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Modelling and parameter estimation for transport processes in zeolite membranes

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Abstract

A mathematical model describing the permeation transport through a zeolite membrane has been developped. It is based on the diffusion mecanism identification from experimental data analysis. The diffusion parameters have been estimated by fitting the mathematical model to experimental data. The experiments were carried out under steady state conditions; permeate flows were measured for a large range of temperature and pressure values. The random search method proposed by Luus and Jaakola was used for the parameters estimation. Statistical analysis was performed to evaluate the confidence interval for the estimates. The results were in good agreement with experimental data.

Keywords: Mass Transport Modelling, Parameters Estimation, Zeolite Microporous Membranes

1. Introduction

Zeolite membranes are already used in several industrial processes. The separation of gaseous mixtures at industrial scale using MFI zeolite membranes is very promising due to the high thermal stability of such materials. The design

of membrane separation equipments requires a good knowledge of the values of diffusion parameters. They can be estimated by experimental data correlations using a mathematical model derived for the permeation transport through such microporous membranes. The diffusion parameters estimation considering the temperature influence, following an Arrhenius type relation, has been intensively reported in literature. The pressure influence can be put into evidence by estimation of the diffusion parameters using several experimental runs, including pressure variation, and subsequent statistical analysis of the estimation quality.

2. Experimental study

The gas transport mechanisms were studied for a MFI zeolite membrane, characterised by pores of about 0.55 nm, grown on and inside a tubular α-Al_2O_3 substrate [1].
A large number of permeation experiments for light hydrocarbons (CH_4, C_2H_6, C_3H_8, *n*-C_4H_{10}) were carried out under steady state conditions at different temperatures and pressures.
The experimental setup, presented in details in [2], has been built respecting the "dead end" concept, as the gas feed inside the membrane is at one end of the membrane module and, at the other end, the outlet of the inner compartment is closed. Experiments were carried out measuring the permeate flow for temperature values in the 288-773 K range and for a pressure variation between $1.2 \cdot 10^5$ Pa and $2 \cdot 10^5$ Pa. The experiments were repeated for all gases investigated keeping the same values of operating parameters. To avoid experimental errors a strong outgasing at 773 K of the entire module was performed before each experiment. The experimental error was put into evidence by replicate measurements in some experimental points and was below 5 %.

3. Mathematical modelling for permeation transport

The mathematical model for the permeation process is focused on the evaluation of diffusion fluxes. The identification of the type of diffusion determining the permeation process is a crucial step in deriving the specific transport equations. Possible transport mechanisms are: viscous flow, molecular diffusion (in macropores), Knudsen diffusion (in intracrystalline holes), surface diffusion, activated gaseous diffusion (in zeolite micropores). Previous investigation of this membrane [3] revealed that intracrystalline holes are no larger than 0.62 nm, and consequently the overall permeation takes place only through micropores. Therefore, two mechanisms were considered to describe correctly the transport process: surface diffusion and activated gaseous diffusion.

In this work the selection of main mechanisms involved was realized by comparing the experimental variation of permeate flowrates with typical diffusion curves (flux and permeance measured in function of pressure and temperature). For all investigated gases the most probable diffusion patterns are the surface diffusion and the activated gaseous diffusion (configurational diffusion), the corresponding permeate fluxes being described by Eq. (1) and Eq. (2) [4, 5]:

$$N_i^s = \frac{\varepsilon}{\tau \cdot \delta_m} \cdot \rho \cdot q_{sat,i} \cdot Đ_i^{s0} \cdot exp\left\{\frac{-E_{a,i}^s}{R \cdot T}\right\} \cdot ln\frac{1 + K_i \cdot p_{F,i}}{1 + K_i \cdot p_{P,i}} \tag{1}$$

$$N_i^g = \frac{\varepsilon}{\tau \cdot \delta_m} \cdot d \cdot \sqrt{\frac{8 \cdot R \cdot T}{\pi \cdot M_i}} \cdot exp\left\{\frac{-E_{a,i}^g}{R \cdot T}\right\} \cdot \frac{\Delta p_i}{R \cdot T} \tag{2}$$

Light hydrocarbons are adsorbable gases which follows a non linear behaviour of the Langmuir isotherm adsorption. In this particular case the adsorbed molecules concentration can be evaluated using Eq. (3), corrected by an empirical factor [4] which considers the temperature variation of the saturation concentration:

$$q_{sat,i} = q_{sat,i,0} + \phi \cdot T \tag{3}$$

The global permeate flux N^t is the sum of the two contributions described by Eq. (1) and Eq. (2) and the permeate flowrate is: $G = N^t \cdot S$, where S is the permeation surface. The mathematical model reflects the variation of permeate flux with temperature and pressure.

