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Organic Vapor/Gas Mixture Separation by Membrane—A Parametric Study

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Abstract

A parametric study was carried out for the membrane separation of organic vapor–gas mixtures. Based on a set of basic transport equations, the effect of the concentration polarization on the membrane surface as a function of mass transfer coefficient is illustrated. It is shown that the concentration polarization is negligible for membranes of low permeability but would be significant for highly permeable and selective membranes. The effects of some operating parameters and membrane permselectivity on the separation performance are also discussed. The results demonstrate the utility of parametric analyses for exploring the effects of variations in the membrane separation of organic vapor–gas mixtures.

Key Words: Concentration polarization; Membrane separation; Organic vapor/gas permeation; Pervaporation

INTRODUCTION

As a relatively new area of application for membranes, the membrane separation of organic vapors from contaminated gas streams is currently being studied with increasing interest for the simultaneous recovery of organic vapor and air pollution control. In this process the feed vapor–gas mixture is usually introduced to one side of the membrane at essentially atmospheric pressure, and the organic vapor permeates through the membrane, preferentially under the driving force provided by a vacuum pump on the permeate side. The membrane-permeated organic vapor is then condensed and collected as organic liquid. Because of its similarity to the conventional pervaporation separation process with respect to operational details, this process is also categorized as pervaporation by some researchers (*1–4*).

In most of the current literature, silicone rubber coated on a porous substrate is commonly used as the membrane for organic vapor–gas separations (*5–8*). As an alternative approach, an asymmetric aromatic polyimide membrane was studied and tested for a number of organic vapor plus air mixtures (*9*). Further studies were then carried out using aromatic polyetherimide membranes with some improvement in data analysis. It was shown that the membranes are applicable for the separation of organic vapor–nitrogen mixtures, and that the transport equations used in the data analysis are valid (*10*). This work has been extended to an experimental study with hollow fiber membranes for volatile hydrocarbon emission control (*11*).

It is well known that concentration polarization is a common phenomenon in membrane separation processes based on the difference in the permeation rates of different permeating components. Due to retention of the slow permeating component on the membrane surface, a concentration gradient is built up in the vicinity of the membrane surface. Consequently, the concentration of the fast permeating component on the membrane surface is lower than that in the bulk phase, while the opposite is true for the slow component, resulting in a lower productivity and a lesser extent of separation. The concentration polarization is generally assumed to be negligible for most of the current membranes used for gas separation and pervaporation due to their limited permselectivity, and only a few papers deal with concentration polarization (*12–14*). It may be expected, however, that the concentration polarization effect would become significant with the development of high performance membranes.

This work has the objective of illustrating the effect of concentration polarization on the membrane separation of organic vapor–gas mixtures. Then, assuming the concentration polarization to be negligible, the effects of two major operating variables (feed concentration and permeate pressure) and membrane permselectivity on the separation performance are also illustrated. For this purpose a parametric study was carried out and the results are reported.

THEORETICAL

A schematic representation of the concentration polarization is shown in Fig. 1. Under steady-state operating conditions, the mass transfer within the concentration boundary layer can be expressed as

$$Q_V = -CD\frac{dX}{dZ} + (Q_V + Q_G)X \qquad (1)$$

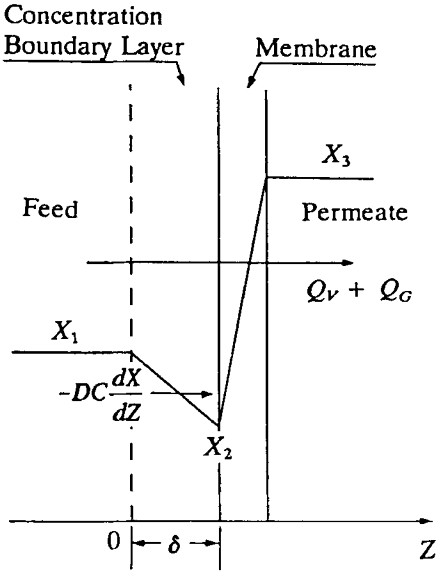

FIG. 1. A schematic of concentration polarization.

