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Modelling a catalytic membrane reactor with plug flow pattern and a hypothetical equilibrium gas-phase reaction with $\Delta n \neq 0$

José M. Sousa [a,b], Adélio Mendes [b,*]

[a] *Universidade de Trás-os-Montes e Alto Douro, Departamento de Química, Apartado 202, 5001-911 Vila-Real Codex, Portugal*

[b] *LEPAE – Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Roberto Frias, 4200-465 Porto, Portugal*

Abstract

The scope of this paper is to present a theoretical study of a catalytic polymeric dense membrane reactor (CPDMR) assuming isothermal conditions, plug flow pattern without pressure drop in both retentate and permeate sides, shell side feed and cocurrent operation. The conversion enhancement over the thermodynamic equilibrium value is studied for a gas-phase reaction of the type $a\mathrm{A} \rightleftharpoons b\mathrm{B}$, considering two different stoichiometric ratios: $\Delta n > 0$ and $\Delta n < 0$, where $\Delta n = b - a$. For each of these cases, the influence of the relative sorption and diffusivity of the reaction species is studied. It is concluded that the conversion of a reversible reaction can be significantly enhanced when the diffusivity of the reaction products is higher than that of the reactants and/or the sorption is lower. It is also concluded that, even for equal sorption and diffusion coefficients, the conversion could also be improved for reactions with $\Delta n \neq 0$. The extension of this enhancement depends on the reaction stoichiometry, the overall concentration inside the membrane, the Thiele modulus, and the contact time.

Keywords: Catalytic membrane reactor; Plug flow pattern; Gas-phase reaction; Equilibrium reaction; Modelling

1. Introduction

A membrane reactor is a generic concept applied to a chemical system that incorporates a catalytic reactor and a membrane, independently of its function, with several configurations proposed and extensively reviewed [1,2]. Among others, two main categories of membrane reactors can be distinguished: the ‘‘catalytic membrane reactor’’ (CMR), where the membrane is catalytic and could be or not permselective and the ‘‘packed-bed membrane reactor’’ (PBMR), where the membrane performs only a separation function.

Most of the nowadays studied and discussed membrane reactors use inorganic membranes, because the chemical reactions to be carried out in such reactors are normally conducted in harsh conditions concerning both temperature and chemical environment. So it is not surprising that polymeric membranes have hardly ever been utilised, except in biocatalysis [2]. However, they have attracted an increasing interest in the last few years, as they offer some advantages over their inorganic counterparts [2–4]. Besides, polymeric membranes can be easily produced with incorporated catalysts (nano-sized dispersed metallic clusters [5,6], zeolites and activated carbons [7] or metallic complexes [8,9]) and can be easily made in different forms (flat, tubes, tubules, hollow fibres, spiral wound) [1,8,10]. The ability of these materials to be, in some way, tailored to the needs makes them very promising for future applications.

As a consequence of such developments, there is a growing need for effective theoretical models that could help to understand the potential and the limitations of polymeric membrane reactors, leading to optimised designs. In the open literature, there are several studies about membrane reactor modelling, although only a few actually deal with CMRs [2,11–14]. To the best of our knowledge and beyond our recent work [12,13], only a few researchers [11,14] actually modelled polymeric catalytic membrane reactors, however for conducting liquid-phase reactions and considering completely mixed flow pattern in both sides.

We have already analysed the performance of a dense polymeric catalytic membrane reactor when running an

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* Corresponding author. Tel.: +351 22 5081695; fax: +351 22 5081449.
E-mail address: mendes@fe.up.pt (A. Mendes).

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Nomenclature

a	stoichiometric coefficient for the reactant [–]
b	stoichiometric coefficient for the reaction product [–]
c	partial concentration [mol/m^3]
C	total concentration [mol/m^3]
D	diffusion coefficient [m^2/s]
H	Henry's sorption coefficient [mol/(m^3 Pa)]
k_d	direct reaction rate constant [(mol/m^3)$^{(1-a)}$/s]
K_e	reaction equilibrium constant [(mol/m^3)$^{b-a}$]
L	reactor's length [m]
p	partial pressure [Pa]
P	total pressure [Pa]
Q	volumetric flowrate [m^3/s]
r	spatial coordinate relative to the membrane [m]
r^s	external membrane radius (shell side) [m]
r^t	internal membrane radius (tube side) [m]
$\Re$	universal gas constant [Pa m^3/(mol K)]
T	absolute temperature [K]
X	conversion [–]
z	spatial coordinate relative to the tube/shell [m]
Greek symbols	
Γ	dimensionless contact time parameter [–]
δ	membrane thickness [m]
Δn	net change of the total moles number [–]
Θ	relative reaction coefficient [–]
λ	dimensionless spatial coordinate relative to the tube/shell [–]
ν	stoichiometric coefficient (positive for products, negative for reactants) [–]
ρ	dimensionless spatial coordinate relative to the membrane [–]
Φ	Thiele modulus [–]
χ_A	relative conversion (X_A/X_A^e) [–]
Subscripts	
i	relative to the ith component [–]
ref	relative to the reference conditions or component [–]
Superscripts	
*	dimensionless variable [–]
F	relative to the feed stream conditions [–]
P	relative to the permeate stream conditions [–]
R	relative to the retentate stream conditions [–]

