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Theoretical study of mechano-chemical couplings in a compartmental enzyme system

I. Analytical treatment

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This paper deals with theoretical aspects of the volume changes of a system in which diffusion, convection and reaction processes are coupled. This study involves a material able to swell in the presence of a chemical effector produced by an enzyme reaction. Three limiting factors of volume change rate were considered: fluid flow, diffusion or reaction limitations. Dimensionless diffusion-reaction and diffusion-convection parameters were introduced to allow quantitative predictions in limit cases. The steady states appear to be independent of convection processes; however, the transient states depend on diffusion, convection and reaction processes.

1. Introduction

Diffusion-reaction processes have been extensively studied both with chemical reactions [1,2] and biochemical reactions (modelling of immobilized enzyme reactions) [3–5]. In the latter case, fundamental studies with enzyme coated on an impermeable surface, immobilized in membranes or beads, or solubilized in compartments have led to an understanding of the reaction limitations by diffusion constraints and of ways in which to decrease them. These studies also revealed a large

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List of symbols: (Latin) A, membrane area; C_i, C_i^0, concentration of species i, corresponding concentration in the reservoir; D, diffusion coefficient; e, membrane thickness; E_0, enzyme concentration for the minimum hydration (H_o); $f(P)$, constitutive law; H, hydration; H_o, minimum hydration (when $P = 0$); H_{max}, maximum hydration; H^*, $H^* = H_{max} - H_o$ range of potential variations of hydration; h, h_i, dimensionless hydration $h = H/H_o$, initial value of h; K, Darcy's constant; k_2, kinetic constant of the enzyme reaction; k_s, k_d, phenomenological coefficients characteristic of the shape of $f(P)$; l, l_o, length of the reactive compartment, value of l corresponding to H_o (minimum hydration); M, dimensionless diffusion-convection criterion: $M = K\xi H_o/\phi D_P$; N, normalization factor $N = 1 + 2(k_s k_d)^{1/2}$; p swelling pressure; $\mathcal{P}$, hydrostatic pressure; P, product concentration; P_{max}, P_1, product concentration corresponding to the maximum hydration; P_2, product concentration corresponding to the minimum hydration; P', dimensionless concentration $P' = P/P_{max}$; t, t', time variable, dimensionless time variable: $t' = t\mu\phi D_P/H_o$; v_{real}, fluid velocity inside the membrane; $v_{average}$, membrane velocity; v_R, enzyme reaction rate. (Greek) α, parameter defined by $\alpha = 0$ when $v_{real} \leq 0$, $\alpha = 1$ when $v_{real} > 0$; Γ_i, ionic flux; Γ_{fluid}, fluid flux; μ, $\mu = (1 + H_o)/(el_o)$; ν_i, stoichiometric coefficient; ξ, factor of potential swelling; π, osmotic pressure; σ', dimensionless diffusion-reaction criterion: $\sigma' = k_2 E_o H_o/(\mu\phi D_P P_{max})$; ϕ, porosity factor.

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variety in behavior: bistability [6–8], pluristability [9], space and space-time oscillations [10]. These studies have led to applications, mainly in biotechnology, for synthesis [11,12] (formation of L-amino acids from racemic mixtures by aminoacylases), production of HFCS (high-fructose corn syrups) from glucose by glucose isomerases, hydrolysis of penicillin G (for production of new penicillins), or for analytical purposes [12–15] (enzyme electrodes for glucose, urea, hydrogen peroxide, amino acids, penicillin, etc.).

On the other hand, diffusion-convection-reaction couplings began to be studied in the sixties to elaborate energy-conversion systems [16–19]. More recently, sophisticated models analyzing the different behaviors depending on the pertinent characteristic times were elaborated for understanding of the mechano-chemical properties of connective tissues (cartilages) [20–22] or cornea [23,24] and eventually fight related diseases.

Mechano-chemical systems were also studied with a view to defining drug-delivery systems, monitored by electric fields [25,26] or by the response of the system itself to a chemical species [27].

Striking experimental results have been obtained with polyacrylamide gels able to change their volume by a factor of several hundred percent [28–30] when changing a chemical parameter (pH, electrolyte concentration, solvent) or a physical parameter (temperature, electric field).

So far, only a few studies have been concerned with chemical reactions (ionization reaction excluded) [27,31].

Our aim is to couple the two areas in order to define new energy-conversion systems and, by taking advantage of specific biochemical reactions, to define new types of biosensors.

In this paper, we were concerned with the dynamics of volume changes (swelling or de-swelling) of a system in which mechanical, diffusion and chemical processes are coupled. For this purpose, a very simple 'homogeneous' model was considered, leading to space-independent phenomena and analytical solutions.

