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M. H. V. Mulder[a]; C. A. Smolders[a]
[a] DEPARTMENT OF CHEMICAL TECHNOLOGY, UNIVERSITY OF TWENTE, AE ENSCHEDE, THE NETHERLANDS

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Mass Transport Phenomena in Pervaporation Processes*

M. H. V. MULDER and C. A. SMOLDERS
DEPARTMENT OF CHEMICAL TECHNOLOGY
UNIVERSITY OF TWENTE
P.O. BOX 217, 7500 AE ENSCHEDE, THE NETHERLANDS

Abstract

Transport in pervaporation takes place in a three-step sequence: 1) (selective) sorption into the membrane, 2) diffusion through the membrane, and 3) desorption into a vapor phase. Diffusion through the membrane is the rate-determinating step. The transport can be described by a solution-diffusion mechanism where the permeation rate is a function of solubility and diffusivity. The basic principles of this model are described. In the case of a liquid mixture, two aspects have to be distinguished with respect to selective transport: flow coupling and thermodynamic interaction. Both aspects are discussed.

INTRODUCTION

When passive transport through a membrane takes place, a driving force is acting on the components on one side of the membrane. This driving force is a potential gradient across the membrane, often a chemical potential gradient. Because of this driving force, molecules permeate across the membrane where they undergo a friction or resistance which is dependent on the membrane structure. Roughly, two different types of structure can be considered: 1) an open porous structure which can be found in microfiltration and ultrafiltration membranes, and 2) a "dense" structure which can be found in pervaporation and gas separation. In the case of porous membranes, only a small driving force is needed to obtain a "relatively" high flux because the membrane resistance is low. However, in the case of dense nonporous membranes, the resistance to transport is much higher.

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Although the same polymeric structure can be used for both pervaporation and gas separation, there is a difference in transport mechanism. This difference is mainly caused by large differences in affinity between the permeating molecules and the polymeric membrane. In the case of gas separation, there is a small interaction between (inert) gas molecules and membrane material, and hence the solubility is very low, i.e., the polymeric structure is not much influenced by the presence of the (permeating) gas molecules.

Table 1 gives the permeability of oxygen and nitrogen in various polymers (*1–3*). From this table it can be seen that for all polymers oxygen has a higher permeability than nitrogen for highly permeable as well as for moderately permeable polymers, making the transport description relatively simple, and often making use of constant diffusion coefficients.

On the other hand, the interaction of condensable vapors and liquids with the polymer is often much higher, and consequently the segmental chain mobility has been increased very much and also the flux will be much higher. In the case of separating a binary organic mixture A/B, some polymers may be selective for component A and other polymers may be selective for component B. This indicates that the transport description of liquid mixtures is much more complicated than that of gas mixtures. Table 2 gives an example of the separation of ethanol/water mixtures by various polymers, and it shows that some polymers are highly selective for water while other are selective for ethanol (*4*).

SINGLE COMPONENT TRANSPORT

The transport of liquid permeants through dense (nonporous) membranes can be described in terms of solubility and diffusivity. For a single

TABLE 1

Permeabilities of Nitrogen and Oxygen in Various Polymers (*1–3*)

Polymer	P_{O_2} (barrer)	P_{N_2} (barrer)	α_{ideal} (P_{O_2}/P_{N_2})
Polytrimethylsilylpropyne	10,040.0	6745.0	1.5
Polydimethylsiloxane	604.0	281.0	2.2
Polymethylpentene	37.2	8.9	4.2
Polystyrene	7.5	2.5	3.0
Cellulose acetate	0.75	0.25	3.0
Polyamide (nylon 6)	0.093	0.025	2.8
Polyvinyl alcohol	0.0019	0.00057	3.3

TABLE 2
Performance of Various Polymers to Ethanol–Water Mixtures (*4*)[a]

Polymer	Flux ($kg \cdot m^{-2} \cdot h^{-1}$)	Selectivity, $\alpha_{H_2O/EtOH}$
Polyacrylonitrile	0.012	650
Cellulose acetate	0.7	4.2
Polydimethylsiloxane	0.07	0.3
Polytrimethylsilylpropyne	0.12	0.25

[a] Feed: 50% by weight ethanol. *T*:20–30°C. Membrane thickness: 25 μm.

component i, the flux J_i is the product of concentration and linear velocity, where the velocity is the product of mobility and driving force:

$$J_i = v_i c_i = -c_i B_i \frac{d\mu_i}{dx} \tag{1}$$

This single-component transport can be described in terms of a permeability coefficient or a diffusion coefficient. Assuming that the vapor pressure at the permeate or downstream side is very low ($p_i'' = c_i'' \rightarrow 0$), then

$$J_i = -P_i p_i' / \Delta x \tag{2}$$

Here P_i is the permeability coefficient, p_i' is the vapor pressure at the feed side, and Δx is the thickness of the membrane.

