

Adsorption Properties and Permeation Performances of DD3R Zeolite Membranes

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This modelling paper is focused on the evaluation of the performance of DD3R zeolite membranes for light gases separation. First, the required adsorption properties are calculated by means of a multivariate regression. Then, the Maxwell-Stefan multicomponent transport equations are implemented considering a quaternary equimolar gas mixture (CH₄, CO₂, CO and N₂) on the high-pressure feed side to evaluate the actual permeance and selectivity of the considered gases keeping the low-pressure permeation side at 100 kPa. After validating the model through experimental data taken from the literature, the simulation is performed in a certain range of temperature and pressure. It is found that in the range of considered conditions, the CO₂ / CH₄ selectivity is higher than 100, increasing with decreasing temperature and pressure. Therefore, the most convenient temperature and pressure conditions where permeance and CO₂ / CH₄ selectivity are good enough to be of interest for industrial applications are identified.

1. Introduction

Membrane technology represents a powerful alternative to more traditional and more energy consuming gas separation processes like, for example, Pressure Swing Adsorption (PSA). Among all types of membranes, the zeolite ones have been nowadays gaining more and more importance in gas separation thanks to their particular crystalline ceramic nanostructures, which are able to selectively adsorb molecules and separate them by adsorption equilibrium, diffusion kinetics and/or molecular sieving. Furthermore, zeolite membranes show a good thermal and mechanical stability.

A crucial factor affecting the separation performance of a zeolite membrane is the composition of the framework, with a particular regard to the Si-Al ratio. For example, zeolites with low Si-Al ratios are suitable for water separation, whereas membranes with high Si-Al ratios are suitable for gas separation thanks to their low content of defects (van den Bergh, 2010a).

In this paper, DD3R (deca-dodecasil 3R) membranes are considered because of their promising performance in gas separation. In particular, they can be used to separate several gas mixtures like CO₂/CH₄, propane/propene and water/ethanol (Zhu et al., 1999; Gascon et al., 2008; Tomita et al., 2004; van den Bergh et al., 2008a, 2008b, 2010a; Kuhn et al., 2008). The pore size of DD3R (0.36 x 0.44 nm), which is smaller than that of other zeolites like Silicalite and FAU (Faujasite), makes this zeolite very interesting for light gases separation.

The transport through zeolite membranes is mostly driven by the surface diffusion, which can be effectively described by the multicomponent Maxwell-Stefan approach, as reported in several literature works (van den Bergh et al., 2007, 2008b, 2010a, 2010b; Lee, 2007; Kangas et al., 2013; Kaptejin et al., 2000; Wirawan et al., 2011; Bakker et al., 1996; Krishna and Wesselingh, 1997; Li et al., 2007; Krishna and Paschek, 2000).

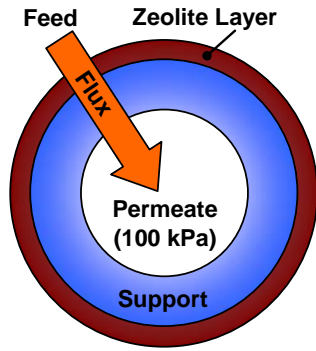


Figure 1: Simulated System

Notation Table

a	Sticking coefficient, -	N	Molar flux, mol m ⁻² s ⁻¹
b_L	Langmuir affinity constant, Pa ⁻¹	P	Pressure, Pa
C_μ	Molecular loading, mol kg ⁻¹	Q_L	Heat of adsorption, J mol ⁻¹
$C_{\mu s,0}$	Saturation molecular loading at T_0 , mol kg ⁻¹	T	Temperature, K
$D_i(0)$	Zero-loading molecular diffusivity, m ² s ⁻¹	T_0	Reference temperature, K
D_i	Maxwell-Stefan self diffusivity, m ² s ⁻¹	χ	Empirical parameter in Eq 5, -
D_{ij}	Maxwell-Stefan exchange diffusivity, m ² s ⁻¹	θ	Fractional surface occupancy, -
$k_{d\infty}$	Desorption rate constant, mol s ⁻¹ m ⁻²	μ	Chemical potential, J mol ⁻¹
M	Molar mass, kg mol ⁻¹	ρ	Density of zeolite, kg m ⁻³

The implementation of such an approach requires the knowledge of several adsorption properties, like saturation loading, heat of adsorption and affinity constant. For this reason, the first part of this paper is dedicated to the evaluation of the required adsorption properties, obtained by a non-linear regression analysis of several experimental isotherms by an optimization routine using the Levenbergh-Marquardt algorithm to fit the data through the Langmuir model. By doing that, the functionality of the adsorption parameters with temperature is achieved. Then, the adsorption parameters are used as input data in the simulation of the permeation of a quaternary equimolar gas mixture (CH₄, CO₂, CO and N₂) through a DD3R membrane adopting the multicomponent approach described below.