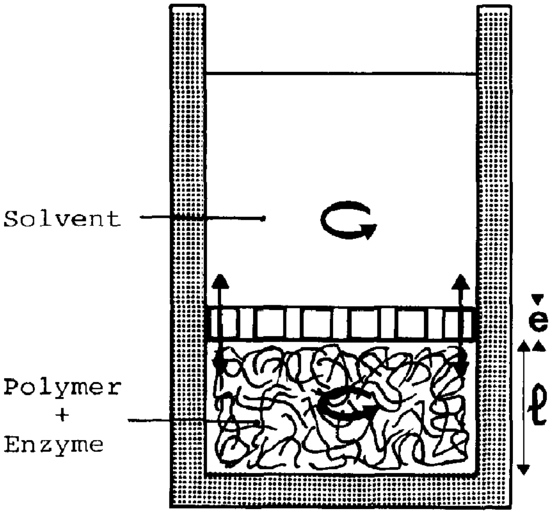

Fig. 1. Structure of the model: a compartment containing a polymer gel and an enzyme is separated from a reservoir containing the solvent (water) and the reactive species, by a membrane (impermeable to the polymer and the enzyme). The enzyme reaction taking place in the compartment produces a species which modifies a property of the polymer which, in turn, may cause a change in the hydration of the system.

2. The model

The system considered is one-dimensional; it is constituted of a 'compartment' of cross-section A and length l, in which a 'gel' containing a solubilized enzyme is trapped (fig. 1). This compartment, assumed to be perfectly homogenized, is separated from a concentration reservoir by a membrane of thickness e. This membrane is fixed on a frame which can move without any friction along the walls of the system; so, this device permits compartmental volume changes.

The 'gel' is made of a material immersed in water and has the property of swelling in the presence of a chemical effector P which is produced by the enzymic reaction. This material may be a polyelectrolyte liable to swell or de-swell with pH, ionic strength, solvent nature, temperature, etc. However, for a greater generality of this theoretical study, we shall not consider precise materials and effectors.

The system is set in such a way that the membrane is horizontal; therefore, the weight of both membrane and frame can be used as a restoring force when de-swelling occurs; however, this force will be neglected in the theoretical treatment since it may be very low compared to the swelling forces involved.

The limiting factors of volume change rate in such a system may be:

a slow response of the material to the effects of the effector (conformation changes of the macromolecules)

a limitation of the fluid flux through the membrane (low porosity, high tortuosity)

a limitation of the chemical effector diffusion through the membrane (low diffusivity)

a limitation by the enzyme reaction rate.

In this study, the first point will not be considered; it will be the subject of an other paper.

When the other three points are coupled, the behavior of the system is governed by diffusion-convection-reaction regimes. For a quantitative study of these regimes, dimensionless criteria have been introduced.

We may note that diffusion and convection couplings with the reaction are two-way couplings: diffusion and convection tend to change the concentration of chemical species which may control enzyme activity (especially substrate S); conversely, the reaction consumes the substrate and produces P; this modifies their concentration by changing the volume of the compartment. However, in the case of zero-order kinetics, there is only a one-way coupling since the reaction becomes independent of any chemical effector.

To take into account steady and transient states, the swelling pressure p in the compartment is assumed to be a function of both the concentration of product (P) and hydration H (defined as the ratio of fluid and dry material volumes):

$$p = \xi(f(P) - H) \tag{1}$$

This relation corresponds to the constitutive law of the system.

Remark: The concentration of any chemical species will be denoted by the corresponding letter without brackets or charge sign.

In eq. 1, ξ characterizes the potential swelling rate and $f(P)$, the dependence of the swelling on P, is defined by:

$$f(P) = H_o + (H_{max} - H_o)NP/(k_s + P + k_d P^2) \tag{2}$$

with

$$N = 1 + 2(k_s k_d)^{1/2}$$

where H_o is the equilibrium hydration in the absence of P and H_{max} the maximum hydration (corresponding to the maximum volume of the compartment); k_s and k_d are phenomenological parameters corresponding to swelling and de-swelling domains, respectively; N is introduced to rationalize $f(P)$ ($\forall P, 0 \leq f(P) \leq 1$).

Although our study was defined to be general enough, eq. 2 fits especially well the behavior of a polyelectrolyte gel and in particular the effects of a base (in the case of a polyacid) on its mechanical properties: in domain I, P (OH^-) ionizes acidic groups (swelling); in domain II, a high concentration of P leads to a screening effect of the charges (or salt effect) and thus to a de-swelling. For a given system, if $f(P)$ is first described forward (P increases from a low initial value, i.e., pH increases), $f(P)$ cannot be described backward since the salt effect remains even if pH decreases (during the increase of pH, ionic species have been brought in the medium).

