

TRANSPORT OF ETHANOL-WATER DIMERS IN PERVAPORATION THROUGH A SILICONE RUBBER MEMBRANE

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Summary

Pervaporation experiments have been performed using a silicone rubber membrane with feed mixtures ranging from pure water to pure ethanol. The pervaporation process is modelled as coupled diffusion driven by activity gradients. Diffusion coefficients are assumed to be constant. Coupling effects are modelled by assuming that water clusters, practically immobilized within the silicone rubber membrane, break down in the presence of ethanol to form mobile ethanol-water dimers that contribute significantly to the overall water flux. Experimental data are consistent with the proposed model.

Introduction

The separation of ethanol-water mixtures by pervaporation has been extensively studied over the past decade. Most of the membranes used in these studies are water selective; only a few, such as silicone rubber membranes, permit preferential permeation of ethanol [1-3].

The transport of permeants through a homogeneous membrane in pervaporation is usually described by a solution-diffusion model [4,5]. The components of a liquid mixture are sorbed at the upstream side of the membrane, diffuse through the membrane, and are desorbed from the membrane phase to the vapor phase at the downstream side of the membrane. The overall selectivity of a membrane for a given liquid mixture depends on both the sorption and diffusion coefficients of the permeants in the membrane.

Component fluxes can be related to the corresponding driving forces by the phenomenological equation [1]:

$$J_i = (Q_i/L) (f_i^\circ a_i - \nu_i p_i), \quad (1)$$

where Q_i is the permeability, f_i° the standard state fugacity, a_i the activity, p_i the partial pressure, and ν_i the fugacity coefficient of component i . L represents

the membrane thickness. For a sufficient low downstream pressure, eqn. (1) reduces to:

$$J_i = (Q_i f_i^\circ / L) a_i \quad (2)$$

If the permeability does not change with feed concentration, the flux of component i is a linear function of the activity of component i in the feed. In most pervaporation systems component interactions are strong and permeabilities can be highly dependent on the feed concentration. Coupled transport often occurs, with coupling present both in the solubility and the kinetic part of the mechanism [5]. However, eqn. (2) can still be used to investigate deviations from the ideal case of constant permeability, and may be helpful in developing a solution-diffusion model for a particular system.

Pervaporation of liquid mixtures is usually modelled assuming Fick's law with diffusion coefficients dependent on the concentrations of both permeants [6-8]. At the membrane-feed interface, Henry's law is assumed to be valid, with concentrations in the membrane being proportional to the corresponding feed activities. No coupling effects due to friction between permeants are considered.

Earlier studies on the sorption and diffusion of pure water and methanol vapors through silicone rubber membranes [9,10] show that when the sorbent vapor pressures are high, both sorbents form clusters through hydrogen bonding. The transport of pure water and methanol can be described by a simple model that takes into account only the diffusion of monomeric species, assuming constant diffusion coefficients, and ignoring the practically immobilized clusters.

Pervaporation of ethanol-water mixtures through silicone rubber membranes has been described as a coupled diffusion process driven by concentration gradients [11]. The approach presented here is a generalization of the model presented earlier, since it takes into account nonideality in the liquid feed.

Theory

The model developed in this work for the pervaporation of ethanol-water mixtures through silicone rubber membranes is based on the assumption that water clusters break down to form ethanol-water dimers in the presence of ethanol. Ethanol has a solubility in silicone rubber that is an order of magnitude greater than that of water. As reported by Strathmann et al. [12], silicone rubber absorbs 0.15 wt.% of water and 4 wt.% of ethanol when contacted with pure components. The affinity of water for ethanol is high, as is demonstrated by the high heat of mixing. *Ab initio* calculations of hydrogen bond energies for water, ethanol, and ethanol-water dimers in the gas phase show that bond energies for all types of dimers are in the range of 5.4-5.85 kcal/mol [13].

