Pergamon

Int. Comm. Heat Mass Transfer, Vol. 28, No. 3, pp. 337–346, 2001

0735-1933/01/$–see front matter

PII: S0735-1933(01)00239-1

DIFFUSION OF BINARY MIXTURES ACROSS ZEOLITE MEMBRANES: ENTROPY EFFECTS ON PERMEATION SELECTIVITY

R. Krishna
Department of Chemical Engineering, University of Amsterdam
Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands
(Fax: +31 20 5255604; email: krishna@its.chem.uva.nl)

(Communicated by J.W. Rose and A. Briggs)

ABSTRACT

Diffusion of binary mixtures across zeolite membranes is strongly influenced by the sorption behaviour of the individual components. When the components in the mixture have significantly different molecular sizes, *size entropy* effects tend to favour the sorption of the smaller species at high molecular loadings. This is the case, for example, for adsorption of methane and n-butane in silicalite. For mixtures of linear and branched alkanes having the same number of carbon atoms, *configurational entropy* effects tend to favour the sorption of the linear alkane because these molecules "pack" more efficiently inside the ordered zeolite structure. In estimating the permeation of mixtures across zeolite membranes, both size and configurational entropy effects need to be properly accounted for. A model to estimate the permeation fluxes across zeolite membranes is developed by combining the Real Adsorbed Solution Theory to describe the mixture sorption, and the Maxwell-Stefan diffusion equations. The utility of the model is demonstrated by means of two case studies: (1) permeation of methane and n-butane, and (2) permeation of n-hexane and 2,2, dimethylbutane across a silicalite membrane.

Introduction

Separation of mixtures using zeolite membranes is attracting increasing attention because of the high selectivities that are achievable [1 – 11]. There are two factors which influence the selectivity of separation: (1) the differences in the sorption characteristics of the individual species, and (2) the differences in the mobilities (diffusivities) of the constituents. For transport within zeolites, sorption and diffusion phenomena are closely interlinked. In this communication we focus on two aspects which influence the sorption, and consequently the diffusion, behaviour of binary mixtures across zeolite membranes: *size* and *configurational entropy* effects.

To begin with we explain size entropy effects by considering sorption of a mixture of methane and n-butane in silicalite at 300 K. The Langmuir isotherm:

$$\Theta_i^0 = \Theta_{i\,sat} \frac{b_i P}{1 + b_i P} \tag{1}$$

has been used to correlate the pure component isotherm data by Van de Graaf et al. [12]. The P in eq. (1) represent the system pressure, expressed in Pa. Methane (1) has a much lower sorption strength than n-butane (2); $b_1 = 2.44\times10^{-6}$ Pa^{-1}; $b_2 = 9.6\times10^{-3}$ Pa^{-1}. On the other hand, methane has a saturation capacity $\Theta_{1,sat}$= 20.4 molecules per unit cell, whereas the larger n-butane has a saturation capacity $\Theta_{2,sat}$= 10 molecules per unit cell. While the sorption strength of methane is significantly lower than that of n-butane, its sorption capacity is significantly higher At high loadings, the sorption tends to favour the methane molecule because the smaller methane finds it easier to fill in the vacant "gaps" in the silicalite matrix. For a mixture of methane and n-butane, the loadings in the mixture are commonly estimated using the multicomponent Langmuir isotherm; see e.g. Ciaverella et al. [9]:

$$\frac{\Theta_i}{\Theta_{i\,sat}} = \frac{b_i p_i}{1 + b_1 p_1 + b_2 p_2}; \quad i = 1,2 \tag{2}$$

where p_i represent the partial pressure of component i. The estimations of the loadings for a 95-5 mixture of methane and n-butane using eq. (1) are shown in Fig. 1 (a). The sorption selectivity

$$S = \frac{\Theta_1}{\Theta_2} \frac{p_2}{p_1} \tag{3}$$

is shown in Fig. 1 (c); this value is predicted to be independent of the pressure, i.e. the loading. The multicomponent Langmuir isotherm as presented in eq. (2) is strictly applicable only when the saturation loadings of the two species are identical. When the loadings are different, eq. (2) is no longer thermodynamically consistent [13]. In order to deal with different saturation loadings we use the Ideal Adsorbed Solution Theory (IAST) to estimate the mixture isotherms. Briefly, the basic equation of IAST theory is the analogue of Raoult's law for vapour-liquid equilibrium [14], i.e.

