# Binary Permeation through a Silicalite-1 Membrane

**Leo J. P. van den Broeke, Wridzer J. W. Bakker, Freek Kapteijn, and Jacob A. Moulijn**
Dept. of Chemical Engineering, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

*Permeation of binary gaseous mixtures through a silicalite-1 membrane was studied. Results are reported for the fluxes and separation factors as a function of the feed composition, the pressure and the temperature. For the various cases a comparison is made between the binary and the single-component permeation behavior. For the permeation of the mixtures the stronger adsorbed component is little affected by the presence of the weaker adsorbed component. On the other hand, for the weaker adsorbed component a clear reduction in the flux is observed. As a consequence, the separation factor for mixtures differs considerably from the so-called ideal separation factor, which is the ratio of the one-component permeances. As expected, the separation factor depends on the temperature. The separation factor is also a function of the composition and the feed pressure. This means that the binary equilibrium adsorption cannot be described with the extended Langmuir model. Binary permeation and separation behavior is described using the ideal adsorption solution theory for equilibrium adsorption.*

## Introduction

Multicomponent diffusion in microporous materials, adsorbents with a pore diameter smaller than 2 nm, is characterized by a strong interaction between the adsorbed species. Coupling between the species can be of kinetic and of equilibrium origin. One of the first results demonstrating the interaction between species adsorbed in microporous materials was presented by Habgood (1958). For the transient uptake of methane and nitrogen in zeolite 4A, a clear overshoot is seen in the faster-moving, weakly adsorbed nitrogen. Similar results have been reported for a number of other systems. Kärger and Bülow (1975) studied, as a function of the time, the amount adsorbed of a mixture of benzene and *n*-heptane in zeolite NaX. A maximum is observed in the uptake curve of *n*-heptane. Karge and Niessen (1991) reported results for the uptake of benzene and ethyl benzene in H-ZSM-5. During codiffusion the faster-moving benzene has an overshoot in the uptake profile. For the transient permeation of a mixture of hydrogen and *n*-butane through a silicalite-1 membrane, an overshoot is observed in the permeation of the faster-diffusing hydrogen (Bakker et al., 1996).

These results can be well described with the Maxwell−Stefan theory for micropore diffusion (Krishna, 1990; Krishna and Van den Broeke, 1995; Van den Broeke, 1995). In the description of multicomponent sorption kinetics one likes to predict the mass transport of mixtures based on one-component equilibrium adsorption and diffusion data. With the Maxwell−Stefan equations the overshoot in the transient uptake of the faster-moving species can be predicted from the single-component diffusion data and the binary isotherm. In the Maxwell−Stefan formulation the kinetic and equilibrium contributions are considered separately, providing clues about the various interactions between the adsorbed species. If there is no interaction between the adsorbed components of a mixture, the uptake profiles of the individual species increase monotonously.

Other descriptions for multicomponent diffusion in microporous materials are available. Do and coworkers (Do et al., 1991; Hu and Do, 1993) used the Fick and Onsager formulation to model the diffusion of hydrocarbons in activated carbon. Yang et al. (1991) used the Onsager theory to describe binary diffusion of carbon dioxide and ethane in zeolite 4A. It has been demonstrated by Krishna (1990) that the Fick and Onsager formulation can be derived from the Maxwell−Stefan equations. Chen and Yang (1991, 1992) presented a description for surface diffusion and zeolitic diffusion based on transition state theory. In this approach the diffusion process is

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Correspondence concerning this article should be addressed to L. J. P. van den Broeke.

Present addresses of: L. J. P. van den Broeke, Process Development Group, Dept. of Chemical Engineering, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands; W.J.W. Bakker, Akzo Nobel Central Research, Dept. RTA, P.O. Box 9300, 6800 SB Arnhem, The Netherlands.

described by a random walk and the mass transport takes place by molecules hopping between sites. The elements of the matrix of Fick diffusion coefficients are expressed in term of a sticking parameter.

In the description of multicomponent sorption kinetics the equilibrium adsorption of mixtures gives rise to some fundamental problems. A proper description of the equilibrium adsorption of mixtures requires a thermodynamically consistent model. Such a model must be capable of dealing with the fact that often the saturation capacities of the adsorbed species are different, and the model must be capable of taking the heterogeneous character of the sorbent into account, if necessary (Mauer, 1997). Gu et al. (1991) extended the Langmuir model for mixtures to the situation where for adsorbed species the saturation capacity is different. Some examples were given for breakthrough curves to indicate the consequence of uneven saturation capacities.

In this work silicalite-1 is the adsorbent. For the description of the equilibrium adsorption of mixtures in silicalite-1 several studies have been reported.

Abdul-Rehman et al. (1990) studied the one-component adsorption of the first four *n*-alkanes and some binary and ternary mixtures of these gases in silicalite-1. Several adsorption models were compared. It was found that the best description of the single-component and multicomponent equilibrium adsorption processes was obtained with the Toth model.

Buss and Heuchel (1997) obtained, as a function of the composition, a variable separation factor for binary mixtures of methane and tetrafluormethane in silicalite-1. The separation factor, toward the stronger adsorbed $CF_4$, decreases with an increase in the mole fraction of tetrafluormethane. A reasonable description of the binary adsorption was given with both the ideal adsorption solution (IAS) theory (Myers and Prausnitz, 1965) and the (binary) multi-site Langmuir model (Nitta et al., 1984). It is noted that the two models describe the binary isotherms better than the binary separation factor. In the IAS theory the Toth model was used to describe the one-component isotherms.

Rees and coworkers studied the equilibrium adsorption of various binary mixtures in silicalite-1 using an isosteric method (Graham et al., 1989; Rees et al., 1992). The Henry's law constant for binary mixtures, including $CO_2-N_2$ and $C_2H_6-C_3H_8$, was found to be linearly proportional to the gas-phase composition. The Henry's law constant was obtained from the initial slope of the mixture isotherm (Hampson and Rees, 1993). The dependence of the Henry's law constant on composition is a consequence of the difference in (isosteric) heat of adsorption of the components.

