Mass transport with varying diffusion- and solubility coefficient through a catalytic membrane layer
Proceedings of European Congress of Chemical Engineering (ECCE-6)
Copenhagen, 16-20 September 2007

Mass transport with varying diffusion- and solubility coefficient through a catalytic membrane layer

E. Nagy,[a]

[a]*Research Institute of Chemical and Process Engineering, University of Pannonia , H-8200 Veszprém,Hungary*

Abstract

The mass transport, accompanied by chemical reaction through membrane reactor has been investigated in the case of varying diffusion coefficient and solubility coefficient. In the reality, both parameters might depend on the concentration and/or on the inhomogeneity of the membrane layer. General mathematical models were developed to describe the mass transport, taking into account the external mass transfer resistances as well, when the solubility coefficient can vary e.g. according to the Langmuir-Hinschelwood adsorption theory or when the value of diffusion coefficient depends on the concentration/inhomogeneity in the membrane. A general solution has been given that can be applied most of the mathematical functions of the parameters mentioned. The concentration distribution and the mass transfer rate will be given in closed mathematical forms. The value of the mass transfer rates could be strongly altered by the varying diffusion- and/or solubility coefficient. The mathematical model and the effect of the varying parameters has been discussed in this paper.

Keywords: catalytic membrane layer, dispersed catalyst particles, variable diffusion coefficient, variable solubility coefficient, nonlinear mass transfer;

1. Introduction

As a catalytic membrane reactor one can use an intrinsically catalytic membrane (e.g. zeolite or metallic membranes) or a membrane that has been made catalytic by dispersion, impregnation, etc. of catalytically active particles, as metallic complexes, metallic clusters or activated carbon, zeolite particles, etc., throughout the dense, polymeric- or inorganic membrane layers (Marcano and Tsotsis, 2002; Saracco et al., 1999). A very important task is to describe the mass transfer rate in order to predict the concentration profile in the feed phases or for planning the measure of a membrane reactor. Recently, Nagy (2007) developed mathematical models which

define the concentration distribution and the mass transfer rate in membrane layer with dispersed catalyst particles. Depending on the catalyst particle size, heterogeneous- (for the case of micro-sized particles) and pseudo-homogeneous models (for sub-micron particles) were recommended. For first-order reaction it will be developed an analytical solution for the mass transport. This model assumes constant diffusion in both membrane layer and catalyst particles and constant solubility coefficient of the reactant in the catalyst particles.
In the reality, both parameters might depend on the concentration and/or on the inhomogeneity of the membrane layer. E.g., in the case of zeolite catalyst particles or membrane, the diffusion of a single organic compound or mixtures of hydrocarbons could strongly vary with the concentration of component(s). The mass transport could be well described by the Maxwell-Stefan approach combination with the Langmuir-Hinschelwood adsorption theory (Krishna and Wesselingh, 1997). The mass transport of barely soluble liquid components can often be described by the Flory-Huggins theory (Meuleman et al., 1999) that gives also a strong concentration dependency of the diffusion coefficient. The solubility depends on the concentration especially in the case of inorganic membrane. According to a Langmuir-isotherm, the solubility coefficient gradually increases with the concentration up to a limiting value. These facts prove that the development of mathematical models should be important for the prediction of the effect of the varying parameters on the mass transport.
The mathematical models developed give the concentration distributions and the mass transfer rates in a membrane reactor in closed mathematical forms. Two important cases are discussed here, separately: the effect of the varying solubility and that of the varying diffusion coefficient. The equations developed give general solution, they can be applied for monotone functions of the value of solubility or any function of the value of diffusion coefficient.

2. Theoretical part

The mass transport through catalytic membrane layer, with dispersed catalyst particles, can be given by means of homogeneous and/or heterogeneous models. When the catalyst particles are enough small, $d_p << \delta$ (d_p<1-3 μm, d_p- particle size, δ-thickness of the membrane layer) then the pseudo-homogeneous model is recommended. In this paper the homogeneous model is applied to predict the mass transfer rate in the case of variable diffusion coefficient and solubility as well as accompanied by first-order, irreversible chemical reaction.

