Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Hennepe, H. J. C. Te , Smolders, C. A. , Bargeman, D. and Mulder, M. H. V.(1991) 'Exclusion and Tortuosity Effects for Alcohol/Water Separation by Zeolite-Filled PDMS Membranes', Separation Science and Technology, 26: 4, 585 — 596

To link to this Article: DOI: 10.1080/01496399108050492

URL: http://dx.doi.org/10.1080/01496399108050492

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SEPARATION SCIENCE AND TECHNOLOGY, 26(4), pp. 585–596, 1991

Exclusion and Tortuosity Effects for Alcohol/Water Separation by Zeolite-Filled PDMS Membranes

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Abstract

A resistance model has been developed to describe the increased pervaporation flux and selectivity for the separation of ethanol/water mixtures with silicalite-filled silicone rubber (SR) membranes as compared to unfilled SR membranes. The model interprets the increased component flux for ethanol in terms of an increasing ethanol permeability of the membrane. Membrane permeability is given as a function of rubber and silicalite permeabilities and of the silicalite content of the membrane. It is shown that silicalite permeability varies with the type of alcohol and the alcohol concentration in the feed mixture. In the series methanol, ethanol, propanol, and butanol, the alcohol permeability of silicalite varies with the length of the alcohol molecule, the lowest permeability being found for butanol. In the presence of propanol and butanol, the silicalite particles are impermeable to water and obstruct water transport through the membrane.

INTRODUCTION

Current research to improve membrane performance for the separation of alcohols from aqueous mixtures is mainly focused at the chemical modification of existing polymers or the development of new materials. We have chosen a different approach. Based on the sorption-diffusion model, we have searched for porous materials which can improve the selective sorption properties and by simply incorporating them into the membrane may lead to a better (composite) membrane. Such a material is the hydrophobic zeolite silicalite. Most of the commonly used zeolites or molec-

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ular sieves are hydrophilic and are used to remove traces of water from organic liquids. Silicalite is the aluminum-free analogue of ZSM-5 (*1*), which was first synthesized by researchers at Mobil Oil (*2*). One of the unique properties of both ZSM-5 and silicalite is that they are hydrophobic (organophilic) in nature and therefore selectively adsorb organics from an aqueous mixture. A lot of research has been carried out to investigate silicalite properties, and one of the major applications is the separation of alcohol–water mixtures (*3–5*).

We have combined silicalite and silicone rubber in a pervaporation membrane and tested this composite membrane for its separation properties. The results of these investigations have been published (*6, 7*). It was shown that for all alcohols tested, the silicalite–silicone rubber composite membrane improves the membrane performance, both flux and selectivity, compared to the pure silicone rubber membrane. To elaborate on the transport mechanism, we have also used hydrophilic zeolites A and X as additives (*8,9*). Although these latter zeolites give an increase in water flux and an undesirable decrease in the selectivity for alcohol, measurements using these zeolites have unambiguously shown that transport occurs through the zeolite particles. This means that the positive effect of the addition of silicalite on membrane properties—an increase in the selectivity for ethanol from about 8 for the pure silicone rubber to about 40 for a membrane with 70% (w/w) silicalite—probably results from a combination of both the enhanced sorption of ethanol into the membrane and the faster transport through the membrane.

THEORY

Development of the Model

The sorption-diffusion model, which is frequently used to describe the transport through pervaporation membranes, involves two steps: selective sorption of feed components into the membrane and, subsequently, diffusional transport through the membrane (*10*). The addition of zeolite particles to the membrane matrix influences both the sorption part as well as the diffusional part of the transport mechanism. Here we will concentrate on the diffusional part and consider diffusion through the membrane to be rate determining.

In the case of a zeolite-filled membrane we are dealing with a composite membrane in which each of the components is located in well-defined domains which in turn may have a different resistance to transport. The flux through such a membrane can be described in terms of a resistance model.

