

Separation and Purification Technology 25 (2001) 287-295



www.elsevier.com/locate/seppur

Diffusion of n-butane, isobutane and ethane in a MFI-zeolite membrane investigated by gas permeation and ZLC measurements

Ming Jiang^a, Mladen Eic^{a,*}, Sylvain Miachon^b, Jean-Alain Dalmon^b, Milan Kocirik^c

^a Department of Chemical Engineering, University of New Brunswick, PO Box 4400, Fredericton, New Brunswick, Canada E3B 5A3

^b Institut de Recherches sur la Catalyse, CNRS, 2, Avenue Albert Einstein, 69626 Villeurbanne Cedex, France ^c Heyrovsky Institute of Physical Chemistry, Dolejskova 3, 188 23 Prague 8, Czech Republic

Abstract

The diffusion of n-butane, isobutane and ethane in a composite-membrane alumina-MFI zeolite has been investigated using gas permeation and ZLC techniques. The diffusion of isobutane in the sample is faster than that of n-butane although isobutane molecule has a larger kinetic diameter, and its activation energy is comparable to the results obtained from the gas permeation and QENS measurements reported in the literature. For ethane, the diffusivity is much higher in comparison to n-butane and isobutane. When isobutane is present at a high concentration, the diffusion of ethane is remarkably hindered due to a relatively strong adsorption of isobutane in the membrane micropores. By comparing the diffusivity data obtained from the permeation and ZLC measurements, it was possible to evaluate the thickness of the zeolite membrane effective for gas permeation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Butane; Diffusion; Ethane; Membrane; Permeation; ZLC

1. Introduction

Membrane reactors have attracted a lot of interest because of their mechanical strength, thermal stability and organic solvent resistance. Considerable research efforts have been undertaken to increase membrane selectivity, permeability and stability in gas separation processes. In this aspect, zeolites used as membrane material exhibit a unique advantage, i.e. a uniform poresize distribution, which may remarkably increase the selectivity for gas separations. Among the zeolite membranes studied up to the present time, MFI membranes supported on alumina or stainless steel have exhibited most reproducible permeance data. Zeolites of the MFI type used as membrane material (silicalite and ZSM-5) have channels defined by 10-membered oxygen rings with diameter of ~0.55 nm, which can separate

^{*} Corresponding author.

E-mail address: meic@unb.ca (M. Eic).

^{1383-5866/01/}\$ - see front matter © 2001 Elsevier Science B.V. All rights reserved. PII: S1383-5866(01)00055-7

gases on a scale of molecular sieving. Membrane separation is based on a combined effect involving differences in adsorption equilibria and diffusion coefficients of species adsorbed in zeolites. In order to predict the diffusion behavior of different hydrocarbon sorbates in zeolite membranes, various techniques including microscopic and macroscopic measurements have been applied and different models proposed for the determination of gas diffusivities [1-6]. However, the transport of sorbates in zeolite pores is still poorly understood. In a previous work [6], permeation of gases (H₂ and/or butane) through a composite alumina-MFI zeolite membrane has been reported. It was concluded that the transport in this membrane was controlled by a composite zeolite-alumina layer formed at the outer surface of the support, viz. zeolite membrane behaves as a molecular sieve. In the present work, the properties of the membrane with respect to the diffusion of n-butane, isobutane and ethane are investigated further by using gas permeation and zero-length column (ZLC) techniques. The diffusivity data obtained by the two techniques have been compared and interpreted. The hindering effect of isobutane upon the diffusion of ethane in the membrane sample has also been explored.

2. Experimental methods

The preparation of composite alumina-MFI membrane sample has been described in detail elsewhere [3,7,8]. The macroporous alumina was supplied by SCT/US Filter (Membralox T1-70). The precursor was a clear solution of te-trapropylammonium hydroxide (TPAOH, 1M solution from Aldrich) and silica (aerosil Degussa 380). A single-step synthesis protocol was employed in the preparation of the membrane [6-8].

NaH-ZSM-5 was synthesized by the standard method [9]. The distribution of crystal sizes was uniform, with dimensions, estimated from a scanning electronic micrograph (SEM), of $14 \times 11 \times 8$ µm, corresponding to an equivalent radius (*R*) of

 $6.7 \ \mu m$ when the crystals were approximated as spheres.