2.1. Variable solubility coefficient

Details of the pseudo-homogeneous model applied, is given in Nagy's paper (Nagy, 2007), in the case of constant solubility and diffusivity.
The concave solubility (adsorption or absorption) isotherm is approached by means of two linear isotherms (Nagy, 1999), for the sake of an analytical solution (Fig. 1A). The isotherms have H_1 and H_2 solubility constant. Thus the concentration boundary

layer in the membrane is divided into two sections (0 to X_1 and X_1 to1), namely, the section of $0 \leq X \leq X_1$ where the dimensionless concentration falls between 1 and A_1 as well as the section of $X_1 < X \leq 1$ with concentration regime from A_1 to 0 (Fig. 1B). Thus the linear isotherms can be generally expressed as follows:

$$A_d = H_i(A - A_i) + C_i \qquad \text{with i=1,2} \qquad (1)$$

The slopes of the linear segments (H_i) and the point of intersection (C_i) between the two linear segments characterize the mathematical equation of the linear isotherm. Thus, for the second zone C_i is equal to zero, C_2=0.
The differential mass balance equation for the two sections in the membrane can be given as follows:

$$D_i \frac{d^2A}{dX^2} - \frac{6\omega\varepsilon}{1-\varepsilon}\beta_p\left(H_i[A - A_i] + C_i\right) = 0 \qquad \text{with i=1,2} \qquad (2)$$

where

$$\beta_p = \frac{D_p}{R}\left(\frac{Ha_p}{\tanh\left(Ha_p\right)} - 1\right) \quad \text{and} \qquad Ha_p = \sqrt{\frac{k_1 R^2}{D_p}}$$

The value of β_p gives the mass transfer coefficient into the catalyst particles (for details see Nagy, 2007), while Ha_p is the dimensionless reaction rate constant (R-radius of particles, D_p diffusion coefficient in the particle, k- reaction rate constant, ε-catalyst phase holdup).

The boundary conditions:

If X=0 then A=1 $\qquad A=a/a^*$, $X=x/\delta$

If X=1 then A=0

if $X=X_1$ then $A\big|_{X=X_1^-} = A\big|_{X=X_1^+}$

if $X=X_1$ then $D\frac{dA}{dX}\Big|_{X=X_1^-} = D\frac{dA}{dX}\Big|_{X=X_1^+}$

The solution of the above equation system gives:

$$A = F_i e^{\lambda_i X} + G_i e^{-\lambda_i X} + K_i \qquad (3)$$

After the solution (details are not given here), the mass transfer rate can be given as follows:

$$J = \frac{D\lambda_1}{\delta}\frac{(1-K_1)(\tanh\lambda_1 \tanh\lambda_2 + \lambda_2/\lambda_1) + K_1/\cosh\lambda_1}{\tanh\lambda_2 + \lambda_2/(\lambda_1 \tanh\lambda_1)}$$

(4)

$$C_1 = K_1 + \frac{\frac{(1-K_1)}{\cosh\lambda_1}\tanh\lambda_2\left(\tanh\lambda_1\tanh\lambda_2 + \right) - \frac{\lambda_2}{\lambda_1}K_1\tanh\lambda_1}{\tanh\lambda_2 + \lambda_2/\left(\lambda_1\tanh\lambda_1\right)} \qquad (5)$$

$$\lambda_1 = X_1\sqrt{\frac{6\beta_p\varepsilon\delta^2 H_1}{(1-\varepsilon)d_p D}} \qquad \lambda_2 = \sqrt{\frac{H_2}{H_1}}\lambda_1\frac{(1-X_1)}{X_1} \qquad K_1 = A_1 - \frac{\lambda_1^2}{X_1}\frac{C_1}{H_1}$$

Applying Eqs. (4) and (5), the mass transfer rate can be predicted as a function of the reaction rate as well as with the different linear approaches of the original, curvature isotherm.

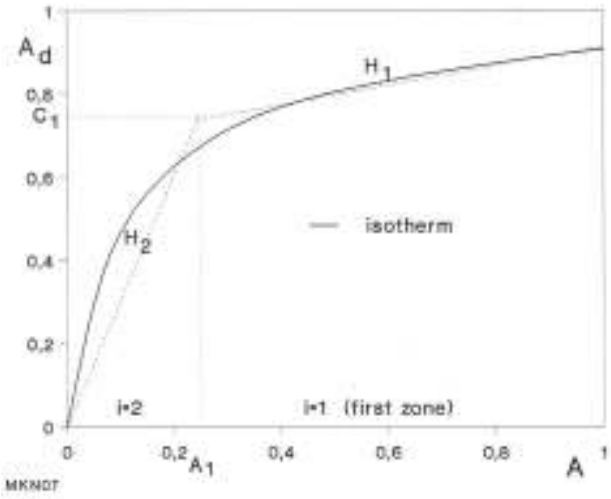

Fig 1A. Illustration of the approach of the curved isotherm (continuous line) by means of two linear isotherms (dotted lines); the concentration distribution in the membrane layer is plotted in Fig. 1B.

