Partial Analytical Solutions for Steady-State Diffusion in Zeolite Membranes

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During the last several years extensive efforts have been made in the study of zeolite membranes. These studies show interesting selective properties for separations as well as the potential for chemical reactors. Recent overviews were given by Kapteijn et al. (1995), Bakker et al. (1996), and Burggraaf (1996). A considerable number of studies were performed on silicalite membranes deposited on a stainless-steel support. Although not quite complete, the best theoretical description of the transport through such membranes is the Maxwell-Stefan approach of Krishna and van den Broeke (1995). For the silicalite, they assumed that cross-diffusion terms for the adsorbates could be neglected. For discussions on this assumption and the relation to "single-file diffusion," the reader is referred to the references, since this is outside the scope of the present article. Krishna and van den Broeke solved the dynamic evolution of permeation of gas mixtures numerically, and their results showed qualitative agreement with experimental data. Upon checking on the steady-state two-component permeation rate, the author recently found an analytical solution that may be of interest as such for the analysis of experimental data and the prediction of selectivity from single-component data.

The system considered is depicted in Figure 1. Resistance to mass transfer is thought to be in a zeolite layer of thickness L, and in a support layer of thickness L_s. Equilibrium is assumed between the partial pressures of components and the occupancies in the adsorbed phase at the gas–membrane interfaces, according to the Langmuir isotherm:

$$\theta_i = \frac{b_i p_i}{1 + \sum_n b_j p_j}. \tag{1}$$

For the vacancy fraction this leads to

$$\theta_v = 1 - \theta_1 - \theta_2 = \frac{1}{1 + \sum_n b_j p_j}. \tag{2}$$

According to Krishna and van den Broeke, the steady-state flux equation reads:

$$\bar{N} = -\rho \epsilon q_{\text{sat}} [\bar{\bar{D}}]_F \frac{d\bar{\theta}}{dz}. \tag{3}$$

For the silicalite they assumed the absence of adsorbate interactions, which led to a Maxwell-Stefan matrix that has only nonzero diagonal elements. Since here the analytical equations are developed for this specific matrix type, the author sees this as a partial solution to the full problem.

In this case, the Fickian diffusion matrix is given by

$$[\bar{\bar{D}}]_F = [\bar{\bar{D}}]_{MS} [\bar{\bar{\Gamma}}]. \tag{4}$$

The thermodynamic factor matrix is given by

$$\Gamma_{ij} = \delta_{ij} + \frac{\theta_i}{\theta_v}. \tag{5}$$

The system can be written in terms of dimensionless variables,

$$Z = z/L \tag{6}$$

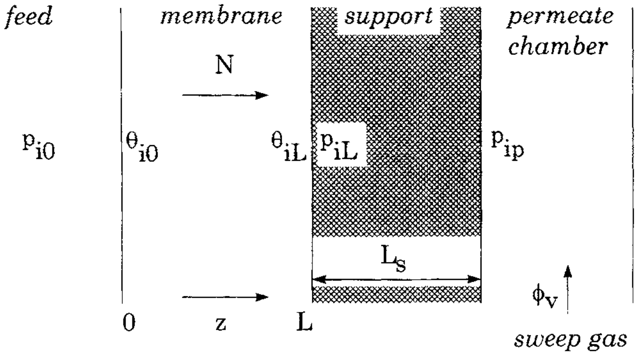

Figure 1. Zeolite membrane system.

$$[\bar{\bar{D}}_r] = [\bar{\bar{D}}]_F \big/ D_{\text{ref}} = \begin{bmatrix} D_{r1} & 0 \\ 0 & D_{r2} \end{bmatrix} [\Gamma]. \tag{7}$$

The normalized flux vector can be written as

$$\bar{N}_r = \frac{\bar{N}L}{\rho \epsilon q_{\text{sat}} D_{\text{ref}}} = -\left[\bar{\bar{D}}_r\right] \frac{d\bar{\theta}}{dZ}. \tag{8}$$