$$P y_i = P_i^0(\pi) x_i \tag{4}$$

where x_i is the mole fraction in the adsorbed phase

$$x_i = \frac{\Theta_i}{\Theta_1 + \Theta_2} \tag{5}$$

and $P_i^0(\pi)$ is the pressure for sorption of every pure component i, which yields the same spreading pressure, π, as that for the mixture. The spreading pressure is defined by the Gibbs adsorption isotherm

$$\frac{\pi A N_A}{RT} = \rho \int_{P=0}^{P=P_i^0} \frac{\Theta_i^0(P)}{P} dP \tag{6}$$

where A is the surface area per m^3 of adsorbent of the adsorbent, ρ is the density of silicalite expressed in terms of the number of unit cells per m^3 , N_A is the Avogadro number, R is the gas constant, T is the absolute temperature, and $\Theta_i^0(P)$ is the pure component isotherm given by eq. (1). The total amount adsorbed is obtained from

$$\Theta_1 + \Theta_2 = \frac{1}{\dfrac{x_1}{\Theta_1^0(P_1^0)} + \dfrac{x_2}{\Theta_2^0(P_2^0)}} \tag{7}$$

The set of equations (1), (4) – (7) need to be solved numerically to obtain the mixture loadings of components 1 and 2. The loadings for a 95-5 mixture calculated from IAST are shown in Fig. 1 (b). We note that the loading of methane increases sharply at higher pressures; this is the consequence of the size entropy effect. The sorption selectivity of n-butane decreases with increasing loading; see Fig. 1 (c). One of the objectives of this communication is to highlight the importance of size entropy effects on permeation across a silicalite membrane.

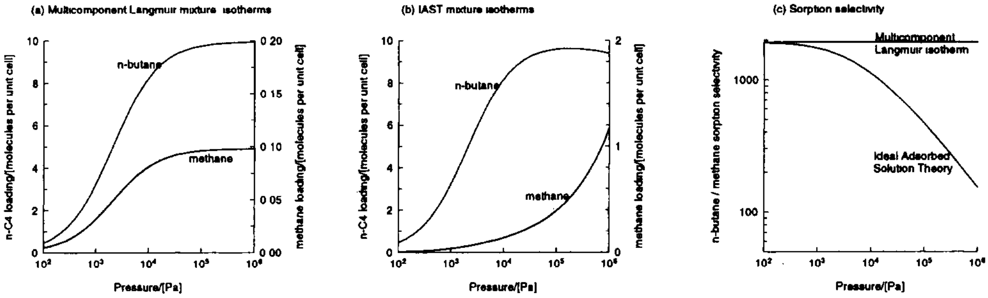

FIG. 1
(a) 95-5 mixture loadings estimated for methane – n-butane at 300 K using eq. (2). (b) 95-5 mxiture loading estimated using IAST. (c) Sorption selectivity

TABLE 1.

Pure component sorption parameters for dual-site Langmuir model applied to silicalite

Component i	Temperature /[K]	Dual-Site Langmuir Parameters, see eq. (7)			
		Site A		Site B	
		$b_{i,A}$ /[Pa^{-1}]	$\Theta_{i,sat,A}$ /[molecules per unit cell]	$b_{i,B}$ /[Pa^{-1}]	$\Theta_{i,sat,B}$ /[molecules per unit cell]
methane	300	2.44×10^{-6}	20.4		
n-butane	300 .	9.6×10^{-3}	10		
n-hexane	398	8.24×10^{-3}	4	1.56×10^{-5}	4
22DMB	398	1.75×10^{-3}	4		