The basic equation of a resistance model is

$$J_i = \Delta p_i/(R_i A) \tag{1}$$

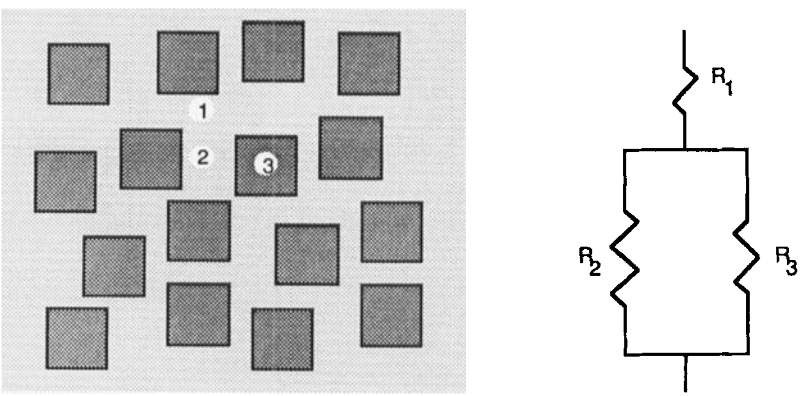
In words: the flux J per unit area is a function of the driving force (the difference in partial vapor pressure across the membrane Δp), the resistance R of the membrane against transport, and the membrane area A. The main objective now is to find an expression for R for feed component i. Since transport can occur through both rubber and zeolite particles, membrane resistance R_i can be written as a combination of the resistances for both materials:

$$R_i = R_{r,i} + R_{z,i} \tag{2}$$

In Eq. (2) the membrane resistance is computed as if rubber and zeolite resistances, $R_{r,i}$ and $R_{z,i}$, are in series. However, if the zeolite particles are impermeable, there is still the transport route around the particles, and this has to be taken into account as a third resistance, $R'_{r,i}$, parallel to the zeolite resistance $R_{z,i}$ in Eq. (2).

Figure 1 gives the resistance model proposed here to describe the transport through zeolite-filled membranes. Membrane resistance is a combination of resistances in series and in parallel. As in the electrical circuit analogue, the total membrane resistance can be computed by

$$R_i = nR_{1,i} + [nR_{2,i}R_{3,i}/(R_{2,i} + R_{3,i})] \tag{3}$$



zeolite filled membrane electrical circuit analog

FIG. 1. Schematic representation of the silicalite/silicone rubber composite membrane and its electrical circuit analogue (transport route through the membrane from top to bottom).

In this equation n is the number of zeolite particles along the transport path. The resistances in Eq. (3) can be evaluated in terms of permeabilities as given in the relations (4a) through (4c):

$$R_{1,i} = R_{r,i} = l_r/(P_{r,i}A_r^0) \tag{4a}$$

$$R_{2,i} = R'_{r,i} = l'_r/(P_{r,i}A_r) \tag{4b}$$

$$R_{3,i} = R_{z,i} = l_z/(P_{z,i}A_z) \tag{4c}$$

In the above relations, l_r is the pathlength between the successive zeolite particles in the direction of transport, l_z is the length of the zeolite particle, and l'_r is the pathlength through the rubber around the zeolite particle. A_z is the area perpendicular to the flow as occupied by the zeolite in a cross section, and A_r is the area between the zeolite particles. The total membrane area is A_r^0; l_r and l_z are related as given in Eq. (5) where d represents the total thickness of the membrane.

$$nl_r + nl_z = d \tag{5}$$

The pathlength around the zeolite particle is a function of the zeolite particle size, particle geometry, and particle orientation. Equation (6) gives a simple relation between l'_r and l_z:

$$l'_r = fl_z \tag{6}$$

For cubical particles orientated as shown in Fig. 2, and in the absence of a lateral concentration gradient, the factor f—which is a tortuosity factor—is 3/2; for spherical particles f is $\pi/2$.