The single component flux can also be written in terms of a diffusion coefficient. By using ideal conditions, Eq. (1) can be transformed in a Fickian equation:

$$J_i = -D_i(c) dc_i / dx \tag{3}$$

Assuming an exponential relation between diffusion coefficient and concentration:

$$D_i = D_{0,i} \exp(\gamma_i c_i) \tag{4}$$

where D_0 is the diffusion coefficient of penetrant i in the membrane at zero concentration ($c_i \rightarrow 0$) and γ_i is a plasticizing constant expressing the influence of the plasticizing action of the liquid on the segmental motions.

Integrating across the membrane gives

$$J_i = (D_{0,i}/\gamma_i)[\exp(\gamma_i c_i) - 1] \tag{5}$$

Both Eqs. (2) and (5) describe single-component transport.

BINARY MIXTURES

In the case of liquid mixtures of components *i* and *j*, the flux can also be described in terms of solubility and diffusivity. However, the solubility of component *i* in the membrane is not only determined by component *i* but also by component *j*. In addition, the diffusivity of component *i* is influenced by the diffusivity of the other component, which means that flow coupling occurs. Therefore, two phenomena have to be distinguished in multicomponent transport: flow coupling and thermodynamic interaction leading to preferential sorption.

Flow coupling is described in terms of the thermodynamics of irreversible processes. For a binary liquid mixture, the following equations are given:

$$-J_1 = L_{11}d\mu_1/dx + L_{12}d\mu_2/dx \tag{6}$$

$$-J_2 = L_{21}d\mu_1/dx + L_{22}d\mu_2/dx \tag{7}$$

The first term on the right-hand side of Eq. (6) describes the flux of component 1 due to its own gradient and the second term describes the flux of component 1 due to the gradient of component 2. This second term describes the coupling effect.

Another approach to describe flow coupling was given by Kedem (*5*):

$$J_1 = -\overline{P}_1dp_1/dx + \overline{Q}Pp_1J_2 \tag{8}$$

$$J_1 = -\overline{P}_2dp_2/dx + \overline{Q}Pp_2J_1 \tag{9}$$

$\overline{P}$ is the local permeability coefficient and $\overline{Q}$ is the local drag factor. In fact, these equations are equal to Eqs. (6) and (7) where the cross term is replaced by the drag term. When no flow coupling takes places, $Q \rightarrow 0$, and Eqs. (8) and (9) reduce to the equations for single component transport (Eq. 2). Integration across the membrane, with $p_1'' = p_2'' \rightarrow 0$, gives for the flux of component 2, with $P_2 = \overline{P}_2/\Delta x$ and $\overline{Q} = Q/\Delta x$:

$$J_2 = P_2p_2'[QJ_1/(1 - \exp(-QJ_1)] \tag{10}$$

Two cases can now be distinguished: weak coupling and strong coupling. In the case of weak coupling, $QJ_1 \ll 1$ and again Eq. (10) reduces to

$$J_2 = P_2p_2' \tag{11}$$

This equation is equal to Eq. (2).

In the case of strong coupling, component 2 is dragged along with component 1. When $QJ_1 > 2$, Eq. (10) is reduced to

$$J_2 = P_2 p_2' Q J_1 \tag{12}$$

Coupling phenomena are difficult to measure quantitatively, and it is difficult to estimate beforehand the extent of the coupling phenomena in relation to the separation properties. However, it is possible to get indirect information from flux measurements and from experimental determination of the concentration of a liquid mixture inside a polymeric film or, in other words, by determining the preferential sorption.

