

Momentum Balance Equation for Nonelectrolytes in Models of Coupling between Chemical Reaction and Diffusion in Membranes

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Abstract. The role of viscosity in coupling between chemical reaction (complex formation) and diffusion in membranes has been investigated. The Fick law was replaced by the momentum balance equation with the viscous term. The irreversible thermodynamics admits coupling of the chemical reaction rate with the gradient of velocity. The proposed model has shown the contrary effect of viscosity and confirmed the experimental results. The chemical reaction rate increases only above the limit value of viscosity. The parameter Q (degree of complex formation) was introduced to investigate coupling. Q equals to the ratio of the chemical contribution into the flux of the complex to the total flux of the substance transported. For different values of the parameters of the model the dependence of Q upon position inside the membrane has been numerically calculated. The assumptions of the model limit it to a specific case and they only roughly model the biological situation.

Key words: Model — Viscosity — Membrane — Coupling — Chemical reaction

Introduction

Theoretical studies of models which allow for simultaneous occurrence of chemical reaction and diffusion have now over a half-century long tradition. The first model of the reaction-diffusion coupling solved dates back to 1909. It was presented by Ferentz Jüttner (1909) from Wrocław. Unfortunately, although based on the latest developments in the theory of differential equations available at that time, his papers have remained unknown up to the fifties. A real and effective contribution to the theory of reaction-diffusion coupling was made in the thirties by Damköhler (1935) in Germany, Zeldovich (1934) in the USSR and Thiele (1939) in the USA. Although the above papers were published independently, they still constitute a basis for the description of the two simultaneously occurring processes, thus contributing to the development of chemical engineering.

It was as late as in the early seventies that the basic achievements and ideas of these papers were explicitly applied to the description of mass transport across biological membranes. Credit for that belongs to professor Caplan and his pupils DeSimone and Bunow (eg. DeSimone and Caplan 1973; Bunow and DeSimone 1977). Papers by Cussler (1971) and Aris and Keller (1972) were of a similar nature, dealing in detail with the local coupling. Almost independently of the studies performed by specialists in chemical engineering a series of papers was published in the 40-ties devoted entirely to the biophysics of mass transport, e. g. Rosenberg (1948), Patlak (1956), Kedem (1960), Blumenthal et al. (1967), Rappaport (1968). These works have dealt with the theory of the active transport and facilitated diffusion thus describing the coupling between metabolic reactions and diffusion. Models developed in those papers have used the language of the thermodynamics of irreversible processes (see Fitts (1962), de Groot and Mazur (1965)), mostly using the formalism of compartmental analysis. In papers published in the 60-ties, e. g. Kedem (1960), Katchalsky and Curran (1967), Mikulecky (1969), emphasis was put on interpretation of the Curie principle, since the reaction-diffusion coupling is one between scalar and vectorial processes. In later papers, e.g. Prigogine et al. (1969), Goldbeter and Lefever (1972), Selegny and Vincet (1980), irreversible thermodynamics was applied to the description of dissipative structures that arise as a result of the coupling, and to the study of their stability and range of occurrence.

The third trend that may be traced back in the history of the reaction-diffusion coupling studies represent numerous kinetic models, e.g. Hill and Kedem (1966), Geck and Heinz (1976), Lieb and Stein (1972), which were used in many cases to describe specific, practical types of active and facilitated transport encountered in experimental practice. The above historical outline and classification of models of reaction-diffusion coupling undoubtedly represents a rough approximation. In our opinion, however, it accurately indicates tendencies in the field. A more detailed analysis with more examples may be found in the paper by Galdzicki (1982).

Along with the description of active and facilitated transport across biological membranes the theory of passive transport has been developed. Making use of latest developments in the statistical theory of transport, the kinetic theory of gases and the theory of mixtures, many physical aspects of the phenomenon for both nonelectrolytes and electrolytes have been clarified. It has been shown that phenomenological flux equations (including Fick's law) result from the momentum conservation law under special assumptions. The phenomenological coefficients have been expressed in terms of the friction and viscosity coefficients as well as in those of electric parameters of both the permeating substance and the membrane.

Some General Remarks on the Model Proposed

In the present paper momentum balance equation has been used to model the coupling between chemical reaction and diffusion. Previous models materialized the essence of this coupling by means of mass balance equation, supplied with the Fick law, or by means of the electroneutrality condition only. In addition the spirit of the present paper as well as many of its approximations were taken from Blumenthal and Katchalsky (1969) and from a continuation of it in a series of papers by Vaidhyanathan (1971a, b).