According to Nielsen (*11*), who described the flux through a polymer membrane filled with inert particles, the space between the particles in the direction of transport is related to the polymer content of the membrane ϕ_p $(=1 - \phi_z)$. The factor n, the number of layers, can thus be eliminated. Combination with Eq. (5) leads to the relations (7a) and (7b) which give the pathlength through the polymer part and through the zeolite part of the membrane, respectively:

$$nl_r = (1 - \phi_z^{1/3})d \tag{7a}$$

$$nl_z = \phi_z^{1/3}d \tag{7b}$$

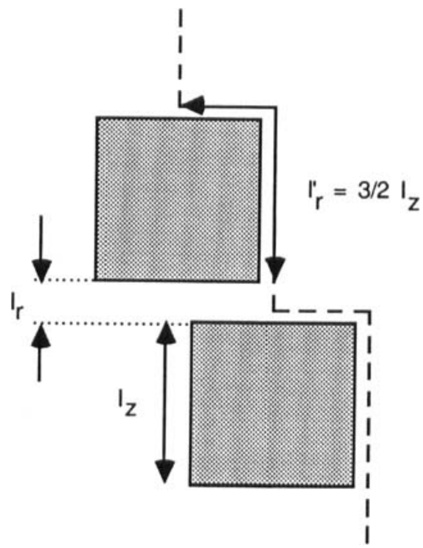


FIG. 2. Schematic representation of zeolite particles in the SR membrane and the pathlengths through and around the particles: l_z and l_r.

Nielsen also gives an expression for the areas A_r and A_z. These areas are related to ϕ_p ($=1 - \phi_z$) and $1 - \phi_p$, respectively. Equations (8a) and (8b) give the expressions for the area of the polymer between the particles and the particle area in a cross section:

$$A_r = A_r^0(1 - \phi_z) \tag{8a}$$

$$A_z = A_r^0\phi_z \tag{8b}$$

By combining the above equations, one obtains Eq. (9) where the component flux is given as a function of the zeolite content of the membrane, membrane thickness, and the permeabilities of the membrane constituents. We have taken f to be 3/2 since the commercially available silicalite which was used in our experiments consists of more or less cubical particles. For strictly cubical particles, the actual value of f may be slightly below 3/2 because of particle orientation.

$$J_i = \Delta p_i \Bigg/ \left(\frac{(1 - \phi_z^{1/3})d}{P_{r,i}} + \frac{\frac{3}{2}\,\phi_z^{1/3}d}{P_{r,i}(1 - \phi_z) + \frac{3}{2}\,P_{z,i}\phi_z}\right) \tag{9}$$

The variables in Eq. (9) are either known or can be obtained by fitting the equation on pervaporation data using $P_{r,i}$ and $P_{z,i}$ as variables.

It has to be noticed here that it is implicitly assumed that both rubber and silicalite permeabilities are independent of the zeolite content of the membrane. Besides, both permeabilities are average values which can be measured only for the membrane as a whole. Both the rubber permeability and the silicalite permeability may vary with the position inside the membrane. The model does not account for these variations.

Permeation Properties Related to $P_{z,i}/P_{r,i}$

The effect of zeolite permeability on flux at a given volume fraction of zeolite can be described by referring to the ratios $P_{z,i}/P_{r,i}$:

$$P_{z,i}/P_{r,i} = 1$$

If zeolite permeability equals rubber permeability for component i, the effect of zeolite on flux will be negligible.

$$P_{z,i}/P_{r,i} \gg 1$$

If zeolite permeability is large compared to rubber permeability, at a high enough zeolite content the increased component flux will be mainly determined by zeolite permeability.

$$P_{z,i}/P_{r,i} \ll 1$$

If zeolite permeability is small, the component flux for i will be lowered and the zeolite particles will obstruct transport due to the tortuosity introduced.

EXPERIMENTAL

The silicone rubber (polydimethylsiloxane/PDMS)/silicalite membranes were prepared according to a procedure described elsewhere (7). Membrane thickness and zeolite content ranged from 80 to 210 μm and from 0 to 70% (w/w), respectively. All membranes were used without further treatment.

The pervaporation measurements on ethanol/water feed mixtures containing between 0 and 10% (w/w) alcohol (PA quality) were performed according to a standard procedure and on a standard pervaporation apparatus as described elsewhere (7). The temperature of the feed was kept constant at 25°C.