For gas-permeation measurements, the membrane (22 cm² active area) was placed in a stainless-steel module equipped with a temperature controller. Graphite cylindrical rings were used as seals between the membrane and the module. Hydrocarbon fluxes were investigated by steadystate permeation measurements using a Wicke-Kallenbach modified method with N₂ as diluting and sweep gas flowing at 75 ml min⁻¹. A gas chromatograph (Shimadzu, GC-14A) was used to measure the feeds, retentate and permeate concentrations. The theoretical analysis of the single gas transport in microporous membrane has been described in Ref. [6], in which the sorption of gas in the membrane sample was assumed to follow a Langmiur isotherm, and the stationary flux of gas, J, through the composite MFI membrane was expressed as:

$$J = \frac{D_0 q_{\text{sat}}}{l} \ln \left(\frac{1 + K P_{\text{R}}}{1 + K P_{\text{P}}} \right), \tag{1}$$

where $P_{\rm P}$ and $P_{\rm R}$ are the pressures at the permeate and retentate sides, respectively, and K is the temperature-dependent Langmiur parameter. q_{sat} is the sorption capacity of zeolite, l the thickness of membrane, and D_0 the intrinsic diffusion coefficient corresponding to the conditions that approach zero concentration of sorbate. Eq. (1) can be expanded by introducing exponential form for the Langmuir parameter, K, and the kinetic parameter D_0 . In this way, the adsorption equilibrium parameters ΔH and ΔS , which can be obtained from the literature, are used for fitting the model to the experimental permeation data to extract the values of D_0^{∞}/l (the ratio of the pre-exponential factor and effective membrane thickness) as well as the activation energies, as described in Ref. [6].

The diffusion of n-butane, isobutane and ethane in the membrane and ZSM-5 samples was directly measured by the ZLC method. The membrane sample was taken from the composite alumina-MFI membrane tube by using a very hard and sharp knife to scrape the surface containing the active zeolite layer. A very small amount of sample was collected and placed in the ZLC column. The column was then equilibrated with sorbate diluted in a helium flow to obtain a low concentration, as required by the ZLC method. It was then purged by pure helium at a flow rate high enough to maintain a very low sorbate concentration at the crystal surfaces, thus ensuring that the process is controlled by diffusion out of the crystals, rather than by convective effects. The relative concentrations (c/c_0) of the effluent sorbates from the ZLC column were determined using a Quadrupole Mass Spectrometer (Dycor Dymaxion, Ametek, USA) by monitoring the mass signals of 30 ($C_3H_6^+$) fragment) for ethane and 43 ($C_3H_7^+$ fragment) for n-butane or isobutane. This experimental armeasurements rangement allows of both single component systems and gas mixtures. Details of the experimental method and analysis of the ZLC curves have been described elsewhere [10]. For a linear system with uniform spherical particles, the relative effluent concentration is given by:

$$\frac{c}{c_0} = \sum_{n=1}^{\infty} \frac{2L}{[\beta_n^2 + L(L-1)]} \exp(-n^2 \beta_n^2 Dt/R^2), \quad (2)$$

where β_n s are the eigenvalues given by the roots of the equation:

$$\beta_n \cot \beta_n + L - 1 = 0 \tag{3}$$

and

$$L = \frac{1}{3} \frac{\varepsilon v}{(1 - \varepsilon)z} \frac{R^2}{K_{\rm H}D} = \frac{1}{3} \frac{\text{purge flow rate}}{\text{crystal volume}} \frac{R^2}{K_{\rm H}D},$$
(4)

where ε is the voidage of particle layer, v the interstitial gas velocity, z the ZLC bed depth, and $K_{\rm H}$ the dimensionless Henry Law constant.

For the long time region, the higher-order terms in the summation can be ignored, and so the function defined by Eq. (2) approaches its asymptote:

$$\frac{c}{c_0} = \frac{2L}{[\beta_1^2 + L(L-1)]} \exp(-\beta_1^2 Dt/R^2).$$
 (5)

From Eq. (5), the values of L and D/R^2 can be easily determined from the slope and intercept of a plot of $\ln(c/c_0)$ vs. time, t.

3. Results

3.1. Permeation measurements

Fig. 1 shows the SEM image of the cross-section of the membrane sample. The zeolitic material is mostly located inside the porous structure of the support alumina tube. In layer 1, as indicated in the figure, large alumina particles (between 20 and 30 μ m) are observed, on which small crystals of the zeolite particles are attached. In layers 2 and 3, the alumina support is difficult to distinguish from the zeolite crystals because the pores are filled by the zeolite crystals. From this image, the average size of the relatively large zeolite crystals can be estimated as $4 \sim 6 \mu$ m.

