One-Component Permeation Maximum: Diagnostic Tool for Silicalite-1 Membranes?

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The permeation flux of single components through MFI-type membranes (Silicalite-1, ZSM-5) as a function of the temperature often exhibits a maximum at a certain temperature (Coronas et al., 1997; Burggraaf et al., 1998; Bakker et al., 1997; van de Graaf et al., 1998a). Also, a weak minimum sometimes is observed at higher temperatures (Bakker et al., 1997). This is well represented by Figure 1 for the C_1–C_4 alkane homologues permeation through a stainless-steel-supported silicalite-1 membrane (van de Graaf, 1999). This can be well described by a major contribution from an adsorption-diffusion process and the additional contribution of activated Knudsen-type diffusion at higher temperatures (van de Graaf et al., 1998c; Bakker et al., 1997). The maximum may be absent, however, as has been found for isobutane over the investigated temperature range (Figure 1). Van de Graaf (1998b) analyzed the occurrence of the maximum based on a permeation model where the driving force is based on the thermodynamic potential gradient. The latter is related to the occupancy in the silicalite-1 through a Langmuir isotherm, which is valid for the linear C_1–C_4 alkanes (Zhu et al., 1998). Neglecting the high temperature contribution, an assumption that is valid for the region around the maximum, the resulting flux expression is given by Eq. 1:

$$N_i(T) = A1 \cdot \text{Đ}_i(T) \cdot \nabla \ln\{1-\theta_i(T)\}$$

$$= \frac{A1}{\delta} \cdot \text{Đ}_i(T) \cdot \ln\left\{\frac{1-\theta_{i,\delta}(T)}{1-\theta_{i,0}(T)}\right\}, \quad (1)$$

where N_i, Đ_i, and θ_i are the flux, the corrected diffusivity, and the occupancy in the silicalite-1, respectively; $A1$ is a proportionality constant containing the saturation capacity of the component, the density of the zeolite, and corrects for surface roughness of the silicalite-1 layer and blocking by the support material; δ represents the effective silicalite-1 membrane thickness; and the subscripts 0 and δ refer to the conditions at the feed and the permeate side of the silicalite layer, respectively.

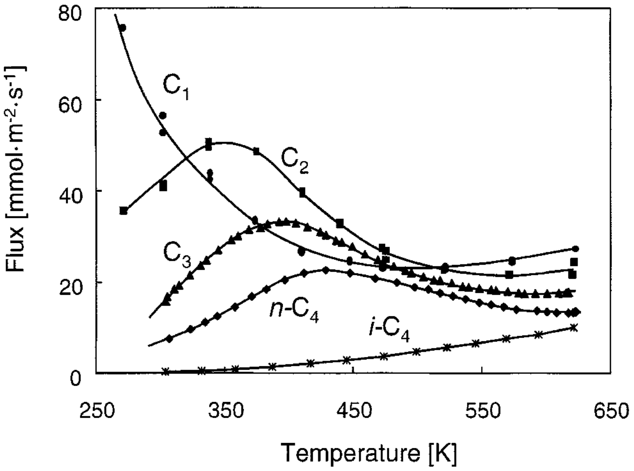

Figure 1. Permeation flux as a function of temperature for *n*-alkanes (C_1–C_4) and *i*-butane through a stainless-steel-supported silicalite-1 membrane, measured in a Wicke-Kallenbach (WK) mode using helium as a sweep gas.

Feed and permeate side pressures 101 kPa, silicalite-1 layer facing the feed side; (●) methane, (■) ethane, (▲) propane, (◆) *n*-butane, (∗) *i*-butane.

The temperature dependency of the flux is contained in that of the corrected diffusivity and the occupancy through Eqs. 2–4:

$$\text{Đ}_i = \text{Đ}_{0i} \exp\left(-\frac{E_{D,i}}{RT}\right) \quad (2)$$

$$\theta_i = \frac{K_i p_i}{1+K_i p_i} \quad (3)$$

$$K_i = K_{0i} \exp\left(\frac{Q_i}{RT}\right). \quad (4)$$

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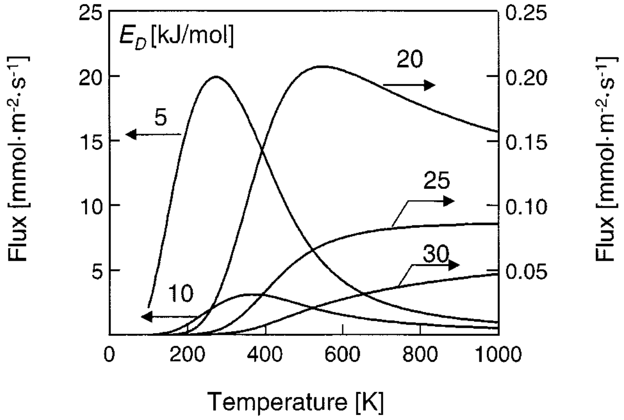

Figure 2. Effect of the activation energy for diffusion E_D (kJ·mol^{-1}) on the permeation flux for the model given by Eqs. 1–4 for a fixed heat of adsorption Q.