equilibrium gas-phase reaction, assuming a plug flow pattern on the retentate and permeate sides and isothermal conditions [13]. In the previous work, a hypothetical reaction described by the scheme $a\mathrm{A} \rightleftharpoons b\mathrm{B}$, with a, $b = 1$ was considered. We treat the same model reaction in the present work, but now with a net change of the total number of moles due to the reaction stoichiometry ($b - a \neq 0$). A systematic study of the reactor performance, that is, the conversion enhancement over a thermodynamic equilibrium value is made, taking into account the influence of the reaction stoichiometry and the relative sorption and diffusion coefficients of the reaction products.

2. Membrane reactor model

Fig. 1 represents a sketch of the catalytic membrane reactor considered in the present study, consisting of a tube and shell chamber separated by a cylindrical catalytic membrane. A shell side feed with cocurrent operation is assumed, because this configuration leads, in most of the situations, to a higher chemical conversion than the tube side feed and/or counter-current operating modes [15]. The proposed model is based on the same main assumptions already described in [13].

The mathematical model comprises the steady state mass balances for the membrane, the retentate, and the permeate sides, as well as the respective boundary conditions. In dimensionless form, the equations are as follows:

2.1 Mass balance and boundary conditions for the membrane

$$D_i^*\left(\frac{\mathrm{d}^2c_i^*}{\mathrm{d}\rho^2}+\frac{1}{\rho+r^t/\delta}\frac{\mathrm{d}c_i^*}{\mathrm{d}\rho}\right)+\nu_i\Phi^2\left((c_A^*)^a-(c_B^*)^b\frac{(C_{\mathrm{ref}})^{\Delta n}}{K_e}\right)=0 \qquad (1)$$

$$\rho=0\,(\forall\lambda),\quad c_i^*(\lambda)=H_i^*P_i^{P^*}(\lambda);\qquad \rho=1\,(\forall\lambda),\quad c_i^*(\lambda)=H_i^*p_i^{R^*}(\lambda) \qquad (2)$$

2.2 Mass balances and boundary conditions for the retentate side

$$\frac{\mathrm{d}(Q^{R^*}p_i^{R^*})}{\mathrm{d}\lambda}-\left(1+\frac{\delta}{r^t}\right)\Gamma D_i^*\left.\frac{\mathrm{d}c_i^*}{\mathrm{d}\rho}\right|_{\rho=1,\lambda}=0 \qquad (3)$$

$$P^{R^*}\frac{\mathrm{d}Q^{R^*}}{\mathrm{d}\lambda}-\left(1+\frac{\delta}{r^t}\right)\Gamma\sum_i D_i^*\left.\frac{\mathrm{d}c_i^*}{\mathrm{d}\rho}\right|_{\rho=1,\lambda}=0 \qquad (4)$$

$$\lambda=0,\quad p_i^{R^*}=p_i^{F^*},\quad \text{and}\quad Q^{R^*}=1 \qquad (5)$$

2.3 Mass balances and boundary conditions for the permeate side

$$\frac{\mathrm{d}(Q^{P^*}p_i^{P^*})}{\mathrm{d}\lambda}+\Gamma D_i^*\left.\frac{\mathrm{d}c_i^*}{\mathrm{d}\rho}\right|_{\rho=0,\lambda}=0 \qquad (6)$$

$$P^{P^*}\frac{\mathrm{d}Q^{P^*}}{\mathrm{d}\lambda}+\Gamma\sum_i D_i^*\left.\frac{\mathrm{d}c_i^*}{\mathrm{d}\rho}\right|_{\rho=0,\lambda}=0 \qquad (7)$$

$$\lambda=1,\quad \frac{\mathrm{d}p_i^{P^*}}{\mathrm{d}\lambda}=0;\qquad \lambda=0,\quad Q^{P^*}=0 \qquad (8)$$

where $c_i^*=c_i/C_{\mathrm{ref}}$, $P^*=P/P_{\mathrm{ref}}$, $p_i^*=p_i/P_{\mathrm{ref}}$, $Q^*=Q/Q_{\mathrm{ref}}$, $D_i^*=D_i/D_{\mathrm{ref}}$, $H_i^*=H_i/H_{\mathrm{ref}}$, $C_{\mathrm{ref}}=H_{\mathrm{ref}}P_{\mathrm{ref}}$, $\lambda=z/L$, $\rho=(r-r^t)/\delta$, $\Gamma=2\pi r^t LD_{\mathrm{ref}}H_{\mathrm{ref}}\Re T/\delta Q_{\mathrm{ref}}$,

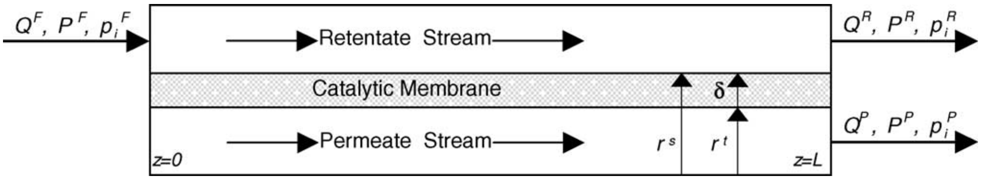

Fig. 1. Schematic diagram of the dense catalytic tubular membrane reactor (for cocurrent flow and shell side feed).

