The Role of Electrical and Volume Transport in Heterogeneous Reaction Systems

E. Kahrig, H. Beßerdich, E. Brecht, and D. Kirstein

Zentralinstitut für Molekularbiologie der Akademie der Wissenschaften der DDR, Selbständige Abteilung Biokatalyse, Berlin

(Z. Naturforsch. **30 c**, 127–128 [1975]; received September 13, 1974)

Transport Reaction Coupling, Periodic Concentration Profiles

For autocatalysis coupled with diffusion the local periodic concentration profiles are influenced essentially by electrical transport and convection.

When diffusion is negligible for Michaelis-Menten-kinetics equations are given to determine the kinetic parameters V_{max} and K_m from transport measurements.

Concentration profiles of substrate and product in enzyme membranes have been computed for diffusion and chemical reaction of zero or first order as well as Michaelis-Menten kinetics [1–6]. A mathematical treatment considering other transport processes (electrical transport, convection) is not known till now, but the consideration of these phenomena can lead to additional parameters valuable for influencing and optimizing the systems.

If the substrate is transported by diffusion, electrical current and volume flow and the following assumptions are made: steady state; electrical field intensity E, electrical mobility u, diffusion coefficient D and convective velocity $v_{conv.}$ are independent of the local coordinate; coupling of the transport processes negligible, the mass balance gives

$$\frac{d^2c}{dx^2} - \frac{u\,E + v_{conv.}}{D}\frac{dc}{dx} = \frac{r}{D} \qquad (1)$$

(c = substrate concentration, x = local coordinate, r = reaction rate).

With the boundary conditions

$$c = c_0 \quad \text{at} \quad x = 0$$
$$c = c_1 \quad \text{at} \quad x = 1$$

the concentration profiles of the substrate are computed in [7] for reactions of zero and first order. They are complicated functions of the parameters

$$a = \frac{u\,E + v_{conv.}}{D}\,,\quad b_0 = \frac{K_0}{D}\,,\quad b_1 = \frac{K_1}{D}$$

(K_0, K_1 = rate constants).

Requests for reprints should be sent to Dr. E. Kahrig, Zentralinstitut für Molekularbiologie der Akademie der Wissenschaften der DDR, Selbständige Abteilung Biokatalyse, *X-1058 Berlin*, Wolliner Str. 71.

Assuming that the reaction includes an autocatalytic step, for instance

$$A + C \xrightarrow{K'} 2\,C$$

with a second substrate A of constant concentration a, the reaction rate is given by

$$r = -K'\,a\,c = -K\,c\,.$$

It can be shown that now – depending on the sign of the discriminant – various solutions are possible. It must be emphasized that a negative discriminant leads to periodic solutions

$$c(x) = e^{\frac{a}{2}x}(A\cos b'\,x + B\sin b'\,x)$$

where

$$b' = \sqrt{b - \frac{a^2}{4}}\,.$$

The onset $\left(\frac{a^2}{4} - b < 0\right)$ and the wave length $\left(\lambda = \frac{2\pi}{b'}\right)$ of the spatial periodic concentration distributions are now dependent on diffusion and reaction as well as on charge and volume transport.

It is important that the latter phenomena inhibit the occurence of the periodicity, because if $a = 0$ there is always a periodical profile [8–11]. When diffusion is negligible compared to the other transport processes $\left(i.\,e.\ \frac{u\,E\,l}{D} \text{ and } \frac{v_{conv.}\,l}{D} \gg 1\right)$, Eq. (1) can be simplified.

Integration gives linear profiles for zero order reaction and exponential profiles for first order reaction [7].

The shape of the concentration profiles depends above all on the parameters

$$a_0 = \frac{K_0}{u\,E + v_{conv.}}\,,\quad a_1 = \frac{K_1}{u\,E + v_{conv.}}\,.$$

For Michaelis-Menten kinetics it follows:

$$(u\,E + v_{conv.})\frac{dc}{dx} + K_2\,E_0\,\frac{c}{K_m + c} = 0 \qquad (2)$$

(K_2 = turnover number, E_0 = enzyme concentration, K_m = Michaelis-constant).

Eq. (2) gives the following implicite relation for the concentration profile:

$$K_m \ln c + c = -a_m\,x + K_m \ln c_0 + c_0 \qquad (3)$$

where

$$a_m = \frac{K_2\,E_0}{u\,E + v_{conv.}}\,.$$

Using Eq. (3) it is possible to determine the important kinetic parameters $v_{max} = K_2\,E_0$ and K_m

by measuring the substrate concentrations c_0 and c_1 in the compartments on both sides of the membrane.

Provided that $c_0, c_1 \gg K_m$, $K_2 E_0$ is given by

$$K_2 E_0 = \frac{c_0 - c_1}{l} (u E + v_{\text{conv.}})$$

and provided that $c_1 \neq c_0$, K_m is given by

$$K_m = \frac{c_0 - c_1 - \dfrac{K_2 E_0 l}{u E + v_{\text{conv.}}}}{\ln \dfrac{c_1}{c_0}}.$$

An experimental verification of these equations is not yet done. This procedure is similar to that of Selegny *et al.* [2, 3] for reaction and diffusion alone.

Summarizing it can be stated that

1. the spatial periodic concentration profiles for autocatalysis are influenced essentially by electrical and volume transport. If charge and volume transport occurs, the dynamic patterns in membranes – first observed by de Simone, Beil and Scriven [11] – should show characteristical changes *e. g.* of wave length and onset.
2. It is possible to determine the kinetic parameters $v_{\max}$ and K_m if diffusion is negligible and a superposition of electrical and/or volume transport with Michaelis-Menten kinetics occurs.

[1] R. Goldman, O. Kedem, and E. Katchalsky, Biochemistry **7**, 4518 [1968].
[2] E. Selegny, S. Avrameas, G. Broun, and D. Thomas, C. R. Acad. Sci., Paris **266**, 1431 [1968].
[3] E. Selegny, G. Broun, J. Geffroy, and D. Thomas, J. Chim. Phys. et Physico. Chim. Biol. **66**, 391 [1969].
[4] E. Selegny, G. Broun, and D. Thomas, Physiol. Veg. **9**, 25 [1971].
[5] E. Selegny, J.-P. Kernevez, G. Broun, and D. Thomas, Physiol. Veg. **9**, 51 [1971].
[6] D. Thomas, G. Broun, and E. Selegny, Biochimie **54**, 229 [1972].
[7] E. Kahrig, H. Besserdich, E. Brecht, and D. Kirstein, Acta Biol. Med. Germ. **34**, Heft 4 [1975].
[8] H. G. Busse, J. Phys. Chem. **73**, 750 [1969].
[9] A. N. Zhaikin and A. M. Zhabotinsky, Nature **225**, 535 [1970].
[10] A. T. Winfree, Science **175**, 634 [1972].
[11] J. A. De Simone, D. L. Beil, and L. E. Scriven, Science **180**, 946 [1973].