In this work the permeation behavior was studied for five binary gaseous systems through a metal-supported silicalite-1 layer. The following experiments were performed:

1. Permeation of mixtures of carbon dioxide and nitrogen as a function of the feed composition using the feed pressure of 101 kPa and the temperature of 303 K.
2. Permeation of air as a function of the temperature (200 to 650 K).
3. Permeation of mixtures of carbon dioxide and methane, as a function of composition, pressure and temperature: (a) the separation factor for a 1:1 mixture of $CO_2$ and $CH_4$ as a function of the temperature and pressure; (b) binary fluxes of $CO_2$ and $CH_4$ over the temperature range of 200 to 675 K for a feed pressure of 101 kPa; and (c) permeation of mixtures of $CO_2$ and $CH_4$ as a function of the composition at 303 K and 101 kPa.
4. Permeation of a binary mixture of methane and ethane, as a function of the temperature (300 K to 525 K) for three pressures (101, 102, and 303 kPa). The feed composition was fixed, $y_{C_2H_6}$: $y_{CH_4} = 1{:}1$.
5. Permeation of a 50 kPa:50 kPa mixture of *n*-butane and hydrogen as a function of the temperature (300 to 675 K).

For most of these binary mixtures a comparison is made between the results for one-component fluxes and the results for two-component fluxes. The one-component permeation through the silicalite-1 membrane for different conditions has been described in Bakker et al. (1997). Furthermore, a comparison is made between the separation factor calculated from the binary fluxes and the so-called ideal separation factor that is obtained from the one-component fluxes. Finally, the experimental results for the binary fluxes and separation factors are compared with numerical predictions made with the extended Langmuir model and the IAS theory.

## Experimental Setup

Experiments with the silicalite-1 membrane are conducted according to the Wicke−Kallenbach method. The permeation results reported here for the binary mixtures were obtained with membrane WTSS-1e (Bakker et al., 1996, 1997). The metal-supported asymmetric membrane is formed by synthesis of a silicalite-1 layer on a stainless-steel porous support. The experimental setup and the membrane synthesis are given in detail in Bakker et al. (1996).

The binary mixtures are obtained by mixing pure gases with two mass flow controllers that were calibrated for each component. The concentrations at the feed, the retentate, and the permeate side of the flat disk membrane were analyzed with a mass spectrometer.

## Diffusion of Mixtures

In the experiments to be presented the results are given in terms of the permeance through the membrane. The permeance, $\Pi$, is related to the flux by taking the partial pressure difference over the membrane into account

$$\Pi_i = \frac{J_i}{\Delta p_i}. \tag{1}$$

In general, the flux in microporous materials is described with the Fick formulation. For a binary mixture we have a matrix of Fick diffusivities, $D_{ij}$, and two concentration differences, $dq_i/d\xi$, with $\xi$ the space coordinate of the membrane. The fluxes are given by the set

$$J_1 = D_{11}\frac{dq_1}{d\xi} + D_{12}\frac{dq_2}{d\xi}$$

$$J_2 = D_{21}\frac{dq_1}{d\xi} + D_{22}\frac{dq_2}{d\xi}. \tag{2}$$

### Binary equilibrium adsorption

For the description of the adsorption of mixtures in micropores essentially two approaches can be followed. One can extend the one-component models to multicomponent isotherm models or one can use a thermodynamic approach. For the first case, the isotherm models describing the adsorption of a mixture can be written in a general way as the Langmuir–Freundlich isotherm

$$\theta_i = \frac{q_i}{q_{i,\mathrm{sat}}} = \frac{b_i p_i}{\left[1 + (b_i p_i)^{n_i} + (b_j p_j)^{n_j}\right]^{1/n_i}}. \tag{3}$$

The well-known extended Langmuir model is obtained for $n_i = 1 = n_j$. For $n_i = n_j$, Eq. 3 gives the multicomponent Toth isotherm.

This line of approach has been used by Abdul-Rehman et al. (1990) to study one- and multicomponent gas adsorption in silicalite-1. For the adsorption of methane and ethane in silicalite-1 Abdul-Rehman et al. (1990) reported values of $n$ equal or close to unity. This means that for the system $CH_4$–$C_2H_6$–silicalite-1 the adsorption can be described by the (extended) Langmuir model. It was found that the saturation capacities decrease with an increase in the temperature. In the modeling of the fluxes the adsorption parameters are required; see Eq. 10 below. As a consequence, the isotherm must be available to determine the adsorption parameters for a given temperature. The only way to obtain the saturation capacity, at a given temperature, is by fitting an isotherm model to an experimental isotherm. It is noted that Abdul-Rehman et al. (1990) did not report separation factors.

The second approach is based on the IAS theory (Myers and Prausnitz, 1965; Ruthven, 1984). In the IAS theory the adsorbed phase is considered as an ideal solution. The partial pressure of a component in an ideal solution is given by the product of the mole fraction, in the solution, and the pressure it would exert as a pure sorbate. For a constant surface area, the IAS description is analogous to the description of a fluid, with the pressure and volume replaced with the spreading pressure and surface area, respectively. The procedure to calculate with the IAS theory the amount adsorbed for a mixture is given in the Appendix.

Buss and Heuchel (1997) used the IAS theory to predict the binary adsorption of $CH_4$ and $CF_4$ in silicalite-1, from single-component adsorption data. The one-component isotherms were described with the Toth model. Good agreement is obtained; especially the variation of the separation factor with the gas-phase composition could be well described.

In this work we use the extended Langmuir model and the IAS theory in the description of the binary permeation behavior. In both cases the one-component adsorption parameters given in the previous article (Bakker et al., 1997; cf. table 4) will be used. The adsorption parameters were obtained from a fit of the isobars with the Langmuir model. Furthermore, in the IAS theory the one-component Langmuir isotherm is used.

### Single-file diffusion

For the description of the mass transport of the mixture through the silicalite-1 membrane the Maxwell–Stefan equations are used (Krishna, 1993; Krishna and Van den Broeke, 1995; Van den Broeke, 1995). In the Maxwell–Stefan description the chemical potential is taken as the driving force for diffusion. From a comparison with the Fick formulation it follows that the Fick diffusion matrix can be separated in a kinetic part, given by the Maxwell–Stefan diffusivities, and in an equilibrium part, in terms of the thermodynamic factor. The Fick diffusion coefficient can be written as

$$[D] = [B]^{-1}[\Gamma]. \tag{4}$$

The elements of the $[B]$ matrix are a function of the Maxwell–Stefan diffusivities, $\mathfrak{D}$. The friction between the adsorbed species and the zeolite lattice is represented by $\mathfrak{D}_i$, and the friction (drag) between the adsorbed species is given by $\mathfrak{D}_{ij}$. In the following we will use the so-called single-file diffusion model to describe the binary diffusion through the silicalite-1 membrane. In single-file diffusion it is assumed that species cannot pass each other in the channels of the zeolite structure. This means that the species exert no drag on each other and the counterexchange coefficient $\mathfrak{D}_{ij}^{-1}$ can be ignored (Van den Broeke, 1995).