$\Phi = \delta[(k_d(C_{\text{ref}})^{a-1})/D_{\text{ref}}]^{1/2}$, Φ is the Thiele modulus and Γ is the dimensionless contact time. Feed conditions are taken as reference for P_{ref} and Q_{ref}. Component A is taken as reference for D_{ref} and H_{ref}. The remaining symbols are described in the nomenclature.

The membrane reactor performance is evaluated based on the obtained relative conversion, χ_A, which is defined as the ratio between the conversion of reactant A reached in the membrane reactor, X_A, and the thermodynamic equilibrium conversion based on the feed conditions, X_A^e. The attained conversion in the reactor is calculated in the usual way:

$$X_A = 1 - \frac{Q^{R^*} p_A^{R^*} + Q^{P^*} p_A^{P^*}}{Q^{F^*} p_A^{F^*}} \tag{9}$$

The relative reaction coefficient, which measures how far the reaction is from the thermodynamic equilibrium, is defined as:

$$\Theta = \frac{(c_B^*)^b}{(c_A^*)^a} \frac{(C_{\text{ref}})^{\Delta n}}{K_e} \tag{10}$$

3. Solution of the model equations

The general strategy used for solving the equations is the same as adopted before [15]: a time derivative term was added to the right-hand side of Eqs. (1), (3), and (6), transforming this problem into a pseudo-transient one. The resulting partial differential equations, connected with Eqs. (4) and (7), were spatially discretised using orthogonal collocation [16]. The time integration routine LSODA [17] was then used to integrate the resulting set of time dependent ordinary differential equations. A suitable variable transformation of the spatial coordinates (collocation points for the membrane and tube/shell) as a function of the Thiele modulus was applied in order to obtain a solution with high accuracy and low computational effort [18]. For all simulations 9 internal collocation points in the tube/shell and 11 internal collocation points in the membrane were used. This number proved to be sufficient for the most extreme operating conditions [18].

4. Results and discussion

This study aims to show how the relative conversion obtained in the present reactor depends on the relative sorption (H_i^*) and diffusion (D_i^*) coefficients of the reacting species, along the contact time and Thiele modulus parametric space, and for reactions with a net change of the total moles number, $\Delta n > 0$ and $\Delta n < 0$. Some of the model parameters and operating variables are considered constant throughout all simulations, namely: the feed composition, $p_A^{F^*} = 1$; the dimensionless permeate pressure, $P^{P^*} = 0.1$; the reference pressure, $P_{\text{ref}} = 100$ kPa; the reference sorption, $H_{\text{ref}} = 1$ mol/(kPa m^3); the ratio between the internal membrane radius and the membrane thickness, $r^t/\delta = 5$. Finally, a thermodynamic equilibrium conversion, X_A^e, equal to 0.2 is assumed. The corresponding value of the thermodynamic equilibrium constant, K_e, was calculated accordingly to the reaction stoichiometry.

4.1. Base case: equal sorption and diffusion for all reaction species

It was shown in a previous study [13] that the maximum conversion reached in a catalytic polymeric dense membrane reactor (CPDMR), for a reaction with equal stoichiometric, sorption, and diffusion coefficients, is the thermodynamic equilibrium value. However, considering the same sorption and diffusion coefficients for reactants and products, the maximum attained conversion in a CPDMR for an equilibrium gas-phase reaction with positive or negative net change of the total number of moles could be higher than the thermodynamic equilibrium value. This would be an expected result for reactions with $\Delta n > 0$ (Fig. 2), as a consequence of Le Chatelier's principle, but not for reactions with $\Delta n < 0$ (Fig. 4). In fact, the results shown in Figs. 2 and 4 are primarily a net result of the two main factors given below.

4.1.1. Total concentration gradient

The gradient of the total pressure between the retentate and the permeate side leads to a total concentration gradient across the membrane. According to Le Chatelier's principle, a decrease in the total concentration of a reactive system is favourable, in terms of the attained conversion, for equilibrium-limited reactions with $\Delta n > 0$ and unfavourable for reactions with $\Delta n < 0$.