$f(P)$ can be used to mimic other behaviors by considering either domain I alone or domain II alone (by an adequate choice of the different parameters) or the complete variations.

For the mathematical treatment, it is convenient to introduce the variable H^*, defined by $H_{max} - H_o$, which characterizes the range of potential hydration changes.

To allow analytical solutions, a piecewise linearized expression of $f(P)$ was defined:

$$\begin{array}{lll} \text{domain I} & 0 \leq P \leq P_1 & f(P) = P/P_1 \\ \text{domain II} & P_1 \leq P \leq P_2 & f(P) = (P_2 - P)/(P_2 - P_1) \\ \text{domain III} & P \geq P_2 & f(P) = 0 \end{array} \tag{3}$$

3. The evolution equations

The theoretical treatment is based on the expression of a fluid balance and a chemical balance (mass balance for each chemical species). To express the fluid balance, it is necessary to know the fluid flow through the membrane and to relate it to the variations of hydration; to express the chemical balance, it is necessary to know the production rate (or consumption rate) of the considered species and its transport flux by diffusion and convection.

Assuming that the system is in a mechanical quasi-equilibrium state $\mathscr{P} + \pi + p = 0$ ($\mathscr{P}$, hydrostatic pressure; π, osmotic pressure; p, swelling pressure); from Darcy's law, the fluid flow (entering fluid flow) can be expressed by:

$$\Gamma_{\text{fluid}} = K(p_{\text{in}} - p_{\text{out}})/e \tag{4}$$

p_{in} and p_{out} are the swelling pressures inside and outside the reactive compartment, respectively; K is Darcy's constant for the membrane and fluid considered. Assuming $p_{\text{out}} = 0$ (no possibility of swelling in the reservoir), it is convenient to denote p_{in} by p; so, eq. 6 reduces to:

$$\Gamma_{\text{fluid}} = Kp/e \tag{5}$$

Now, consider the liquid volume vol_{liq} at time t:

$$\text{vol}_{\text{liq}} = AlH/(1+H) \tag{6}$$

In time dt, the volume of liquid which enters the system is $KpA\ \mathrm{d}t/e$; it is balanced by a variation in liquid volume which is $A\ \mathrm{d}(lH/(1+H))$:

$$\mathrm{d}(lH/(1+H)) = Kp\ \mathrm{d}t/e \tag{7}$$

Then l is expressed as a function of H and l_{o} (the length of the system corresponding to H_{o}):

$$l = l_{\text{o}}(1+H)/(1+H_{\text{o}}) \tag{8}$$

Combining eqs. 6 and 8 and introducing $\mu = (1 + H_{\text{o}})/(el_{\text{o}})$, leads to the fluid balance equation:

$$\mathrm{d}H/\mathrm{d}t = K\mu p \tag{9}$$

Assuming that diffusion and convection are the only transport processes considered here (no electromigration in particular), the chemical flux Γ_i (flux density) for species i (concentration C_i) is:

$$\Gamma_i = -D(C_i^{\text{o}} - C_i)/e + (v_{\text{real}} + |v_{\text{real}}|)C_i/2 + (v_{\text{real}} - |v_{\text{real}}|)C_i^{\text{o}}/2 \tag{10}$$

C_i^{o} denotes the concentration of species i in the reservoir; v_{real} is the fluid velocity inside the membrane. To simplify the expression of eq. 10, a new parameter α is defined; when $v_{\text{real}} > 0$, $\alpha = 1$ and when $v_{\text{real}} \leq 0$, $\alpha = 0$.

The velocity of the membrane (the boundary of the reactive system) dl/dt is defined by the following relation:

$$\mathrm{d}l/\mathrm{d}t = -v_{\text{average}} = -v_{\text{real}}\phi \tag{11}$$

where ϕ is a parameter characterizing the porosity of the membrane.

Remark: v_{average} is equal to Γ_{fluid}.

The two last terms of eq. 10 are introduced to take into account the possibilities of swelling and de-swelling and the discontinuity of our system (a species enters the system with a concentration C_i^{o} and leaves with a concentration C_i).

At time t, the amount of ions in the total volume of the compartment is: $C_iAlH/(1+H) = C_iAHl_{\text{o}}/(1+H_{\text{o}})$. In time d$t$, the amount of ions entering or produced in the system is: $-\Gamma_i\ \mathrm{d}tA\phi + \nu_i v_{\text{R}}\ \mathrm{d}tAHl_{\text{o}}/(1+H_{\text{o}})$ (v_{R} is the enzyme reaction rate and ν_i a stoichiometric coefficient).