Parameter values: $A1 = 3.6 \times 10^{-3}$ mol·m^{-3}; $\delta = 10^{-5}$ m; $Đ_{0i} = 10^{-7}$ m^2·s^{-1}; $Q_i = 25$ kJ·mol^{-1}; $K_{0i} = 1.2 \times 10^{-7}$ Pa^{-1}. Partial-pressure feed side, 101-kPa; permeate side, 0 Pa.

Van de Graaf (1998b) showed that if the activation energy of the diffusivity is smaller than the heat of adsorption, $E_{D,i} < Q_i$, a maximum appears; if it is larger, the flux increases monotonically; and if they are equal, the flux approaches an asymptotic value. Figure 2 illustrates these situations.

In catalysis several temperature programming techniques, such as reduction (TPR) and desorption (TPD), are used for characterization purposes. The observed concentration profile is a fingerprint of the catalyst system and the position of a maximum is related to the activation energy of the studied process. In an analogy, one might wonder if the position of the permeation maximum is some unique property of the permeating component, what relation exists for this maximum, and if it can be used as a diagnostic tool for a quick determination of a system parameter like Q_i or $E_{D,i}$. These questions are addressed in the following.

Mathematical Derivation

The position of the maximum in the surface flux as a function of temperature can be determined from the permeation expression (Eq. 1) by setting the first derivative of the permeation flux with respect to the temperature equal to zero:

$$\frac{\partial N_i(T)}{\partial T} = 0 = \frac{\partial Đ_i(T)}{\partial T} \cdot \ln\left\{\frac{1-\theta_{i,\delta}(T)}{1-\theta_{i,0}(T)}\right\} + Đ_i(T) \cdot \left\{\frac{1-\theta_{i,\delta}(T)}{1-\theta_{i,0}(T)}\right\}^{-1} \cdot \frac{\partial\left\{\dfrac{1-\theta_{i,\delta}(T)}{1-\theta_{i,0}(T)}\right\}}{\partial T}, \quad (5)$$

in which

$$\frac{\partial Đ_i(T)}{\partial T} = \frac{E_{D,i}}{RT^2} \cdot Đ_i(T) \quad (6)$$

and

$$\frac{\partial\left\{\dfrac{1-\theta_{i,\delta}(T)}{1-\theta_{i,0}(T)}\right\}}{\partial T} = \frac{\partial\left\{\dfrac{1+K(T)_i \cdot p_{i,0}}{1+K(T)_i \cdot p_{i,\delta}}\right\}}{\partial T} = -\frac{Q}{R \cdot T^2} \cdot \left\{\frac{1-\theta_{i,\delta}}{1-\theta_{i,0}}\right\} \cdot (\theta_{i,0} - \theta_{i,\delta}). \quad (7)$$

Combining Eqs. 5–7 yields Eq. 8 for the situation of a flux maximum. This expression relates the logarithmic mean of the unoccupied fraction sites, $\theta_{\text{vac}} = (1-\theta_i)$, over the silicalite layer to the ratio of the activation energy for diffusion and the heat of adsorption of a component i:

$$(1-\theta_i)_{\ln} = (\theta_{\text{vac}})_{\ln} = \frac{(1-\theta_{i,\delta}) - (1-\theta_{i,0})}{\ln\left\{\dfrac{1-\theta_{i,\delta}}{1-\theta_{i,0}}\right\}} = \frac{E_{D,i}}{Q_i}. \quad (8)$$

Discussion

From Eq. 8 it follows that the maximum in the surface flux occurs when the logarithmic mean of $(1-\theta_i)$ equals the ratio between the activation energy for diffusion and the heat of adsorption. This expression defines the conditions for which a maximum occurs, since only physically realistic values for the occupancy are allowed, that is, the lefthand side may only vary between 0 and 1.