4.1.2. Sorption capacity of the membrane

For reactions with $\Delta n \neq 0$ the reaction rate depends also on the total concentration at reference conditions, $C_{\text{ref}} = H_{\text{ref}}P_{\text{ref}}$ (see Eq. (1)). So, the affinity of the membrane for the reaction species, set by the H_i values, is another factor that defines the conversion level attained in the catalytic

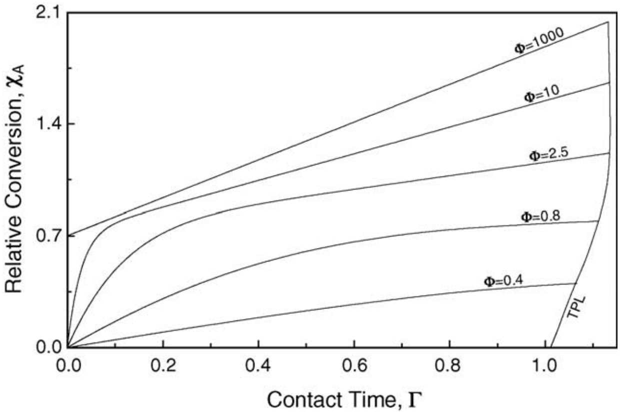

Fig. 2. Relative conversion as a function of the contact time for different values of the Thiele and a reaction with $\Delta n > 0$. $D_i^* = 1$, $H_i^* = 1$, $\nu_A = 1$, $\nu_B = 2$, and $K_e = 8.020$ mol/m^3.

membrane reactor. We should mention that, though the value of C_{ref} depends also on P_{ref}, the thermodynamic equilibrium conversion is affected as well by the same value. So, only the parameter H_{ref} effectively influences the reactor performance. The global conversion is favoured by a C_{ref} value as low as possible for reactions with $\Delta n > 0$ and as high as possible for reactions with $\Delta n < 0$ [12].

Fig. 2 shows the relative conversion of species A as a function of the contact time, for several values of the Thiele modulus and a reaction with $\Delta n > 0$. Globally, these results express the influence of the total concentration gradient and the overall sorption capacity, as explained above. However, a deeper analysis of the results is more subtle and interesting. For low values of the Thiele modulus, where the chemical reaction stage is below or at the thermodynamic equilibrium condition over the whole membrane thickness and along the whole reactor length (Fig. 3A and C), conversion increases more or less linearly with contact time until the total permeation condition (no retentate flow rate is leaving the reactor) is reached, essentially due to the decrease of the reactant loss with the retentate stream (Fig. 2). As the Thiele modulus increases, two different regions along the contact time parameter become evident (Fig. 2). For the low contact time region, conversion increases at a rate strongly dependent on the Thiele modulus. For the remaining contact time range, conversion increases along this parameter at a slower rate and much less dependent on the Thiele modulus. The locus of the endpoints corresponding to the total permeation condition defines the total permeation line, TPL.

For the low contact time region, the chemical reaction stage is always below or at the thermodynamic equilibrium (see Fig. 3B). Thus, an increase of the contact time, i.e., an increase of the feed fraction that penetrates into the membrane, as well as an increase of the Thiele modulus, leads to a more effective use of the catalyst and conversion increases more or less quickly with the Thiele modulus (Fig. 2). For these low contact time values, the whole reactor length contributes to the increase of conversion (Fig. 3D).