Preferential sorption or selective sorption is given by the difference in composition of a binary liquid mixture inside the polymeric membrane and outside in the feed solution. If the concentration of a component of a binary liquid mixture in the polymeric membrane is given by

$$u_i = \phi_i/(\phi_1 + \phi_2) = \phi_i/(1 - \phi_3), \qquad i = 1, 2 \tag{13}$$

and the concentration in the binary liquid phase by v_i, then the preferential sorption ϵ is given by

$$\epsilon = u_i - v_1 = v_2 - u_2 \tag{14}$$

Equilibrium between the binary liquid phase and the ternary polymer phase is expressed by equality of the chemical potentials in the two phases. The chemical potentials can be obtained from Flory-Huggins thermodynamics (*6*). The following equation is obtained for the preferential sorption (*7*):

$$\ln(\phi_1/\phi_2) - \ln(v_1/v_2) = (\ell - 1)\ln(\phi_2/v_2) - \chi_{12}(\phi_2 - \phi_1) \\ - \chi_{12}(v_1 - v_2) - \phi_3(\chi_{13} - \ell\chi_{23})$$

where $\ell = V_1/V_2$. It is assumed here that the interaction parameters χ_{12}, χ_{13}, and χ_{23} are concentration independent, which is generally not the case. By taking concentration dependency into account, the equations become more complex (*7*) but the concept does not change.

By defining the sorption selectivity as

$$\alpha_{\mathrm{sorp}} = (\phi_1/\phi_2)/(v_1/v_2) \tag{16}$$

then

$$\ln \alpha_{\mathrm{sorp}} = \ln (\phi_1/\phi_2) - \ln (v_1/v_2) \tag{17}$$

Hence the left-hand side of Eq. (15) is equal to the logarithm of the sorption selectivity (Eq. 17). The main problem in calculating the sorption selectivity is to obtain numerical values for the interaction parameters, especially when they are concentration dependent. However, it is possible to see from Eq. (15) which factors are important: difference in molar volume, difference in affinity toward the membrane, and mutual affinity between both permeants.

It is also possible to determine the preferential sorption experimentally by a distillation technique (7). A few examples will be given where both preferential sorption and pervaporation have been determined.

The first example is the system *o*-xylene/*p*-xylene/cellulose tripropionate (CTP) (*18*). The mixture *o*-xylene/*p*-xylene can be considered as a rather ideal mixture, and it is interesting to see how such a mixture behaves.

Figure 1 shows the overall sorption as a function of the *o*-xylene concentration in the feed. From this figure it can be seen that the interaction of *o*-xylene with the polymeric membrane is higher than of *p*-xylene, and consequently a higher sorption or swelling can be observed. Overall sorption increases with increasing *o*-xylene concentration in the feed.

It is possible to estimate the concentration in the membrane by using

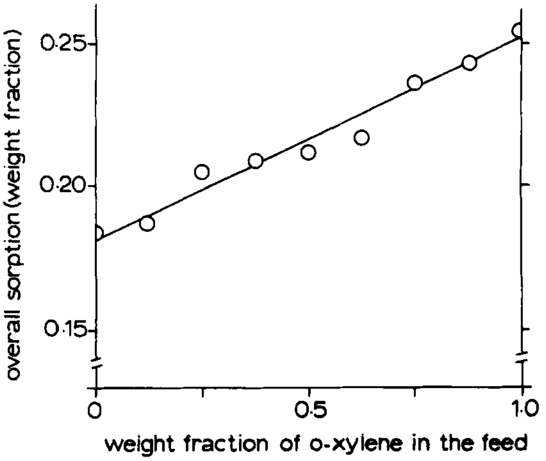

FIG. 1. Total sorption of *o*-xylene/*p*-xylene in cellulose tripropionate (CTP) as a function of the *o*-xylene concentration in the feed.