In the case of single-file diffusion there is no interaction in the kinetic part of the Fick diffusion coefficient matrix. The single-file diffusion model was successfully used by Quereshi and Wei (1990a, 1990b) to describe the binary diffusion of benzene and toluene in ZSM-5. Van den Broeke (1994) used the single-file diffusion model to describe the transient uptake of a mixture of benzene and ethyl benzene in ZSM-5. This means that for these two systems it is possible to describe the binary diffusion with the intrinsic, or single-component Maxwell–Stefan, diffusivities, $\mathfrak{D}_i(0)$, and the binary isotherm.

For binary single-file diffusion the inverse of the $[B]$ matrix is given by

$$[B]^{-1} = \begin{pmatrix} \mathfrak{D}_1(0) & 0 \\ 0 & \mathfrak{D}_2(0) \end{pmatrix}. \tag{5}$$

The matrix of thermodynamic factors, $[\Gamma]$, is given by

$$\Gamma_{ij} = \theta_i \frac{\partial \mu_i}{\partial \theta_j} = RT\theta_i \frac{\partial \ln p_i}{\partial \theta_j}. \tag{6}$$

The Langmuir model will be used to outline the procedure to calculate the binary fluxes. In this case, an explicit expression is obtained. For the IAS theory no analytical relation can be derived for the thermodynamic factor, and a numerical solution is required. For the binary adsorption described with the extended Langmuir model we have

$$[D] = \begin{pmatrix} \mathfrak{D}_1(0) & 0 \\ 0 & \mathfrak{D}_2(0) \end{pmatrix} \frac{1}{1-\theta_1-\theta_2} \begin{pmatrix} 1-\theta_2 & \theta_1 \\ \theta_2 & 1-\theta_1 \end{pmatrix}. \tag{7}$$

This results in the following relations for the fluxes

$$J_1 = \frac{\mathfrak{D}_1(0)}{1-\theta_1-\theta_2}\left[(1-\theta_2)\frac{d\theta_1}{d\xi}+\theta_1\frac{d\theta_2}{d\xi}\right]$$

$$J_2 = \frac{\mathfrak{D}_2(0)}{1-\theta_1-\theta_2}\left[\theta_2\frac{d\theta_1}{d\xi}+(1-\theta_1)\frac{d\theta_2}{d\xi}\right]. \tag{8}$$

In Eqs. 7 and 8 there is only a coupling through the binary equilibrium isotherm. In the following the stronger adsorbed component in the mixture is referred to as component 1, and the weaker adsorbed component is referred to as component 2.

From the temperature dependency of the one-component fluxes it follows that the total flux through the silicalite-1 membrane consists of two contributions (Bakker et al., 1997). For species $i$ in the mixture we have

$$J_i = J_{S,i} + J_{GT,i}. \tag{9}$$

The first term on the righthand side (rhs) is given by Eq. 8 and is referred to as surface diffusion. The second term, on the rhs, is given by the so-called gas translation diffusion (Xiao and Wei, 1992; Bakker et al., 1997). Both mass-transport processes are activated processes.

For the surface diffusion flux through the silicalite-1 membrane, we then have

$$J_{S,i} = \epsilon\rho q_{i,\mathrm{sat}}\,\mathfrak{D}_i(0)\Gamma\frac{d\theta}{d\xi}, \tag{10}$$

with

$$\mathfrak{D}_i(0) = \frac{\lambda^2\nu_i}{z}\exp\left(\frac{-E_{S,i}}{RT}\right)$$

$$= \mathfrak{D}_i^0(0)\exp\left(\frac{-E_{S,i}}{RT}\right). \tag{11}$$

For the flux related to gas translation diffusion we have

$$J_{GT,i} = \epsilon D_{GT,i}\frac{1}{RT}\frac{dp}{d\xi}, \tag{12}$$

with

$$D_{GT,i} = \frac{\lambda}{z}\sqrt{\frac{8RT}{\pi M}}\exp\left(\frac{-E_{GT,i}}{RT}\right). \tag{13}$$

The values for the diffusion and adsorption parameters are given in a previous article (Bakker et al., 1997; cf. tables 3 and 4). For the silicalite-1 membrane we have the following properties. The porosity of the membrane support, $\epsilon$, is equal to 0.52, the thickness of the silicalite-1 layer, $\delta$, is equal to 50 $\mu$m, and the density of silicalite-1, $\rho$, is equal to 1.76 $\mathrm{g\cdot cm^{-3}}$ (Bakker et al., 1997; cf. table 2).

It is noted that Nishiyama et al. (1997) developed a similar model to describe the temperature dependence of the one-component permeance of small molecules (He, $H_2$, $O_2$, $N_2$, $CH_4$, and $CO_2$) through mordenite and ferrierite membranes. In their so-called parallel-diffusion model two paths for micropore diffusion are assumed. A fraction of the molecules are adsorbed on the wall of the zeolite pores, and another fraction of the molecules remain in the central region of the pores.

### *Temperature dependence of adsorption*

Besides being a function of the pressure, the amount adsorbed is also a function of the temperature; when the temperature is increased, the amount adsorbed decreases. This is given by the adsorption parameter, $b$, which follows an Arrhenius relation (Ruthven, 1984). For the Langmuir model

$$q = q_{sat}\frac{bp}{1+bp} \tag{14}$$

one has the following temperature dependence for equilibrium adsorption

$$b = b_0\exp\left(\frac{-\Delta H}{RT}\right)$$

$$= \exp\left(\frac{-\Delta S}{R}\right)\exp\left(\frac{-\Delta H}{RT}\right). \tag{15}$$

It is clear that the surface flux depends on the temperature through the amount adsorbed and through the diffusivity.

### *Separation factors*

In this work the separation factor is calculated from the permeance (Kärger and Ruthven, 1992). For a binary mixture the separation factor is given by

$$\alpha_{1,2} = \frac{\Pi_1}{\Pi_2}$$

$$= \frac{J_1}{J_2}\frac{\Delta p_2}{\Delta p_1}, \tag{16}$$

with $J_i$ the flux of component $i$ in the binary mixture.