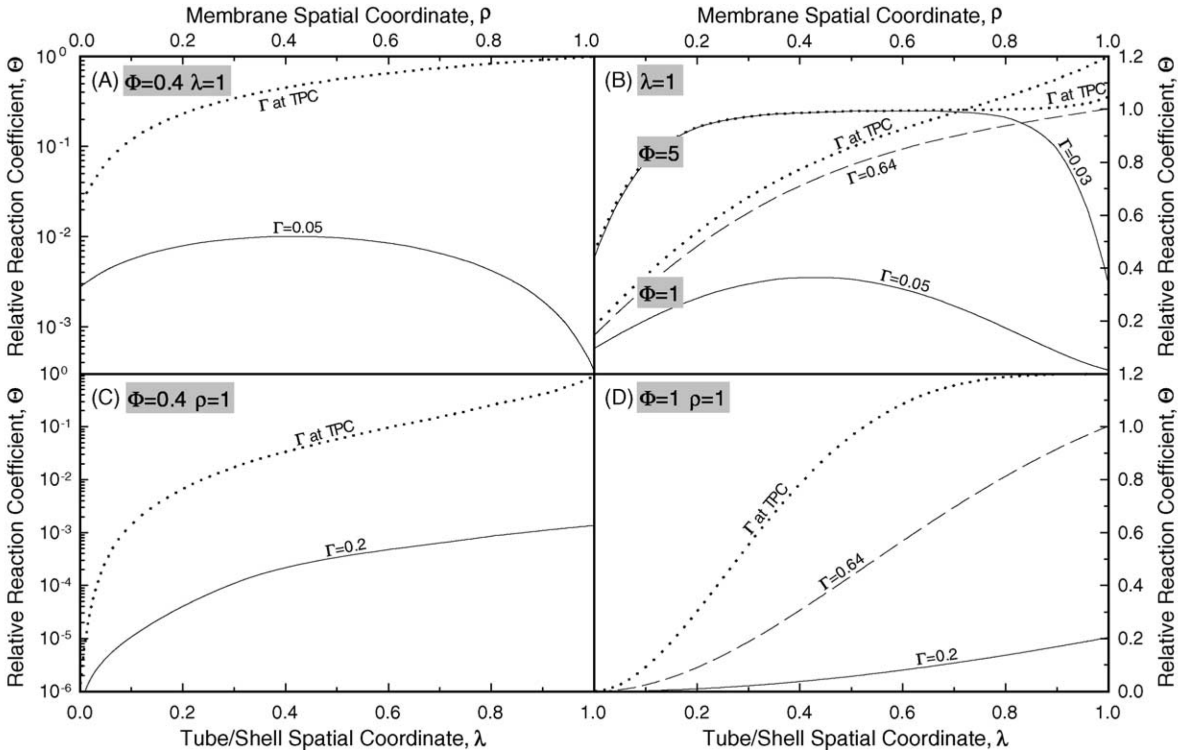

Fig. 3. Relative reaction coefficient at the reactor exit as a function of the membrane radial coordinate (A and B) and as a function of the axial coordinate for the shell side membrane surface (C and D) for some values of the Thiele modulus and the contact time, and for a reaction with $\Delta n > 0$. $D_i^* = 1$, $H_i^* = 1$, $\nu_A = 1$, $\nu_B = 2$, and $K_e = 8.020$ mol/m^3.

However, for a certain contact time, lower than the one at total permeation, which depends on the Thiele modulus, the reaction coefficient becomes unitary (the chemical reaction is at the thermodynamic equilibrium) on the upstream membrane surface and for the reactor exit ($z = L$), as it can be seen in Fig. 3B and D for $\Phi = 1$ and $\Gamma = 0.64$. A further increase of the contact time leads to a displacement of this condition of $\Theta = 1$ towards lower values of the axial coordinate and to a chemical reaction stage beyond the thermodynamic equilibrium in an inward fraction of the membrane thickness upstream, as shown in Fig. 3B and D. As a consequence, the reverse reaction and the backward diffusion (to the membrane) of component B produced upstream (i.e., for lower z values) slow down the conversion increase or even decrease conversion, for what concerns the retentate stream contribution. On the other hand, due to the imposed total concentration gradient across the membrane, the reaction coefficient pulls down in a downstream membrane fraction (Fig. 3A and B), allowing then a more effective usage of the catalyst along the contact time and the Thiele modulus parameters. As a result, the contribution to conversion that comes from the permeate stream is always positive. The net balance of these two contributions (retentate and permeate streams) results in the slow down of the conversion increase after a certain contact time, as shown in Fig. 2.

Analysing the conversion evolution for an instantaneous reaction ($\Phi = 1000$) and for very low contact time, the negative impact of the overall sorption capacity on the reactor performance becomes clear, expressed in terms of the lowering of the conversion relative to the thermodynamic equilibrium value ($\chi_A \approx 0.7$, Fig. 2). For this set of parameters, the reaction occurs at the upstream membrane surface, so at the highest possible concentration. Therefore, the beneficial gradient of the total concentration across the membrane does not influence the attained conversion, because the contribution to the reactor performance depends almost exclusively on the retentate stream conditions. Comparing the assumed value of C_{ref} for the membrane (100 mol/m^3) and the equivalent value in the gas-phase ($P_{\mathrm{ref}}/T_{\mathrm{ref}} \approx 40$ mol/m^3) it becomes clear that the membrane actuates as an overall concentrator.

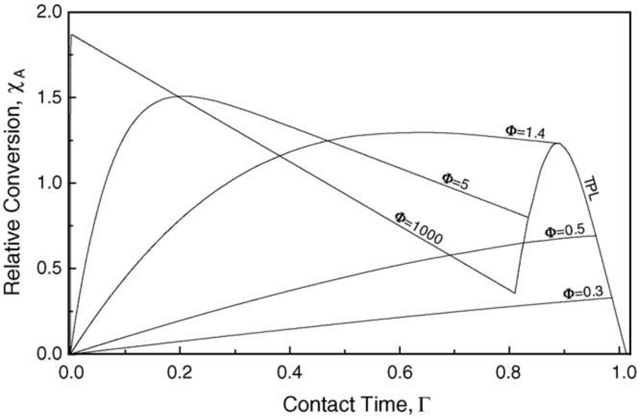

Fig. 4. Relative conversion as a function of the contact time for different values of the Thiele modulus and a reaction with $\Delta n < 0$. $D_i^* = 1$, $H_i^* = 1$, $\nu_A = 2$, $\nu_B = 1$, and $K_e = 0.004$ m^3/mol.

Following the same reasoning, the large positive impact of the overall sorption capacity on the attained conversion for the reaction considered can be seen when $\Delta n < 0$ (Fig. 4). Despite the negative impact of the total concentration gradient, it is still possible to attain some conversion enhancement relative to the thermodynamic equilibrium value in a considerable region of the parameter space concerning the contact time and the Thiele modulus.