By equating the flows of ions entering or produced with the variation of their amount in the same time, the chemical balance equation in the compartment is obtained:

$$\mathrm{d}(C_iH)/\mathrm{d}t = -\Gamma_i\phi(1+H_{\text{o}})/l_{\text{o}} + \nu_i v_{\text{R}}H \tag{12}$$

The system is governed by the combination of eqs. 1, 2, 5 and 9.

Since our aim here was to obtain analytical solutions, it was necessary to assume zero-order enzyme kinetics; in this case, the term v_{R} becomes:

$$v_{\text{R}} = k_2E_{\text{o}}H_{\text{o}}/H \tag{13}$$

With the assumption of a zero-order kinetics, the behavior of the system is independent of the substrate concentration, and the chemical balance (eq. 12) has only to be expressed for product P.

The behavior of the system is now governed by a set of equations including eq. 9 and the following two equations:

$$H\,\mathrm{d}P/\mathrm{d}t = -\mu P(\phi D_{\mathrm{P}} + Kp(1-\alpha)) + k_2 E_o H_o \tag{14}$$

$$p = \xi(H_o - H + H^* f(P)) \tag{15}$$

4. Dimensionless equations and criteria

To obtain dimensionless equations, which is often useful to define meaningful evolution criteria, new variables were considered: the first of these is the rationalized hydration h:

$$h = H/H_o \tag{16}$$

The dimensionless concentration of P, P', is defined as the ratio of the current concentration over its particular value $P_{\max}$ corresponding to the maximum of $f(P)$; when the linearized form of $f(P)$ is considered, $P_{\max} = P_1$:

$$P' = P/P_{\max} \tag{17}$$

To take into account this new variable, a new function was introduced to replace $f(P)$:

$$f_1(P') = H_o + (H_{\max} - H_o)NP'P_{\max}/\left(k_s + P'P_{\max} + k_d P'^2 P_{\max}^2\right) \tag{18}$$

The dimensionless time variable is defined by:

$$t' = t\mu\phi D_{\mathrm{P}}/H_o \tag{19}$$

The introduction of these variables in the dimensional equations lead to the definition of two dimensionless criteria, a diffusion-reaction criterion:

$$\sigma' = k_2 E_o H_o/(\mu\phi D_{\mathrm{P}} P_{\max}) = k_2 E_o e l_o H_o/(P_{\max}\phi D_{\mathrm{P}}(1 + H_o)) \tag{20}$$

and a diffusion-convection criterion M:

$$M = K\xi H_o/\phi D_{\mathrm{P}} \tag{21}$$

Remark: the notation σ' was adopted instead of σ already used to denote a diffusion-reaction criterion in constant-volume systems; its expression is a little different [4,30]: σ' is the square root of a Thiele-type modulus, in which the classical parameters are adapted to the particular structure and mechanical properties: two characteristic lengths (e and l_o) instead of one, and $H_o/(1 + H_o)$ which leads to the true concentrations of the enzyme in the liquid phase.

Replacing p in eqs. 9 and 14 by its expression in eq. 15, the set of dimensionless equations corresponding to the new variables and parameters is now:

$$h\,\mathrm{d}P'/\mathrm{d}t' = -P'(1 + \alpha M(1 - h + h^* f_1(P')) + \sigma' \tag{22}$$

$$\mathrm{d}h/\mathrm{d}t' = M(1 - h + h^* f_1(P')) \tag{23}$$

From these two differential equations, the values of the hydration and of P concentration corresponding to the steady states (denoted by subscript st) can be calculated:

$$P'_{\mathrm{st}} = \sigma' \tag{24}$$

$$h_{\mathrm{st}} = 1 + h^* f_1(\sigma') \tag{25}$$

It is clear from eqs. 24 and 25 that the steady state (which is unique for zero-order kinetics) does not depend on the diffusion-convection parameter and is only governed by a diffusion-reaction process.

However, as we shall see with the following results, the transient states generally depend both on diffusion, convection and reaction processes.

In order to obtain analytical solutions, the linearized form of $f(P)$ was used and two expressions were derived from eq. 25 to take into account the two domains of $f(P)$:

$$h_{\mathrm{st}} = 1 + h^*\sigma' \qquad \text{domain I} \tag{26}$$

$$h_{\mathrm{st}} = 1 + h^*(P'_2 - \sigma')/(P'_2 - 1) \qquad \text{domain II} \tag{27}$$

5. Analytical solutions for the transient states

We considered the cases of swelling and deswelling of the system and for each case the possibility of control by the fluid flow (convection control: $M \ll 1$) or by the diffusion constraints (diffusion control: $M \gg 1$).