The total flux was calculated from Eq. (10). Flux times ethanol weight fraction in the feed gives the component flux for ethanol. Membrane selectivity was calculated using Eq. (11).

$$J_{d=100\mu m} = [w/(\Delta t A_r^0)][d/100] \qquad (g/m^2 \cdot h) \tag{10}$$

$$\alpha = (x_{alc}/x_{H_2O})_{permeate}/(x_{alc}/x_{H_2O})_{feed} \qquad (—) \tag{11}$$

In Eqs. (11) and (12), w = weight (g) of permeate, Δt = permeation time (h), A_r^0 = membrane area (m^2), and d = membrane thickness (μm); x is the weight fraction. As can be seen from Eq. (11), the fluxes are normalized to a membrane thickness of 100 μm.

The value for $\Delta p_i = (p_{i,\text{feed side}} - p_{i,\text{permeate side}})$ in Eq. (9) is calculated by taking $p_{i,\text{permeate side}} = 0$ and using Eq. (12) to calculate $p_{i,\text{feed side}}$:

$$p_{i,\text{feed side}} = c_{i,\text{ feed side}}\gamma p_i^0 \qquad (\text{mmHg}) \tag{12}$$

$c_{i,\text{feed side}}$ is the concentration in the liquid feed mixture in a mole fraction. The activity coefficient γ is calculated from the Margules equation; p_i^0 is calculated from the Antoine equation. The numerical values for the parameters in these equations were taken from Ref. *12*.

RESULTS AND DISCUSSION

The resistance model is based on the assumption that the diffusional transport through the membrane is rate determining. To test both the model and this latter assumption, pervaporation experiments have been performed by using membranes with a thickness varying from 80 to 210 μm. The results of the experiments are summarized in Figs. 3 and 4. These figures show that Eq. (9) fits well to the observed pervaporation fluxes.

The differences between measured and calculated flux values at low silicalite content [<20% (w/w)] indicate that rubber permeability decreases when silicalite is added to the membrane. In the model it is assumed that the permeabilities of both rubber and zeolite are independent of the zeolite content of the membrane. Obviously the addition of the zeolite influences rubber permeability to some extent. The explanation could be either that the zeolite particles act as physical crosslinks for the rubber phase or that the silicalite particles catalyze the chemical crosslinking of the membrane during membrane preparation, or a combination of both effects.

At a higher silicalite content of the membrane [above 20% (w/w)], the proposed model explains the influence of zeolite addition on membrane performance properly. Upon addition of silicalite, ethanol transport

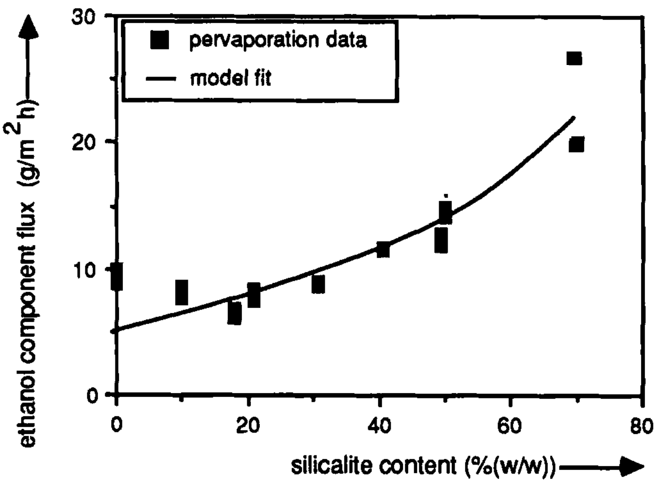


FIG. 3. Component flux for ethanol in silicone rubber membranes filled with silicalite as a function of the silicalite content of the membrane; fluxes are recalculated to 100 μm membrane thickness; ethanol concentration 5% (w/w).

through the membrane as a whole is increased because of the high permeability of silicalite for ethanol. Water permeability through the silicalite particles and through the rubber matrix is lower and roughly the same for both materials, and the addition of silicalite has only a slight effect on water transport. The positive effect of silicalite on membrane selectivity is thus the combined effect of two factors: $P_{z,eth}/P_{r,eth} \gg 1$ and $P_{z,w}/P_{r,w} \approx 1$.