Writing out the equations in terms of the normalized fluxes, we obtain

$$N_{r1} = -D_{r1}\left(1 + \frac{\theta_1}{\theta_v}\right)\frac{d\theta_1}{dZ} - D_{r1}\left(\frac{\theta_1}{\theta_v}\right)\frac{d\theta_2}{dZ}$$

$$N_{r2} = -D_{r2}\frac{\theta_2}{\theta_v}\frac{d\theta_1}{dZ} - D_{r2}\left(1 + \frac{\theta_2}{\theta_v}\right)\frac{d\theta_2}{dZ}. \tag{9}$$

Inversion of the set of Eqs. 9 gives

$$\frac{d\theta_1}{dZ} = -(1 - \theta_1)N_{r1}/D_{r1} + \theta_1 N_{r2}/D_{r2} \tag{10}$$

$$\frac{d\theta_2}{dZ} = \theta_2 N_{r1}/D_{r1} - (1 - \theta_2)N_{r2}/D_{r2}. \tag{11}$$

Further, addition of Eqs. 10 and 11 gives

$$\frac{d\theta_v}{dZ} = -\theta_v\left(\frac{N_{r1}}{D_{r1}} + \frac{N_{r2}}{D_{r2}}\right). \tag{12}$$

Equations 10–12 have been presented in a somewhat different form by Kapteijn et al. (1995).

Now, to save space, we introduce

$$\mu = \frac{N_{r1}}{D_{r1}}\frac{D_{r2}}{N_{r2}}, \tag{13}$$

and so we obtain:

$$\frac{d\theta_1}{dZ} = N_{r2}/D_{r2}[\theta_1(\mu + 1) - \mu] \tag{14}$$

$$\frac{d\theta_2}{dZ} = N_{r2}/D_{r2}[\theta_2(\mu + 1) - 1]. \tag{15}$$

Integration from $Z = 0$ gives

$$\frac{N_{r2}}{D_{r2}}(\mu + 1)Z = \ln\left\{\frac{\theta_1(\mu + 1) - \mu}{\theta_{10}(\mu + 1) - \mu}\right\} \tag{16}$$

$$\frac{N_{r2}}{D_{r2}}(\mu + 1)Z = \ln\left\{\frac{\theta_2(\mu + 1) - 1}{\theta_{20}(\mu + 1) - 1}\right\}, \tag{17}$$

or in terms of the occupancies at $Z = 1$,

$$\frac{N_{r2}}{D_{r2}}(\mu + 1) = \ln\left\{\frac{\theta_{1L}(\mu + 1) - \mu}{\theta_{10}(\mu + 1) - \mu}\right\} \tag{18}$$

$$\frac{N_{r2}}{D_{r2}}(\mu + 1) = \ln\left\{\frac{\theta_{2L}(\mu + 1) - 1}{\theta_{20}(\mu + 1) - 1}\right\}. \tag{19}$$

From this we can obtain the expression for μ:

$$\mu = \frac{\theta_{10}(1 - \theta_{2L}) - \theta_{1L}(1 - \theta_{20})}{\theta_{20}(1 - \theta_{1L}) - \theta_{2L}(1 - \theta_{10})} = \frac{\theta_{10}\theta_{vL} - \theta_{1L}\theta_{v0}}{\theta_{20}\theta_{vL} - \theta_{2L}\theta_{v0}}, \tag{20}$$

leading to the expressions for the reduced fluxes:

$$N_{r1} = D_{r1}\frac{\theta_{10}\theta_{vL} - \theta_{1L}\theta_{v0}}{\theta_{vL} - \theta_{v0}}\ln\left(\frac{\theta_{vL}}{\theta_{v0}}\right) \tag{21}$$

$$N_{r2} = D_{r2}\frac{\theta_{20}\theta_{vL} - \theta_{2L}\theta_{v0}}{\theta_{vL} - \theta_{v0}}\ln\left(\frac{\theta_{vL}}{\theta_{v0}}\right). \tag{22}$$

As an additional result, straightforward integration of Eq. 12 gives

$$\left(\frac{N_{r1}}{D_{r1}} + \frac{N_{r2}}{D_{r2}}\right) = -\ln\left(\frac{\theta_{vL}}{\theta_{v0}}\right), \tag{23}$$

which, of course, can also be obtained from Eqs. 21 and 22.