4. Parameters estimation

Concerning the parameters, the mathematical model proposed according Eq. (1) and Eq. (2) is nonlinear and then it can not be simplified by linearization. The model parameters are:

$\delta_m \cdot \tau/\varepsilon$ – membrane effective thickness, m;
$q_{sat,i,0}$ – saturation concentration of adsorbed molecules, mmol/g;
ϕ – empirical factor for temperature correlation, $mmol \cdot g^{-1} \cdot K^{-1}$;
K^0 – preexponential constant from Langmuir constant equation, Pa^{-1};
Q – adsorption heat, $kJ \cdot mol^{-1}$;
$Đ^{s0}$ – Maxwell-Stefan coefficient for surface diffusion, at zero concentration, $m^2 \cdot s^{-1}$;
E_a^s – activation energy for surface diffusion, $kJ \cdot mol^{-1}$;

E_a^g – activation energy for activated gaseous diffusion, kJ·mol^{-1}.

The number of the parameters describing the process is too large to be accurately estimated just from permeation data and consequently some experiments have been added (helium permeation for the membrane effective thickness estimation $(\tau/\varepsilon)\cdot\delta_m$ [3]). The adsorption parameters were taken from literature [4]. By these considerations the parameter space is reduced to the three diffusion parameters: $Đ^{s0}$, E_a^s and E_a^g.

The model parameters are calculated by solving an optimisation problem considering as objective function the least squares criterion:

$$fob = \sqrt{\sum_{j=1}^{n} \left(G_{exp,j} - G_{calc,j}\right)^2} \tag{4}$$

where $G_{exp,j}$ stay for the measured values of the permeate flowrate, and $G_{calc,j}$ the estimated values with the proposed mathematical model; n is the total number of measurements.

The objective function minimisation has been carried out by the adaptive-random method proposed by Luus and Jaakola [6]. The procedure is characterised by two steps of extreme research. In the first step the regions where the objective function has minimum values are selected, while in the second step the minimum zone is iteratively restricted. The Luus – Jaakola method was chosen for its ability to identify the optimum of multimodal function in a reasonable computing time.

Statistical tests were used to verify the estimates reliability. An approximation of the confidence interval for the parameters assuming model linearity in the optimum zone [7] is realised with the matrix $W_{kj} = \left(df/dx_k\right)_j$, where f is the mathematical expression of the model, and x_k are the parameters; $1 \le j \le n$, n being the number of experiments, $1 \le k \le p$, p being the number of parameters. The matrix computations were carried out with Matlab™ software. The confidence interval was calculated using Student distribution for a confidence level of 95 %. The data dispersion was approximated with SSE/(n-p), where SSE is the sum of squared errors between experimental data and the model. Considering the possibility of parameters interaction, the inter-correlation matrix was calculated and a correlation between $Đ^{s0}$ and E_a^s was revealed. This is not an unexpected result as these two parameters interfere in an Arrhenius-type relation [7, 8].

5. Results& discussions

Table 1 presents the model coefficients values with their confidence intervals and the mean relative errors between experimental and calculated flowrates.

Table 1. Model parameters estimated with 95 % confidence level

Gas	$Đ^{s0} \cdot 10^8$ $m^2.s^{-1}$	E_a^s $kJ \cdot mol^{-1}$	E_a^g $kJ \cdot mol^{-1}$	Mean relative error (%)
CH_4	25.87 ± 1.11	11.15 ± 0.15	18.23 ± 0.17	5.622
C_2H_6	18.90 ± 2.16	15.60 ± 0.34	19.00 ± 0.28	5.283
C_3H_8	6.34 ± 0.19	16.00 ± 0.10	18.70 ± 0.10	3.967
C_4H_{10}	3.71 ± 0.71	16.61 ± 0.27	18.10 ± 0.43	4.571

Fig. 1 presents experimental data and values calculated with the estimated parameters, as well as the contributions of diffusion types considered (dotted lines) in Eq. (1) and Eq. (2).