The cited papers were among the first ones introducing local coupling by mass balance equation and Fick's law. The momentum balance equations applied to our model were, in their general form for multicomponent mixtures, first derived by Snell, Aranow and Spangler (1967) from statistical considerations. In its final form the derivation differs from that reported by Bearman and Kirkwood (1958) in that the partial stress tensor is totally expressed in terms of fluxes of individual components.

The equation has the form:

$$\frac{\partial}{\partial t} (\rho_i \vec{u}_i) = -\vec{\nabla}(\tau_i + \rho_i \vec{u}_i \vec{u}_i) - c_i \vec{\nabla} \mu_i + c_i \sum_j c_j \zeta_{ij} (\vec{u}_j - \vec{u}_i) + c_i \vec{F}_i \quad (1)$$

where ρ_i is the density of the i -th component; $\vec{u}_i$ is the local velocity of the mass centre of the i -th component; c_i is the concentration of the i -th component; ζ_{ij} is the coefficient of friction between the i -th and the j -th components; F_i is the external force acting on the i -th component; and $\vec{\nabla}$ is the nabla operator.

The partial viscosity tensor, τ_i , is defined as follows :

$$\tau_i = -c_i \sum_j g_{ij} \vec{\nabla} \rho_j \vec{u}_j \quad (2)$$

$$g_{ij} = \delta_i \zeta_{ij} \delta_j \quad (3)$$

where δ_i , δ_j are interpreted as the maximum distances at which the interactions between the components still contribute to the stress tensor. Summing Eq. (1) over all species, we obtain an equation of motion for a fluid element as a whole. It is just the Navier-Stokes equation of motion however. Equation 1 does not take account of partial momentum that may arise during chemical reactions. In order to do that an additional term must be considered (Bowen (1976), Baranowski (1974), Miękisz et al. (1979))

$$\vec{J}_{Rl}^m = \vec{u}_i \sum_l \nu_{il} m_l J_{Rl} \quad (4)$$

where J_{Rl} is the rate of the l -th reaction: ν_{il} are the stochiometric coefficients, and

m_i is the molecular mass of the i -th component. The upper index m denotes momentum.

To adapt Eq. (1) to the description of transport across membranes, an additional term should be considered which allows for interaction between permeating components and the membrane molecules. For that purpose the frictional term of Eq. (1) can be used, assuming that membrane molecules are considered as mixture components fixed in space, i.e. $u_m = 0$, where the lower index m denotes the membrane component. Thus, the term will take the form $F_{im} = -c_i f_{im} \vec{u}_i$ (see e.g. Richardson and Miękisz (1976) or Mason and Viehland (1978)).

The momentum balance equation will thus take the form:

$$\frac{\partial}{\partial t} (\rho_i \vec{u}_i) = -\vec{\nabla}(\tau_i + \rho_i \vec{u}_i \vec{u}_i) - c_i \vec{\nabla} \mu_i + c_i \sum_j \zeta_{ij} c_j (\vec{u}_j - \vec{u}_i) + \vec{F}_{im} + J_{Ri}^m \quad (5)$$

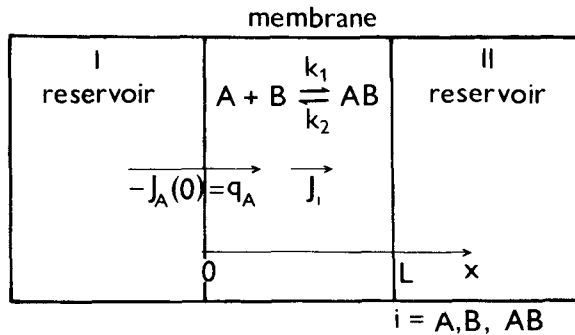
Adaptation of momentum balance to transport processes across membranes seems to be a very simple procedure (with the summation condition changed). The momentum balance equations for the membrane components were not explicitly written. An excellent review of these problems for nonreacting mixtures only was presented by Mason and Viehland (1978). Two approaches to mixture transport across membranes were compared. The first one was based on the "dusty gas" model, the other one arose from fluid dynamics.

The inclusion of chemical reactions to the theory of transport across membranes was discussed from the hierarchical point of view in the work by Miękisz et al. (1979).