These arguments support the hypothesis that, in the excess of ethanol, water in silicone rubber forms mixed clusters with ethanol in preference to pure water clusters. Similar phenomena were observed in ethanol–water liquid solutions where pure water clusters in the presence of excess ethanol are less stable than ethanol hydrated clusters [13]. Also, concentrations of ethanol and water in silicone rubber are two to three orders of magnitude smaller than in a liquid solution, which could favor the formation of mixed aggregates of smaller size. Therefore, as a first approximation, the transport of ethanol and water can be expected to occur by a coupled diffusion mechanism, where the coupling of fluxes can be interpreted as the diffusion of ethanol–water dimers. The following assumptions are used:

(1) Fick's law of diffusion with constant diffusion coefficients holds for each species. This assumption implies that permeant mobilities do not change significantly with concentration in the case of a low-swelling, rubbery polymer such as silicone rubber.

(2) Frictional interactions between permeating species are insignificant for the low concentrations found in the membrane; cross-terms in generalized transport equations are neglected. However, besides the independent diffusion of water and ethanol monomers, an allowance is made for coupling effects due to ethanol–water dimerization.

(3) The diffusional contribution of clusters other than ethanol–water dimers is negligible, due to low diffusion coefficients and negligible concentrations expected for the higher-order aggregates.

(4) Monomer concentrations, C'_i , of ethanol and water in the membrane at the upstream side are related to corresponding activities in the feed by Henry's law:

$$C'_i = K_i a'_i \quad (3)$$

The use of Henry's law for monomers, instead of total membrane concentrations [6–8] is supported by Barrie's work on the sorption of pure components in silicone rubber [10]. A constant partition coefficient reflects the assumption of an ideal, dilute solution of monomers in the membrane phase. This assumption should hold for a low-swelling, rubbery polymer.

(5) The dimerization reaction $\text{H}_2\text{O} + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}$ is at equilibrium, thus:

$$C_{\text{dim}} = K_{\text{eq}} C_{\text{H}_2\text{O}} C_{\text{EtOH}} \quad (4)$$

(6) At the downstream side of the membrane, the pressure is low enough that the corresponding concentrations of permeants in the membrane are zero.

Diffusion equations for the permeants are written as:

$$\begin{aligned} J_{\text{H}_2\text{O}} &= -D_{\text{H}_2\text{O}} (dC_{\text{H}_2\text{O}}/dz) - D_{\text{dim}} (dC_{\text{dim}}/dz) \\ J_{\text{EtOH}} &= -D_{\text{EtOH}} (dC_{\text{EtOH}}/dz) - D_{\text{dim}} (dC_{\text{dim}}/dz) \end{aligned} \quad (5)$$

where the D_i s and C_i s represent diffusion coefficients and concentrations in the membrane, the J_i s are fluxes measured relative to stationary coordinates, and z is the distance in the direction of diffusion.

Integrating eqns. (5) across the membrane and substituting eqns. (3) and (4) gives:

$$J_{\text{H}_2\text{O}} = (D_{\text{H}_2\text{O}} K_{\text{H}_2\text{O}} / L) a'_{\text{H}_2\text{O}} + (D_{\text{dim}} K / L) a'_{\text{H}_2\text{O}} a'_{\text{EtOH}} \quad (6)$$

$$J_{\text{EtOH}} = (D_{\text{EtOH}} K_{\text{EtOH}} / L) a'_{\text{EtOH}} + (D_{\text{dim}} K / L) a'_{\text{H}_2\text{O}} a'_{\text{EtOH}}$$

The constant K is defined as:

$$K = K_{\text{eq}} K_{\text{H}_2\text{O}} K_{\text{EtOH}}. \quad (7)$$

Equations (6) and (7) are proposed to describe the transport of ethanol and water through silicone rubber membranes.

Experimental

A flat silicone rubber membrane with a thickness of $50 \mu\text{m}$ was used. Ethanol-water solutions were prepared from ultrapure deionized water and pure dehydrated ethanol.