Let us now consider a mixture of n-hexane (n-C6) and its isomer 2,2 dimethylbutane (22DMB). The pure component isotherms, estimated from Configurational-Bias Monte Carlo simulations (CBMC) are shown in Fig. 2 (a). The CBMC methodology is explained in detail in our earlier publications [7,8,10,11,15,16]. Extensive comparisons of CBMC simulations with experimental data have established the accuracy of the CBMC simulations [15,16] and therefore we treat the CBMC simulations as "experimental data". We note from Fig. 2 (a) that n- hexane exhibits a slight inflection at a loading of 4 molecules per unit cell and the pure component isotherms are best represented by a dual-site Langmuir isotherm

$$\Theta_i^0(P) = \frac{\Theta_{i,sat,A} b_{i,A} P}{1 + b_{i,A} P} + \frac{\Theta_{i,sat,B} b_{i,B} P}{1 + b_{i,B} P} \tag{8}$$

where we identify two sites within the silicalite matrix A (corresponding to the intersections) and B (corresponding to the channel interiors). The pure component parameters are listed in Table 1. For a 50-50 mixture CBMC simulations of the loadings are shown in Fig. 2 (b). The branched alkane 22DMB exhibits a curious maximum with respect to molecular loading within the silicalite structure. As the partial pressures increase to 1000 Pa, the sorbate loading of both linear and branched alkanes increase till a maximum is reached in the loading of 2DMB. This occurs at a total mixture loading of 4 molecules per unit cell. Up to this point there is really no competition between n-C_6 and 22DMB. As the pressure is increased beyond 1000 Pa, it is more efficient to obtain higher loading by "replacing" the 22DMB with n-C_6; this *configurational entropy* effect is the reason behind the curious maximum in the22DMB isotherm. The IAS theory is not adequate to precisely describe the mixture behaviour and non-ideality effects need to be taken into account [8]. The mixture non-ideality effects can be quantified by the introduction of activity coefficients into eq. (4). The resulting Real Adsorbed Solution (RAS) theory is described by

$$P y_i = P_i^0(\pi) x_i \gamma_i \tag{9}$$

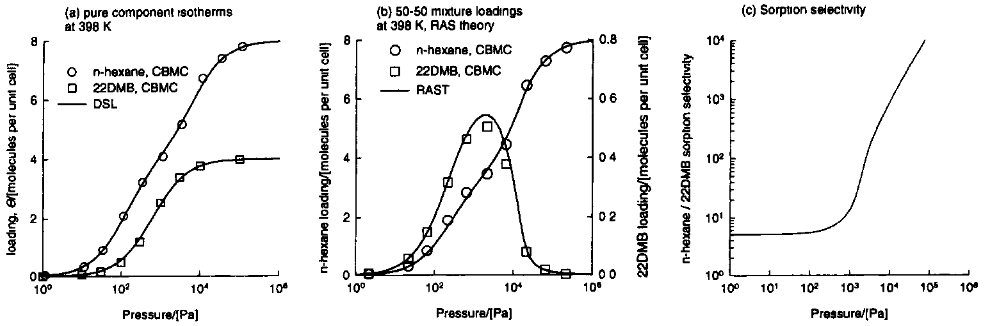

FIG. 2
(a) pure component isotherm for n-C6 and 22DMB at 398 K; CBMC simulations compared with Dual -site Langmuir model fits using parameters from Table 1. (b) 50-50 mixture loadings estimated using RAST. (c) Sorption selectivity calculated using RAST.

Following the work of Calleja et al. [17] we have used the Wilson model for the activity coefficients:

$$\begin{aligned} \ln(\gamma_1) &= 1-\ln(x_1+x_2\Lambda_{12})-\frac{x_1}{x_1+x_2\Lambda_{12}}-\frac{x_2\Lambda_{21}}{x_2+x_1\Lambda_{21}} \\ \ln(\gamma_2) &= 1-\ln(x_2+x_1\Lambda_{21})-\frac{x_2}{x_2+x_1\Lambda_{21}}-\frac{x_1\Lambda_{12}}{x_1+x_2\Lambda_{12}} \end{aligned} \qquad (10)$$

The values of the fitted Wilson parameters are Λ_{12} = 2.6; Λ_{12} = 0.01. The calculations using RAST are compared with the CBMC mixture simulations in Fig. 2 (b); the agreement is very good. The sorption selectivity of n-C6 with respect to 22DMB is seen to rise sharply beyond a pressure of 1000 Pa (cf. Fig. 2 (c)); configurational entropy effects have a profound effect on the selectivity. The second objective of this communication is to study the influence of configurational entropy effects on mixture permeation.