Eq. (5) will henceforth be used to construct our model. Moreover, it is assumed that water flows through the membrane much slower than other components. This assumption means that, in our model, the membrane permeability for water is a very small value. The contributions from water permeating molecules interactions are incorporated into terms describing the membrane permeating molecules interaction. In our one-dimensional model the viscosity effect of water may be omitted due to the incompressibility of it. In the opposite case the viscosity of the solvent can be allowed for by using the more general form of the coefficients f_{im} and ζ_{ij} in the momentum balance equation (for details, see Mehta et al. (1976) or Mason and Viehland (1978)).

Description of the Model

We consider a membrane separating two reservoirs, I and II. Also let us assume that both external solutions are well stirred and that they are homogenous. The concentrations of the species remain uniform up to the region close to the boundary surfaces of the membrane. Reservoir I contains only solute A (with no B or AB present). The substance A permeating across the membrane participates



in an association-dissociation reaction, $A + B \xrightleftharpoons[k_2]{k_1} AB$. This reaction will be considered inside the membrane only. For simplicity, any conditions for the content of reservoir II were not considered. Here, the one-dimensional case of a stationary state far from equilibrium is described. The system is thermodynamically open and the steady state is maintained by a constant influx of A ($J_A(0)$). Also, isothermic conditions are assumed. For further considerations interphase conditions need not to be particularly specified. They only change the numerical values of $c_A(0)$ and $J_A(0)$.

According to the above assumptions, the local rate of the chemical reaction can be expressed as:

$$J_R(x) = k_1 c_A(x) c_B(x) - k_2 c_{AB}(x) \quad (6)$$

where $[A] = a$; $[B] = b$; $[AB] = d$ denote local concentrations of the reactants, respectively. Following mass balance equations apply for the respective components:

$$\begin{aligned} -\frac{dJ_A}{dx} - v_A J_R &= 0 \\ -\frac{dJ_B}{dx} - v_B J_R &= 0 \\ -\frac{dJ_{AB}}{dx} - v_{AB} J_R &= 0 \end{aligned} \quad (7)$$

where $v_A = v_B = 1$; $v_{AB} = -1$. The respective momentum balance equations according to Eq. (5) are as follows:

$$\begin{aligned} 0 &= -\frac{d}{dx} (\tau_A + a m_A u_A u_A) - a \frac{d\mu_A}{dx} + a \sum_{j=1}^3 \zeta_{Aj} c_j (u_j - u_A) - a f_{Am} u_A + u_A m_A J_R \\ 0 &= -\frac{d}{dx} (\tau_B + b m_B u_B u_B) - b \frac{d\mu_B}{dx} + b \sum_{j=1}^3 \zeta_{Bj} c_j (u_j - u_B) - b f_{Bm} u_B + u_B m_B J_R \end{aligned} \quad (8)$$

$$0 = -\frac{d}{dx}(\tau_{AB} + dm_{AB}u_{AB}u_{AB}) - d\frac{d\mu_{AB}}{dx} + d\sum_{j=1}^3 \zeta_{ABj}c_j(u_j - u_{AB}) - df_{ABm}u_{AB} - u_{AB}m_{AB}J_R$$

where $c_A = a$; $c_B = b$; $c_{AB} = d$. Here, τ_i depends on δ_i and δ_j the respective radii of interaction within the membrane (see Eqs. (2), (3)). They are henceforth assumed to be equal (symmetry of interaction) $\delta_A = \delta_B = \delta_{AB} = 3 \times 10^{-10}$ m.

Eqs. (7) and (8) form a set of nonlinear differential-integral equations, and hence they are very difficult to solve. Applying an approximation similarly as that in Vaidhyanathan's papers (Vaidhyanathan 1971a, b), concerning the x -coordinate dependence of concentration (x being the distance from the left surface of the membrane), an approximate solution may be obtained. We assume that the concentrations a , b , d are analytical functions and can be expressed as the Taylor series:

$$a = \sum_{i=0}^{\infty} a_i x^i, \quad b = \sum_{i=0}^{\infty} b_i x^i, \quad d = \sum_{i=0}^{\infty} d_i x^i \quad (9)$$

With that assumption Eqs. (7) and (8) can be rewritten as a set of algebraic equations. The assumption (9) implies that all the physico-chemical quantities inside the membrane are continuous and that they vary smoothly in it.