$$Q_G = CD\frac{dX}{dZ} + (Q_V + Q_G)(1 - X) \tag{2}$$

The boundary conditions for Eqs. (1) and (2) are:

$$\text{when } Z = 0, \qquad X = X_1$$

and:

$$\text{when } Z = \delta, \qquad X = X_2$$

Using the relation

$$X_3 = \frac{Q_V}{Q_V + Q_G} \tag{3}$$

and integrating Eq. (1) with the above boundary conditions, the molar flux can be expressed as

$$Q_V + Q_G = \frac{D}{\delta}C \ln\left(\frac{X_3 - X_2}{X_3 - X_1}\right) \tag{4}$$

or

$$Q_V = \frac{D}{\delta} C X_3 \ln \left(\frac{X_3 - X_2}{X_3 - X_1} \right) \tag{5}$$

where D is the gas diffusion coefficient, C is the total molar concentration of the feed gas mixture in the bulk phase, and the X's are the molar fractions of the organic vapor.

Neglecting the pressure gradient vertical to the membrane surface and assuming the organic vapor–gas mixture to be ideal, the molar concentration C can be written in terms of the ideal gas equation to give

$$C = C_V + C_G = P_1/RT \tag{6}$$

Defining the Colburn–Drew mass transfer coefficient k in the conventional manner (*15*),

$$k = D/\delta \tag{7}$$

Eq. (5) becomes

$$Q_V = k X_3 \frac{P_1}{RT} \ln \left(\frac{X_3 - X_2}{X_3 - X_1} \right) \tag{8}$$

The mass transfer within the membrane can be described phenomenologically by the following equations (*10, 11*):

$$Q_G = A[P_1(1 - X_2) - P_3(1 - X_3)] \tag{9}$$

$$Q_V = B[(P_1X_2)^2 - (P_3X_3)^2] \tag{10}$$

where A and B are the transport parameters characterizing the organic vapor–gas–membrane system, and they are independent of feed mixture concentration but dependent on the permeants–membrane interactions and membrane morphology.

Note that Eqs. (3), (8), (9), and (10) describe the mass transport in the membrane and the concentration boundary layer simultaneously, and thus constitute the basic transport equations. Considering these equations, P_1, P_3, X_1, and T are operating parameters, while Q_V and X_3 (and hence Q_G) are known quantities from the primary organic vapor–gas permeation experiment. Therefore the four unknowns A, B, k, and X_2 can be solved from the above equations. Conversely, when the membrane system is specified in terms of A, B, and k at given operating conditions, the quantities Q_V, Q_G, X_2, and X_3 can be calculated. This parametric analysis is similar to that for reverse osmosis separations (*16*).

It should be noted that the magnitude of k is a function of the chemical nature of the permeating components, the turbulence condition of the feed flow, and the operating pressure and temperature on the feed side of the membrane. For finite values of k, $X_2 < X_1$. When k is infinity, $X_2 = X_1$, and the transport equations simplify to be

$$\frac{Q_G}{Q_V} = \frac{A[P_1(1 - X_1) - P_3(1 - X_3)]}{B[(P_1X_1)^2 - (P_3X_3)^2]} = \frac{1 - X_3}{X_3} \tag{11}$$

The ratio X_2/X_1 can thus be defined as an index to measure the effect of concentration polarization.

RESULTS AND DISCUSSION

A set of three combinations of A and B values, as given in Table 1, is arbitrarily chosen to illustrate the effect of mass transfer coefficient k. Case I is close to the data of a polyetherimide membrane for the separation of organic vapor–nitrogen mixtures (*10*, *11*); Cases II and III represent more permselective membranes.