In order to calculate the permeation fluxes and selectivities, we use the Maxwell-Stefan diffusion equations.

The Maxwell-Stefan Theory for Binary Mixture Diffusion

The Maxwell-Stefan theory for n-component diffusion within a zeolite matrix is given by the following equation (details are available in our earlier publications [8, 18 - 23])

$$-\rho\frac{\theta_i}{RT}\nabla\mu_i=\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{\Theta_j \mathbf{N}_i-\Theta_i \mathbf{N}_j}{\Theta_{i,sat}\Theta_{j,sat}Đ_{ij}}+\frac{\mathbf{N}_i}{\Theta_{i,sat}Đ_i};\quad i=1,2...n \qquad (11)$$

The fractional occupancy θ_i of the sorbate within the zeolite matrix is defined as

$$\theta_i \equiv \Theta_i/\Theta_{i,sat};\quad i=1,2,...n \qquad (12)$$

For a binary mixture, n = 2, eq. (11) may be cast into 2-dimensional matrix notation to give

$$(\mathbf{N})=-\rho[\Theta_{sat}][B]^{-1}[\Gamma]\nabla(\theta)=-\rho[\Theta_{sat}][D]\nabla(\theta) \qquad (13)$$

where $[D]$ is the two-dimensional Fick diffusvity matrix and $[\Theta_{sat}]$ is a diagonal matrix with the saturation loadings $\Theta_{i,sat}$. The matrix $[B]$ has the elements

$$B_{ii}=\frac{1}{Đ_i}+\sum_{\substack{j=1\\ j\neq i}}^{2}\frac{\theta_j}{Đ_{ij}};\quad B_{ij}=-\frac{\theta_i}{Đ_{ij}};\quad i,j=1,2 \qquad (14)$$

Taking the inverse of matrix $[B]$, we obtain

$$[B]^{-1}=\frac{1}{\left(1+\theta_1\frac{Đ_2}{Đ_{12}}+\theta_2\frac{Đ_1}{Đ_{12}}\right)}\begin{bmatrix} Đ_1+\theta_1\frac{Đ_1Đ_2}{Đ_{12}} & \theta_1\frac{Đ_1Đ_2}{Đ_{12}} \\ \theta_2\frac{Đ_1Đ_2}{Đ_{12}} & Đ_2+\theta_2\frac{Đ_1Đ_2}{Đ_{12}} \end{bmatrix} \qquad (15)$$

For calculation of the fluxes $\mathbf{N}_i$ using eq. (13), we require data on the Maxwell-Stefan diffusivities: $Đ_1$, $Đ_2$ and $Đ_{12}$. The $Đ_i$ are the diffusivites that reflect interactions between species i and the zeolite matrix. Mixture diffusion introduces an additional complication due to sorbate-sorbate interactions. This interaction is embodied in the coefficients $Đ_{12}$. We can consider this coefficient as representing the facility for counter-exchange, *i.e.* at a sorption site the sorbed species *j* is replaced by the species *i*. The net effect of this counter-exchange is a slowing down of a faster moving species due to interactions with a species of lower mobility. Also, a species of lower mobility is accelerated by interactions with another species of higher mobility. A logarithmic interpolation procedure for the estimation of the counter-exchange coefficient $Đ_{12}$ has been suggested by Krishna and Wesselingh [18]:

$$Đ_{12} = Đ_1^{x_1}\, Đ_2^{x_2} \tag{16}$$

The matrix $[\Gamma]$ is the thermodynamic correction factor matrix, which can be determined from the mixture isotherm.

$$\Gamma_{ij} \equiv \left(\frac{\Theta_{j,sat}}{\Theta_{i,sat}}\right)\frac{\Theta_i}{p_i}\frac{\partial p_i}{\partial \Theta_j}; \quad i,j = 1,2\ldots n \tag{17}$$

When the saturation loadings of the two components, $\Theta_{i,sat}$, are equal to each other, and the isotherms of the pure components can be described by a single-site Langmuir isotherm, the matrix of thermodynamic correction factors can be determined from

$$[\Gamma] = \begin{bmatrix} \Gamma_{11} & \Gamma_{12} \\ \Gamma_{21} & \Gamma_{22} \end{bmatrix} = \frac{\begin{bmatrix} 1-\theta_2 & \theta_1 \\ \theta_2 & 1-\theta_1 \end{bmatrix}}{1-\theta_1-\theta_2} \tag{18}$$

In the general case, when the saturation loadings of the two components are different we must use the Rdeal Adsorbed Solution theory to calculate the mixture isotherms [8, 19, 21]. However, we have established after several numerical computations that eq. (18) can also be used with acceptable accuracy for the general case where the saturation loadings of the constituents are different, provided the fractional occupancies are calculated using eq. (12).