The negative impact of the total concentration gradient shown in Fig. 4 can be better understood through analysis of Fig. 5. For low values of the Thiele modulus, the efficiency of utilisation of the catalyst, i.e., the fraction of the reactant that contacts the catalyst increases with increasing contact time, thus leading to an increase of conversion (see Figs. 4 and 5A). On the other hand, the chemical reaction stage gets beyond the thermodynamic equilibrium somewhere in an inward fraction of the membrane thickness further downstream, promoting this way the reverse reaction and, consequently, decreasing conversion (Fig. 5A). While the impact of the reverse reaction is low, for a kinetically controlled regime, the net balance between these two factors favours the first one, thus resulting

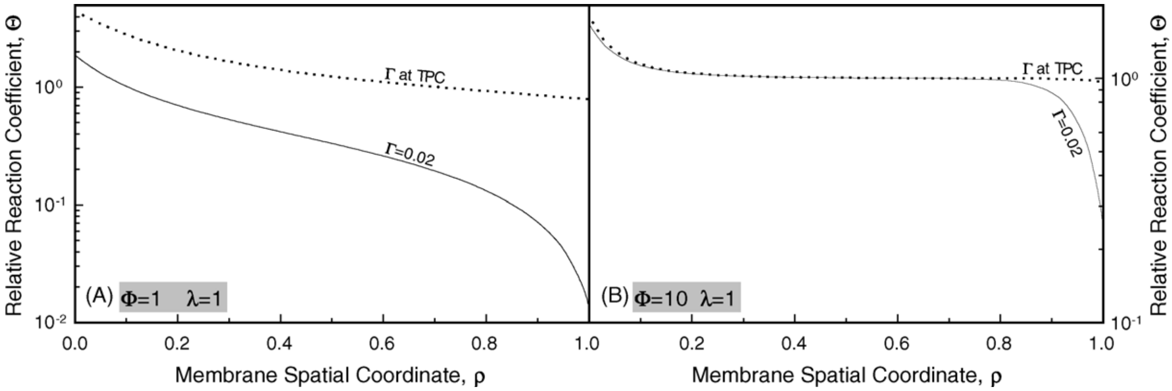

Fig. 5. Relative reaction coefficient at the reactor exit as a function of the radial coordinate for some values of the Thiele modulus and the contact time, and for a reaction with $\Delta n < 0$. $D_i^* = 1$, $H_i^* = 1$, $\nu_A = 2$, $\nu_B = 1$, and $K_e = 0.004$ m^3/mol.

in a monotonous increase of conversion with contact time until the total permeation condition (Fig. 4).

Increasing the Thiele modulus, for its turn, increases accordingly the rate of both direct and reverse reactions and the contributions to conversion from the retentate and permeate streams cancel out partially. That is, the chemical reaction reaches the thermodynamic equilibrium closer and closer to the upstream membrane surface, thus contributing positively to conversion. On the other hand, the reverse reaction prevents that the chemical reaction stage goes beyond the thermodynamic equilibrium, thus contributing negatively to the conversion increase (Fig. 5B). The impact of the reverse reaction becomes noticeable only in the contribution from the permeate stream. So, the conversion increases more or less quickly for low contact times, depending on the Thiele modulus, essentially due to the much higher contribution of the retentate stream (high pressure side, favourable for the reaction). At a certain contact time, the retentate stream conditions at the end of the reactor become unchangeable, because, for some internal axial position, the chemical composition on the upstream membrane surface reaches equilibrium. From this contact time on, the conversion decreases continuously until to the total permeation condition, because of the higher and higher contribution of the permeate stream (low pressure side, unfavourable for the reaction).

4.2. Higher permeability for the reaction product

Fig. 6 shows the relative conversion as a function of contact time and Thiele modulus for the case with $\Delta n > 0$ and a diffusion coefficient of the reaction product higher than that of the reactant. Comparing such results with those from Fig. 2 (where only the effect of the total concentration gradient is present) and those from the previous work [13] (where only the separation effect is present) it is possible to identify clearly the influence of each of these two factors in different regions of the Thiele modulus/contact time parametric space. Firstly, it is possible to identify, for relatively low values of the Thiele modulus ($\Phi < 4$), the synergy coming from the influence of the reaction stoichiometry (total concentration gradient) and, essentially, the separation effect. The combination of both, total concentration gradient and separation effect, results in a fast increase of conversion with the Thiele modulus, for medium to high contact time values. For higher and higher values of the Thiele modulus, the separation effect is progressively reduced until it completely vanishes for an instantaneous reaction and then the reactor conversion behaviour reflects more and more only the influence of the total concentration gradient. The evolution of the contact time at the total permeation condition (line TPL) shows the dominant influence of the separation effect. We should mention at this point that the effect of the overall sorption capacity is not taken into account for the analysis of the present (and future) results, because it does not change the global pattern of the results.

Fig. 7 shows the relative conversion as a function of the contact time and the Thiele modulus for a diffusion coefficient of the reaction product higher than that of the reactant, but now for the case of $\Delta n < 0$. As in the case of $\Delta n > 0$, the evolution of conversion along the region of low values of the Thiele modulus and for medium to high contact times reflects the conjugated influence of the total concentration gradient, and, essentially, the separation effect. For medium to high values of the Thiele modulus, the conversion behaviour reflects more and more only the influence of the total concentration gradient. The evolution of the contact time and conversion at the total permeation condition (line TPL) shows the conjugated effect of the total concentration gradient and the separation effect.