The average values of temperature-independent D_0^{∞}/l data for n-butane, isobutane and ethane were obtained from fitting the permeation model (Eq. (1)) to the experimental flux data at different temperatures. These values are presented in Table 1. A graphical example of this procedure for isobutane is shown in Fig. 2.



Fig. 1. SEM image of the cross-section of the composite alumina-MFI zeolite membrane.

Table 1

290

Diffusivity data for the diffusion of butane and ethane in the membrane sample obtained from the gas permeation and ZLC measurements^a

Sorbate	Gas permeation $D^{\infty}/1 \times 10^3$	ZLC measurements					
		Purge rate (ml min ⁻¹)	<i>T</i> (°C)	$\frac{D/R^2}{(s^{-1})} \times 10^3$	$\frac{D^{\infty}/R^2}{(s^{-1})} \times 10^{-3}$	$E (kJ mol^{-1})$	$l/R^2 ~(\mu m^{-1})$
n-Butane	6.7	60	10	3.5	0.9	29.0	0.14
		60	20	4.4			
		60	30	7.1			
		60	40	11.1			
Isobutane	21.0	60	0	4.8	7.3	32.5	0.35
		60	10	6.7			
		60	20	10.4			
		60	30	20.3			
		90	20	9.9			
		120	20	11.3			
		60	-40	28.8			
Ethane	20.7	60	-30	44.6	3.0	22.4	0.50
		60	-20	72.0			
Ethane/ isobutane		60	30	13.6			
		60	60	15.6			
		60	90	16.7			

^a L>5 was kept in all experimental runs except for the ethane/isobutane mixture (L<2).

It can be seen from the table that there is no essential difference between the values of the parameter D_0^{∞}/l for isobutane and ethane, but the values for isobutane are higher than for n-butane.

3.2. ZLC measurements

Diffusion of single component gases such as n-butane, isobutane and ethane in the membrane sample was investigated by the ZLC technique. The sorbate concentration at the ZLC column was adjusted to 0.025 vol%, and the flow rate of helium used as the purge gas was set to 60 or 120 ml/min⁻¹. For measurements involving a binary mixture of ethane/isobutane in the membrane sample, the concentration of ethane was maintained at 0.025 vol%, while that of isobutane was adjusted to a relatively high value of 5.0 vol% to check if the ethane diffusion was significantly affected by the presence of isobutane.

Fig. 3 shows the representative ZLC curves for n-butane and isobutane in the membrane sample.

Since the sample taken from the membrane contained alumina support (crystals) in addition to zeolite crystals grown on the support, additional experimental checks were carried out using a pure alumina support. The ZLC results of these runs confirmed negligible effects with respect to the



Fig. 2. Fitting of the permeation model (line) to the experimental isobutane flux (symbol). (Wicke-Kallenbach experiment, P = 125 kPa, $\Delta P_{\text{total}} = 0$ kPa).



Fig. 3. ZLC curves of n-butane (a) and isobutane (b) in the membrane sample (helium purge flow rate: 60 ml min^{-1}).

diffusion through the alumina crystals, thus validating the assumption that the effective diffusion through the membrane is completely controlled by intracrystalline diffusion involving the zeolite layer only. Comparing the curves obtained for the two sorbates at the same temperature (e.g. 20°C), one can find that n-butane diffusion is slower than isobutane. The diffusivity data derived from the theoretical analysis of the ZLC curves are summarized in Table 1. At the same temperature, the values of D/R^2 of isobutane are two or three times higher than for n-butane. Based upon the diffusivity data obtained from ZLC measurements, Arrhenius plots of $\ln(D/R^2)$ vs. T^{-1} for the diffusion of n-butane and isobutane in the membrane sample are shown in Fig. 4. Good linear trends for the temperature range employed in the measurements can be observed. The activation energies derived from the plots are listed in Table 1. It can also be found from the table that the diffusivities of isobutane measured at 20°C at different purge flow rates (60 ~ 120 ml min⁻¹) are



Fig. 4. Arrhenius plots for the diffusion of n-butane (a) and isobutane (b) in the membrane sample and n-butane (c) and isobutane (d) in the ZSM-5 sample.

essentially the same (the values of D/R^2 vary between 9.9 and 11.3 s⁻¹). This indicates the validity of the simple theoretical ZLC model.