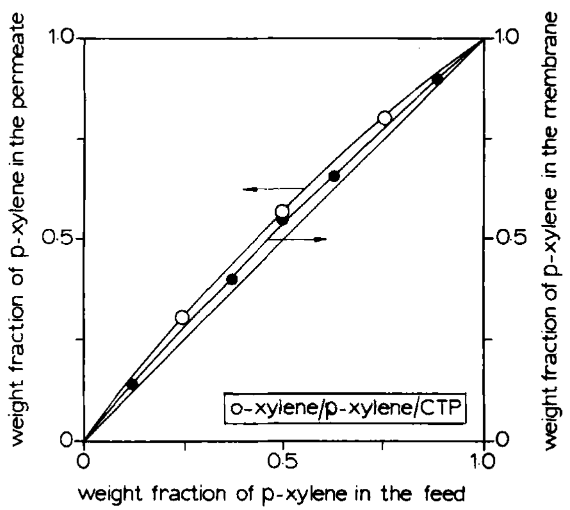

FIG. 2. Experimental values for preferential sorption and pervaporation for the system *o*-xylene/*p*-xylene/cellulose tripropionate.

simple Henry-type equations (*8*). According to this Henry-type relation, *o*-xylene is the component that will be preferentially sorbed.

In Fig. 2, both preferential sorption and pervaporation are given. This figure shows that over the entire composition range, *p*-xylene, the component that is preferentially sorbed, also permeates preferentially. This figure also shows that over the entire composition it is *p*-xylene that is preferentially sorbed, while on the basis of the pure component solubilities it would be expected that *o*-xylene would be the preferentially sorbed component.

This example of a glassy polymer and an isomeric xylene mixture shows that the component that is sorbed preferentially also permeates preferentially.

Chain mobility is much higher in elastomeric polymers compared to glassy polymers, and it is interesting to compare the effects of thermodynamic interaction and flow coupling in both types of polymers.

Table 3 shows the solubility of water and some alcohols in polydimethylsiloxane (PDMS). From this table it can be seen that water has a very low interaction and consequently a low solubility is found, whereas the solubility of the alcohols increases with increasing chain length or with increasing hydrophobicity.

Table 4 shows the overall and preferential sorption of some alcohol/water mixtures (5 wt% alcohol) in PDMS. The overall or total sorption values are rather low because the alcohol content of the mixture is rather

TABLE 3
Solubility of Water and Some Alcohols in Polydimethylsiloxane

Component	Solubility (g/100 g)
Water	<0.1
Methanol	2.1
Ethanol	6.3
Propanol	13.0
Butanol	16.5

low. The overall sorption increases in going from methanol to butanol. By considering the individual components, it can be seen that the solubility of water increases a little in going from methanol to butanol, but that the solubility of the alcohol increases drastically, resulting in a strong increase in sorption selectivity or preferential sorption. When the preferential sorption results are compared with the pervaporation results, it can be seen that both follow the same line qualitatively. Also, it seems that the component that is sorbed preferentially also permeates preferentially; in other words, thermodynamic interaction or preferential sorption is the leading step in selective transport. The extent of selective transport is also determined by flow coupling, which means that the results on preferential sorption cannot be used quantitatively.

The last system discussed here is nitrile-butadiene rubber with 18% acrylonitrile (NBR-18) and a mixture of trichloroethylene and water (*16*). Pervaporation seems to be very promising in removing volatile organic components from (waste) water. The concentration of the organic component is very low (less than 500 ppm), and a number of elastomeric membranes show a very high selectivity for the organic component.

Figure 3 gives both the preferential sorption and pervaporation results of a mixture of trichloroethylene and water as a function of the organic

TABLE 4
Overall and Preferential Sorption of Some Alcohol/Water Mixtures in Polydimethylsiloxane

Alcohol in mixture	Total sorption (g/100 g)	H_2O sorption (g/100 g)	Alcohol sorption (g/100 g)	α_{sorp}	α_{perv}
Methanol	0.16	0.13	0.03	4.6	7.7
Ethanol	0.21	0.14	0.07	8.2	8.2
Propanol	0.41	0.17	0.24	23.0	18.1
Butanol	1.27	0.22	1.05	86.0	47.0