2.2. Variable diffusion coefficient

The diffusion coefficient might vary as a function of the concentration [D=D(a)] and/or space coordinate [D=D(x)]. For an analytical solution of these systems, the membrane layer is divided into M sub-layers (M value must be high enough due to the assumption of constant diffusivity in these sub-layers, see Nagy, 2007) with constant diffusivity. Thus, you can get ordinary differential equation system with constant parameters. This equation system can be solved analytically. For the case of the concentration dependent diffusivity the concentration distribution in the membrane layer must be known in order to determine the correct values of D(a). This calculation process needs 3-4 steps of iteration. When the diffusion coefficient

depends on the space coordinate, the mass transfer rate at the membrane interface can be expressed without knowing the concentration distribution in the catalytic membrane layer. The concentration distribution and the mass transfer rates are expressed by closed, explicit mathematical equations for pseudo first-order, irreversible chemical reaction.

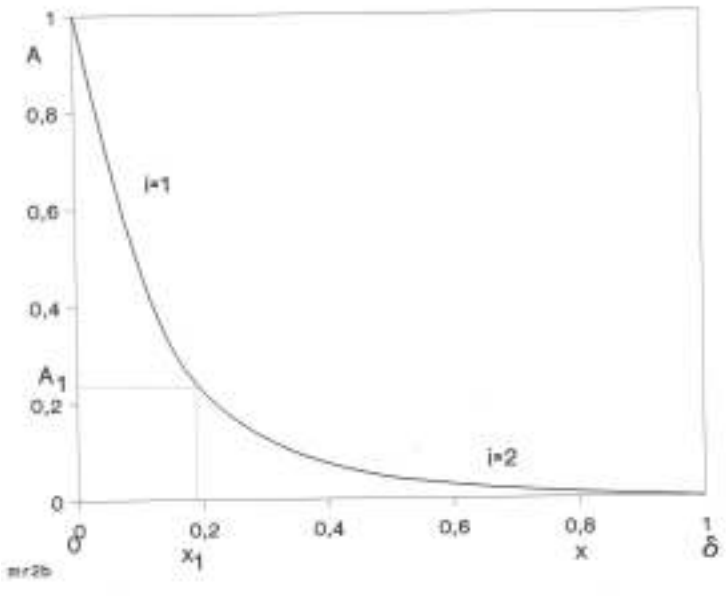

Fig. 1B. Illustration of the concentration distribution in the two zones of the membrane layer

For one-dimensional transport in rectangular coordinates the general molar species continuity equation is:

$$\frac{d}{dx}\left(D\frac{da}{dx}\right)-Q=0 \qquad (6)$$

In general case the diffusion coefficient and the convective velocity can depend on the space coordinate, thus D=D(x), D=D(a) or D=D(a,x). As a source term, Q we consider first-order kinetics, $Q=k_1a$ (very easy to consider the zero order reaction as well, but not discussed here). In the boundary conditions the external mass transfer resistance should be taken into account.
The external boundary conditions are as follows:

$$\text{if} \quad x=0 \quad \text{then} \quad \beta_1^o\left(a_{1f}-a_{1f}^*\right)=-D_1\left.\frac{da_1}{dx}\right|_{x=0^+} \qquad (7)$$

$$\text{if} \quad x=\delta \quad \text{then} \quad \beta_2^o\left(a_{2f}^* - a_{2f}\right) = -D_M \left.\frac{da_M}{dx}\right|_{x=\delta^-}$$

For the solution the membrane should be divided M sub-layer, in the direction of the mass transport, that is perpendicular to the membrane interface, with thickness of $\Delta\delta$ ($\Delta\delta=\delta/M$). In each section the parameters D_m, can be regarded as constant parameter (m denotes the m^{th} sub-layer perpendicular to the interface). For the m^{th} sub-layer of the membrane layer, using dimensionless quantities, it can be given (the value of λ is equal to the well known Hatta-number, $\lambda \equiv Ha$) :

$$\frac{d^2A_m}{dX^2} - \lambda_m^2 A_m = 0 \tag{8}$$

where

$$\lambda_m = \sqrt{\frac{k_1\delta^2}{D_m}}$$

The solution of Eq. (8) is as follows:

$$A_m = T_m e^{(\lambda_m X)} + P_m e^{(-\lambda_m X)} \qquad \text{with } X_{m-1} < X < X_m \tag{9}$$