The so-called ideal separation factor is obtained in the case where one uses the ratio of the one-component permeances

$$\alpha_{id} = \frac{\tilde{\Pi}_1}{\tilde{\Pi}_2}. \tag{17}$$

It is understood that the two single-component permeances, $\tilde{\Pi}$, are obtained for the same conditions. In the following, a comparison is made between the binary separation factor and the ideal separation factor.

The binary permeation is studied as a function of composition, as a function of the pressure, and as a function of the temperature. For all three situations a variable binary separation factor, $\alpha_{1,2}$, is obtained. For the separation factor as a function of the temperature, this is understood in terms of a change in the amount adsorbed, given by Eq. 15. However, the dependence of the separation factor on the composition and on the total pressure is a consequence of the binary equilibrium adsorption model. For a equilibrium-based separation process the separation factor is

$$\alpha_{1,2}^{\mathrm{eq}} = \frac{x_1}{y_1}\frac{y_2}{x_2} \tag{18}$$

with $x$ and $y$ the mole fraction of the feed and of the permeate, respectively.

From the extended Langmuir model it follows that the separation factor, based on equilibrium alone, is independent of the composition and the pressure.

The separation factor for the extendend Langmuir model is obtained by taking $n_1 = 1 = n_2$ in Eq. 3. Equation 18 gives, with $q_i = x_i$ and with $p_i = y_i p_{\mathrm{tot}}$, a constant separation factor

$$\alpha_{1,2}^{\mathrm{eq}} = \frac{q_{1,\mathrm{sat}} b_1}{q_{2,\mathrm{sat}} b_2} = \frac{K_1}{K_2}. \tag{19}$$

We have added the superscript, *eq*, to make a distinction between the separation factor calculated from the mole fractions, obtained for an equilibrium process, and the separation factor calculated from the permeances. Numerical simulations have been performed to calculate the separation factor for concentration-dependent diffusion through the silicalite-1 membrane with the thermodynamic factor obtained from the extendend Langmuir model. In that case, the separation factor is also independent of the pressure and the composition.

## Binary Permeation: Results and Discussion

In the following, the results for the permeation of five binary mixtures through the silicalite-1 membrane are discussed. In Table 1 an overview is given of the various mixtures studied and the experimental conditions applied.

### *Effect of the feed composition*

In Figure 1 the fluxes for mixtures of carbon dioxide and nitrogen are given as a function of composition. The feed pressure was kept constant at 101 kPa, and the temperature was set at 303 K. A comparison is made between the one- and two-component fluxes. In the one-component case the fraction of the adsorbing component is balanced by helium to give a constant feed pressure of 101 kPa. The results for the binary fluxes are plotted as a function of the fraction carbon dioxide, $y_{\mathrm{CO_2}}$, in the feed. The single-component flux for nitrogen is, of course, given as a function of the fraction nitrogen. If the amount of carbon dioxide in the feed is increased, the binary flux of carbon dioxide increases in an almost linear way. The binary flux of carbon dioxide is hardly affected by the presence of nitrogen in the mixture. On the other hand, a clear reduction is seen in the binary flux of nitrogen, as compared to the one-component flux. The binary flux for nitrogen decreases clearly in a nonlinear manner. As a consequence, the separation factor increases with an increase in the amount of carbon dioxide in the feed.

**Table 1. Experimental Conditions Used to Study the Permeation of Binary Mixtures Through the Silicalite-1 Membrane**

| Mixture | Composition | $p_f$ [kPa] | $T$ [K] |
|---|---|---|---|
| $N_2$:$O_2$ | 0.2:0.8 | 101 | 200–675 |
| $CO_2$:$N_2$ | $y_{\mathrm{CO_2}} + y_{\mathrm{N_2}} = 1$ | 101 | 303 |
| $CO_2$:$CH_4$ | $y_{\mathrm{CO_2}} + y_{\mathrm{CH_4}} = 1$ | 101 | 303 |
| $CO_2$:$CH_4$ | 0.5:0.5 | 101–450 | 225–545 |
| $CO_2$:$CH_4$ | 0.5:0.5 | 101 | 200–675 |
| $C_2H_6$:$CH_4$ | 0.5:0.5 | 101 | 300–500 |
| $n$-$C_4H_{10}$:$H_2$ | 0.5:0.5 | 101 | 300–675 |

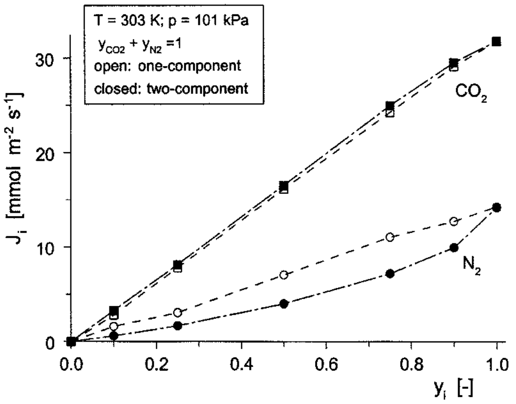


**Figure 1. Comparison between one- and two-component fluxes for carbon dioxide and nitrogen as function of the feed composition.**

Permeation results are for the silicalite-1 membrane at 101 kPa and 303 K.

In Figure 2 the separation factors obtained from the permeation of two mixtures, $CO_2$–$N_2$ and $CO_2$–$CH_4$, are compared with the ideal separation factors. The ideal separation

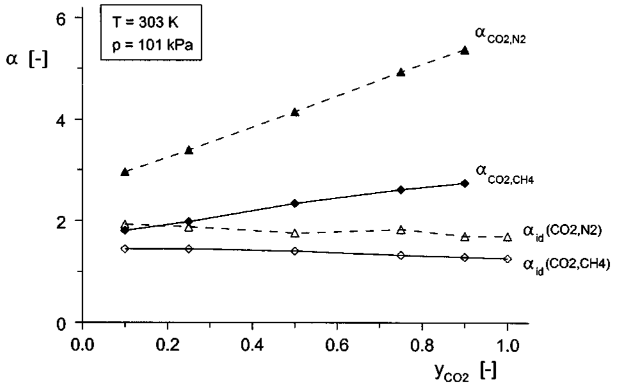


**Figure 2. Separation factors for the systems $CO_2$–$N_2$–silicalite-1 and $CO_2$–$CH_4$–silicalite-1, as a function of the feed composition.**

Comparison between ideal separation factor and separation factor for mixtures at 101 kPa and 303 K.

factor is calculated by dividing the one-component flux for carbon dioxide by the one-component flux of nitrogen or methane, at a given composition. Due to the difference in the adsorption isotherms, the ideal separation factor decreases slightly if the fraction of carbon dioxide is increased. At 303 K the adsorption isotherm of carbon dioxide is nonlinear. At the same temperature the adsorption isotherms of nitrogen and methane are almost linear. For the permeation of the $CO_2-N_2$ mixture the separation factor is two to three times higher, as expected from the one-component data. The same trend is seen for the permeation of the $CO_2-CH_4$ mixture. This clearly demonstrates the effect of competitive adsorption on the binary permeation. In silicalite-1 methane is more strongly adsorbed than nitrogen; therefore, the separation factors for the $CO_2-CH_4$ system are smaller than the separation factors obtained for the $CO_2-N_2$ system.