Pervaporation experiments were performed using the equipment schematically presented in Fig. 1. The feed mixture was recirculated between the feed tank and pervaporation cell using a positive displacement peristaltic pump. The temperature was monitored with a thermocouple inside the pervaporation cell, and was kept constant at $30 \pm 0.1^\circ\text{C}$. The cell was stirred with an exter-

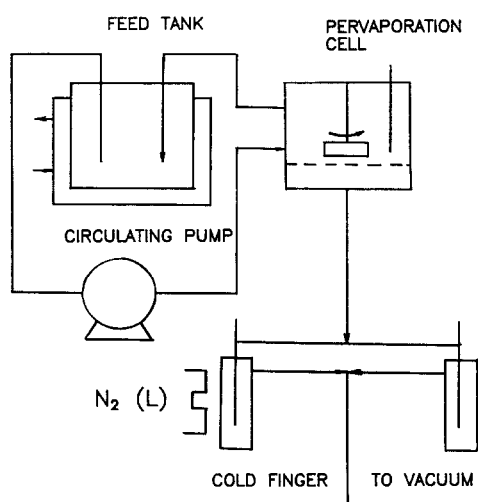


Fig. 1. Pervaporation equipment.

nally operated magnetic stirrer, at a minimum stirring speed of 150 rpm. Downstream pressures of up to 1.6 mmHg were measured with an electronic manometer with sensitivity of ± 0.01 mmHg. The permeate was collected in cold traps cooled with liquid nitrogen, and the total flux was calculated from the amounts collected for a given time period after steady state was reached. The relative error in the flux measurements was estimated to be less than 1%.

Permeate compositions were determined by gas chromatography using n-propanol as an internal standard. The relative error in composition measurements was estimated to be less than 1%.

Results and discussion

Water and ethanol fluxes are shown in Figs. 2 and 3 as functions of the corresponding feed activities. Activities were calculated using Wilson's equation [14]. The water flux exhibits a positive deviation from linearity over the entire activity range, suggesting enhanced transport of water in the presence of ethanol. The ethanol flux linearly increases with activity at low ethanol activities in the feed. From eqns. (6), the flux of a component is linear with respect to the feed activity of that component, but is also a function of the feed activity of the other component due to dimerization. Based on eqns. (6), $J_{\text{H}_2\text{O}}/a'_{\text{H}_2\text{O}}$ is shown as a function of a'_{EtOH} in Fig. 4. An analysis of variance was carried out for the water flux; the results of that analysis are given in Table 1. The large value of the regression f -statistic, calculated as the ratio of the

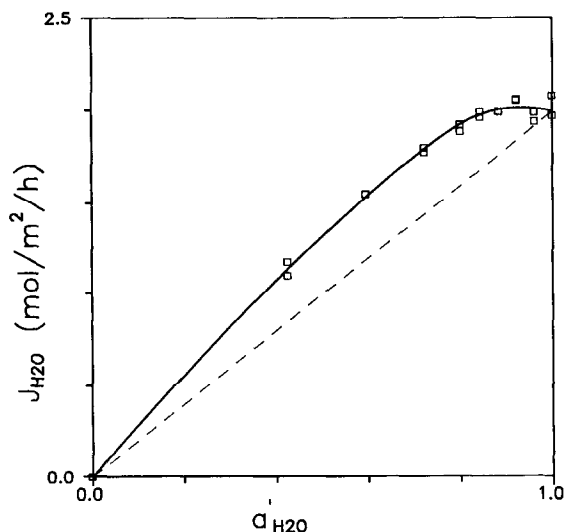


Fig. 2. Water flux vs. water activity in the feed.