T_m and P_m are parameters can be determined by means of the boundary conditions for the m^{th} sub-layer (with $1 \le m \le M$). The boundary conditions at the internal interfaces of the sub-layers ($1 \le m \le M-1$; $X_m=m\Delta X$) can be obtained by the following, well known equations:

$$-\frac{dA_m}{dX} = \frac{D_{m+1}}{D_m}\frac{dA_{m+1}}{dX} \qquad \text{at } X=X_m \tag{10a}$$

$$H_m A_m = A_{m+1} \qquad \text{at } X=X_m \tag{10b}$$

The mass transfer rate on the upstream side of the membrane can be given:

$$J_1 = -D_1(T_1 - P_1)\lambda_1 \tag{11}$$

with

$$T_1 = \frac{\left(\frac{1}{H_1^*} - \frac{F_{M-1}}{n_1 E_{M-1}}\right) r_0 e^{-\lambda_1 \Delta X} + \frac{r_\delta F_{M-1}}{H_1^* n_1 E_{M-1}} Q_{M-1}(1+\Theta)}{\frac{1}{n_1}(\Theta + \tanh(\lambda_1 \Delta X))\frac{F_{M-1}}{E_{M-1}} + \left(\Theta \tanh(\lambda_1 \Delta X) + \frac{1}{H_1^*}\right)} \frac{1}{2\cosh(\lambda_1 \Delta X)} \tag{12}$$

and

$$\Theta = H_0^* \lambda_1 Sh_1$$

$$P_1 = \frac{r_0 - T_1(1-\Theta)}{1+\Theta} \tag{13}$$

with $r_0 = A_{f1} H_0^*$

where

$$E_i = \frac{F_{i-1}}{n_{M+1-i} E_{i-1}} \tanh(\lambda_{M+1-i} \Delta X) + \frac{1}{H_{M+1-i}^*} \qquad \text{for i=2,3,…,M}$$

$$F_i = \frac{F_{i-1}}{n_{M+1-i} E_{i-1}} + \frac{\tanh(\lambda_{M+1-i} \Delta X)}{H_{M+1-i}^*} \qquad \text{for i=2,3,…,M-1}$$

with

$$E_1 = \tanh(\lambda_M \Delta X) + \frac{Sh_M \lambda_M}{H_M^*}$$

and

$$F_1 = 1 + \frac{Sh_M \lambda_M}{H_M^*} \tanh(\lambda_M \Delta X)$$

as well as

$$Q_i = B_i + C_i \frac{E_i}{F_i} \qquad \text{for i=2,3,…,M-1}$$

where

$$C_i = \bar{r}_{M-i} - Q_{i-1} \sinh(\lambda_{M+1-i} \Delta X) \qquad \text{for i=2,3,…,M-1}$$

$$B_i = r_{M-i} + Q_{i-1} \cosh(\lambda_{M+1-i} \Delta X) \qquad \text{for i=2,3,…,M-1}$$

with

$$C_1 = \bar{r}_{M-1} - r_\delta \sinh(\lambda_M \Delta X)$$

$$B_1 = r_{M-1} + r_\delta \cosh(\lambda_M \Delta X)$$

$$r_\delta = \frac{A^o_{f2}}{H^*_M}$$

with

$$n_i = \frac{D_i \lambda_i}{D_{i+1} \lambda_{i+1}}; \qquad H^*_i = \frac{H_i}{H_{i+1}} \quad (H_{M+1}=H_\delta) \qquad \text{for } i=1,2,3,\ldots,M-1$$

Applying the above equations, the mass transfer rate can be obtained easily using Eq. (11). The concentration distribution can be simply obtained from the boundary conditions (10a) and (10b) in the knowledge of the T_1 and P_1 values. About the solution details will be given elsewhere.

The mass transfer rate should be replaced into the differential mass balance equation given for the tube (or shell) side of the membrane layer and the effect of the concentration dependency of the parameters on the outlet concentration can be simulated.