### *Permeation as a function of pressure*

In Figure 3 results for a 1:1 mixture of carbon dioxide and methane are presented. The separation factor, toward $CO_2$, is given as a function of temperature and pressure. For a temperature of 225 K the separation factor, obtained from the binary fluxes, decreases as the feed pressure is increased from 100 to 450 kPa. For higher temperatures only a small change in the separation factor is observed, if the pressure is increased. This is due to the fact that, at high temperatures the isotherms become more linear. At the highest temperature studied, $T = 543$ K, the separation factor is almost independent of the pressure.

The fact that at a temperature of 225 K the separation factor changes with pressure is a strong indication that the extended Langmuir model cannot be used to describe the adsorption of mixtures in silicalite-1. This is also clear from the predictions; the extended Langmuir model gives a separation factor that is independent of the pressure. In the calculations the activated gas translation contribution is neglected because it is much smaller than the contribution given by surface diffusion. This means that the observed behavior at 225 K is governed by adsorption and surface diffusion. The *b* parameter in the (extended) Langmuir model is calculated with Eq. 15, using the data given in Table 2. The decreasing trend is reasonably well described with the IAS theory. So, the IAS theory, using the one-component Langmuir model, gives a concentration-dependent separation factor. It is stressed that both models use only single-component equilibrium and diffusion data.

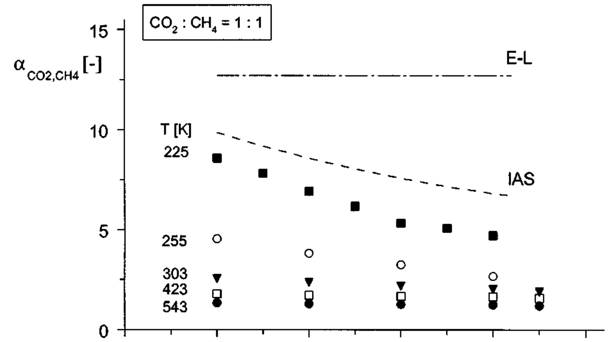


**Figure 3. Binary separation factor (symbols) for a 1:1 mixture of carbon dioxide and methane as a function of the pressure, for five different temperatures.**

Experimental results are compared with predictions (lines) using the extended Langmuir (E-L) model and the ideal adsorbed solution (IAS) theory.

**Table 2. Adsorption and Diffusion Parameters Used in the Predictions of the Permeation of the Binary Mixtures**

| Property | Unit | $CH_4$ | $CO_2$ | $n$-$C_4H_{10}$ | $i$-$C_4H_{10}$ |
|---|---|---|---|---|---|
| $-\Delta H$ | $kJ \cdot mol^{-1} \cdot K^{-1}$ | 22.6 | 24.1 | 45.9 | 34.1 |
| $\Delta S$ | $kJ \cdot mol^{-1} \cdot {}^{-1}$ | −70 | −58 | −85 | −82 |
| $q_{sat}$ | $mmol \cdot g^{-1}$ | 4.5 | 5.0 | 2.2 | 1.5 |
| $\mathfrak{D}^0(0)$ | $10^{-8}\ m^2 \cdot s^{-1}$ | 3.9 | 0.70 | 0.40 | 0.15 |
| $E_S$ | $kJ \cdot mol^{-1}$ | 8.8 | 9.6 | 13.7 | 15.1 |
| $\lambda$ | nm | 1.0 | 0.9 | 0.8 | 0.8 |
| $E_{GT}$ | $kJ \cdot mol^{-1}$ | 7.9 | 10.3 | 13.1 | 13.5 |

Note: In the IAS theory the one-component Langmuir equation is used.

The fact that the separation factor calculated with the IAS model is a function of the pressure is due to the difference in saturation capacity. Some simulations have been performed with the same saturation capacity. In that case the separation factor is independent of the gas-phase composition (these results are not shown). On the other hand, the extended Langmuir model with a concentration-dependent Fick diffusion-coefficient matrix (always) gives a constant separation factor.

### *Permeation as a function of temperature*

The interaction between the species adsorbed in the silicalite-1 crystals of the membrane becomes clear when permeation is studied as a function of temperature. For four different binary systems permeance as a function of temperature has been measured (see Table 1). The adsorption and diffusion properties of the various gases in the silicalite-1 crystals were given in the previous article (Bakker et al., 1997).

In Figure 4 the binary permeation of air, permeance of nitrogen and oxygen, is given as a function of the tempera-

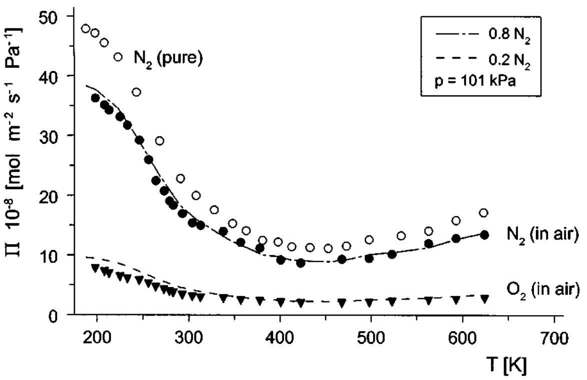
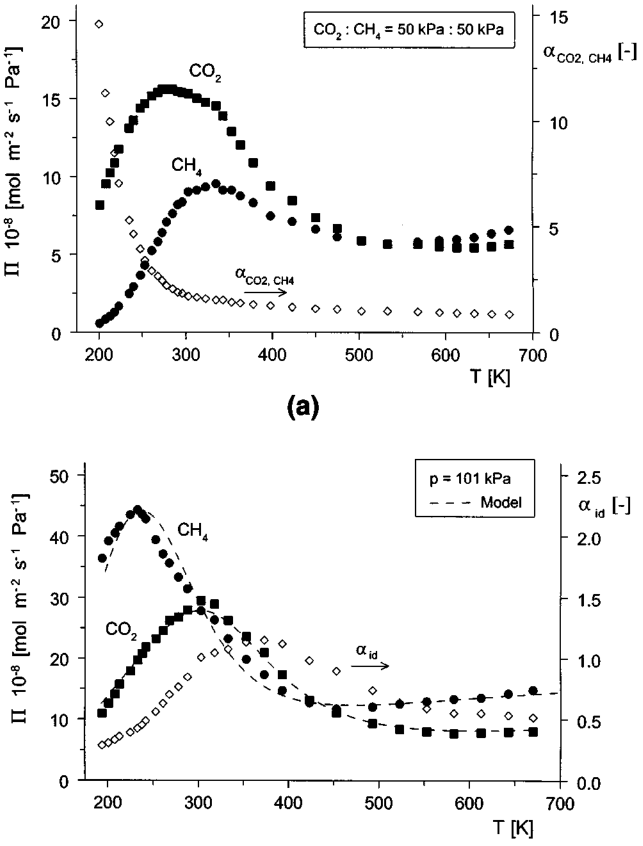