We have considered for the initial conditions a

Table 1

Typical variations of hydration for the different considered cases: swelling or de-swelling of the system ($\sigma' < 1$ or $\sigma' > 1$), swelling or de-swelling limitations by diffusion or fluid flow ($M \gg 1$ or $M \ll 1$)

Conditions of validity				Results		
Swelling or de-swelling	M	σ'	Other assumptions	Steady state	$M \nearrow$	$\sigma' \nearrow$
S	$\ll 1$	$\leqslant 1$	$Mh^* \ll 1$	$h_{st} = 1 + h^*\sigma'$	$\left(\frac{dh}{dt'}\right)_{t'=0}^{\nearrow}$	$h_{st} \nearrow$ $\left(\frac{dh}{dt'}\right)_{t'=0}^{\nearrow}$
S	$\gg 1$	$\leqslant 1$		$h_{st} = 1 + h^*\sigma'$	–	$h_{st} \nearrow$ $\left(\frac{dh}{dt'}\right)_{t'=0}^{\nearrow}$
D	$\ll 1$	$\geqslant 1$ $\leqslant P_2'$	$h \leqslant 3/2$	$h_{st} = 1 + h^* \frac{P_2' - \sigma'}{P_2' - 1}$	$\left(\frac{dh}{dt'}\right)_{t'=0}^{\searrow}$	$h_{st} \searrow$ $\left(\frac{dh}{dt'}\right)_{t'=0}^{\searrow}$
D	$\gg 1$	$\geqslant 1$ $\leqslant P_2'$	$h \leqslant 3/2$	$h_{st} = 1 + h^* \frac{P_2' - \sigma'}{P_2' - 1}$	–	$h_{st} \searrow$ $\left(\frac{dh}{dt'}\right)_{t'=0}^{\searrow}$

zero P concentration inside the reactive compartment when the system swells, and a value corresponding to the maximum of $f(P)$ (P_1) when the system de-swells, and we assumed when the system is de-swelling that it is in domain II; with the considered initial condition, the concentration of the effector P always tends to increase in the system.

To respect these assumptions, the analytical solutions corresponding to P concentrations have to remain in the adequate domains; for this reason, it is clear from eqs. 26 and 27 that the diffusion-reaction parameter has to satisfy one or the other of the two following conditions:

$0 < \sigma' < 1$ in domain I
$1 < \sigma' < P_2'$ in domain II

For the calculations, we used classical approximations for small terms when M was very large or small compared to 1. The accuracy of the analytical solutions was tested by a comparison with numerical solutions. In a general way, there is a good agreement between the analytical and the numerical results.

Typical variations of hydration for the different cases are summarized in table 1.

5.1. Swelling

5.1.1. Fluid flow limitations $M \ll 1$

The expression of the variations of the hydration in terms of time is as follows:

$$h = (h_i - h_{st})\exp(-2h_{st}Mt'/3) + h_{st} \tag{28}$$

$h(t')$ variations are illustrated in fig. 2A for $\sigma' = 0.99$ and for different values of M, and in fig. 2B for $M = 0.03$ and for different values of σ'. It is clear that the lower the M, the higher is the time necessary to reach the steady state (the same for all values of M).

Moreover, the lower the M (i.e., the better the assumption $M \ll 1$), the better is the approximation of the exact solution, especially for short times.