3. Results and discussion

3.1. Variable solubility coefficient

Fig. 2 contains two nonlinear solubility curves (curves 1 and 2), each of them were approached by two linear isotherms given by dotted lines. The expressions of the linear isotherms e. g. for the more curvature curve 1 are as follows: A_d=0.164(A-A_1)+0.77 for the regime of $X_1 \leq X \leq 1$ as well as A_d=5.1A for $0 \leq X \leq X_1$. The value of A_1 in this case is equal to 0.151. The essential of the calculation methodology, that you should vary the value of X_1 until the Eq. (5) is fulfilled in order to get the value of X_1. Then one can calculate the mass transfer rate, J, by means of Eq. (4). Typical curves illustrate the effect of the nonlinearity on the mass transfer rate in Fig. 3. The solubility curve with higher curvature has much higher value of the enhancement in the mass transfer (curve 1 in Fig. 3). (E gives the mass transfer rate related to that of physical mass transfer). The curve denoted by "lin" in Fig. 3. gives the enhancement with linear solubility isotherm (straight line, curve 3, in Fig. 2). Using a single linear solubility for the curve 3 in Fig.2, one can simply get that H=0.91 (H=A_d/A at X=1). With increasing reaction rate the E value increases more significantly than the E_{lin} value. These results prove that the curvature of the solubility isotherms could have significant influence on the mass transfer rate into the catalytic membrane layer. It will be demonstrated the effect of the curvature on the mass transfer rate of hydrocarbons into zeolite membrane as a function of the reaction rate.

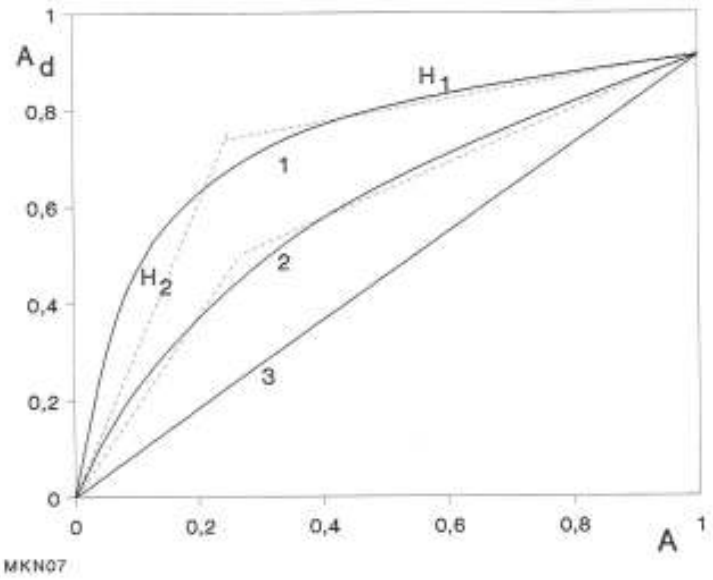

Fig. 2. Different curved solubility curves and their approaching by two linear isotherms

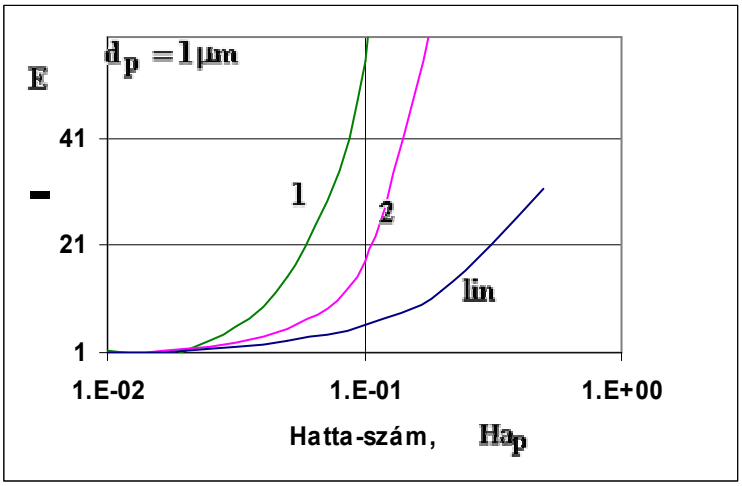

Fig. 3 Enhancement of the mass transfer rate as a function of the reaction rate applying the solubility curves given in Fig. 2. Parameter values used for calculation: $D=D_p= 1x10^{-10}$ m^2/s, δ=100 µm, ε=0.1, for the linear isotherm: H=0.91)