- If $Q_i < E_{D,i}$, Eq. 8 has no solution and there is no maximum in the flux as a function of temperature. In other words, the activated nature of the diffusion process then dominates at all temperatures. This is experimentally observed with our silicalite-1 membrane for bulky components like *i*-butane and neopentane.
- If $Q_i = E_{D,i}$, the only solution is for the occupancy approaching zero. This represents an asymptotic solution for high temperatures where the flux becomes independent of temperature. The other trivial solution for zero occupancy, at infinitely low pressure, yields no flux at all.
- A maximum in the flux can be observed for only $0 < E_{D,i} < Q_i$. Figure 2 shows the different situations.

Under the last condition, it follows from Eq. 8 that the position (temperature) of the maximum permeation flux for a given component is determined by two variables, the feed- and the permeate-side concentrations in the silicalite layer. These concentrations depend on the temperature and on the boundary conditions during the experiments. The boundary conditions are not only determined by the composition of the feed and the permeate, but also on the experimental method and membrane configuration (van de Graaf et al., 1998a). The membrane used in Figure 1 consists of a 50-μm-thin silicalite-1 layer supported by a 3-mm-thick porous sintered stainless-steel layer (van de Graaf et al., 1999). The silicalite-1 faces the feed side (“WK-feed”). The steel support layer has a certain resistance and a concentration gradient exists, so the local concentration at the silicalite-1 is higher than in the permeate gas. If the membrane is turned around, so the silicalite-1 faces the permeate side (“WK-perm”), then the helium immediately sweeps away the permeated gas molecules, maintaining a lower concentration at the permeate side than in the former orientation. Also, vacuum can be applied at the permeate side instead of using a sweep gas (“batch method”). These three situations are compared in Figure 3a for the permeation flux of propane, and in Figure 3b for ethane. It is obvious that the experimental method used affects the observed position of the maximum, due to the dependency on the occupancy at both the feed and permeate sides. The maximum may even disappear in the investigated temperature range.

Equation 8 is graphically represented in Figure 4a. For fixed values of the permeate-side occupancy, $\theta_{i,\delta}$, the corresponding feed-side occupancy, $\theta_{i,0}$, is given as a function of the ratio $E_{D,i}/Q_i$. This immediately reveals the following constraints for the presence of a maximum in the permeation flux:

$$0 \le \theta_{i,\delta} < \left(1-\frac{E_{D,i}}{Q_i}\right) < \theta_{i,0} \le \theta_{i,0}^{\max}. \qquad (9)$$

The upper limit for the feed-side occupancy, $\theta_{i,0}^{\max}$, corresponds to a zero permeate occupancy $\theta_{i,\delta} = 0$. Only a certain range of feasible combinations of occupancies will result in a maximum in the permeation flux, indicated by the shaded area. If the feed occupancy is too high, a flux maximum will be found at higher temperatures where the occupancies will be lower, and vice versa. On the other hand, maintaining a large occupancy at the permeate side can eliminate the possibility of observing a maximum in the permeation flux for higher values of $E_{D,i}/Q_i$.

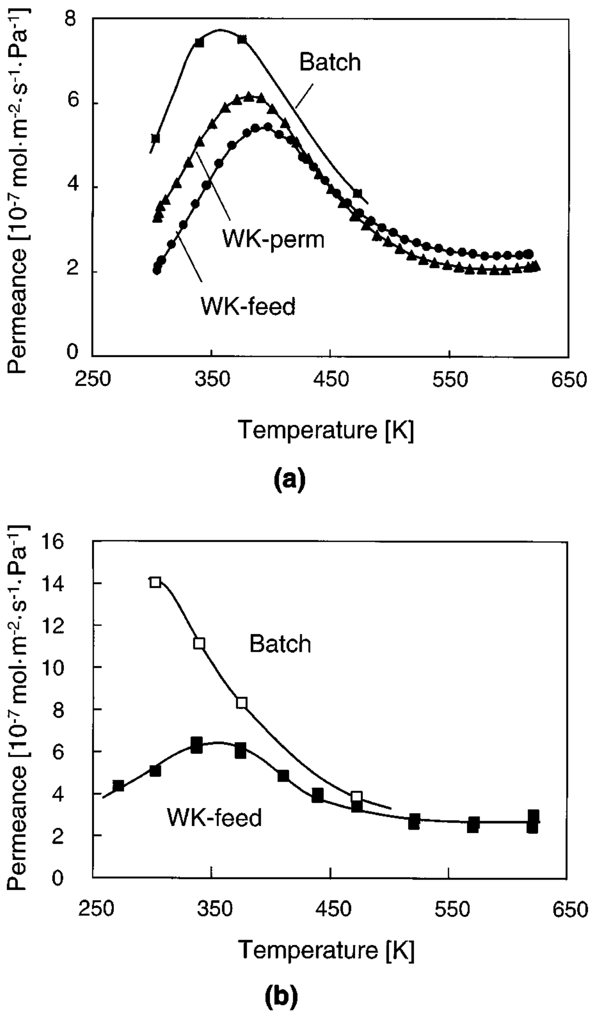

Figure 3. Permeance (flux divided by the partial-pressure difference over the membrane) as a function of the temperature for different experimental methods for (a) propane and (b) ethane (feed: 101 kPa).