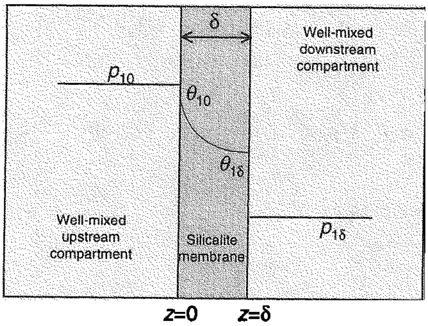

FIG. 3
Schematic of membrane separation device.

The above set of Maxwell-Stefan equations are applied below to calculate the permeation rates across a zeolite membrane, pictured in Fig. 3.

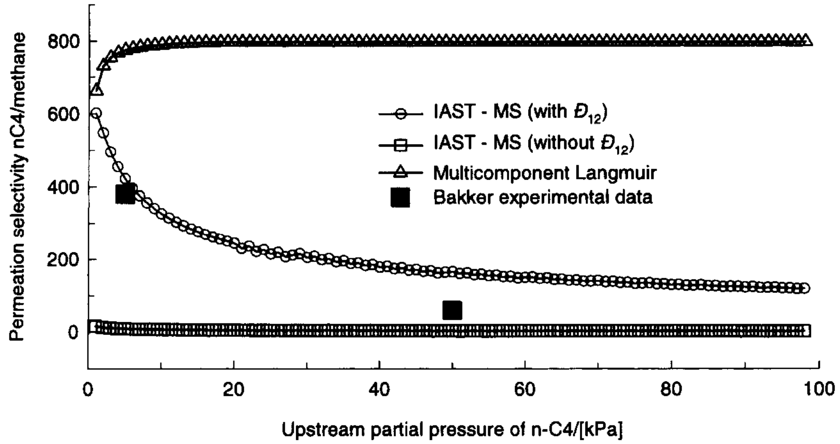

FIG. 4
Permeation selectivity for methane – n-butane mixture at 300 K.

Permeation of Methane – n-Butane Across Silicalite Membrane at 300 K; Size Entropy Effects

Let us consider steady-state permeation of a mixture of methane (1) and n-butane (2) across a silicalite membrane at 300 K. The Maxwell-Stefan diffusivities are given by Van de Graaf [12] to be $Đ_1 = 1\times10^{-9}$ m^2 s^{-1}; $Đ_2 = 1\times10^{-11}$ m^2 s^{-1}. We take the total upstream pressure to be 100 kPa. The downstream compartment is flushed with sweep gas and we assume in the calculations below that the partial pressures of the permeating components are negligibly small, i.e. $p_{1\delta} \approx p_{2\delta} \approx 0$. The occupancy gradients are calculated by assuming

$$\nabla\theta_i = \frac{\theta_{i0} - \theta_{i\delta}}{\delta} \approx \frac{\theta_{i0}}{\delta} \tag{19}$$

where δ is the membrane thickness. The fluxes can be calculated using eq. (13) and the permeation selectivity determined from:

$$S_P = \frac{N_2/N_1}{p_{20}/p_{10}} \tag{20}$$

for a range of values of p_{20}, keeping $p_{10} + p_{20} = 100$ kPa. The selectivity values are shown in Fig. 4. We note the strong decrease in S_P with increasing partial pressure of n-butane. The large filled square symbols represent the experimental data of Bakker [6], which verify the strong decrease in butane selectivity with increasing butane partial pressure. A model which ignores sorbate-sorbate interchange (quantified by $Đ_{12}$) predicts a significantly lower permeation selectivity, not in conformity with experiment. This conclusion has been earlier reached also by Van de Graaf et al. [5]. Also shown in Fig. 4 are calculations assuming both components have equal saturation capacities (= 10 molecules per unit cell) and employing the multicomponent Langmuir relations (2). The permeation selectivity in this case is practically independent of the butane partial pressure, not in conformity with experiment. Consider the situation for which p_{20} = 5 kPa. The value of S_P for the IAST – MS model including $Đ_{12}$ is 422. Ignoring $Đ_{12}$ yields a S_P value of 9.2. For equal saturation loadings and use of the Langmuir mixture rule (eq. (2)) the value of S_P is 768. The experimental value of S_P obtained by Bakker [6] is 380.