3.2. Variable diffusion coefficient

The value of T_m and P_m were determined by means of the boundary conditions obtained for the internal and external interfaces. According to the Maxwell-Stefan, the Flory-Huggins theories or the Vignes equations (Bitter, 1991), there can be given several different mathematical functions between concentration and diffusion coefficient. As illustrations, it is shown here some typical examples how the varying

diffusion coefficient can alter the concentration distribution and the mass transfer rate in the catalytic membrane layer. For the sake of simplicity a linear change of the D(a) value was assumed [$D=D_o(1\pm Km/M)$] in these examples. Two typical figures illustrate the change of the concentration in the membrane layer when the diffusion coefficient increases with increasing concentration (Fig. 4a) or when it decreases with increasing concentration (Fig. 4b). The tendency of curves is well known, thus, their detailed discussion here is not necessary. For physical mass transport, the mass transfer rate and/or the concentration distribution can be calculated by means a simpler equation, namely:

$$A_m = T_m m\Delta X + P_m \qquad \text{with } m=1,2,\ldots,M \qquad (16)$$

$$T_m = -\frac{1}{D_m}\frac{1-A^o_{f2}}{\frac{1}{D_1 Sh_1}+\frac{1}{D_M Sh_M}+\Delta X\sum_{j=1}^{M}\frac{1}{D_j}} \qquad (17)$$

$$P_m = \left(1+\frac{T_1}{Sh_1}\right)+\sum_{j=1}^{m-1} T_j\Delta X - T_m(m-1)\Delta X \qquad (18)$$

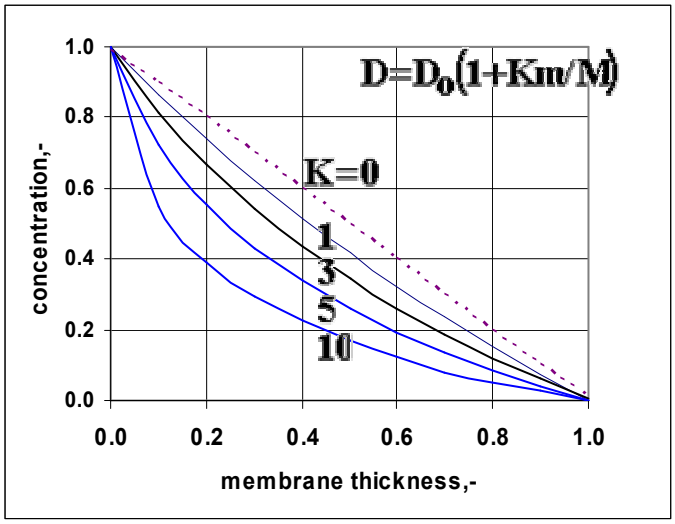

Fig. 4a. Concentration distribution in the membrane without chemical reaction (Ha=0, $A^{o}_{f2}=0$, $\beta^{o}_{1}=\beta^{o}_{2}\to\infty$)

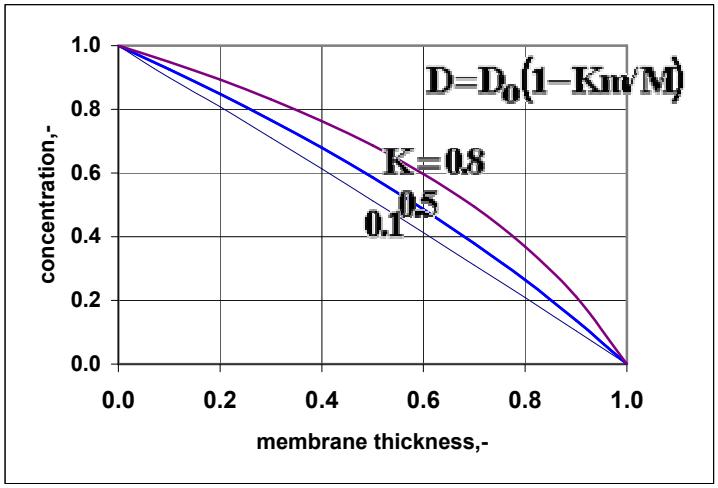

Fig. 4b Concentration distribution in the membrane without chemical reaction (Ha=0, $A^{o}_{f2}=0$, $\beta^{o}_{1}=\beta^{o}_{2}\to\infty$)

How the chemical reaction alters the enhancement is plotted in Fig. 5, in the case when the diffusion coefficient increases with the concentration. The value of K parameter changes between 0 and 10. The dotted line gives the mass transfer rate with constant diffusion coefficient. The actual mass transfer rate is related to that obtained by D_o constant diffusion coefficient and without chemical reaction. The mass transfer rate gradually increases with the Hatta-number. As can be seen the varying diffusion coefficient has strong effect on the mass transfer rate at even at higher value of Ha.