In another set of simulations (results not shown here), the influence of the relative sorption coefficients was studied. All diffusion coefficients were assumed to be equal and the same relative permeability as in the previous case (reported in Figs. 6 and 7) was assumed. Globally, the trend of the

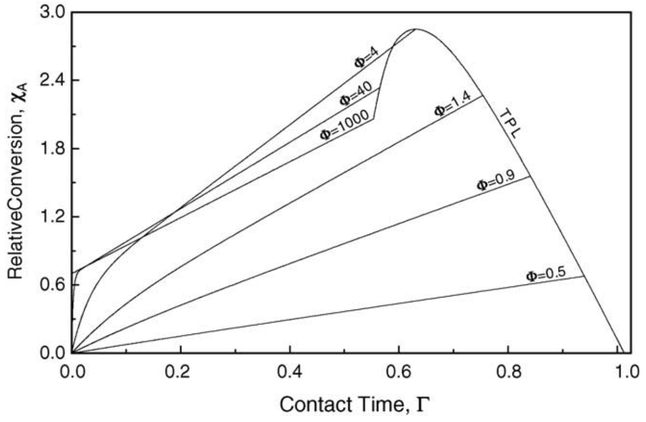

Fig. 6. Relative conversion as a function of the contact time for different values of the Thiele modulus and a reaction with $\Delta n > 0$. $D_A^* = 1, D_B^* = 10$, $H_i^* = 1$, $\nu_A = 1$, $\nu_B = 2$, and $K_e = 8.020$ mol/m^3.

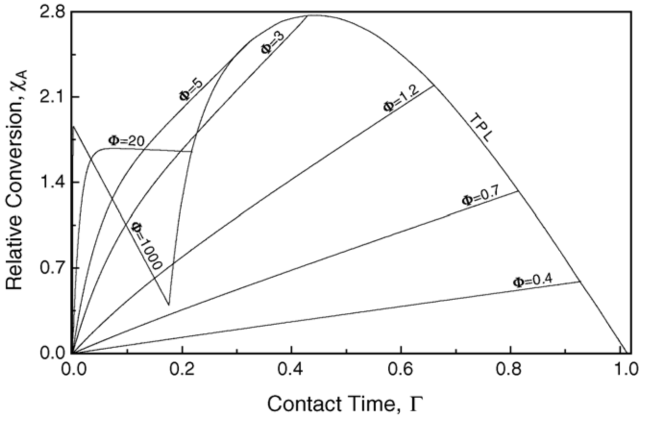

Fig. 7. Relative conversion as a function of the contact time for different values of the Thiele modulus and a reaction with $\Delta n < 0$. $D_A^* = 1, D_B^* = 10$, $H_i^* = 1$, $\nu_A = 2$, $\nu_B = 1$, and $K_e = 0.004$ m^3/mol.

conversion for the entire contact time and Thiele modulus parametric region is essentially the same as that shown in Figs. 6 and 7, but a distinct difference is seen in quantitative terms, depending on the reaction stoichiometry.

For the reaction case of $\Delta n > 0$ and with a sorption coefficient of the reaction product higher than that of the reactant, for example, the conversion is strongly penalised in the entire contact time/Thiele modulus parametric region relative to the results presented in Fig. 6. Even the maximum conversion, which is also reached for an intermediate value of the Thiele modulus at the total permeation condition (because of the unchanged separation effect) is lower than the corresponding value attained when solely the separation effect is present ($\Delta n = 0$), for equal diffusion coefficients. These results show that the effect of the total concentration gradient for a reaction of such stoichiometry is negative when the reaction product has a higher sorption coefficient. Beyond the excess of the reaction product in the reaction medium, due to the membrane capacity to concentrate such species, the reaction stoichiometry leads to a relative production of the reaction product higher than for the case of $\Delta n = 0$. Thus, conversion is doubly penalised.

For a reaction with $\Delta n > 0$ and a higher sorption coefficient of the reaction product, on the other hand, conversion is only moderately penalised relative to the results presented in Fig. 7. Actually, its maximum is even significantly higher than the corresponding one reached when solely the separation effect is present, $\Delta n = 0$, for equal diffusion coefficients. Now, the effect of the total concentration gradient for a reaction of such stoichiometry is positive when the reaction product has a higher sorption coefficient. In a certain way, the excess of such species in the reaction medium, due to the ability of the membrane to concentrate them, is partially attenuated by the reaction stoichiometry, because the relative production of the reaction product is lower than for the case of $\Delta n = 0$.

4.3. Lower permeability for the reaction product

Fig. 8 shows the relative conversion as a function of contact time and Thiele modulus for the case of $\Delta n > 0$ and a sorption coefficient of the reaction product lower than that of the reactant. For this set of parameter values, the negative effect caused by the relative "excess" of the reaction product promoted by the stoichiometry, relative to the case with $\Delta n = 0$, is partially cancelled by the low sorption capacity of the membrane for such species. Thus, even for the region of high values for the Thiele modulus, where the total concentration gradient effect dominates the separation effect, there is a great enhancement of conversion (Fig. 8).