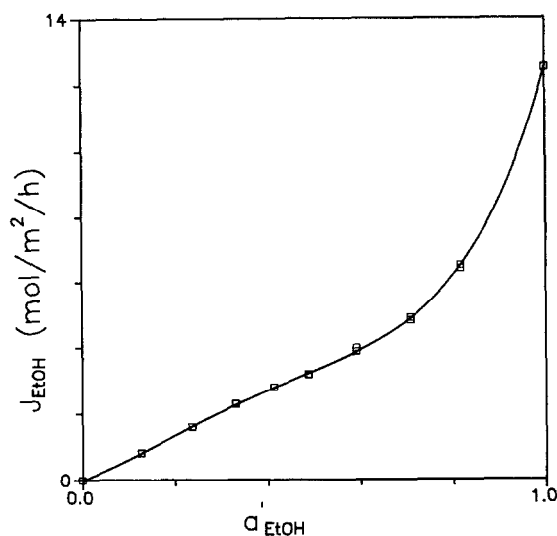


Fig. 3. Ethanol flux vs. ethanol activity in the feed.

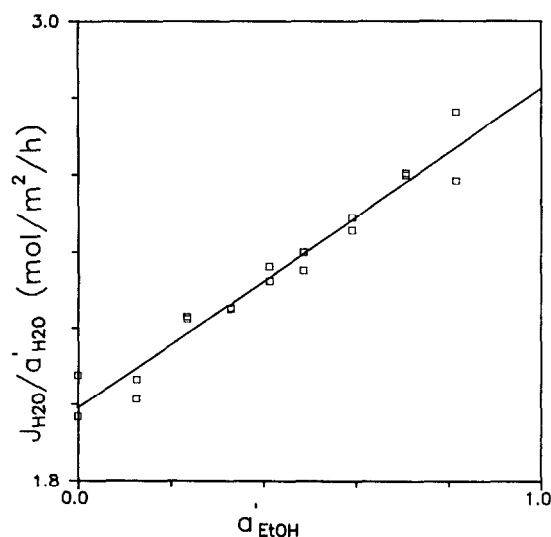


Fig. 4. Linear regression for water flux.

regression mean square to the pure error mean square, shows that the hypothesis of a linear relationship between $J_{\text{H}_2\text{O}}/a'_{\text{H}_2\text{O}}$ and a'_{EtOH} can be accepted at 0.01 level of significance. The small value of the lack of fit f -statistic shows that higher-order terms, representing the diffusion of larger clusters, need not be considered. Since the ethanol flux at a given feed concentration is often at

TABLE 1

Analysis of variance for water flux

Source of variation	Sum of squares	Degrees of freedom	Mean square	Computed <i>f</i>
Regression	0.8055	1	0.8055	283.7351
Error	0.0396	16		
Lack of fit	0.0140	7	0.0020	0.7057
Pure error	0.0255	9	0.0028	
Total	0.8451	17		
Critical region: $f_{0.01}(7,9)=5.61$				
Linear regression: $r^2=0.953$				
$D_{H_2O}K_{H_2O}/L=1.99 \text{ mol}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$				
$D_{\text{dim}}K/L=0.835 \text{ mol}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$				

least an order of magnitude greater than the water flux, the dimer contribution to the ethanol flux cannot be accurately determined from a correlation of $J_{\text{EtOH}}/a'_{\text{EtOH}}$ as a function of $a'_{\text{H}_2\text{O}}$. Instead, the dimer contribution to J_{EtOH} was used to determine the flux of monomeric ethanol, J_{EtOH}^* .

Using the regression coefficients obtained in the analysis of the water flux, the flux of monomeric ethanol was calculated from the experimental data using the equation:

$$J_{\text{EtOH}}^* = J_{\text{EtOH}} - (D_{\text{dim}}K/L)a'_{\text{H}_2\text{O}}a'_{\text{EtOH}} \quad (8)$$

J_{EtOH}^* is shown as a function of ethanol activity in the feed in Fig. 5. An analysis of variance was carried out for the flux of monomeric ethanol; the results of that analysis are given in Table 2. The large value of the regression *f*-statistic, calculated as the ratio of the regression mean square to the pure error mean square, shows that the hypothesis of a linear relationship between J_{EtOH}^* and a'_{EtOH} can be accepted at the 0.01 level of significance when the ethanol activity is in the range of 0–0.6. The small value of the lack of fit *f*-statistic shows that higher-order terms, representing the diffusion of larger clusters, need not be considered. At higher ethanol activities, the ethanol flux shows pronounced deviations from linear behavior. A more refined model is needed to explain these observations.