Fig. 5 presents the ZLC curves for the diffusion of ethane in the membrane sample. Compared with those shown in Fig. 3, the diffusivities of ethane are much higher than for n-butane and isobutane because of the smaller kinetic diameter of the sorbate molecule. Actually, the reliable ZLC curves were only obtained at rather low temperatures (below -20° C). The diffusivity data derived from the ZLC curves are summarized in Table 1. From the temperature dependence of the diffusivity, the activation energy of ethane diffusion in the membrane was estimated as 22.4 kJ mol⁻¹.



Fig. 5. ZLC curves of ethane in the membrane sample (helium purge flow rate: 60 ml min^{-1}).



Fig. 6. ZLC curves of ethane in the membrane sample in the presence of isobutane of a high concentration.

Fig. 6 displays the ZLC curves for diffusion of ethane in the membrane sample in the presence of isobutane at a high concentration (5.0%). Compared with the single gas (Fig. 4), the diffusion of ethane is significantly reduced and, therefore, the ZLC curves can be obtained even at rather high temperatures ($> 30^{\circ}$ C). The evaluated diffusivity data are presented in Table 1.

In order to make a comparison of the diffusion properties of n-butane, isobutane and ethane in the composite alumina-MFI membrane with those in pure MFI zeolites, a NaH-ZSM-5 sample was subjected to the same ZLC measurements as the membrane sample. The representative ZLC curves for n-butane and isobutane diffusion in this sample are presented in Fig. 7. The diffusivity data evaluated from the analysis of the ZLC curves are summarized in Table 2. Similar to the case involving the membrane sample, the diffusivities of isobutane are also higher than for n-butane, indicating the similarity in diffusion of the hydrocarbons in NaH-ZSM-5 and the membrane samples of the similar structure. From the analysis of Arrhenius plots, the activation energies of n-butane and isobutane in the ZSM-5 sample are smaller compared to the membrane sample (Tables 1 and 2). The diffusion of ethane in the ZSM-5 sample was also measured. It was found that the ZLC measurements have to be performed at an even lower temperature than that with the membrane sample (the reliable ZLC curves were obtained only at temperatures below -30° C).

4. Discussion

Millot et al. measured the diffusivities of n-butane and isobutane in MFI zeolite membrane and ZSM-5 using quasi-elastic neutron scattering (QENS) technique [1]. They reported that the diffusivities were significantly affected by the kinetic diameters of sorbate molecules. The diffusion coefficient of isobutane in ZSM-5 zeolite was found to be three orders of magnitude lower than that of n-butane in the same zeolite because of the larger kinetic diameter of isobutane. In contrast, the present work shows that the diffusivities of isobutane in the membrane and ZSM-5 samples obtained by ZLC measurements are somewhat higher than those of n-butane. Furthermore, these results are in reasonable agreement with the results for n-butane and isobutane on silicalite reported by Hufton and Ruthven [11]. The discrepancy of our results from those of Millot et al. may be due to the large differences between the



Fig. 7. ZLC curves of n-butane (helium purge flow rate: 120 ml min⁻¹): (a) and isobutane (helium purge flow rate: 60 ml min⁻¹); (b) in the ZSM-5 sample.

M. Jiang et al. / Separation/Purification Technology 25 (2001) 287-295

Sorbate	Purge rate (ml min ⁻¹)	<i>T</i> (°C)	$D \; (\mu m^2 \; s^{-1})$	$E (kJ mol^{-1})$
n-Butane	120	40	0.16	16.8
	120	60	0.27	
	120	80	0.34	
Isobutane	60	0	0.08	24.5
	60	20	0.14	
	60	40	0.30	
	60	60	0.53	
Ethane	120	-40	0.43	13.7
	120	-30	0.57	

Table 2 Diffusivity data for the diffusion of butane and ethane in the ZSM-5 sample obtained from the ZLC measurements^a

^a $L \ge 5$ for n-butane systems, 3 < L < 4 for isobutane and ethane systems.

microscopic and macroscopic measurements, e.g. the different time scale, equilibrium versus transient measurement conditions, etc. This may also have an effect on the determination of the activation energy of diffusion. It was found that the activation energies for isobutane diffusion obtained from gas permeation and QENS measurements differ by a factor of 2 [1]. However, the diffusivities for n-butane in the membrane sample at ambient temperature obtained from gas permeation experiments (calculated from the D^{∞}/l listed in Table 1 and the activation energy of 11.9 kJ/mol, as given in Ref. [12]) are also about three orders of magnitude higher than that for isobutane. The reasons for the discrepancies between different techniques remain unclear and should be a subject of further investigation.