From Eqs. (9) and (6) the reaction rates can be expressed as functions of x in the following way:

$$J_R = \sum_{i=0}^{\infty} R_i x^i \quad (10)$$

where $R_0 = k_1 a(0)b(0) - k_2 d(0)$

$$R_i = k_1 [a(0)b_i + b(0)a_i + \sum_{j=1}^{i-1} a_j b_{i-j}] - k_2 d_i \quad (11)$$

Using Eq. (10) and integrating directly Eq. (7) over x , we obtain explicit expressions for the fluxes of substances A, B and AB as functions of x :

$$\begin{aligned} J_A &= -q_A - R(x) & J_A(0) &= -q_A \\ J_B &= -q_B - R(x) & J_B(0) &= -q_B \\ J_{AB} &= q_{AB} + R(x) & J_{AB}(0) &= q_{AB} \end{aligned} \quad (12)$$

where $R(x) = \sum_{i=0}^{\infty} R_i / (i+1) x^{i+1}$

q_i are the integration constants of the mass balance equations (7). Further we assume that both q_B and q_{AB} equal to zero, which means that neither the substance B nor the complex AB may cross the left side of the membrane (it is in full agreement with the assumptions of the model)

In the momentum balance equations (8) gradients of chemical potentials appear. We express them (as we consider nonelectrolytes) as follows:

$$\frac{d\mu_i}{dx} = \bar{v}_i \frac{dp}{dx} + RT \frac{d}{dx} \left[\ln \left(c_i / \sum_i c_i \right) \right] \quad (13)$$

where p is the pressure; R is the gas constant; T is the temperature; and $\bar{v}_i$ is the partial volume of the i -th substance.

Eq. (13) introduces a new quantity to the balance equation, namely the pressure, which has not yet been expressed as a function of x . In order to obtain this relationship, we sum up momentum balance equations for each component and thus get a momentum balance equation for the mixture as a whole. In the stationary state the terms with ζ_{ij} vanish owing to the symmetry with respect to i and j .

$$\frac{dp}{dx} = -\frac{d}{dx} \left(\sum_{i=1}^3 c_i \sum_{j=1}^3 g_{ij} \frac{d}{dx} (c_j u_j) + \sum_{i=1}^3 m_i c_i u_i \right) - \sum_{i=1}^3 f_{im} c_i u_i \quad (14)$$

From the hierarchy condition — that the Navier-Stokes equation for the whole mixture must result from the momentum balance equations for individual components (Richardson and Miękisz 1976) it may be assumed that:

$$\sum_{i=1}^3 c_i \bar{\nabla} \mu_i = \bar{\nabla} p \quad (15)$$

Although this equation reminds the Gibbs-Duhem equation applicable only to mechanical equilibrium, here it follows from the hierarchy of dynamical description of mixtures.

In the final stage of the calculations two cases have been considered: one in which partial viscosities were neglected and another with full balance equations, so as to investigate the role of viscosity in the coupling.

It is assumed here, and it is a customary assumption in models of this kind, that the total carrier amount is locally the same throughout the membrane regardless of the dependence of both b and d on x (it turned out that this assumption cannot be met if partial viscosities of the components are taken into account).

On inserting Eqs. (12), (13), (14), (11), and (9) into Eqs. (8) a set of three algebraic equations is obtained. Then, assembling terms of the same order with respect to x , and equating the coefficients of the respective powers of x to zero (the equations become identities), sets of equations for the coefficients a_i , b_i , d_i , respectively, are obtained. In this way, recurrence formulae for the expansion coefficients are obtained. Equations for these coefficients (Galdzicki 1982) express the fact that the knowledge of the lower order Taylor expansion coefficients allows to compute the higher order coefficients. In this way, both the reaction rate and the concentrations of species profiles can be computed to any order of accuracy desired using experimentally available information. In our paper only the first and the second order terms were used in numerical calculations. The third order terms obtained turned out to give negligible corrections to calculated quantities similarly as in Vaidhyanathan (1971a). The fact that the membrane thickness is 10^{-8} m and

that higher order Taylor expansion coefficients are of decreasing importance, are employed to terminate the Taylor series with finite term.

This assumption allows to calculate the fluxes given by Eqs. (12) up to the third power of x (Galdzicki 1982).