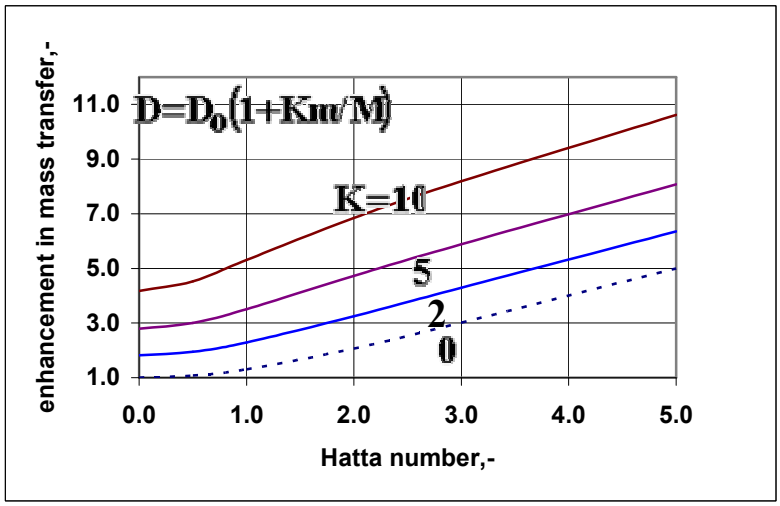

Fig. 5. The effect of the chemical reaction rate on the mass transfer rate related to that without chemical reaction and constant D_o diffusion coefficient in the catalytic

membrane layer. The value of diffusion coefficient increases with the concentration [$D=D_o(1+Km/M)$, $A^o_{f2}=0$, $\beta^o_1=\beta^o_2\to\infty$]

4. Conclusion

Relatively simple mathematical equations are presented in order to predict the mass transport in membrane reactor in the case of nonlinear mass transfer. Closed equations were developed to calculate the effect of varying solubility and/or diffusion coefficient. Figures presented prove strong effect of the concentration dependency of the diffusion coefficient and solubility.

Acknowledgement

This work was supported by the Hungarian research Foundation under Grants OTKA 63615/2006

Notation

a	concentration, mol/m^3
a_{1f}	concentration in the bulk feed phase, mol/m^3
a^*_{1f}	concentration on the membrane interface on the feed side, mol/m^3
A	dimensionless concentration, (=a/a^o_{f1})
A_d	concentration in particles, mol/m^3
A^o_{f1}	external bulk phase concentration in the feed side, mol/m^3
D	diffusion coefficient, m^2/s
D_p	diffusion coefficient in particles, m^2/s
d_p	particle size, m
H	solubility coefficient, -
H^*_m	$=H_m/H_{m+1}$
k_1	reaction rate constant, 1/sec
M	number of sub-layer with constant parameters in the membrane layer, m
R	particle radius, m
Sh_1	$=D_1/(\delta\beta^o_1)$
Sh_M	$=D_M/(\delta\beta^o_2)$

Greek letters

β	mass transfer coefficient, m/s
ε	holdup

ω specific area of the catalyst particles in the membrane, m^2/m^3

Indices

1 feed phase
2 down stream phase

References

Bitter, J.G.A., *Transport mechanisms in membrane separation processes*, 1991, Amsterdam
Krishna, R., J.A. Wesselingh, 1997, *Chem. Eng. Sci*., 52, 861-911.
Markano, J.G.S., Tsotsis, T.T., *Catalytic Membranes and Membrane Reactors*, Wiley-VCH, (2002).
Meuleman, K., B.B. Bosch, M.H.V. Mulder, H. Stratmann, 1999, *AIChE J*., 45, 2153-2160
Saracco, G. Neomagus, H.W.J.P., Versteeg, G.F., van Swaaij, W.P.M., (1999), *Chem. Eng. Sci.* 54 1997-2017
Nagy E., (2007), *Industrial & Engineering Chemistry Research*, 46, 2295-2306.
Nagy E., (1999), *Chem. Eng. Journal*, 72, 43-51