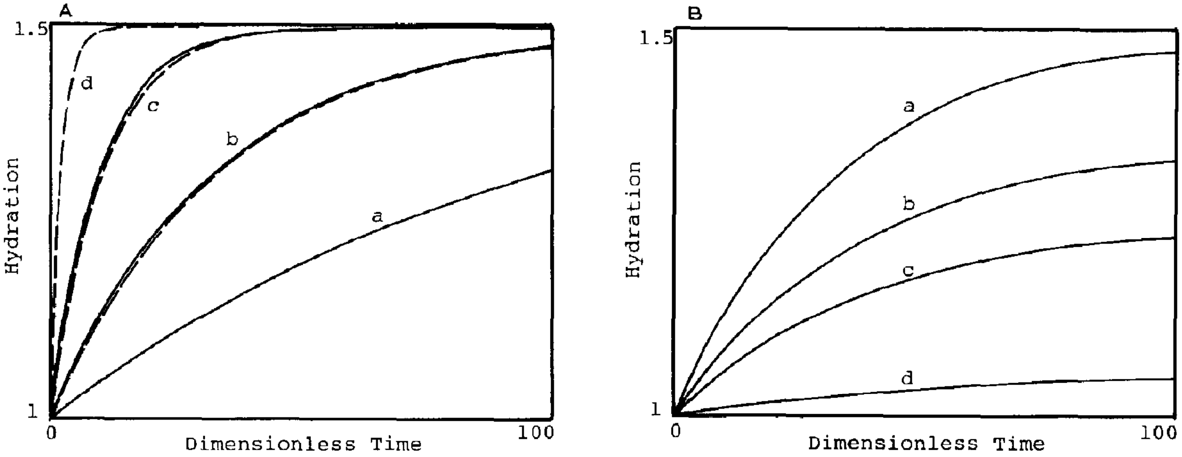

Fig. 2. (A) Hydration variations in terms of dimensionless time, obtained for different values of the diffusion-convection parameter M and for a given value of the diffusion-reaction parameter σ': (———) analytical solutions (obtained for $M \ll 1$ and $\sigma' < 1$), (- - - - - -) numerical solutions (obtained like analytical solutions, with the piecewise linearized form of $f(P)$ (domain I)); $\sigma' = 0.99$; (a) $M = 0.01$, (b) $M = 0.03$, (c) $M = 0.1$, (d) $M = 1$. (B) Hydration variations in terms of dimensionless time, obtained for different values of the diffusion-reaction parameter and for a given value of the diffusion-convection parameter (analytical solutions obtained for $M \ll 1$ and $\sigma' < 1$); $M = 0.03$; (a) $\sigma' = 0.99$, (b) $\sigma' = 0.7$, (c) $\sigma' = 0.5$, (d) $\sigma' = 0.1$.

For a given value of M (fig. 2B), the higher the σ', the higher is the steady-state hydration and the longer the time to reach this steady state.

5.1.2. Diffusion limitations $M \gg 1$

Two limiting cases were considered: (a) the concentration of P is low (short times), (b) the

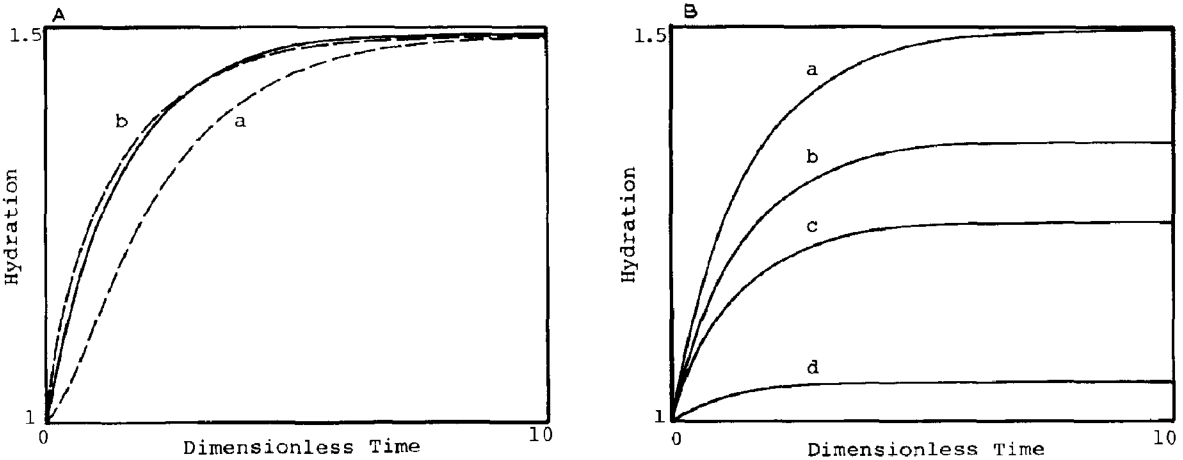

Fig. 3. (A) Hydration variations in terms of dimensionless time, obtained for different values of the diffusion-convection parameter M and for a given value of the diffusion-reaction parameter σ': (———) analytical solutions (obtained for $M \gg 1$ and $\sigma' < 1$), (- - - - - -) numerical solutions (obtained like analytical solutions, with the piecewise linearized form of $f(P)$ (domain I)); $\sigma' = 0.99$; (a) $M = 1$, (b) $M = 100$. (B) Hydration variations in terms of dimensionless time, obtained for different values of the diffusion-reaction parameter and for a given value of the diffusion-convection parameter (analytical solutions obtained for $M \gg 1$ and $\sigma' < 1$); $M = 100$; (a) $\sigma' = 0.99$, (b) $\sigma' = 0.7$, (c) $\sigma' = 0.5$, (d) $\sigma' = 0.1$.