The above example illustrates the need for proper modelling of the mixture isotherm and of the binary diffusion equations. We conclude that size entropy effects have a significant influence on permeation fluxes and selectivities.

Permeation of n-Hezane – 22 DMB Across Silicalite Membrane; Configurational Entropy Effects

Let us consider steady-state permeation of a 50-50 mixture of n-hexane (1) and 22DMB (2) across a silicalite membrane at 398 K. For this isomer mixture, there are no size entropy effects and the mixture sorption and diffusion behaviour is governed by differences in the molecular *configuration*. The ratio of Maxwell-Stefan diffusivities has been determined by Krishna and Paschek [10] to be $Đ_1/Đ_2 = 3.5$ from an analysis of the pure component permeation experiments of Gump et al. [4]. We consider variation in the total upstream pressure, keeping the downstream pressure such that $p_{1\delta} \approx p_{2\delta} \approx 0$. The permeation selectivity calculated using eqs (13) and (20), combined with the RAST are shown in Fig. 5 for varying upstream total pressures. The increase in the permeation selectivity for total upstream pressures beyond 1000 Pa can be understood by considering the mixture isotherm shown in Fig. 2 (b). The total mixture loading at P = 1000 Pa is 4 molecules per unit cell. Beyond this loading packing efficiency differences between n-hexane and 22DMB comes into play. The length of n-hexane is commensurate with the size of the zig-zag channels and this molecule can be packed into the silicalite matrix much more efficiently. As seen in Fig. 2 (c) the sorption selectivity S increases sharply beyond P = 1000 Pa. From Fig. 5 we see that there is a concomitant increase in the permeation selectivity S_P. The experimental data of Gump et al. [4] for 50-50 mixture permeation confirm the predicted trends with the RAST-Maxwell-Stefan modelling approach.

Conclusions

The Maxwell-Stefan formulation for zeolite diffusion developed by us earlier [8, 18 - 23] has been used to highlight the influence of size and configurational entropy effects on binary mixture permeation across zeolite membranes. The following major observations and conclusions can be drawn from the two case studies presented.

- For permeation of a mixture containing components with different saturation capacities, size entropy effects tend to favour the smaller molecule at high loadings. The smaller molecule can easily fill the gaps in the zeolite structure. Experimental data of Bakker [6] for methane – n-butane confirm that the importance of size entropy.
- The interaction coefficient $Đ_{12}$ has a significant influence on the permeation fluxes and selectivity. This interaction tends to slow down the faster molecules and accelerate the larger molecules. For the case of permeation of methane – n-butane, the inclusion $Đ_{12}$ tends to vastly increase the permeation selectivity of n-butane. Experimental data of Bakker [6] confirm the selectivity predictions.
- For mixtures of linear and branched alkanes, the sorption selectivity increases in favour of the linear alkane at high loadings because of higher packing efficiency or configurational entropy effects. The simulations for 50-50 mixtures n-C6 – 22DMB show the strong influence of configurational entropy effects on permeation fluxes and selectivities. The model calculations for the permeation selectivity are in good agreement with the experimental results of Gump et al. [4].

This communication presents a general approach to modelling binary mixture permeation across zeolite membranes.