(●) WK-feed method: silicalite facing the feed side (sweep gas helium, 101 kPa); (▲) WK-perm method: silicalite facing the permeate side (sweep gas helium, 101 kPa); (■) Batch method: silicalite facing the feed side (permeate-side vacuum).

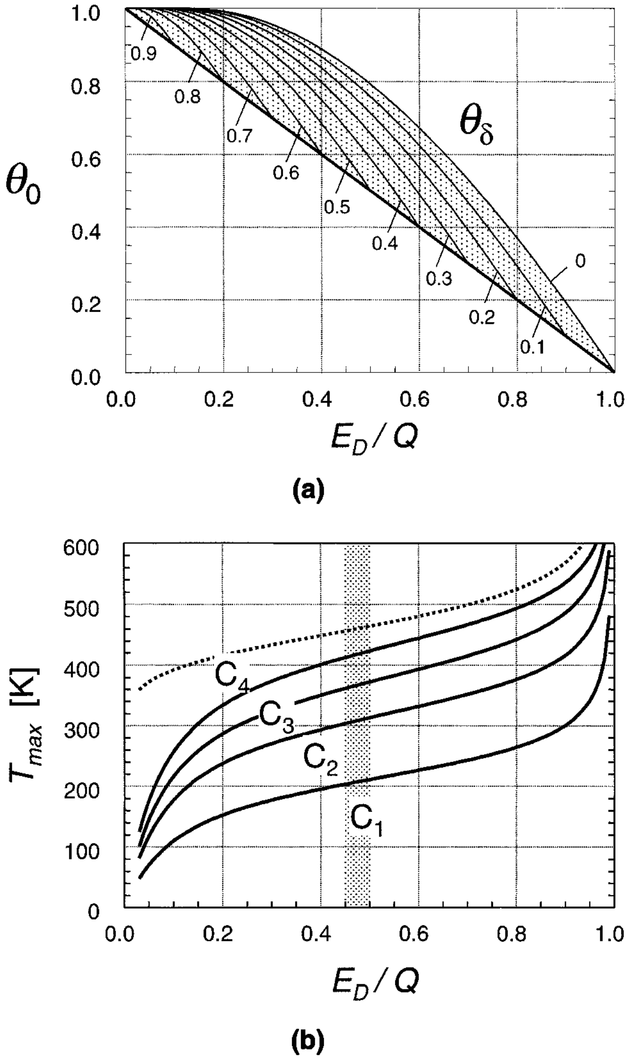

Figure 4. Parametric charts for Eq. 8.

(a) Feed-side occupancy θ_0 as a function of E_D/Q for constant permeate-side occupancy values θ_δ; (b) temperature of the maximum for 101-kPa feed pressure and vacuum at permeate side as a function of E_D/Q for C_1–C_4 alkanes (solid lines). Dashed line represents the upper temperature limit for the butanes if the permeate pressure is increased.

Table 1. Predicted vs. Experimental Occupancies Calculated for the Maximum Surface Flux at 101-kPa Feed Pressure With Wicke-Kallenbach and Batch Methods*

Gas	Methane	Ethane	Propane	*n*-Butane
Batch				
$E_{D,i}$ [kJ·mol^{-1}]**	7.2	13.2	18.1	
Q_i [kJ·mol^{-1}]**	16.4	29.3	37	
θ_{i0} (Theory)†	0.44	0.45	0.49	
θ_{i0} (Exp.)†	n.d.	0.42	0.43	
Wicke-Kallenbach				
$E_{D,i}$ [kJ/mol^{-1}]**	6.3	15.4	18.7	21.0
Q_i [kJ·mol^{-1}]**	16.4	29.3	37	47
$\Delta_{\ln}(1-\theta_i)$ (Theory)	0.38	0.53	0.51	0.45
$\Delta_{\ln}(1-\theta_i)$ (Exp.)	n.d.	0.48	0.48	0.38

*In both cases the silicalite-1 layer faced the feed side.