**Figure 4. Binary fluxes of air, nitrogen and oxygen, as a function of the temperature; comparison with one-component flux for nitrogen.**

ture. For comparison the permeance for pure nitrogen, at 101 kPa, is also given. The results for pure nitrogen is used to predict the permeance of air, using the mole fractions of $N_2$:$O_2$ = 0.8:0.2. Because of the fact that nitrogen and oxygen have similar adsorption and diffusion properties in silicalite-1, the results for air can be predicted reasonably well over the whole temperature range, using the pure-nitrogen data.

The results for the permeances of a mixture of carbon dioxide and methane, 50 kPa:50 kPa, over the temperature range of 200 K to 675 K are given in Figure 5a. To illustrate the interaction in the case of diffusion of binary mixtures, the one-component permeance and the ideal separation factor are given in Figure 5b for comparison. The results for the one-component permeances were presented before (Bakker et al., 1997). In the single-component case the maximum in the permeance of methane occurs at a lower temperature than the maximum of carbon dioxide. In the mixture the methane maximum occurs at a slightly higher temperature than the carbon dioxide maximum. If we compare the one-component results with the binary results, we see that for carbon dioxide, in both cases, the maximum in the permeance occurs around 275 K. For methane we see that above a temperature of about 450 K the one-component flux and the binary flux show the same behavior. This means that one can say that up to 450 K the permeation of methane is affected by the presence of carbon dioxide. Above 450 K there is no longer any competitive adsorption, and carbon dioxide and methane are permeating more or less independently.

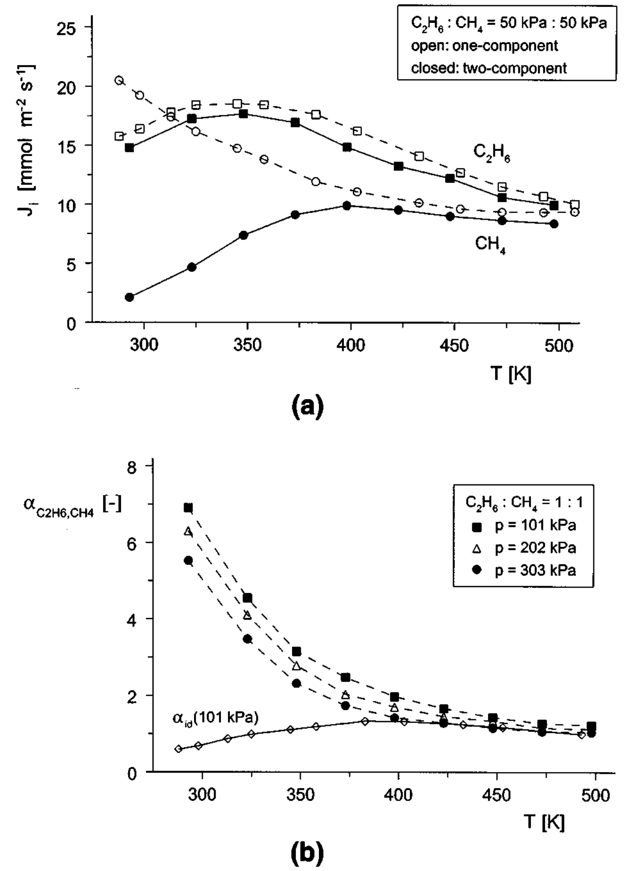


(a)

(b)

**Figure 5. Permeation and separation factor for a 1:1 mixture of carbon dioxide and methane as a function of the temperature.**

(a) Binary permeances and separation factor. (b) One-component permeances and ideal separation factor.



(a)

(b)

**Figure 6. Binary fluxes of a 1:1 mixture of ethane and methane through the silicalite-1 membrane as a function of the temperature (300–500 K) at 101 kPa.**

(a) Comparison between one- and two-component fluxes. In the one-component case the feed pressure was 50 kPa of ethane or methane plus 50 kPa helium. (b) Separation factor for a 1:1 mixture of ethane and methane for three different pressures. Comparison with the ideal separation factor.

For the third system, a 1:1 mixture of ethane and methane, the permeance was obtained over the temperature range of 300 K to 500 K, for three pressures. The results for the one- and two-component permeances at 101 kPa are compared in Figure 6a. In the one-component case the feed consisted of 50 kPa of methane or ethane and 50 kPa of helium. The results for the separation factors at a pressure of 101, 202, and 303 kPa are given in Figure 6b. Again, the permeance of ethane in the mixture is hardly affected as compared to the one-component result. For methane the maximum in the permeance occurs at a higher temperature than the maximum of ethane. The separation factor at a given pressure decreases with an increase in the temperature. For a given temperature, the separation factor decreases if the pressure is increased. At high temperatures the separation factor is almost independent of the pressure, indicating that the relevant transport mechanism has shifted from surface diffusion to activated gas translation diffusion. Again, there is no significant interaction between the two components in the silicalite-1 crystals above, say, 450 K.

The fact that at low temperatures the separation factor toward ethane decreases if the pressure is increased is caused by the nonlinearity of the $C_2H_6$ isotherms. An increase in the $C_2H_6$ pressure results in a smaller increase in the amount adsorbed, as compared to $CH_4$, which has a more linear isotherm. The difference between the amount adsorbed at the feed and the permeate side determines the driving force for diffusion. By increasing the pressure, the amount of methane adsorbed increases more than the amount adsorbed of ethane. As a result the separation factor toward the stronger adsorbed component will decrease if the pressure is increased.