The results of the calculation for the concentration polarization index as a function of the mass transfer coefficient are shown in Fig. 2. For the purpose of calculation, the following numerical values were used: $P_1 = 101.3$ kPa, $P_3 = 0$, $X_1 = 0.2$, and $T = 298$ K. The figure shows that X_2/X_1 tends to increase with an increase in k. When k is sufficiently large, X_2/X_1 approaches unity, indicating the effect of concentration polarization is negligible. Note that there is a critical value of mass transfer beyond which the concentration polarization is insignificant, and below which X_2/X_1 decreases rapidly as k decreases. The critical k value depends on the relative magnitude of the mass transfer resistances of the membrane

TABLE 1
The Arbitrarily Chosen A and B Values for the Parametric Studies

Case	A [mol/(m^2·s·Pa)]	B [mol/(m^2·s·Pa^2)]
I	10^{-11}	10^{-13}
II	10^{-10}	10^{-12}
III	10^{-9}	10^{-10}

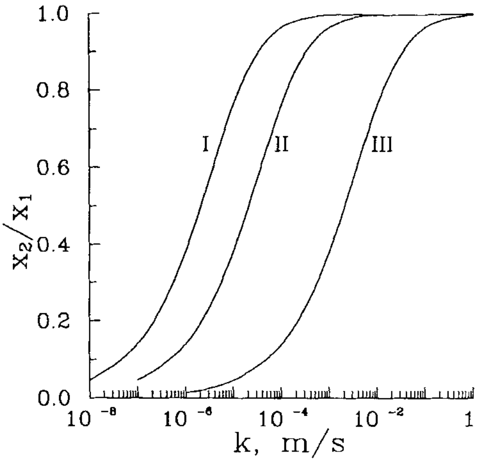

FIG. 2. The concentration polarization index versus mass transfer coefficient. $P_3/P_1 = 0$, $X_1 = 0.2$; the membrane parameters A and B for Cases I to III are given in Table 1.

and the concentration boundary layer, and it is estimated to be approximately 10^{-4}, 10^{-3}, and 10^{-1} m/s, respectively, for the three cases under study. In consideration that the gas-phase diffusivity has a value on the order of 10^{-5} m^2/s for a pressure of 101.3 kPa (*15*), the corresponding thickness of the concentration boundary layer is on the order of 0.1, 0.01, and 0.0001 m, respectively. Therefore, under normal operating conditions, the concentration polarization is not significant for most of the present membranes which may be represented by Cases I and II. However, it is expected that the effect of concentration polarization might not be neglected for high performance membranes whose permselectivities are superior to that represented by Case III.

The effects of mass transfer coefficient on the permeate concentration and vapor flux are shown in Fig. 3 with respect to the three cases. Only when the concentration polarization effect is minimal, i.e., the mass transfer coefficient k is sufficiently large, the separation is determined primarily by the membrane properties. If k is significantly small, an asymptotic relationship between vapor flux and mass transfer coefficient is observed, as represented by the dashed line in Fig. 3. In this case the concentration boundary layer dominates the mass transfer, and thus the separation is low. Consequently, there is a sharp decrease in permeate concentration when the mass transfer coefficient is decreasing.

As mentioned above, the concentration polarization is insignificant for most of the current membranes due to their limited permeability and se-