2. Description of the system

The system considered in this investigation is a cross-section of a tubular membrane composed of a thin DD3R layer (60 μm) deposited on a porous support (Figure 1). The high-pressure side is located on the zeolite layer side, whereas the low-pressure one is on the support side. The characteristic pore size of support is supposed to be sufficiently large to provide a negligible effect to mass transfer.

3. Mathematical approach

Langmuir model is used to fit the collected experimental isotherms. Eqs(1-5) provide the details of the single-component Langmuir isotherms (Do, 1998):

$$C_\mu = C_{\mu s} \frac{(b_L P)}{1 + (b_L P)}, \quad b_L = b_{\infty, L} \exp\left[\frac{Q_L}{RT}\right], \quad b_{\infty, L} = \frac{b_0}{\sqrt{T}}, \quad b_0 = \frac{a}{k_{d\infty} \sqrt{2\pi MR}}, \quad C_{\mu s} = C_{\mu s,0} \exp\left[\chi\left(1 - \frac{T}{T_0}\right)\right] \quad (1-5)$$

3.1 Maxwell-Stefan approach to mass transport

According to the Maxwell-Stefan theory, the driving force for mass transport, given by the chemical potential gradient, is balanced by the friction that a single species with a certain velocity has with zeolite and the other species in mixture (Kaptejin et al., 2000; Krishna and Wesselingh, 1997; Krishna and Paschek, 2000):

$$-\rho\theta_i \frac{\nabla\mu_i}{RT} = \sum_{j=1}^n \frac{C_{\mu_j} N_i - C_{\mu_i} N_j}{C_{\mu s_i} C_{\mu s_j} D_{ij}} + \frac{N_i}{C_{\mu s_i} D_i} \quad (6)$$

The Maxwell-Stefan surface diffusivity D_i describes the interactions between the i^{th} species and zeolite, whereas the exchange diffusivity D_{ij} describes the interactions between two generic species. Eq(6) can be represented using matrices, from which the form of the flux vector can be obtained as expressed in Eqs(7-9).

$$(N) = -\frac{\rho}{RT} [B]^{-1} [C_\mu] (\nabla\mu), \quad B_{ii} = \frac{1}{D_i} + \sum_{j=1}^n \frac{C_{\mu_j}}{C_{\mu s_j} D_{ij}}, \quad B_{ij} = -\frac{C_{\mu_j}}{C_{\mu s_j} D_{ij}} \quad D_i = D_i(0)(1 - \theta), \quad \theta = \frac{C_\mu}{C_{\mu s}} \quad (7-11)$$

For the mathematical closure of the system, the Maxwell-Stefan equations (Eqs(7-9)) are coupled to the mass balance of the i^{th} species through the zeolite layer along with the appropriate boundary conditions. The system considered for simulation is shown in Figure 1.

The boundary conditions are given in terms of fixed pressures on both membrane sides. The simulation hypotheses are: (1) negligible effect of porous support; (2) negligible effect of external mass transfer; (3) single loadings described by Langmuir isotherm; (4) strong confinement scenario. The hypothesis of strong confinement scenario corresponds to a linear relation between the diffusivity D_i with the occupancy degree θ (Lee, 2007).

4. Results and Discussion

4.1 Adsorption Properties

The optimal values of some key-adsorption properties (saturation loading and heat of adsorption) are reported along with their respective confidence intervals at 95% (Figure 2a and b). Figure 2a shows quite narrow confidence intervals of the optimal values of the saturation loadings for all species, indicating the good calculation accuracy. The confidence intervals for the heat of adsorption (Figure 2b) are sufficiently narrow (within around $\pm 10\%$) for all species but hydrogen, for which the large calculation uncertainty is due to the weak hydrogen-zeolite physical bond. In Table 1, optimal values of parameters and corresponding confidence intervals are reported for CO₂.

4.2 Simulation results

Before simulation, the model was validated collecting some experimental data from the literature in terms of CO₂ permeability and selectivity with respect to CH₄ (van den Bergh et al., 2008b), running simulations in the same conditions as those reported in the paper. The model predicts quite well the experimental behaviour at a temperature higher than around 10°C (3), which are of direct interest for industrial applications. In particular, the CO₂ permeability decreases with increasing temperature, this owing to the weaker adsorption strength on which surface diffusion is based.

The calculated permeability and selectivity trends are reported in Figure -6. Figure a shows that the CH₄ permeability decreases with increasing pressure, as well as that of CO₂ (Figure b), CO (Figure a) and N₂ (Figure b). Such a common trend is due to the increasing species-zeolite interactions caused by the higher concentration in the pores. However, for CH₄, an increase of the feed pressure does not significantly affect permeability. Feed pressure has a stronger influence on the permeability of the other components, especially at the lower pressures (up to ≈ 600 kPa).