In the present work, the activation energy for diffusion of isobutane in the membrane obtained from gas-permeation measurements has been evaluated as 31 kJ mol⁻¹, which is in a good agreement with those obtained by Millot et al. (34 kJ mol⁻¹) using gas-permeation techniques on the same type of membranes [1]. This finding is also consistent with that obtained from the ZLC measurements in the present study (i.e. 32.5 kJ/mol^{-1} ; cf. Table 1). In NaH-ZSM-5, the activation energies of diffusion of n-butane, isobutane and ethane are lower than those in the membrane sample. This may result from the inhomogeneity of the zeolite material and the possible effects of the surface barrier due to the existence of crystal defects in the membrane sample.

As described above, the diffusivity of ethane in the membrane sample is significantly decreased when isobutane is present. This is due to the difference in adsorption affinities of the two sorbates. It has been postulated that the strongly adsorbed molecules form a barrier to the diffusion of weakly adsorbed molecules and hence reduce their transport across the membrane. The ZLC curves of ethane shown in Fig. 6 are in fact similar to the adsorption curves that are obtained under the surface barrier conditions [13]. It has been observed earlier that the diffusivity and permeability of hydrogen in the membrane sample are drastically reduced in the presence of n-butane or isobutane [6,14–17]. From Table 1, the diffusivity of ethane in the presence of isobutane derived from the analysis of the ZLC curves is comparable to that of pure isobutane. The effect of isobutane upon the diffusion of ethane in the membrane sample depends on the concentrations of the two sorbates. We have also measured the diffusion of the mixture of ethane and isobutane both at the low concentrations of 0.025 vol%. However, the obtained ZLC curves were essentially the same as those corresponding to single components. This clearly indicates that there is no interaction between the sorbates at the very low concentration levels.

In order to obtain the diffusivity, D, the equivalent radius of the zeolite crystals, R (for the ZLC measurements), or the thickness of membrane, l(for the gas permeation measurements), have to be determined. From the SEM image of the membrane sample, the size of the zeolite crystals on the membrane sample is not uniformly distributed, and therefore the radius of R seems difficult to evaluate. However, based on Eqs. (2) and (5), the contribution of the large zeolite crystals to the overall diffusion process is much more significant compared to the small crystals. In previous work, it has been proved that the properties of gas permeation through the membrane sample are controlled by the zeolite micropores, i.e. controlled by the relatively larger crystals of the zeolites. From this point of view, the average size of the relatively larger zeolite crystals can be estimated to fall between 4 and 6 µm, as described above. By assuming that the equivalent radius, R, of the relatively larger zeolite crystals is about 3 µm, the diffusion coefficients of n-butane, isobutane and ethane in the membrane sample can be calculated and compared with those in the ZSM-5 sample (Table 3). It can be seen that at the same temperatures, the diffusivities of the sorbates in the membrane sample are generally smaller than those in the ZSM-5 sample. One plausible explanation could be related to the existence of structural defects in the membrane sample, which gives additional resistance in the diffusion. Nevertheless, the diffusivity data for the two samples are in reasonable agreement, as expected, because of the similar structures of the ZSM-5 and membrane crystals.

Comparing D^{∞}/l with D^{∞}/R^2 data for the different systems obtained from the permeation and ZLC measurements, respectively, one can calculate the l/R^2 ratios, which are presented in the last column of Table 1. These values can be used to

Table 3

Comparison of the selected diffusivity data for butane and ethane in the membrane and ZSM-5 samples obtained from the ZLC measurements

Sorbate	<i>T</i> (°C)	Membrane $D \ (\mu m^2 \ s^{-1})$	ZSM-5 $D \ (\mu m^2 \ s^{-1})$
n-Butane	40	0.10	0.16
Isobutane	0	0.04	0.08
	20	0.09	0.14
Ethane	-40	0.26	0.43
	-30	0.40	0.57