**Data from Zhu et al. (1998); van de Graaf et al. (1999).

†Since vacuum is applied at the permeate side, the feed side occupancy can be given.

Figure 4b contains the temperature where the maximum of the permeation flux will be found, as a function of the ratio $E_{D,i}/Q_i$ for 100-kPa feed pressure and zero permeate pressure, globally corresponding to the batch method. The various curves correspond to the adsorption data for the C_1–C_4 alkanes, that is, the curves for normal and isobutane nearly coincide and are not given separately. For these *n*-alkanes the range of $E_{D,i}/Q_i$ values is globally 0.45–0.50, so Figure 4b (shaded area) indicates the temperatures where the maximum in the flux can be expected for the various components in the batch experiments. This corresponds well with Figure 3a for propane. The maximum for ethane is not visible; it is located at the lower-temperature end of the experiments. The maximum in the WK experiments are shifted to higher temperatures, since the permeate occupancy is larger in these experiments.

Generally, for higher permeate pressures the curves in Figure 4b will shift upward until the upper limit is reached for $T_{\max}$, since only conditions where $\theta_{\delta,i} < (1 - E_{D,i}/Q_i)$ are acceptable. This is indicated for butane in Figure 4b by the dashed line.

In Table 1 the theoretical values of the occupancy at which the maximum in the flux is expected for the different *n*-alkanes are compared with the experimental values of the average occupancy at the temperature of the maximum in the surface flux. To calculate the experimental values, the effect of the experimental method was taken into account (van de Graaf et al., 1998a), and the theoretical occupancies were based on values for the diffusivity activation energy from isothermal determinations (van de Graaf et al., 1999). The heat of adsorption had been determined separately (Zhu et al., 1998), and there is good agreement between the predicted and experimental values. This implies that if the adsorption data of a component and the experimental conditions (partial pressures at both sides) are known, the position of the maximum gives a reasonable estimate of the activation energy of diffusion through application of Eq. 8.

To illustrate this, the graph of Figure 4a is applied to the data for isobutane of Millot et al. (1999). The authors observed a maximum in the permeation flux through an alumina-supported ZSM-5 membrane around 600 K and feed pressures of 1.5–1.7 bar. According to Zhu et al.'s data for the adsorption of isobutane, the feed occupancy ranges between 0.10 and 0.12. Since no data for the permeate partial pressure are available, the occupancy at that side cannot be established, but from Figure 4a a range of feasible $E_{D,i-C_4}/Q_{i-C_4}$ values between 0.88 and 0.95 follows, depending on the permeate occupancy, and correspondingly $E_{D,i-C_4} \approx 41-44$ kJ/mol. Millot et al. reported an apparent diffusivity activation energy of 34 kJ/mol. This is obviously too low to explain the maximum. Their diffusivity data at lower temperatures, however, clearly deviate from the Arrhenius trend. It is suggested that at these lower temperatures the dual-site adsorption (Vlugt et al., 1998; Zhu et al., 1998) affects the permeation, yielding deviating diffusivity values. Ignoring these data, the resulting estimated 40.7 kJ/mol for the diffusivity activation energy is well in agreement with the analysis described earlier. The absence of a maximum in our data can be attributed to the low upper temperature limit in the experiments or to a higher apparent activation energy for diffusion. The separation layer of intergrown crystals exhibits higher values for the diffusivity activation energy than does a pure silicalite-1 crystal (van de Graaf et al., 1999) and values differ from membrane to membrane. In the *i*-butane case, the values are close to the heat of adsorption and small changes can lead to the appearance or disappearance of the maximum. A similar case is given by Coronas et al. (1997). They synthesized different alumina-supported ZSM-5 membranes and observed a maximum for one membrane of around 450 K, whereas for another membrane, the *n*-butane flux approached asymptotically a maximum level. The latter suggests an activation energy for diffusion that is about equal to the heat of adsorption (cf. Figure 2).

In general, adsorption equilibrium data are less affected by crystal intergrowth than is diffusion, which suffers much more from internal barriers. Therefore independently determined adsorption data can be used in the present analysis to determine the apparent diffusivity activation energy for a zeolite membrane.

In conclusion, analysis of the permeation maximum presented, appearing in single-component permeation through zeolitic membranes as a function of the temperature, demonstrates that the position (temperature) of this maximum can be used to estimate the apparent activation energy of the diffusivity, provided the applied partial pressures at both sides of the membrane and the adsorption parameters are known.

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