The examples given so far for the binary mixtures are controlled by equilibrium adsorption. This means that at low temperatures the largest difference is seen between the results for the mixtures and the results for the one-component systems. So, separation is preferably performed at low temperatures. For high-temperature applications, with a silicalite-1 membrane, only the separation of hydrogen from a mixture containing butane isomers seems interesting (cf. fig. 9 of Bakker et al. (1997)). At high temperatures the permeance is determined by gas translation diffusion, and the difference in mobility determines the separation. In Figure 7 the permeation and separation factor for a 1:1 mixture of *n*-butane and hydrogen is presented. This is a clear example of where the permeation is controlled by equilibrium at low temperatures, say, between 300 and 400 K, and where at high temperatures the separation is a consequence of the difference in mobility. The fact that two different mechanisms contribute to the permeation causes a reversal in the separation factor. At room temperature the separation factor is about 31 toward *n*-butane. At the other end, for a temperature of 675 K, the separation factor is 7.8, but now toward the faster-moving hydrogen.

### *Comparison of binary and ideal separation factors*

In Figure 8 the separation factor of a 1:1 mixture of $CO_2$ and $CH_4$ as a function of the temperature is compared with two predictions. The decreasing trend for the separation factor can be described reasonably well with both the extended Langmuir model and the IAS theory.

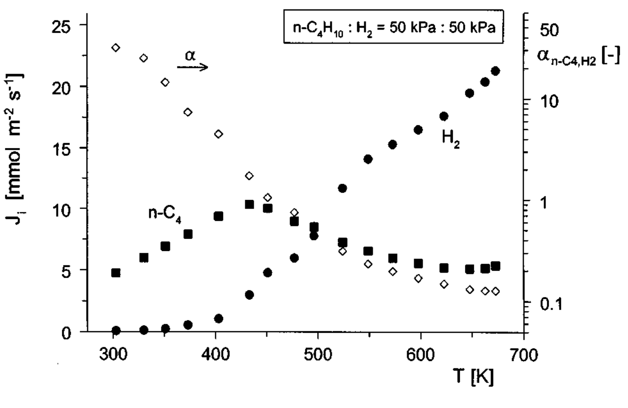


**Figure 7. Binary flux and separation factor for a 1:1 mixture of *n*-butane and hydrogen through the silicalite-1 membrane as a function of the temperature (300–675 K) at 101 kPa.**

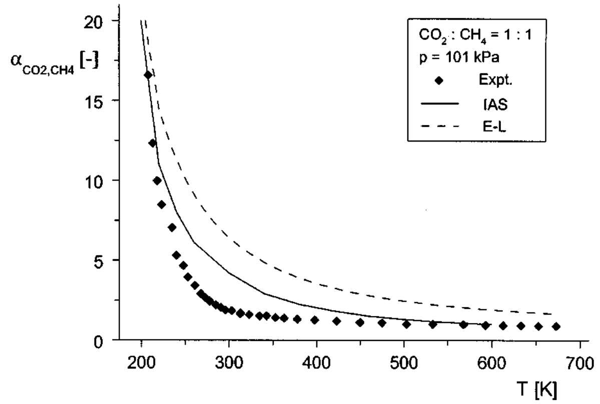


**Figure 8. Predictions with the extended Langmuir (E-L) model and with the ideal adsorbed solution (IAS) theory for the separation factor for a 1:1 mixture of carbon dioxide and methane, as a function of the temperature.**

In Figure 9a the ideal separation factor as a function of the temperature is compared for a number of systems containing light alkanes. The ideal separation factors are obtained from the modeling results of the one-component permeances, as presented by Bakker et al. (1997). The various ideal separation factors show more or less the same dependence on the temperature. If the temperature is increased, the ideal separation factor toward the stronger adsorbed *n*-butane goes through a maximum. Except for the system of *n*-butane and *i*-butane, the ideal separation factors toward the stronger adsorbed *n*-butane are smaller than unity

This behavior of the ideal separation factor is also seen for most of the other systems (see Figure 5b for the result for $CO_2$ and $CH_4$, and Figure 6b for the result for the $C_2H_6$ and $CH_4$). From the results presented in Figures 5 and 6, it follows that for low temperatures the binary separation factor is much higher than the corresponding ideal separation factor. At high temperatures the binary separation factor approaches the ideal separation factor. It is also noted that the ideal separation factors do not change strongly with temperature. The ideal separation factor for $n\text{-}C_4H_{10}\text{–}CH_4$ increases by a factor of 5.7, from 0.07 to 0.4, between 300 and 450 K. On the other hand, for the $CO_2$ and $CH_4$ and the $n\text{-}C_4H_{10}$ and $H_2$ mixtures, the separation factor changes by factors of 18 and 250, respectively, over the temperature range studied.

Figure 9b shows calculations for the separation factor for a 50 kPa:50 kPa mixture of *n*-butane and *i*-butane as a function of the temperature. Results for binary permeation of *n*-butane and *i*-butane have been reported by Coronas et al. (1997). However, the permeance and the separation factor were found to depend on the synthesis procedure. It is, therefore, interesting to have some theoretical results for the separation factor of this mixture. The extendend Langmuir model was used to predict the binary fluxes, which were used to calculate the separation factor as a function of the temper-