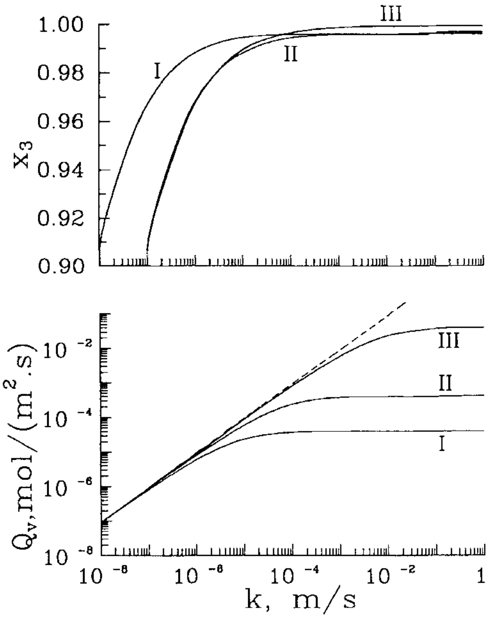

FIG. 3. The effect of mass transfer coefficient on the permeate concentration and vapor flux. The membrane parameters and operating conditions used in the calculation are the same as in Fig. 2.

lectivity. In what follows, the effects of some operating conditions and membrane permselectivity are discussed, assuming an infinite value of mass transfer coefficient.

Figure 4 illustrates the effect of feed vapor concentration on the vapor permeation flux and permeate concentration for Case I. The figure shows that the vapor permeation flux increases with an increase in the feed vapor concentration, but the rate of such an increase is smaller for higher feed vapor concentration. The gas flux naturally decreases when the feed vapor concentration is increasing, resulting in a sharp increase in permeate vapor concentration. However, as permeate vapor concentration X_3 approaches unity, the feed vapor concentration has little effect on X_3. Therefore, membrane is especially effective for the separation of organic vapor–gas mixtures when the vapor content is considerably low, but not so effective when the vapor content is high. The curves in Fig. 4 have the same trends as observed from experimental data (*11*).

Q_V and X_3 as a function of the permeate/feed pressure ratio are shown in Fig. 5. It can be seen that both Q_V and X_3 increase with a decrease in

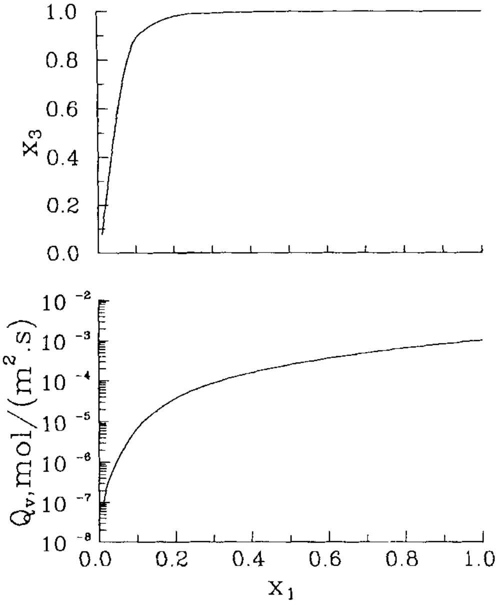

FIG. 4. The effect of feed vapor concentration on the permeate concentration and vapor flux. $k = \infty$, $P_3/P_1 = 0$. Membrane parameters: $A = 10^{-11}$ mol/(m^2·s·Pa) and $B = 10^{-13}$ mol/(m^2·s·Pa^2).

the pressure ratio. A very low permeate pressure, however, is not appropriate due to the limitations in the available vacuum pumps, especially for evacuating streams containing condensible vapors. Moreover, the figure shows that in the range of the pressure ratio below 0.1, Q_V and X_3 vary only slightly for the case under study, indicating it is unlikely to apply very high vacuum on the permeate side of the membrane in order to improve separation performance significantly. It should be pointed out that the appropriate pressure ratio depends on the membrane permeability to the components to be separated, as experimentally observed (*11*).

The effect of membrane permselectivity on the separation performance is shown in Fig. 6. The figure shows that for a given gas permeation parameters A, the permeate vapor concentration increases with an increase in vapor permeation parameter B. However, when the membrane selectivity is substantially high, further increase in selectivity does not improve the permeate vapor concentration significantly, as represented by the plateau part of the curves in Fig. 6. Nevertheless, the vapor flux changes almost linearly with the vapor permeation parameter, regardless of the gas permeability.

