - \lambda_i\}/k_{-3} \tag{A10}$$

$$r_{i4} = r_{i1}k_{-2}/\{k_{-2} - \lambda_i\} \tag{A11}$$

The limiting conditions for the system, for $t = 0$ and $x \geqslant 0$, and $t > 0$ and $x \to \infty$, are

$$\psi_i = 0 \quad \text{for } i = 1,2,3 \tag{A12}$$

$$\psi_4 = 1 \tag{A13}$$

Thus, the solutions to eqns. (A3) and (A4) are of the form [5]

$$\frac{d\psi_i}{dx}\bigg|_{x=0} = -F(\lambda_i)\frac{\psi_i}{\delta}\bigg|_{x=0} \quad \text{for } i = 1,2,3 \tag{A14}$$

$$\frac{d\psi_4}{dx}\bigg|_{x=0} = \frac{1 - \psi_4}{\delta}\bigg|_{x=0} \tag{A15}$$

where

$$\delta = (3\pi Dt/7)^{1/2} \tag{A16}$$

$$F(\lambda_i) \cong \left\{1.349(\lambda_i t)^{1/2}\right\}^{1.091} \coth\left\{1.349(\lambda_i t)^{1/2}\right\}^{1.091} \tag{A17}$$

and for $x = 0$ and $t \geqslant 0$

$$a_3 = a_4 = 0 \tag{A18}$$

$$(da_3/dx) + (da_4/dx) = I/\delta \tag{A19}$$

with

$$I = i_k/i_D \tag{A20}$$

$$i_D = nDFAc^\circ/\delta \tag{A21}$$

I can be obtained by eliminating a_1 and a_2 from eqns. (A6), (A7), (A14), (A15) and (A19).
The final solution is

$$\frac{I}{1-I} = \frac{A_1 B_2 - A_2 B_1}{C_1 B_2 - C_2 B_1} \tag{A22}$$

with

$$A_1 = \frac{F(\lambda_1)r_{11}}{1 - r_{14}} - \frac{F(\lambda_2)r_{21}}{1 - r_{24}} \tag{A23}$$

$$A_2 = \frac{F(\lambda_1)r_{11}}{1 - r_{14}} - \frac{F(\lambda_3)r_{31}}{1 - r_{34}} \tag{A24}$$

$$B_1 = \frac{F(\lambda_1)\{r_{12} - r_{11}\}}{1 - r_{14}} - \frac{F(\lambda_2)\{r_{21} - r_{22}\}}{1 - r_{24}} \tag{A25}$$

$$B_2 = \frac{F(\lambda_1)\{r_{12} - r_{11}\}}{1 - r_{14}} - \frac{F(\lambda_3)\{r_{31} - r_{32}\}}{1 - r_{34}} \tag{A26}$$

$$C_1 = \{1/(1 - r_{24})\} - \{1/(1 - r_{14})\} \tag{A27}$$

$$C_2 = \{1/(1 - r_{34})\} - \{1/(1 - r_{14})\} \tag{A28}$$

Treatment of Scheme 4

In this case, the linear combinations of the equation of mass transport have the form [5]

$$\nabla\psi_5 = -\lambda_5\psi_5 \tag{A29}$$

$$\nabla\psi_6 = -\lambda_6\psi_6 \tag{A30}$$

$$\nabla\psi_7 = 0 \tag{A31}$$

where ψ_5 and ψ_6 are given by

$$\psi_i = r_{i3}a_3 + a_2 + r_{i5}a_5 \qquad i = 5,6 \tag{A32}$$

$$\psi_7 = a_3 + a_2 + a_5 \tag{A33}$$

in which we have taken $r_{i2} = 1$ [5] and

$$r_{53} = 1/\{1 - (\lambda_5/k_{-3})\} \tag{A34}$$

$$r_{63} = 1/\{1 - (\lambda_6/k_{-3})\} \tag{A35}$$

$$r_{55} = 1/\{1 - (\lambda_5/k_{-5})\} \tag{A36}$$

$$r_{65} = 1/\{1 - (\lambda_6/k_{-5})\} \tag{A37}$$

$$\lambda_5 = \left\{ k + (k^2 - 4s)^{1/2} \right\}/2 \tag{A38}$$

$$\lambda_6 = k - \lambda_5 \tag{A39}$$

$$k = k_3(1 + K_3) + k_5\left(1 + \frac{1}{K_5}\right) \tag{A40}$$

$$s = k_3 k_5 \left(K_3 + \frac{1}{K_5} + \frac{K_3}{K_5} \right) \tag{A41}$$

By taking into account that for $x \geqslant 0$ and $t = 0$, and for $t > 0$ and $x \to \infty$

$$\psi_5 = \psi_6 = 0 \tag{A42}$$

$$\psi_7 = 1 \tag{A43}$$

and that for $x = 0$ and $t \geqslant 0$

$$(da_3/dx) = I/\delta \tag{A44}$$

we may eliminate a_2 and a_5 in much the same way as in the previous case, taking

into account relations similar to eqns. (A14) and (A15), which allow us to obtain the value of I:

$$\frac{I}{1-I} = \frac{\{r_{65} - r_{55}\} F(\lambda_5) F(\lambda_6)}{r_{53}\{1 - r_{65}\} F(\lambda_6) - r_{63}\{1 - r_{55}\} F(\lambda_5)} \tag{A45}$$

where $F(\lambda_5)$ and $F(\lambda_6)$ are related to λ_5 and λ_6 as in eqns. (A17).

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