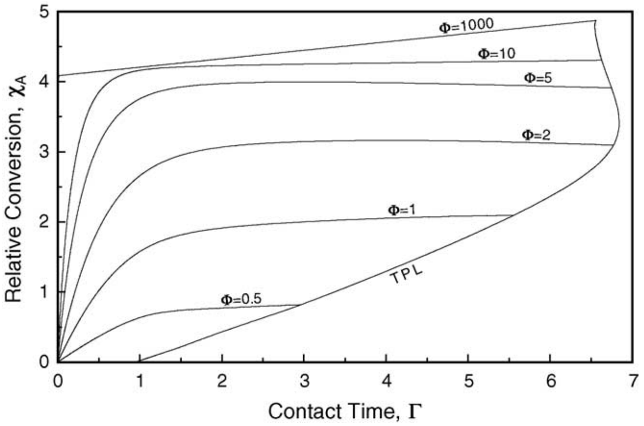

Fig. 8. Relative conversion as a function of the contact time for different values of the Thiele modulus and a reaction with $\Delta n > 0$. $D_i^* = 1$, $H_A^* = 1$, $H_B^* = 0.1$, $\nu_A = 1$, $\nu_B = 2$, and $K_e = 8.020$ mol/m^3.

Fig. 9 shows the relative conversion as a function of the contact time and the Thiele modulus for the case of $\Delta n < 0$ and a sorption coefficient of the reaction product lower than that of the reactant. Generically, such results express the balance between two opposite trends: on one hand, the lower sorption of the reaction product favours conversion. On the other hand, lower sorption penalises conversion for a reaction of the stoichiometry considered, because the relative production of the reaction product is lower than for a reaction with $\Delta n = 0$.

The evolution of the contact time and the conversion at the total permeation condition (line TPL), for both reaction cases, shows the conjugated effect of the transmembrane concentration gradient and the separation effect. In particular for the case where $\Delta n < 0$ (Fig. 9), it is clear that the relative influence of each factor depends on the Thiele modulus, though the most important influence is due to the separation effect.

In a separate set of simulations (results not shown here), the influence of the relative diffusion coefficients was studied. All sorption coefficients were assumed equal and the same relative permeability as in the previous case (Figs. 8 and 9) was used. Globally, the trend of conversion for the entire contact time/Thiele modulus parametric region is essentially the same as that shown in Figs. 8 and 9. That is, the separation effect is the most important factor for the low to medium

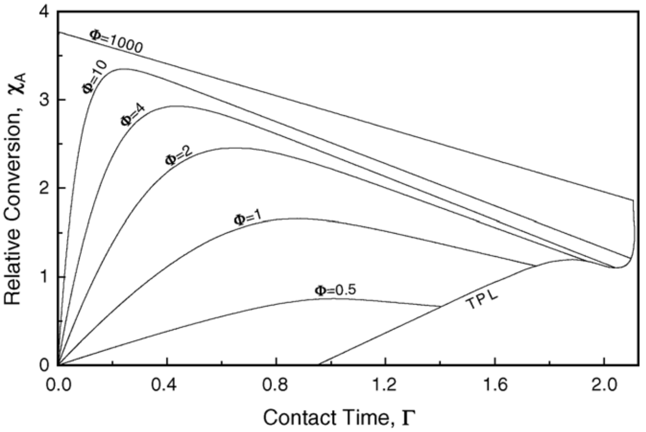

Fig. 9. Relative conversion as a function of the contact time for different values of the Thiele modulus and a reaction with $\Delta n < 0$. $D_i^* = 1$, $H_A^* = 1$, $H_B^* = 0.1$, $\nu_A = 2$, $\nu_B = 1$, and $K_e = 0.004$ m^3/mol.

Thiele modulus parametric region, while the influence of the total concentration gradient becomes more and more important for the medium to high Thiele modulus region.

5. Conclusions

The results presented show that the attained conversion in this membrane reactor can be significantly enhanced when the diffusion coefficient of the reaction product is higher than that of the reactant and/or the reverse relation holds for the sorption coefficients, for a given stoichiometry ratio and overall intramembrane concentration of the reactive system. It was found that conversion is favoured by a high overall sorption capacity of the membrane for reactions with $\Delta n < 0$ and, conversely, by a low overall sorption capacity for reactions with $\Delta n > 0$. On the other hand, a reaction with $\Delta n > 0$ is favoured by the trans-membrane total concentration gradient, while a reaction with $\Delta n < 0$ is disfavoured by the same gradient.

Generally, the conversion for a reaction system with higher diffusivity of the product compared to the reactant is favoured for low to medium values of the Thiele modulus and medium to high contact times, irrespective of the reaction stoichiometry. For a reaction where the sorption coefficient of the product is lower than that of the reactant, conversion is higher for higher values of the Thiele modulus. The contact time region that maximises conversion in this case is in the range of low to medium values for reactions with $\Delta n < 0$ and in the range of medium to high values for reactions with $\Delta n > 0$.

The analysis of such reactors cannot be based solely on the permeability of the reaction components, as the sorption and diffusivity parameters have a different impact on the performance. However, the permeability values are sufficient to analyse qualitatively the conversion behaviour along the Thiele modulus and contact time parametric space.

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