Differently, permeability shows an increasing trend with temperature for CH₄, CO and N₂. As for CO₂, its trend with temperature exhibits a maximum (Figure a), owing to the contrasting effects of adsorption and diffusion with temperature. Moreover, the temperature at the maximum is found to increase at higher pressure, changing from 293 K at 200 kPa to 313 K at 1000 kPa. Comparison among permeabilities shows that the less polar molecules (N₂ and CH₄) pass slower than the more polar ones (CO₂ and CO). This can be due to the preferentially CO₂ and CO adsorption into the zeolite layer, this representing a barrier for adsorption and consequent diffusion of N₂ and CH₄. Figure shows that the CO₂/CH₄ selectivity decreases with both feed pressure and temperature, keeping values between 100 and 1000. These results are also observed by van den Bergh et al. (2008b), but, additionally, our work indicates temperature and pressure range for an effective CO₂/CH₄ separation.

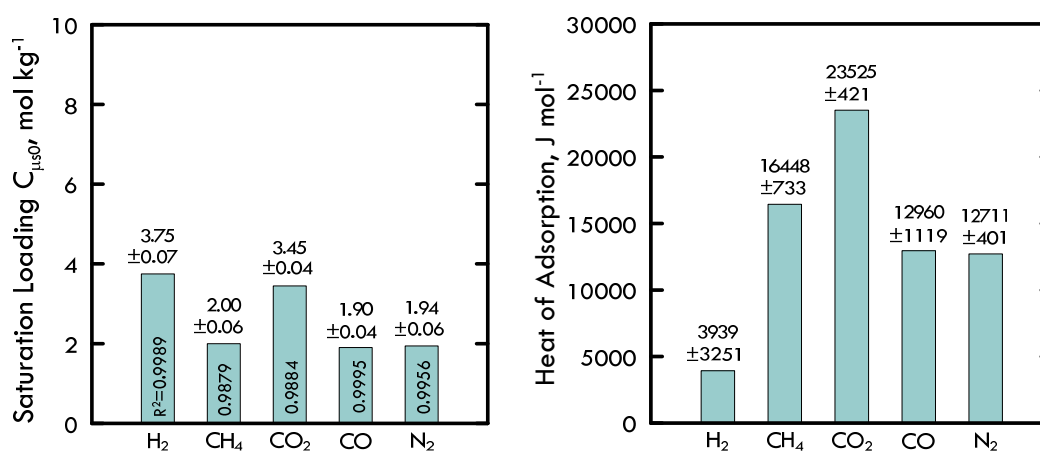


Figure 2: Calculated values of (a) saturation loadings and (b) heat of adsorption.

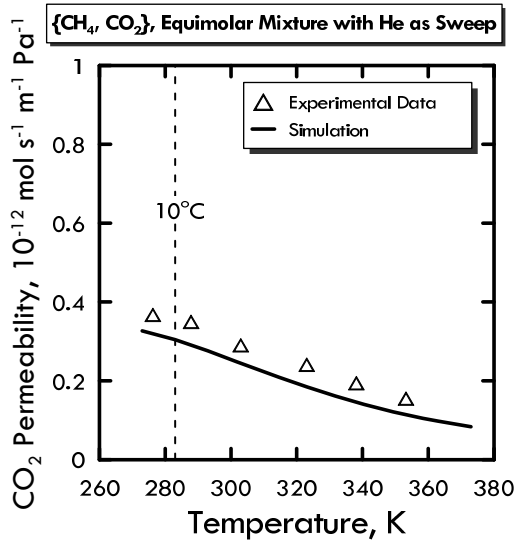


Figure 3: Model validation using literature data (van den Bergh et al., 2008b).

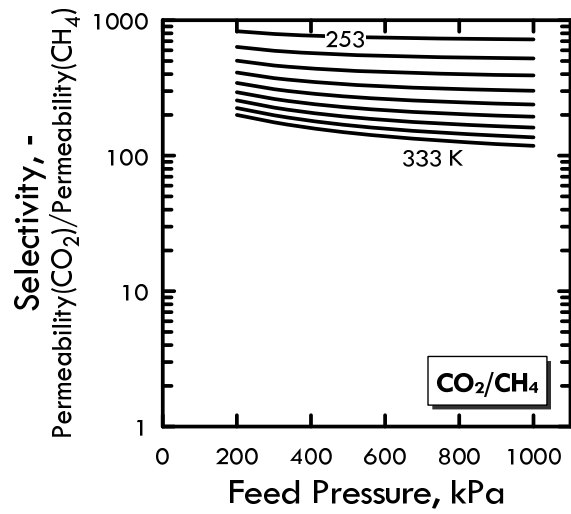


Figure 4: Calculated CO₂/CH₄ selectivity vs. feed pressure at different temperatures