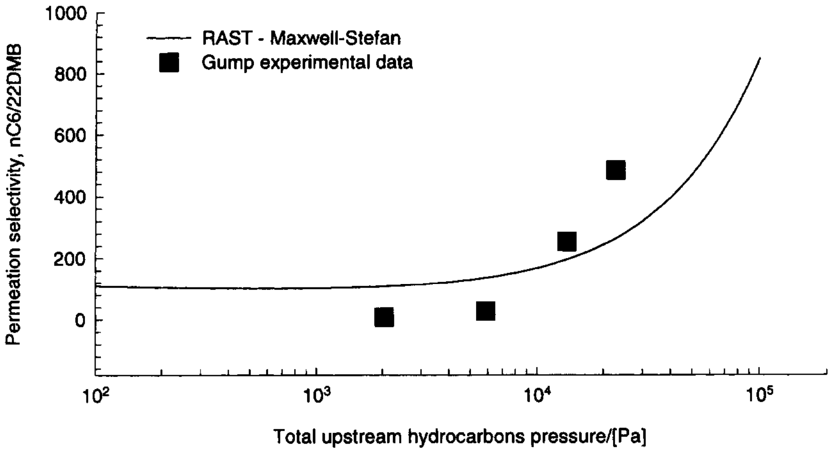

FIG. 5
Permeation selectivity for n-hexane – 22DMB 50-50 mixture at 398 K.

Acknowledgment

RK acknowledges a grant *Programmasubsidie* from the Netherlands Organisation for Scientific Research (NWO) for development of novel concepts in reactive separations technology.

References

1. H.H. Funke, A.M. Argo, J.L. Falconer and R.M. Noble, *Ind. Eng. Chem. Research*, **36**, 137 (1997).
2. A. Tavolaro and E. Drioli, *Advanced Materials*, **11,** 975 (1999).
3. K. Huddersman and M. Klimczyk, *A.I.Ch.E.J.*, **42,** 405 (1996).
4. C.J. Gump, R.D. Noble, and J.L. Falconer, *Ind. Eng. Chem. Research*, **38**, 2775 (1999).
5. J.M. van de Graaf, F. Kapteijn and J.A. Moulijn, *A.I.Ch.E.J.*, **45,** 497 (1999).
6. W.J.W. Bakker, *Structured systems in gas separation*, Ph.D. dissertation, Delft University of Technology, Delft, 1999.
7. R. Krishna, B. Smit and T.J.H. Vlugt, *J.Phys.Chem. A*, **102**, 7727 (1998).
8. R. Krishna and D. Paschek, *Separation and Purification Technology*, **21,** 111 (2000).
9. P. Ciaverella, H. Moueddeb, S. Miachon, K. Fiaty and J.A. Dalmon, *Catalysis Today*, **56,** 253 (2000).
10. R. Krishna and D. Paschek, *Ind.Eng.Chem. Research*, **39**, 2618 (2000).
11. R. Krishna, T.J.H. Vlugt and B. Smit, *Chem. Eng. Sci.*, **54**, 1751 (1999).
12. J.M. van de Graaf, F. Kapteijn and J.A. Moulijn, *Microporous and Mesoporous Materials*, **35,** 267 (2000).
13. M.B. Rao and S. Sircar, *Langmuir*, **15,** 7258 (1999).
14. A.L. Myers and J.M. Prausnitz, *A.I.Ch.E. J.*, **11,** 121 (1965).
15. T.J.H. Vlugt, R. Krishna and B. Smit, *J.Phys.Chem. B*, **103,** 1102 (1999).
16. T.J.H. Vlugt, W. Zhu, F. Kapteijn, J.A. Moulijn, B. Smit and R. Krishna, *J.Am.Chem.Soc.*, **120**, 5599 (1998).
17. G. Calleja, A., Jimenez, J. Pau, L. Dominguez and P. Perez, *Gas Separation and Purification*, **8,** 247 (1994).
18. R. Krishna and J.A. Wesselingh, *Chem. Eng. Sci.*, **52,** 861 (1997).
19. F. Kapteijn, J.A. Moulijn and R. Krishna, *Chem. Eng. Sci.*, **55**, 2923 (2000).
20. D. Paschek and R. Krishna, *Physical Chemistry Chemical Physics*, **2**, 2389 (2000).
21. R. Krishna, *Chemical Physics Letters*, **326**, 477 (2000).
22. F.J. Keil, R. Krishna and M.-O. Coppens, *Reviews in Chemical Engineering*, **16**, 71 (2000).
23. R. Krishna, *Int. Commn. Heat Mass Transfer*, **27**, 893 (2000)

Received January 7, 2001