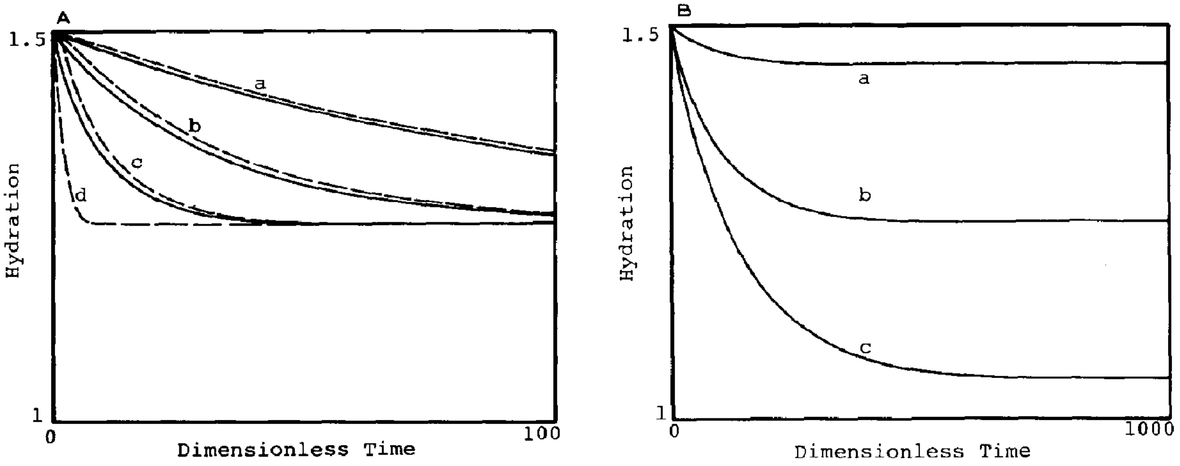

Fig. 4. (A) Hydration variations in terms of dimensionless time, obtained for different values of the diffusion-convection parameter M and for a given value of the diffusion-reaction parameter σ': (———) analytical solutions (obtained for $M \ll 1$ and $P_2' > \sigma' > 1$), (- - - - - -) numerical solutions (obtained like analytical solutions, with the piecewise linearized form of $f(P)$ (domain II)); $\sigma' = 50$; (a) $M = 0.01$, (b) $M = 0.03$, (c) $M = 0.1$, (d) $M = 1$. (B) Hydration variations in terms of dimensionless time, obtained for different values of the diffusion-reaction parameter and for a given value of the diffusion-convection parameter (analytical solutions obtained for $M \ll 1$ and $P_2' > \sigma' > 1$); $M = 0.01$; (a) $\sigma' = 10$, (b) $\sigma' = 50$, (c) $\sigma' = 90$.

system is near the steady state.

For the first case, the expression of the variations of the hydration in terms of time is:

$$h = 1 + \sigma' h^* t' \tag{29}$$

and for the second limit case (fig. 3A and B):

$$h = 1 + \sigma' h^* (1 - \exp(-t'/h_{\text{st}})) \tag{30}$$

Remark 1: Dimensionless eqs. 29 and 30 show that in the two cases σ' is the only parameter of the evolution of the system and thus that the system is governed by a diffusion-reaction regime. However, we have to keep in mind that in this dimensionless representation, the time is not an absolute time but is dependent on the diffusion characteristics of the system and, as a matter of fact, the above conclusion is not exact: the dimensional form of eq. 29:

$$h = 1 + k_2 E_0 h^* t / P_1 \tag{31}$$

shows clearly that the hydration depends only on the reaction for the short times. However, when the system is near the steady state, the conclusion is correct: the system is dependent on both reaction and diffusion processes (in agreement with the expression of the steady-state expression of the hydration).

Remark 2: It is also possible to show that the lower the $h^* \sigma'$, the better eq. 30 fits the entire time course.

As in the previous case, for a given value of M (fig. 3B), the higher the σ', the larger is the steady-state hydration and the longer the time to reach this steady state.

5.2. De-swelling

5.2.1. Fluid flow limitations $M \ll 1$

In this case, in order to obtain an analytical solution, it was necessary to make a supplementary assumption concerning the domain of hydration: $h < 3/2$.

The expression of the hydration in terms of time is (fig. 4A and B):

$$h = (h_i - h_{\text{st}}) \times \exp(-2 M h_{\text{st}} h^* (h_{\max}/h^* - \sigma'/P_2') t'/3) + h_{\text{st}} \tag{32}$$