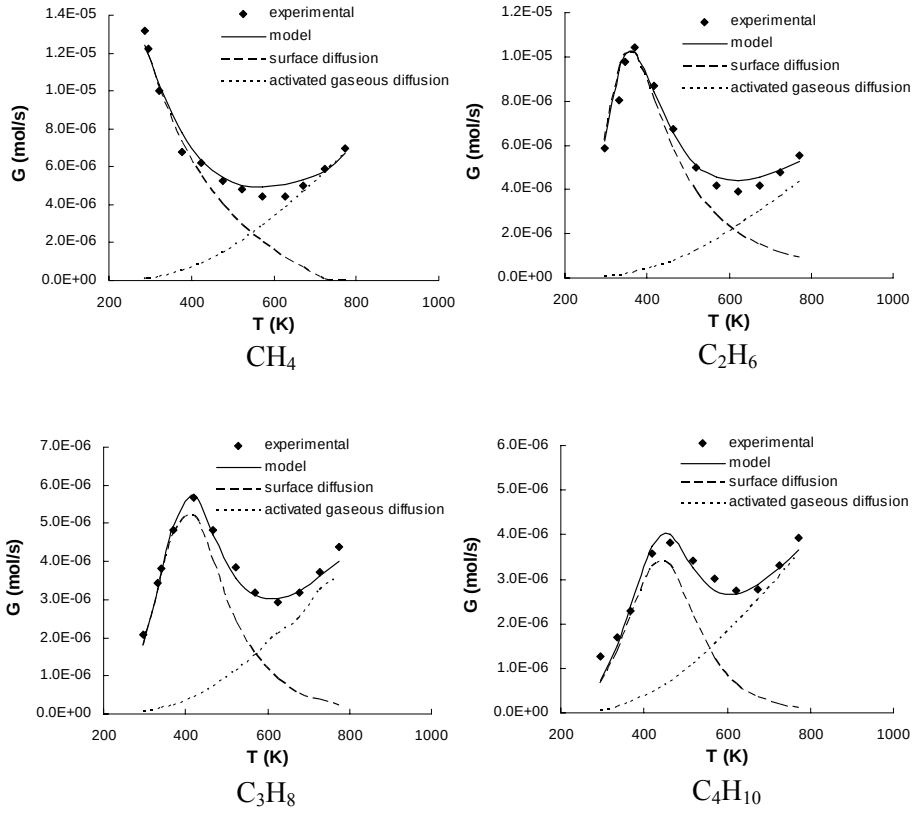

Figure 1. Comparison between experimental and calculated permeate flowrates

The selection of variable boundaries, necessary in the optimisation step, was based on theoretical assumptions and a trial and error procedure. Reasonable boundaries specifications, especially for the preexponential factor, $Đ^{s0}$, and for the activation energy of surface diffusion, E_a^s, avoided the identification of suboptimal solution generated by the intercorrelation of these two parameters. Several runs were necessary to obtain a good solution of the optimisation problem. We can notice that the simulation curves are in good agreement with experimental results. Moreover, these results are also in good agreement with previously reported results in the literature for other type of zeolite membranes [4]. It is very interesting to mention that the global model simulation curve is obtained always as a contribution of the surface diffusion and gaseous activated diffusion.

6. Conclusions and future work

The calculation of the model parameters (from experimental data sets with temperature and pressure variation) proved that reliable estimates can be obtained for a large range of operating conditions. These results demonstrate that, at least in the pressure range used for experiments, the diffusion parameters are pressure independent. The estimation accuracy has been tested by statistical analysis. The good agreement between calculated permeates flowrates and experimental data confirms that the diffusion mechanisms considered in the mathematical model formulation have been correctly assumed.
Future work will focus on a large scale experimentation of gas permeation with application in separation processes in petrochemical plants and parameters estimation in order to create a database for membrane separators design.

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