Results

The algebraic equations obtained for a_1 , b_1 , d_1 , a_2 , b_2 , and d_2 make it possible to calculate the fluxes J_A , J_B , and J_{AB} , and the chemical reaction rate, as functions of x . From the mass balance equations it follows that in stationary state $J_A^{\text{total}} = J_A + J_{AB}$. To investigate the coupling of chemical reaction with diffusion, a quantity should be introduced which would characterize the strength and effectiveness of the coupling. Such a quantity, we call it factor Q , is defined as follows:

$$Q = (J_{AB} - q_{AB})/J_A^{\text{total}} \quad (16)$$

The contribution of chemical reaction to the flux of the complex AB is expressed by the subtraction of q_{AB} from J_{AB} (Eq. (12)). Q characterizes the degree of the complex formation of the substance A, i.e. it provides information about how the flux of the complex varies relative to the total flux of A due to chemical reaction occurring within the membrane. The degree of the complex formation, Q , is a more general form of facilitation factor which was first introduced in similar topics by Kaper et al. (1980). The factor Q depends on all parameters that characterize the system. This dependence was examined in the final phase of our study. The results are shown in the plots.

It was shown that values of Q within the interval (0.1) correspond to situations with fluxes J_A and J_{AB} being in the same direction, and J_B in the opposite direction. Such situations prevail in many models of facilitated transport. It should be pointed out here that the model presented will be a model of facilitated transport of physiological substances if one of the following applies:

a) additional boundary conditions are assumed: $J_B(L) = J_{AB}(L) = 0$; in that case the rate of chemical reaction is reserved and hence both the carrier and the complex do not leave the membrane;

b) the complex disintegrates while crossing the righthand surface of the membrane, and hence the carrier is allowed to exist outside the membrane. The carrier might also be undetectable if it entered rapidly further metabolic reactions.

Situations for which $Q > 1$ correspond to models in which the whole transport of substance A goes against its own concentration gradient, this being often referred to in the literature as active transport.

Values of $Q < 0$ correspond to situations with negative coupling and are due to a marked reversal of the chemical reaction rate within the membrane. No example situation in the biophysics of transport is known to us to which this could apply.

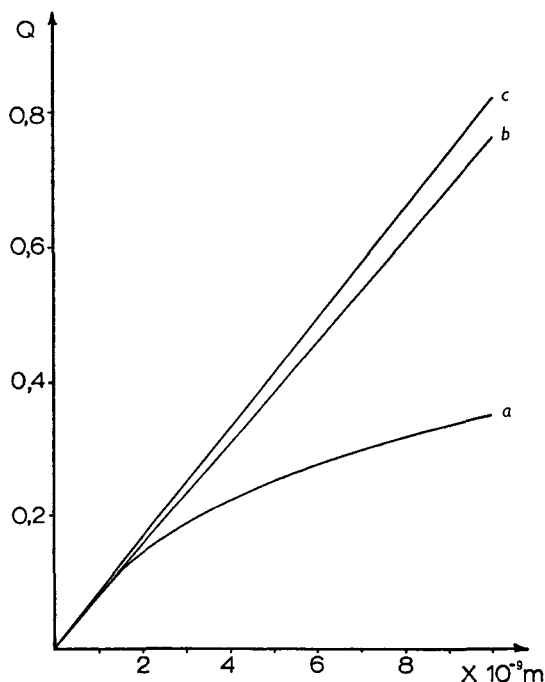


Fig. 1. The complex formation degree versus the location in the membrane for various component-membrane friction coefficients a $f_{im} \sim 10^{16}$, b $f_{im} \sim 10^{15}$, c $f_{im} \sim 10^{13}$. For symbols, see text

The study of the dependence of Q and J_R on values of parameters ξ_{ij} , f_{im} , k_1 , k_2 , and partial viscosities respectively has been performed using a small computer of the Commodore 4016 CBM series, and results are presented in six plots. Numerical values of parameters of the model used for the calculations are presented in Appendix.

Analysis of the plots enables to draw final conclusions concerning both the behaviour of the factor Q and the rate of chemical reaction in the membrane.

Collisions within the membrane are of different nature than in gases or in solutions. Molecules of the permeating substance have to make their way through the membrane and hence the frequency of collisions as well as their effectiveness are substantially greater than in ordinary solutions or gases. Also, with large friction coefficients f_{im} the degree of complex formation must be smaller, (see Fig. 1 and Appendix) since the reaction rate suddenly decreases.