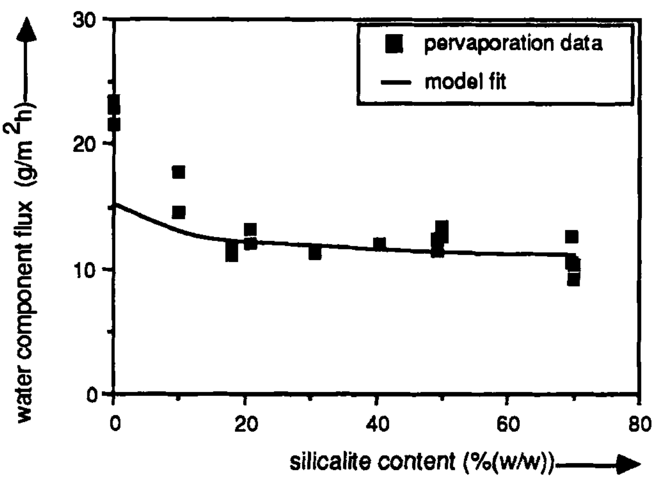


FIG. 4. Component flux for water in silicone rubber membranes filled with silicalite as a function of the silicalite content of the membrane; ethanol concentration 5% (w/w).

TABLE 1
Calculated Permeabilities for Silicone Rubber and Silicalite for Some Alcohols

Alcohol	$P_{r,alc} \times 10^{-4}$ ($g \cdot m/m^2 \cdot h \cdot mmHg$)	$P_{z,alc} \times 10^{-4}$ ($g \cdot m/m^2 \cdot h \cdot mmHg$)
MeOH	1.1	37
EtOH	2.0	11
PrOH	6.2	3
BuOH	16.0	4

Table 1 gives the calculated permeabilities for several alcohols. For comparison: water permeabilities in the presence of ethanol for rubber and zeolite are 9.9×10^{-5} and 4.6×10^{-5} $g \cdot m/m^2 \cdot h \cdot mmHg$, respectively.

The increase in ethanol flux with increasing zeolite content is attributed to the higher silicalite permeability compared to the rubber permeability for ethanol. For propanol the lower silicalite permeability for the alcohol will result in a decrease in propanol flux with zeolite content. This is illustrated in Fig. 5. In this figure the propanol component flux is given as a function of the feed concentration for membranes with different silicalite content. The lines are fitted by using Eq. (9).

Figure 6 gives the water component flux in the presence of propanol. Water flux strongly decreases with the silicalite content of the membrane.

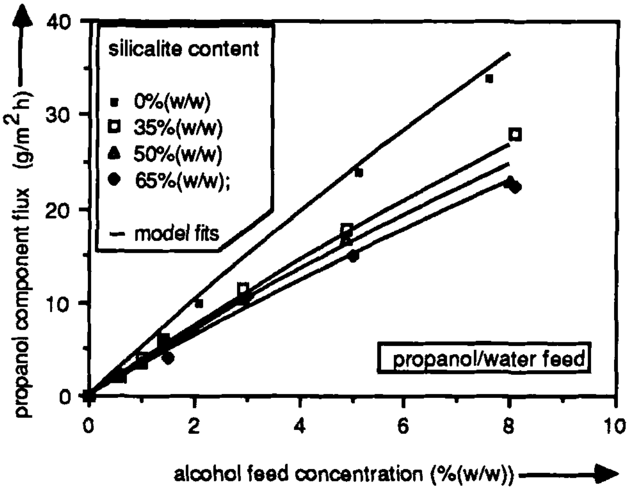


FIG. 5. Propanol component flux for the pervaporation of a propanol/water feed mixture using silicalite-filled membranes with different silicalite content as a function of the feed composition; feed temperature about 25°C.