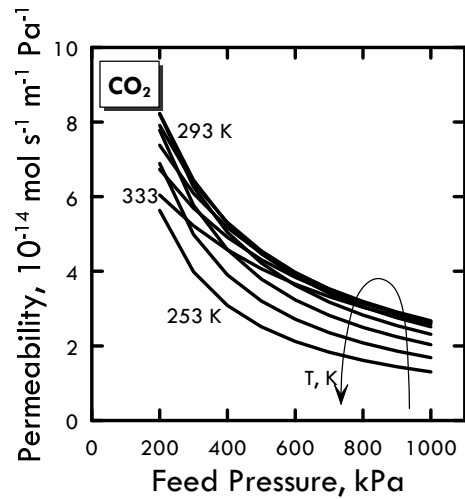
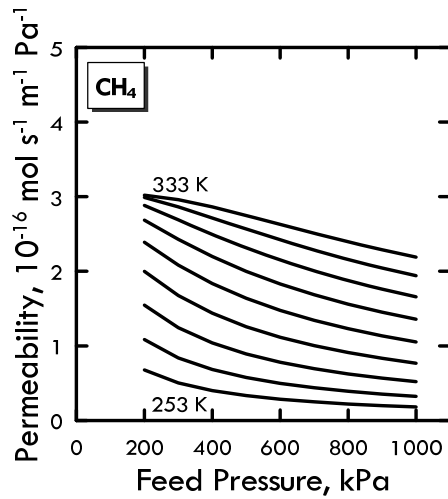


Figure 5: (a) CH₄ and (b) CO₂ permeability vs. feed pressure at different temperatures.

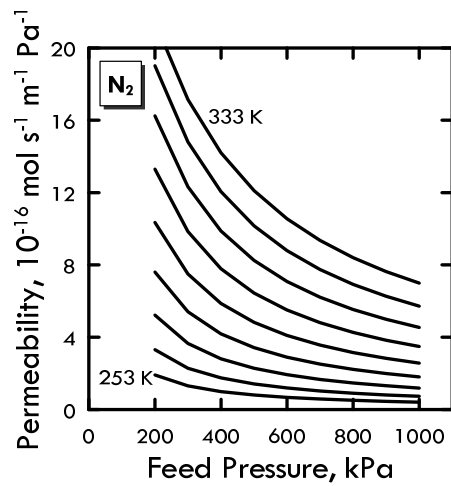
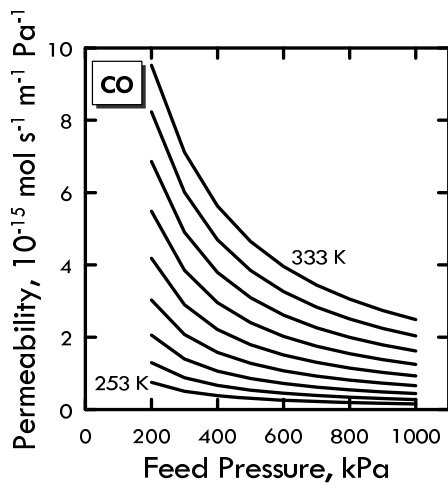


Figure 6: (a) CO and (b) N₂ permeability vs. feed pressure at different temperatures.

Table 1: Optimal value of the model parameters and corresponding confidence intervals for CO₂ in DD3R

Parameters	Optimal Value	Confidence Intervals
$C_{\mu s0}$, mol kg ⁻¹	3.45	± 0.04
χ , -	0.23	± 0.04
b_0 , 10 ⁻⁸ K ^{0.5} Pa ⁻¹	1.19	± 0.36
Q_L , kJ mol ⁻¹	23.525	± 0.421

5. Conclusions

The separation performances of DD3R zeolite membranes were investigated using the multicomponent Maxwell-Stefan approach. For this investigation, the permeation of an equimolar gas mixture (CH₄, CO₂, CO, N₂) was simulated as a function of temperature and feed pressures. The model adopted was preliminary validated using experimental data from the literature. The simulation results showed that the permeabilities of the less polar molecules (N₂ and CH₄) are lower than the more polar ones (CO₂ and CO). The most important results consisted in predicting the membrane behaviour at high feed pressures and in a wide range of temperature, this providing the optimal usage conditions for the DD3R membranes. In particular, the CO₂/CH₄ selectivity is found to be very high (100-1000), especially at lower temperatures and feed pressures, whereas a gradual decrease is observed with increasing both variables.

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