For *single-component permeation* relations, Eqs. 21 and 22 result in

$$N_{ri} = D_{ri}\ln\left(\frac{1 - \theta_{iL}}{1 - \theta_{i0}}\right). \tag{24}$$

For the special case of *zero partial pressure* at the permeate side, as was assumed by Krishna and van den Broeke, we obtain the following equations:

$$\mu = \frac{\theta_{10}}{\theta_{20}}, \tag{25}$$

and so

$$N_{r1} = D_{r1}\frac{\theta_{10}}{\theta_{10} + \theta_{20}}\ln\left\{\frac{1}{1 - \theta_{10} - \theta_{20}}\right\} \tag{26}$$

$$N_{r2} = D_{r2}\frac{\theta_{20}}{\theta_{10} + \theta_{20}}\ln\left\{\frac{1}{1 - \theta_{10} - \theta_{20}}\right\}. \tag{27}$$

For the flux ratio, we find from Eqs. 8, 20, 26 and 27:

$$\frac{N_1}{N_2} = \frac{D_1}{D_2}\mu = \frac{D_1}{D_2}\frac{\theta_{10}}{\theta_{20}} = \frac{D_1}{D_2}\frac{b_1}{b_2}\frac{p_{10}}{p_{20}}. \tag{28}$$

We now illustrate the use of these analytical equations with two examples. The first one is an analysis of the data of Kapteijn et al. on the permeation of propane (1)–propene (2) at 292 K. In order to interpret these data, two additional equations are needed. The first is the balance over the permeate chamber; if it is assumed to be ideally mixed, the permeate partial pressure of the components is given by:

$$p_{ip} = \frac{N_i ART}{\phi_v}. \tag{29}$$

The second necessary equation is one for transport inside the stainless-steel support. In principle this should be treated as a multicomponent transport problem in an inert porous medium, such as was described by Kerkhof (1996). In view of the large size of the pores, as can be seen in the photographs of Bakker et al., and the relatively low mole fractions of permeating components, a reasonable approach is to take dilute independent diffusion of the components in the sweep gas, with a hindering factor because of support porosity and tortuosity:

$$N_i \approx \frac{D_{i,s}}{L_s}\frac{1}{RT}(p_{iL}-p_{ip}) = \frac{\xi D_{i,\mathrm{mol}}}{L_s}\frac{1}{RT}(p_{iL}-p_{ip}). \tag{30}$$

From Bakker et al.'s article, follow the following data:

Membrane thickness: $L = 40\ \mu\mathrm{m}$
Support porosity: $\epsilon = 0.4$
Support layer thickness: $L_s = 3.10^{-3}$ m
Silicalite density: $\rho = 1{,}800\ \mathrm{kg/m^3}$
Membrane area: $A = 3.14 \times 10^{-4}\ \mathrm{m^2}$
Sweep gas flow: $\phi_v = 1.67 \times 10^{-6}\ \mathrm{m^3/s}$
Saturation load: $q_{\mathrm{sat}} = 2.18 \times 10^{-3}$ kmol/kg
Langmuir slope: $b_1 = 1.1$ (1/kPa), $b_2 = 0.75$ (1/kPa)

At partial feed pressures of 50 kPa for both components, the following data can be found in Bakker et al.'s article:

	N_{single} (10^{-6} kmol/m^2·s)	N_{mixture} (10^{-6} kmol/m^2·s)	D_{single} (10^{-10} m^2/s)	D_{mixture} (10^{-10} m^2/s)
C_3H_8 (1)	7.07	4.78	0.63–0.70	0.789
C_3H_6 (2)	8.97	3.65	1.02	0.768

As can be concluded from their discussion, Bakker et al. neglected the resistance of the support layer, but took into account the pressure in the permeate chamber. First, we can use Eq. 23 as a consistency test for the mixture results. The permeate-chamber partial pressures were calculated from the fluxes. For the situation in which the support-layer resistance is neglected, the θ_{iL} follow from the Langmuir equation. We then find the following results:

	θ_{i0}	θ_{iL}	N_{ri}/D_{ri}
C_3H_8 (1)	0.588	0.518	1.54
C_3H_6 (2)	0.401	0.269	1.21

and so we find $\ln(\theta_{vL}/\theta_{v0}) = \ln(0.213/0.0107) = 2.99$. For the sum of the N_{ri}/D_{ri}, we find $1.54 + 1.21 = 2.75$. Thus we see that this test is reasonably met. From the analytical equations (Eqs. 21 and 22), however, we can also evaluate the diffusion coefficients, thus finding values of 0.69 and 0.76 (10^{-10} m^2/s) for Eqs. 1 and 2, respectively, which fully agree with the consistency criterion. If we take into account the resistance of the support layer, estimating the hindrance factor at $\xi = 0.25$, and estimating the gaseous binary diffusion coefficients with He according to the Neufeld method of Reid et al. (1977), the analysis presented here gives:

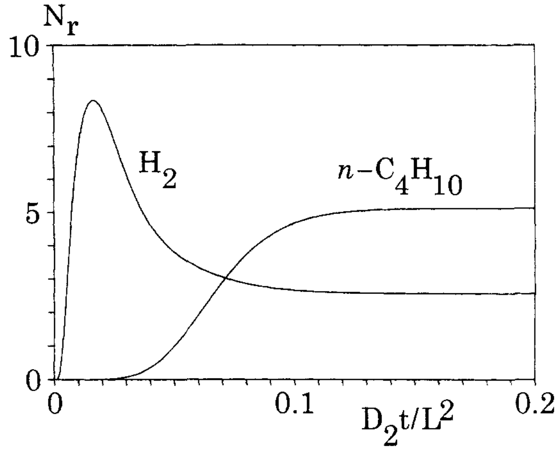

Figure 2. Breakthrough curves for the system hydrogen (1)-*n*-butane (2) through zeolite membrane at each 50-kPa feed pressure and zero permeate pressure.

Resistance of support layer neglected. Physical data used in this calculation: $D_1/D_2 = 20$, $b_2/b_1 = 40$, $b_1 = 0.1$ kPa^{-1} (Krishna and van den Broeke (1995) cited $D_1/D_2 = 40$, $b_2/b_1 = 20$ in their article).

	θ_{i0}	$D_{i,\mathrm{mol}}$ (10^{-5} m^2/s)	θ_{iL}	$D_{i,\mathrm{mix}}$ (10^{-10} m^2/s)
C_3H_8 (1)	0.588	4.11	0.605	0.94
C_3H_6 (2)	0.401	4.53	0.297	1.02

It is not the author's intention here to go into a deeper discussion of these and other results, but only to indicate how the analytical equations can be used in data analysis.

The second example is concerned with numerical results. An often used figure from Krishna and van den Broeke (1995) is shown in Figure 2, which looks similar to the experimental results of Kapteijn et al. (1995) for the simultaneous permeation of H_2 and n-C_4H_{10}. According to Krishna and van den Broeke, the parameters used were $D_1/D_2 = 40$ and $b_2/b_1 = 20$, for equal partial pressures of 50 kPa for the feed. However, a numerical calculation by the present author using these data failed to produce this figure. For the parameter values of Krishna and van den Broeke, one should obtain $N_1/N_2 = 2$, according to Eq. 28; in their figure, however, a value of 0.5 is found. The most probable explanation is that the authors switched the numbers 20 and 40 in the input of their computer program; this does indeed give the graphs in Figure 2.

Thus we may conclude that the analytical equations presented here may help in both experimental evaluation and numerical simulation.

Notation

q = load in adsorbed phase, kmol/kg
R = gas constant, J/kmol·K
T = absolute temperature, K
z = distance coordinate, m
Z = dimensionless distance coordinate, m
δ_{ij} = Kronecker delta
μ = flux ratio factor, Eq. 13
ξ = diffusion hindrance factor

Subscripts

0 = at $z = 0$
i, j = component
L = at $z = L$
mol = molecular
n = number of components
r = reduced
ref = reference
s = support

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