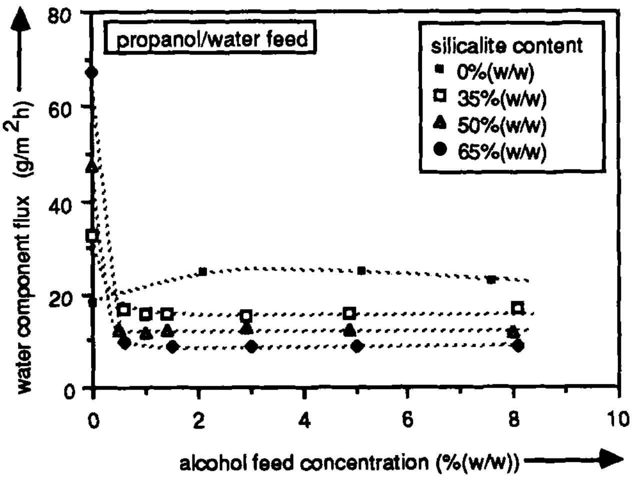


FIG. 6. Water component flux for the pervaporation of a propanol/water feed mixture using silicalite-filled membranes with different silicalite content as a function of the feed composition; feed temperature about 25°C.

The water flux data from Fig. 6 are represented in Fig. 7 as a function of the silicalite content of the membrane. Equation (9) was fitted on these data by using $P_{z,w} = 0$. In other words, in the presence of propanol, water flux decreases as a function of the silicalite content, and this decrease can be accounted for by the increased tortuosity of the transport route through the membrane. The same behavior is found for butanol/water mixtures.

CONCLUSION

A model has been developed that explains the permeability of a silicalite-filled silicone rubber membrane in terms of the permeabilities of the membrane constituents. The model holds for the situation where the diffusional transport through the membrane is flux determining. The resistance model accurately describes the transport through silicalite-filled silicone rubber membranes for various alcohols and for different feed concentrations. The model permits the calculation of permeabilities for both the silicone rubber matrix and the suspended silicalite particles. Silicalite permeability for water is shown to be a function of the alcohol concentration in the feed mixture and of the type of alcohol. It is demonstrated that the strength of the alcohol/silicalite interaction has a strong effect on both the silicalite permeability for alcohol and on the silicalite permeability for water: Stronger interaction between alcohol and silicalite means a decrease in

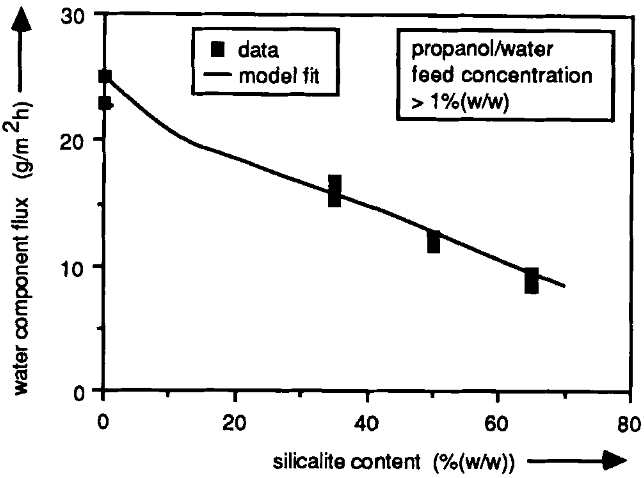


FIG. 7. Water component flux for the pervaporation of a propanol/water feed mixture with a propanol concentration above 1% (w/w) using silicalite-filled membranes as a function of the silicalite content of the membrane; data from Fig. 6; model fit using Eq. (9) with $P_{z,w} = 0$.

$P_{z,\mathrm{alc}}$ and through exclusion of water also leads to a decrease in $P_{z,w}$. The lowest values for alcohol permeability are found for propanol and butanol, while the water permeability is nil for these two alcohols.

The calculated permeabilities $P_{z,i}$ and $P_{r,i}$ show that the increased membrane selectivity for ethanol is due to an increase in the overall ethanol flux whereas the water flux stays constant. The increase in membrane performance is a combination of two factors: $P_{z,\mathrm{eth}}/P_{r,\mathrm{eth}} \gg 1$ and $P_{z,w}/P_{r,w} \approx 1$. For propanol the increase in selectivity is caused by the obstruction of water transport due to the tortuosity introduced by the impermeable zeolite particles.

Acknowledgments

We thank Zandrie Borneman, Freddy Odolphy, and Henk Olthof for performing the pervaporation experiments. The work was financially supported by the Ministry of Economical Affairs in The Netherlands.

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Received by editor March 2, 1990