A further important factors are the interaction between the components and the partial viscosities. These factors, when strong enough, cause the interacting pair of particles to stay longer at an effective distance from one another and thus increase the probability of chemical reaction between them, especially with large

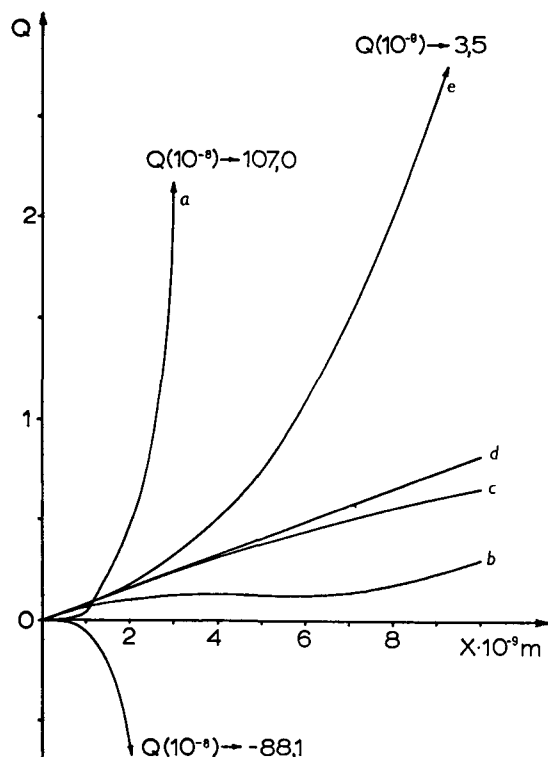


Fig. 2. The complex formation degree versus the location in the membrane for various component-component friction coefficients. *a*: $\zeta_{ij} \sim 10^{16}$, *b*: $\zeta_{ij} \sim 10^{15}$, *c*: $\zeta_{ij} \sim 10^{14}$, *d*: $\zeta_{ij} \sim 10^{11}$, *e*: $\zeta_{AB} \sim 10^{16}$, *f*: $\zeta_{AAB} \sim 10^{16}$, (other ζ_{ij} equal to zero). For symbols, see text.

ζ_{AB} . However, the decrease in velocity of the permeating components (see Fig. 2 and curves *a*, *b*, *d*) is in competition with this effect.

In situation with sufficiently large ζ_{AAB} and relatively small other coefficients ζ_{ij} the effective dissociation constant (not equal to k_2) becomes much larger than the effective association constant (not equal to k_1). In this case the degree of complex formation suddenly decreases and becomes even negative, as the rate of chemical reaction reverses.

When we take account of partial viscosities (putting $\delta_i = 3 \times 10^{-10}$ m) we get a marked increase in the degree of complex formation. Shinitzky et al. (1980) have shown experimentally that the regulatory role of viscosity is reflected in two contrary effects:

- a) a decrease in velocities of diffusing molecules, particularly of the large ones
- b) an increase in the probability of complex formation due to increasing accessibility of the carrier to the molecules of the substance transported.

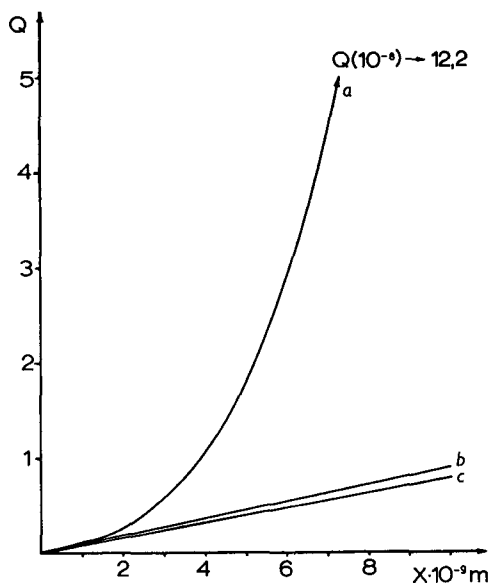


Fig. 3. The complex formation degree versus the location in the membrane regarding partial viscosity for various component-component friction coefficients. *a*: $\zeta_{ij} \sim 10^{13}$, *b*: $\zeta_{ij} \sim 10^{12}$, *c*: $\zeta_{ij} \sim 10^{11}$ and $\delta_i = 3 \times 10^{-10}$ m. For symbols, see text.

As can be seen from curves *b* and *c*, both effects change the value of the factor *Q* for $\zeta_{ij} = 10^{-11} \div 10^{-12}$ kg · m³/(mol² · s) in a similar way.