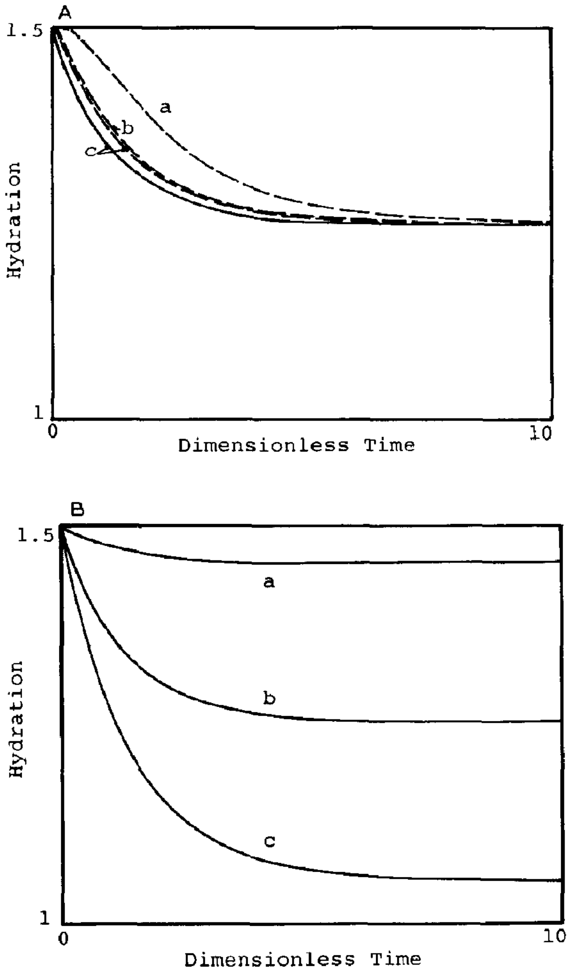

Fig. 5. (A) Hydration variations in terms of dimensionless time, obtained for different values of the diffusion-convection parameter M and for a given value of the diffusion-reaction parameter σ': (———) analytical solutions (obtained for $M \gg 1$ and $P_2' > \sigma' > 1$), (- - - - - -) numerical solutions (obtained like analytical solutions, with the piecewise linearized form of $f(P)$ (domain II)); $\sigma' = 50$; (a) $M = 1$, (b) $M = 10$, (c) $M = 100$. (B) Hydration variations in terms of dimensionless time, obtained for different values of the diffusion-reaction parameter and for a given value of the diffusion-convection parameter (analytical solutions obtained for $M \gg 1$ and $P_2' > \sigma' > 1$); $M = 100$; (a) $\sigma' = 10$, (b) $\sigma' = 50$, (c) $\sigma' = 90$.

It appears (fig. 4A) that the lower the M, the better is the agreement between our approximate analytical solutions and the numerical solutions.

It is possible to conclude that the lower the M, the longer is the time necessary to reach the steady state. Moreover, the higher the σ', the lower is the steady-state hydration level and the longer the time necessary to reach this steady state.

5.2.2. Diffusion limitations $M \gg 1$

As for the latter case, we assume that the dimensionless hydration is lower than 3/2, and the expression of the hydration in terms of time is (fig. 5A and B):

$$h = (h_i - h_{st}) \exp(-2h^*(h_{max}/h^* - \sigma'/P_2')t'/3) + h_{st} \qquad (33)$$

With diffusion limitations, there appears, especially for short times, a greater discrepancy between our analytical solution and the 'exact' computed solution ($M = 500$, $\sigma' = 50$) (fig. 5A).

In this case, the higher the σ', the lower is the steady-state hydration and the longer the time necessary to reach this steady state (fig. 5B).

6. Discussion

In this paper, we have studied the dynamics of volume changes of a model system, in which mechanical, diffusion and reaction processes were coupled.

The study was based on the use of a material which has the property of swelling in the presence of a chemical effector produced by an enzymic reaction.

Three limiting factors of volume change rate were considered: fluid flow limitation, diffusion limitation or reaction limitation.

Hydration instead of volume was preferred in this study for an easier theoretical formulation and all results were expressed in terms of hydration.

The separation in space of transport and reaction processes thanks to a compartmental structure, and the use of a piecewise linearized form of the constitutive law (swelling and de-swelling regimes) allowed, in conjunction with other assumptions, analytical solutions of the evolution differential equations which were compared to exact numerical solutions.

Dimensionless parameters were introduced: σ', the diffusion-reaction parameter and M, the diffusion-convection parameter, allowing predictions in limiting cases.

The results show that the steady states are independent of convection processes and depend only on diffusion-reaction characteristics. However, the transient states depend both on diffusion, convection and reaction.

General conclusions (see table 1) are that the higher the σ', the higher are the variations in hydration but the longer the time necessary to reach the steady state. Conversely, the lower the M, the longer is the time necessary to reach the steady state.

These first results limited to analytical solutions in particular cases were extended to general cases by extensive numerical solutions which will be reported elsewhere.

This first approach will have to be developed to take into account other types of structures, more complex chemical schemes (considering substrate dependences in particular), and materials with more precisely defined characteristics, in order to be able to elaborate original systems for energetic or analytical applications.

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