estimate the effective thickness of the zeolite membrane. From the SEM image of the membrane sample, one may obtain the "geometric" thickness of the zeolite membrane, as estimated in the range of $20-30 \mu m$ (Fig. 1). In this wide range of thicknesses, however, the zeolite crystals are stacked together, starting from the alumina support with many pinholes in between, through which, instead of through the zeolite micropores, gases can pass without resistance. Considering that the micropores of the zeolite control the gas permeation, it is most likely that a dense layer of the zeolite membrane is involved. However, the boundary of such a dense zeolite membrane cannot be visualized from the SEM image itself, which makes the determination of the thickness of the membrane difficult. However, from the l/R^2 ratios shown in Table 1, the thickness of the membrane can be estimated. For n-butane, isobutane and ethane, the values of l/R^2 should be theoretically constant since the ratio represents geometrical properties relevant to the experimental systems studied. However, the values listed in Table 1 vary between 0.14 and 0.5 μ m⁻¹. As mentioned above, because of the large difference in diffusivity value for n-butane in the membrane sample obtained by the gas permeation and ZLC techniques, only the l/R^2 values for isobutane and ethane diffusion should be considered for the estimation of *l*. From the Table 1, the average l/R^2 value could be estimated at about 0.4 μ m⁻¹. Assuming that the equivalent radius, R, of the relatively larger zeolite crystals is about 3 µm, the calculated thickness of the membrane, l, is about 4 µm, which corresponds to about one to two lavers of zeolite crystals. A similar membrane effective thickness was reported earlier in Ref. [6]. Hence, the effective thickness of the membrane for gas permeation through the micropores of the zeolite is much smaller than the geometric thickness of the membrane as observed from the SEM image.

5. Conclusion

The diffusion of n-butane, isobutane and ethane in a composite alumina-MFI zeolite membrane sample was investigated by using the gas permeation and ZLC techniques. It was found that the diffusivity data of ethane and isobutane obtained from the two techniques are in good agreement within the margin of experimental errors. The activation energy of isobutane diffusion is also comparable to those obtained from the gas permeation and QENS measurements reported in the literature. Although isobutane has a larger kinetic diameter than n-butane, the diffusivities of isobutane in the membrane and ZSM-5 samples are surprisingly higher than for n-butane. In the presence of isobutane at a high concentration, the ZLC measurements indicate that the diffusion of ethane is remarkably hindered because of the relatively stronger adsorption of isobutane in the sample. By comparing the diffusivity data obtained from the permeation and ZLC measurements, the effective thickness of the zeolite membrane for the gas permeation can be reasonably estimated.

Acknowledgements

Financial supports for this project provided by the NATO Linkage Grant No CRG. LG974432, NSERC (Canadian government) and Grant Agency of the Academy of Sciences of the Czech Republic Grant No IAA 4040901 are gratefully acknowledged.

References

- B. Millot, A. Methivier, H. Jobic, H. Moueddeb, M. Bee, J. Phys. Chem. 103 (1999) 103.
- [2] H. Jobic, M. Bee, J. Caro, in: D. Oslon, A. Bisio (Eds.), Proceedings of the 9th International Zeolites Conference, Butterworths, Stoneham, MA, 1993, p. 121.
- [3] H. Moueddeb, P. Ciavarella, S. Miachon, J.A. Dalmon, J. Membr. Sci. submitted for publication.
- [4] W.J.W. Bakker, L.J.P.V.D. Broeke, F. Kapteijn, J.A. Moulijin, AIChE J. 43 (1997) 2203.
- [5] R.M. Barrer, J. Chem. Soc. Faraday Tans. 86 (1990) 1123.
- [6] P. Ciavarella, H. Moueddeb, S. Miachon, K. Fiaty, J.A. Dalmon, Catal. Today 56 (2000) 253.
- [7] J. Ramsay, A.G. Fendler, A. Julbe, J.A. Dalmon, French Patent No. 005652, 1994.
- [8] E. Piera, A. G. Fendler, J.A. Dalmon, H. Moueddeb, J. Coronas, M. Mendez, J. Santamaria, J. Membr. Sci. 142 (1998) 97.
- [9] A. Zikanova, D. Derewinski, Zeolites 15 (1995) 148.
- [10] M. Eic, D.M. Ruthven, Zeolites 8 (1988) 40.
- [11] J.R. Hufton, D.M. Ruthven, Ind. Eng. Chem. Res. 32 (1993) 2379.
- [12] P. Ciavarella, Ph.D. thesis. Institut de Recherches sur la Catalyse, CNRS, Lyon, France, 1999.
- [13] D.M. Ruthven, in: M.D. Levan (Ed.), Fundamentals of Adsorption, Kluwer Academic, Boston, MA, 1996, p. 529.
- [14] A. Ash, R.M. Barrer, R.T. Lowson, J. Chem. Soc. Faraday Trans. I 69 (1973) 2166.
- [15] A. Yammasaki, H. Inoue, J. Membr. Sci. 59 (1991) 233.
- [16] M.B. Rao, S. Sircar, J. Membr. Sci. 110 (1996) 109.
- [17] M. Yang, B.D. Crittenden, S.P. Perera, H. Moueddeb, J.A. Dalmon, J. Membr. Sci. 156 (1999) 1.