Tables 1 and 2 also give values of parameters related to diffusion and sorption of monomers (D_iK_i/L), and the value of $D_{\text{dim}}K/L$, which shows the magnitude of the coupling effects. From these values and the estimated diffusion coefficients of mobile species (monomers and dimers), Henry's law constants and the equilibrium constant of the dimerization reaction can be calculated. The diffusion coefficients of water and ethanol reported in literature [12] are overall, averaged values that take into account the total amount of sorbed water

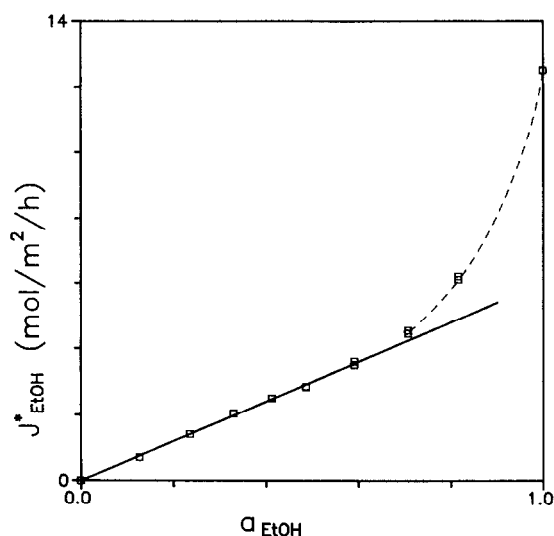


Fig. 5. Linear regression for ethanol flux.

TABLE 2

Analysis of variance for ethanol flux

Source of variation	Sum of squares	Degrees of freedom	Mean square	Computed <i>f</i>
Regression	18.4949	1	18.4949	23030.7809
Error	0.0302	12		
Lack of fit	0.0246	5	0.0049	6.1181
Pure error	0.0056	7	0.0008	
Total	18.5250	13		

Critical region: $f_{0.01}(5.7) = 10.46$ Linear regression: $r^2 = 0.998$

$$D_{\text{EtOH}} K_{\text{EtOH}} / L = 6.00 \text{ mol} \cdot \text{m}^{-2} \cdot \text{hr}^{-1}$$

or ethanol, including clusters that do not contribute significantly to water or ethanol flux. To estimate the unknown diffusion coefficients of monomeric species, experimental values of diffusion coefficients in the limit of low permeant concentration, when only monomers are present, were used [9,10]. These values are 4.4×10^{-9} and 1.0×10^{-9} m^2/sec for water and methanol, respectively. A correlation for diffusion coefficients of a series of *n*-alcohols in silicone rubber [15] was used to estimate $D_{\text{EtOH}} = 0.60 \times 10^{-9}$ and $D_{\text{dim}} = 0.37 \times 10^{-9}$ m^2/sec . This correlation was based on vapor sorption and permeation experiments in the region of low relative vapor pressures (0 to 0.4)