Only when $\zeta_{ij} = 10^{-13}$ kg · m³/(mol² · s) a substantial increase in *Q* (curve *a*), is observed i.e. the second effect begins to dominate, as confirmed by results given in Fig. 6.

It is very interesting that even the factor *Q* varies only linearly for large values of the association coefficients k_1 and for small values of the dissociation coefficient k_2 . Most likely, this is due to the condition of stationarity — compare Vaidhyanathan (1979b).

Figure 5 shows how *Q* increases with the increasing rate of penetration q_A , of A into the membrane. This is due to an increase in the probability of association at lower velocities.

The results presented show that the proposed model of reaction-diffusion coupling offers great possibilities to study the effect of the interactions mentioned (the chemical ones expressed by constants k_1 and k_2 and those of frictional-viscous nature) on the coupling strength.

Discussion

Description of coupling between chemical reaction and diffusion by introducing the general form of the momentum balance equation made enabled the investigation of

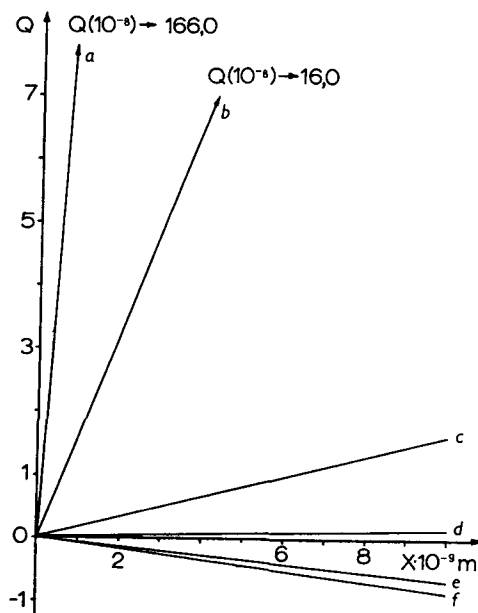


Fig. 4. The complex formation degree versus the location in the membrane for various rate constants for the association and dissociation reactions, respectively. *a*: $k_1 = 1000$, $k_2 = 10$, *b*: $k_1 = 100$, $k_2 = 10$ *c*: $k_1 = k_2 = 10$, *d*: $k_1 = 1$, $k_2 = 10$ *e*: $k_1 = 1$, $k_2 = 1000$, *f*: $k_1 = 0.1$, $k_2 = 1000$. For symbols, see text.

the regulatory role of viscosity in phenomena associated with the transport across membranes.

It would be difficult to compare the obtained results with known experimental data on a quantitative level as parameters necessary for calculations are unavailable. We therefore performed a qualitative comparison and have tried to throw light on the problems of coupling.

Gavish analyzed in his papers the viscosity effect on enzyme catalysis in experimental and theoretical studies (Gavish and Werber 1979; Gavish 1980). The fact that the dynamic state of the molecular structure of the enzyme-substrate complex is governed by interaction with surrounding molecules through two competing processes: random collisions and the action of friction forces, is the most important thesis of those papers. The action of the former increases the kinetic energy of the various modes of motion, and the latter dissipates their energy by viscous damping. This is the reason why "the transient state" becomes the engine of enzyme catalysis, especially for membrane-bound proteins. These predictions and results are compatible with other experimental facts, e.g. Lass and Fischbach (1976), Read and McElhaney (1976), Shinitzky et al. (1980). Both regulatory aspects of viscosity (Fig. 3) have yielded equal contributions; similar results were also obtained by Shinitzky et al. 1980. The effect producing an increase in the