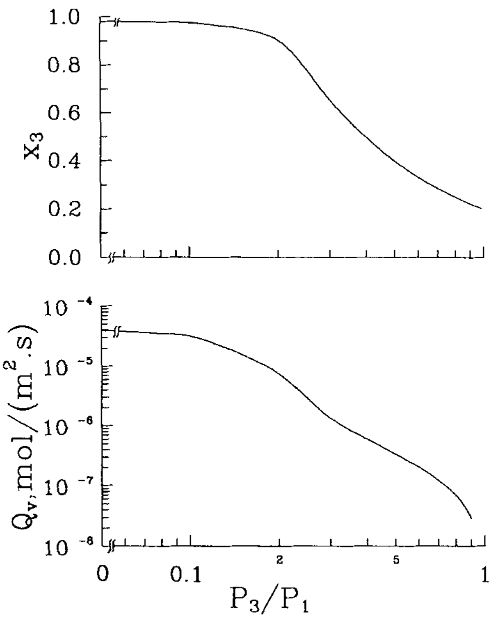

FIG. 5. The effect of permeate/feed pressure ratio on the permeate concentration and vapor flux. $k = \infty$, $X_1 = 0.2$. Membrane parameters: Same as those given in Fig. 4.

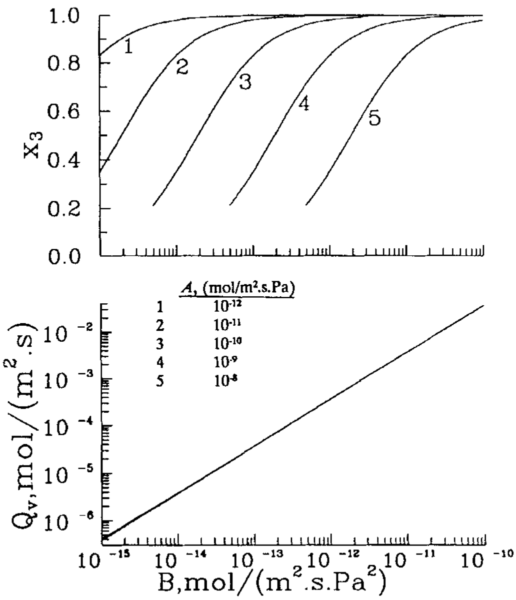

FIG. 6. The effect of membrane parameters on the permeate concentration and vapor flux. $k = \infty$, $X_1 = 0.2$, $P_3/P_1 = 0$.

CONCLUSIONS

The following conclusions can be drawn from the results of the parametric analyses on the separation of organic vapor–gas mixtures made in this study.

(1) The effect of concentration polarization is negligible for membranes of low permeability, but would be significant for highly permeable and selective membranes.
(2) Membrane separation is especially effective for the organic vapor–gas mixtures of low vapor content, but not so effective when the vapor content is considerably high.
(3) The permeation flux and the permeate concentration increase with an increase in permeate/feed pressure ratio. However, the effect of the pressure ratio is insignificant when it is sufficiently small.
(4) For a membrane of high selectivity, the vapor permeation parameter B has little effect on permeate concentration, but the permeation flux increases almost linearly with B.

NOTATIONS

A	gas permeation parameter [mol/(m^2·s·Pa)]
B	organic vapor permeation parameter [mol/(m^2·s·Pa^2)]
C	molar concentration (mol/m^3)
D	gas-phase diffusion coefficient (m^2/s)
k	Colburn–Drew mass transfer coefficient (m/s)
Q_V, Q_G	molar flux of organic vapor and gas, respectively [mol/(m^2·s)]
R	universal gas constant, 8.314 N·m/(mol·K)
T	temperature (K)
X	molar fraction of organic vapor
δ	thickness of concentration boundary layer (m)

Subscripts

1, 2, 3	feed, membrane surface, and permeate, respectively

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