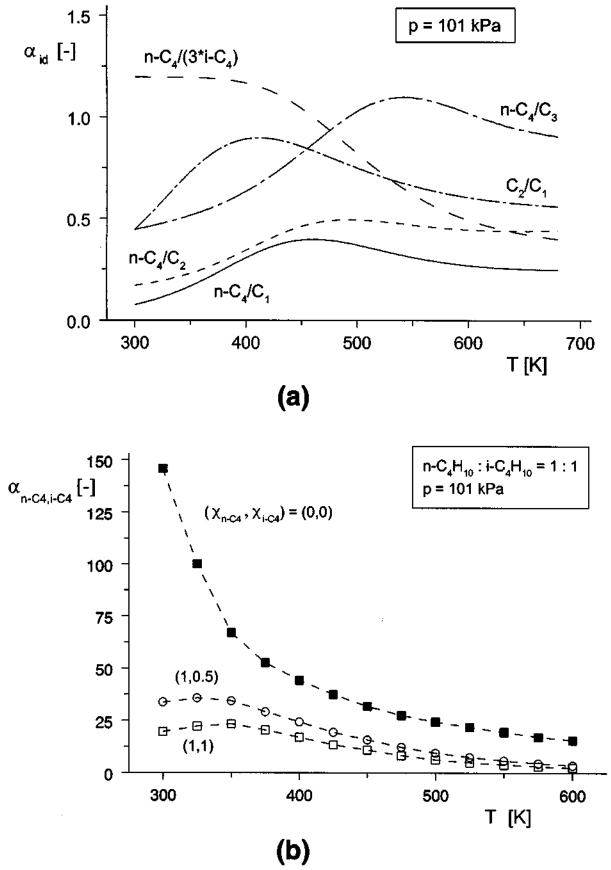


**Figure 9. Ideal and binary separation factors as a function of the temperature.**

(a) Ideal separation factor for systems with C1 to C4 alkanes. (b) Predictions of the separation factor with Eq. 20, for a 50 kPa:50 kPa mixture of *n*-butane and *i*-butane using the extended Langmuir model.

ature. The parameters given in Table 2, taken from Bakker et al. (1997), were used in the simulations.

Due to the fact that there are two contributions to the mass transport, the separation factor is given by

$$\alpha_{n-C_4,i-C_4} = \frac{\Pi_{S,n-C_4} + \chi_{n-C_4}\Pi_{GT,n-C_4}}{\Pi_{S,i-C_4} + \chi_{i-C_4}\Pi_{GT,i-C_4}}. \tag{20}$$

The relative contributions of the two mass-transport mechanisms are taken into account by the parameter $\chi$.

In Figure 9b three situations are analyzed parametrically. For the case where the permeation and the separation are determined solely by adsorption and surface diffusion we have $(\chi_{n-C_4}, \chi_{i-C_4}) = (0.0)$. If the mass transport by gas translation is through defects between the silicalite-1 crystals, one expects no effect of the stronger adsorbed *n*-butane on the permeation of *i*-butane. For this situation one has $(\chi_{n-C_4}, \chi_{i-C_4}) = (1,1)$. It is also possible that the stronger adsorbed *n*-butane hinders the gas translation transport of *i*-butane. This is the situation where the gas translation diffusion is an intracrystalline transport. For this case, $\chi_{i-C_4}$ is smaller than $\chi_{n-C_4}$, and we have, for example, $(\chi_{n-C_4}, \chi_{i-C_4}) = (1, 0.5)$.

For the situation of only surface diffusion, the separation factor decreases with an increase in temperature. For the situation where gas translation also contributes, a different behavior is seen; the separation factor has a maximum and is considerably lower than the separation factor calculated with only surface diffusion. It is noted that the results with gas translation are in reasonable agreement with the experimental results presented by Coronas et al. (1998). These results imply that by carefully measuring binary equilibrium and permeation it will be possible to identify the origin of the gas-translation diffusion.

## Conclusions

From the results for the binary permeation through the silicalite-1 membrane, the following main points are noted. For the permeation of binary mixtures it is seen that the permeation of the stronger adsorbed component in the mixture is hardly affected by the presence of a weaker adsorbed component. On the other hand, the permeation of the weaker adsorbed component is considerably reduced in the presence of a stronger adsorbed component.

At low temperatures the separation factor for the mixtures deviates considerably from the so-called ideal separation factor. Clearly, the competitive equilibrium adsorption has a definite effect on the permeation and separation behavior.

Some conclusions about the binary adsorption model can be drawn from a comparison of the binary permeance for three different operating conditions. From the results for the binary permeation as a function of composition and pressure, it can be concluded that it is not possible to describe the observed behavior for the separation factor with the extended Langmuir model. The extended Langmuir model gives, as a function of the composition or the pressure, a constant separation factor. The separation behavior of binary mixtures with a silicalite-1 can be described reasonably well with the ideal adsorption solution theory.

## Acknowledgment

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## Notation

$b^0$ = pre-exponential factor
$\mathfrak{D}^0$ = limiting Maxwell–Stefan diffusion coefficient
$E$ = activation energy for diffusion
$K$ = Henry's law constant
$M$ = molair mass
$p$ = pressure
$q$ = amount adsorbed
$R$ = gas constant
$T$ = temperature
$z$ = probability factor
$\Delta H$ = heat of adsorption
$\Delta S$ = entropy of adsorption
$\theta$ = fractional occupancy
$\lambda$ = diffusional length
$\mu$ = chemical potential
$\nu$ = jump frequency for surface diffusion

### *Superscripts and subscripts*

1,2 = component 1, 2
$f$ = feed
$i, j$ = components $i$, $j$
sat = saturation capacity
tot = total

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## Appendix: IAS Theory

For a thermodynamically ideal adsorbed phase, the equilibrium isotherm of an adsorbed mixture can be predicted from the pure-component data. This is known as the ideal adsorbed solution (IAS) theory; the spreading pressure of the adsorbed mixture is equal to pure-component spreading pressure (Myers and Prausnitz, 1965; Ruthven, 1984). Considering equilibrium between the vapor phase and the adsorbed phase, we have

$$p = p^0(\pi)\gamma x. \tag{A1}$$

For an ideal binary system, this reduces to

$$\begin{aligned} p_1 &= p_1^0(\pi)x_1 \\ p_2 &= p_2^0(\pi)x_2. \end{aligned} \tag{A2}$$

In these equation $p^0$ refers to the pure component. The relation between the single-component isotherm and the spreading pressure $\pi$ is given by

$$\frac{\pi A}{RT} = \int_0^p \frac{q^0(p)}{p} dp. \tag{A3}$$

Equation A3 is derived under the conditions of mixing taking place at constant temperature and spreading pressure

$$\pi_1^0 = \pi_{\text{mix}} = \pi_2^0. \tag{A4}$$

For a binary mixture we have the following additional conditions for the adsorbed phase and the bulk phase

$$\begin{aligned} x_1 + x_2 &= 1 \\ y_1 + y_2 &= 1. \end{aligned} \tag{A5}$$

Assuming there is no change in area upon mixing of the sorbents, the total amount adsorbed for the mixture is given by

$$\frac{1}{q_1 + q_2} = \frac{x_1}{q_1^0} + \frac{x_2}{q_2^0}. \tag{A6}$$

Equations A2 to A6 form a set of seven equations with nine unknowns. This means that at the start of an adsorption isotherm measurement, two independent variables must be known. For example, the total pressure $p$ and the bulk mole fraction $y_1$ are used as input.

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