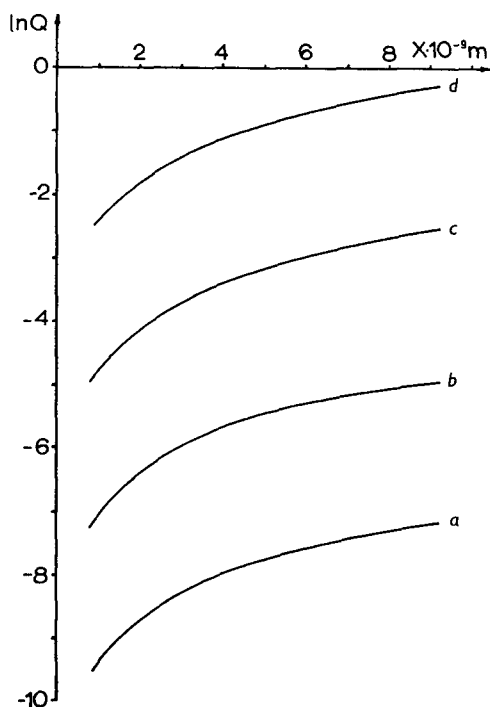


Fig. 5. The logarithm of the complex formation degree versus the location in the membrane for various influxes. $a: q_A = 1.2 \times 10^{-2}$, $b: q_A = 1.2 \times 10^{-3}$, $c: q_A = 1.2 \times 10^{-4}$, $d: q_A = 1.2 \times 10^{-5}$. For symbols, see text.

chemical reaction rate and resulting in higher values of factor Q just dominate over the limiting value of viscosity (MacDonald and MacNaughtan 1979). The latter value depends on values of other parameters.

It has been known from thermodynamics of irreversible processes that chemical reaction is directly coupled, with the gradient of velocity, i.e. with the viscous effects even in isotropic systems. The dynamic-kinetic considerations presented above strictly confirmed this fact. It would be also interesting to investigate for which values of k_1 and k_2 the influence of viscosity becomes negligible.*

In its present form the model seems especially suitable for the description of transport of drugs (see Vaidhaynathan 19871a) and nonelectrolytes across biological membranes (see Kotyk 1973). It could be an alternative description of carrier transport of ions after making some corrections for the presence of electric field.

* A personal suggestion of Dr. J. Sandblom.

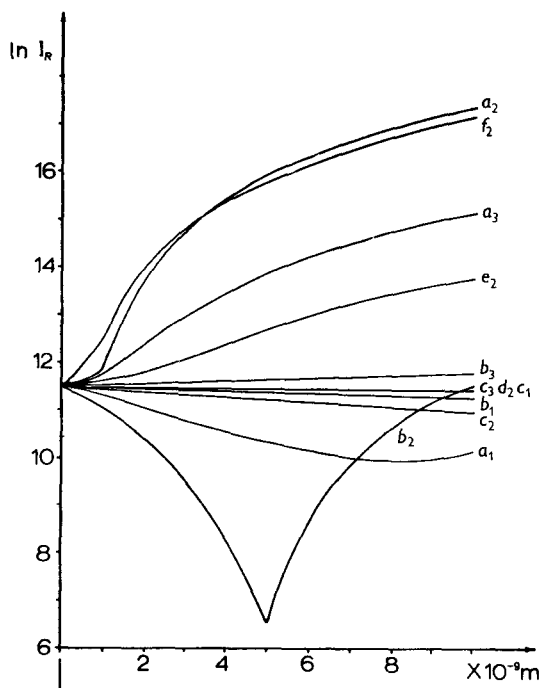


Fig. 6. The logarithm of the reaction rates versus the location in the membrane. The numbers denote respective curves (subscripts) in previous figures (Figs. 1—5).

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Appendix

In numerical calculation data close to results obtained experimentally were used (see Vaidhyanathan 1971a,b, 1975; Katchalsky and Curran 1967).

$$\zeta_{AB} = \zeta_{BA} = 1.6 \times 10^{12} \text{ kg} \cdot \text{m}^3 / (\text{s} \cdot \text{mol}^2)$$

$$\zeta_{AAB} = \zeta_{ABA} = \zeta_{BAB} = \zeta_{ABA} = 1 \times 10^{11} \text{ kg} \cdot \text{m}^3 / (\text{s} \cdot \text{mol}^2)$$

$$f_{Am} = 6 \times 10^{11} \text{ kg} / (\text{s} \cdot \text{mol})$$

$$f_{Bm} = f_{ABm} = 1 \times 10^{11} \text{ kg} / (\text{s} \cdot \text{mol})$$

$$k_1 = 10 \text{ m}^3 / (\text{mol} \cdot \text{s}) \quad k_2 = 1000 \text{ 1/s}$$

$$q_A = 1.2 \times 10^{-3} \text{ mol} / (\text{m}^2 \cdot \text{s})$$

$$\begin{array}{ll} a_0 = 200 \text{ mol/m}^3 & b_0 = d_0 = 100 \text{ mol/m}^3 \\ m_A = 0.2 \text{ kg/mol} & m_B = 0.2 \text{ kg/mol} \end{array}$$

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