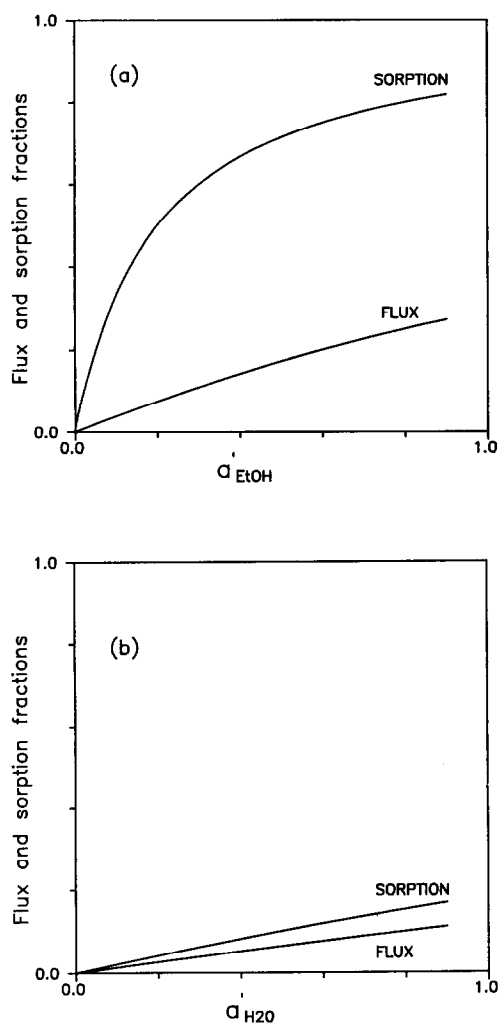


Fig. 6. Contribution of dimers to component sorption and flux: (a) water; (b) ethanol.

where monomers are expected to be the dominant sorbed form. These values are all an order of magnitude greater than overall diffusion coefficients reported in literature. The difference is the result of the small proportion of monomers in the total amounts sorbed at high feed activities. Estimated diffusion coefficients were used to calculate the contribution of the dimers to the sorption and flux of both water and ethanol. The dimer sorption fraction of component i is the number of dimers sorbed at the upstream side of the membrane divided by the total number of sorbed mobile molecules (monomers and dimers) of component i . Figure 6 shows the calculated dimer sorption fraction

and dimer flux fraction as functions of component feed activities for water and ethanol. The contribution of the dimers to sorption is particularly pronounced in the case of water: when the ethanol activity in the feed is high, it is calculated that 80% of the mobile water at the upstream side of the membrane is present as ethanol–water dimers. Figure 6 shows that the contribution of the dimers to ethanol sorption and flux is much smaller.

Conclusions

The transport of ethanol and water during pervaporation through silicone rubber membrane has been modelled, taking into account possible coupling effects due to the formation of ethanol–water dimers within the membrane. The model is consistent with experiments for water over the entire activity range, and for ethanol up to an activity of 0.6. The results show that the presence of ethanol in the membrane significantly increases water sorption, due to the formation of ethanol–water dimers. Further research is needed to explain the observed ethanol fluxes at high ethanol activities in the feed.

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List of symbols

a_i	activity of component i , [dimensionless]
C_i	concentration of species i in the membrane [$\text{mol}\cdot\text{m}^{-3}$]
D_i	diffusion coefficient of species i in the membrane [$\text{m}^2\cdot\text{sec}^{-1}$]
f_i°	standard-state fugacity of component i [Pa]
J_i	flux of component i [$\text{mol}\cdot\text{m}^{-2}\cdot\text{sec}^{-1}$]
K	constant defined by eqn. (7) [$\text{mol}\cdot\text{m}^{-3}$]
K_i	Henry's law constant for species i [$\text{mol}\cdot\text{m}^{-3}$]
K_{eq}	equilibrium constant for the dimerization reaction [$\text{m}^3\cdot\text{mol}^{-1}$]
L	membrane thickness [m]
Q_i	permeability of component i [$\text{mol}\cdot\text{Pa}^{-1}\cdot\text{m}^{-1}\cdot\text{sec}^{-1}$]
P_i	partial pressure of component i at the downstream side of the membrane [Pa]
z	position within the membrane [m]
ν_i	fugacity coefficient of component i [dimensionless]

Subscripts

H ₂ O	water
EtOH	ethanol
dim	ethanol-water dimer

Superscripts

'	upstream side of the membrane
*	monomer

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