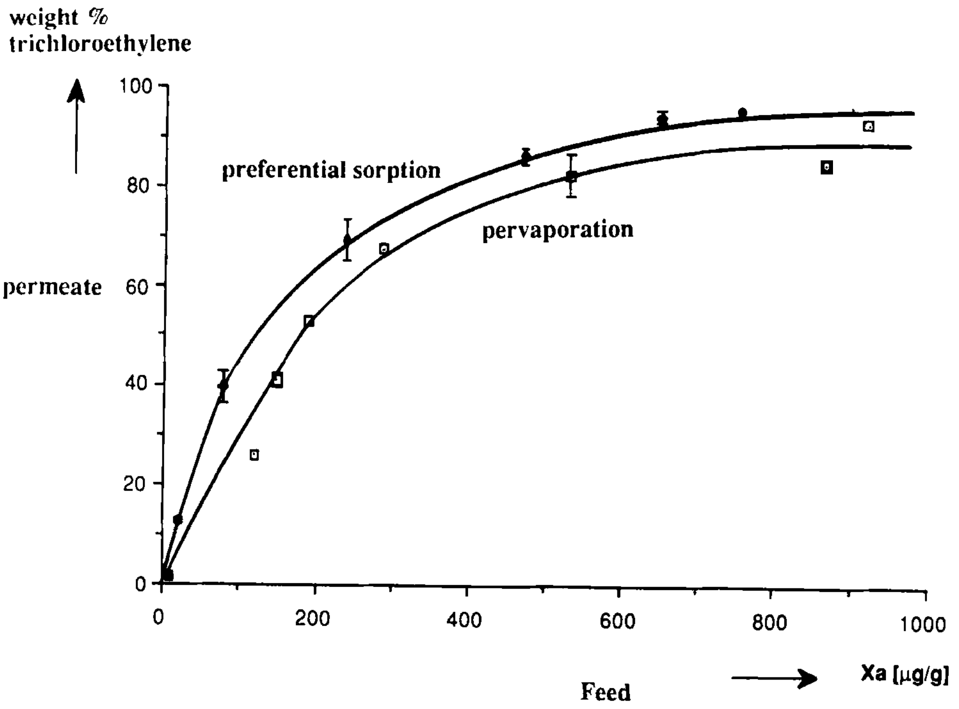

FIG. 3. Experimental values of preferential sorption and pervaporation for the system trichloroethylene/water/NBR-18.

component concentration. This figure shows that the selectivity for trichloroethylene increases exponentially with feed concentration, and the same behavior is found for the preferential sorption results. Preferential sorption and pervaporation for this system also show the same behavior.

Aside from the systems described here, there are a number of other systems described in the literature, all indicating that preferential sorption is the leading factor in selective transport. An overview of these literature sources is given in Table 5. So far one exception has been described in the literature where an ion-exchange membrane is used for the separation of carboxylic acid/water mixtures. Here the membrane preferentially sorbs the acid whereas water is the component that is selectively transported. An explanation for this phenomenon has not been given, but compared with the other systems where mainly neutral polymers and nonelectrolytes are considered, here the polymer is a polyelectrolyte and also the carboxylic acids are electrolytes, indicating that charge effects also have to be taken into account.

TABLE 5
Literature Sources

Binary mixture	Polymer	Reference
Water/methanol	PMG	*9*
Water/methanol	PDMS	This work
Water/ethanol	PVA	*10*
Water/ethanol	PVA	*11*
Water/ethanol	CA	*7*
Water/ethanol	PAN	*7*
Water/ethanol	PMMA	*12*
Water/ethanol	Selemion	*13*
Water/ethanol	PDMS	This work
Water-propanol	PDMS	This work
Water/butanol	PDMS	This work
Ethanol/1,2-dichloroethylene	PTFE/PVP	*14*
Ethanol/chloroform	PTFE/PVP	*14*
Acetic acid/1,2-dichloroethylene	PTFE/PVP	*14*
Chloroform/water	SBR	*15*
Chloroform/water	NBR	*15*
Trichloroethylene/water	NBR	*16*
Trichloroethylene/water	BR	*16*
Benzene/water	NBR	*15*
Toluene/water	NBR	*15*
Toluene/water	NBR	*16*
Toluene/water	BR	*16*
Benzene/cyclohexane	PMG	*12*
Benzene/heptane	NBR	*17*
o-Xylene/*p*-xylene	CTP	*18*

CONCLUSION

The main conclusion is that the transport of binary mixtures in pervaporation cannot be quantitatively predicted from pure component permeation experiments because of flow coupling and thermodynamic interaction.

The results given in this paper as well as results presented by others show that preferential sorption is the factor that determines selective transport. Preferential sorption gives only a qualitative indication. In order to describe the transport of binary or multicomponent mixtures quantitatively, flow coupling has to be taken into account.

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