Separation of Volatile Organic Compound/Nitrogen Mixtures

by Polymeric Membranes

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ABSTRACT

Dry asymmetric polyetherimide membranes were prepared by phase inversion technique under different conditions to investigate their performance for separating volatile organic compounds/nitrogen gas mixtures. The membrane performance was further tested under different operating conditions such as operating temperature, feed vapour concentration and the pressure on the permeate side of the membrane. A set of transport equations was proposed for the membrane permeation of organic vapour/gas mixtures. The validity of the transport equations was tested by their applicability to describe the experimental data.

INTRODUCTION

Volatile organic compounds produce a large amount of waste emissions which cause not only a severe environmental pollution problem but also a significant economic loss. The recovery of volatile organic compounds from loading, unloading and other handling operations has been under scrutiny from both environmental and economic points of view. However, most existing techniques for organic vapour emissions control have so far proved to be unsatisfactory in view of safety, performance, operating cost and facility space.[1] Membrane technology, which has been successfully applied in sea water desalination and gas-gas mixture separations is expected to provide an alternative to the conventional methods.

The concept of organic vapour separation by membrane is not new, but only recently did interest increase in this process. The separation of organic vapour from waste gas streams is different from gas-gas separations. Besides permeability and selectivity requirements, the membrane material has to be highly resistant to organic vapour attack. Though this process is a low-pressure membrane process and involves vapour components in the permeate, it also differs from pervaporation since the membrane is dry.

Most of the experimental works reported so far on membrane vapour recovery are concentrated on composite silicone rubber membranes. Pinnau et al.[2], Kimmerle et al.[3], Strathmann et al.[4] and Paul et al.[5] tested silicone rubber membranes coated on a porous polysulfone substrate. Behling et al.[6,7] chose polyetherimide as the supporting material because it is much more stable to organic vapours than polysulfone. Buys et al.[8] used polyhydantoine and polyimide as the porous support to silicone rubber coating layer in their study. A membrane system for the treatment of low-volume, high vapour concentration gas streams was tested, but no information was disclosed concerning membrane materials.[9]

The resistance of silicone rubber to some organic vapours, for example gasoline, is however poor.[10] An attempt was made, therefore, by the authors to prepare membranes from a single polymeric material of high organic resistance. In our previous studies, asymmetric aromatic polyimide membranes were investigated for this purpose.[11,12] It was shown that membranes of both high selectivity and reasonably high permeability could be produced by controlling the conditions of the membrane preparation properly. In this study aromatic polyetherimide membranes are also included. In order to reduce the resistance to the membrane permeation, asymmetry is introduced to the membrane structure using phase inversion technique in the preparation of membranes. Membranes prepared under different conditions were tested for various operating conditions and the results are reported.

The mathematical modelling of the transport involved in the membrane permeation of gas–vapour mixtures is another objective of this study. In comparison with other membrane processes such as separations of liquid-liquid and gas-gas mixtures, the transport study for gas-vapour mixture permeation is in a far less advanced state primarily due to the lack of experimental data. For this purpose a new set of transport equations is proposed and its validity is examined by experimental data. It has to be noted that the origin of this transport model is traced back to the pore flow models proposed to understand transport phenomena involved in reverse osmosis, membrane gas separation and pervaporation. Therefore, this work is one of the attempts to understand various membrane separation processes from a single view point of "flow in the pore under the influence of membrane material".

THEORETICAL

The molar permeation flux of nitrogen gas through the membrane, Q_N (mol/m^2·s), is

obtained by

$$Q_N = \frac{V}{A} \frac{273.15}{273.15 + 23} \frac{1}{22400 \times 60} \tag{1}$$

where V is the volumetric permeation rate (mL/min) of nitrogen gas, A is the effective film area (m^2). The permeability of nitrogen gas, J_N (mol/m$^2 \cdot$s$\cdot$Pa), is given by

$$J_N = Q_N / \Delta P \tag{2}$$

where ΔP is the pressure difference across the membrane (Pa).

The following transport equations are used for the analysis of membrane permeation data when the feed is a nitrogen gas/organic vapor mixture.

$$Q_N = A[P_1(1 - Y_1) - P_3(1 - Y_3)] \tag{3}$$

$$Q_v = B[(P_1 Y_1)^2 - (P_3 Y_3)^2] \tag{4}$$

$$Y_3 = \frac{Q_v}{Q_v + Q_N} \tag{5}$$

where Q's are permeation fluxes; P's are pressures and Y's are mole fractions of the organic vapour. Subscripts N and v represent nitrogen and organic vapour, respectively. Subscripts 1 and 3 represent the feed and the permeate, respectively. It should be noted that, unlike our previous paper,[12] eq. 4 assumes that Q_v is proportional to the difference in the square of the partial vapour pressure on both sides of the membrane rather than the difference in the partial pressure itself. This assumption was necessary because of the nonlinear dependence of the permeation flux on partial vapour pressure as shown later in the experimental section. Assuming further that the permeability of nitrogen gas is unaffected by the presence of organic vapours in the feed,

$$A = J_N \tag{6}$$

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Looking into eqs. 3–5, Q_v, P_1, P_3, Y_1 and A are known quantities from the permeation experiment for pure nitrogen gas and from the permeation experiment for feed nitrogen gas/organic vapour mixtures. Consequently, three unknown quantities B, Q_N and Y_3 can be calculated from above three equations. Conversely, when P_1, P_3, Y_1, A and B are given, Q_N, Q_v and Y_3 can be calculated. Therefore, there are two possibilities of calculating Y_3, either by giving experimental Q_v or by giving a parameter B. It should be further noted that the quantity B remains constant for a given organic vapour and for a given temperature, if the above equations are valid.

EXPERIMENTAL

Materials. Aromatic polyimide (PI) (2080 grade) powder, supplied by Upjohn Company, was dried at 140°C for 16 h before use. Aromatic polyetherimide (PEI) (1000 grade) was supplied by General Electric Co. in a pellet form. The pellets were dried at 150°C for 4 h in an oven with forced air circulation as suggested by the supplier. Lithium chloride (LiCl) and lithium nitrate (LiNO$_3$) from Fisher Scientific Co. were dried at 140°C for 4 h before being used as additives in membrane preparation. All organic chemicals were supplied by BDH Inc. and were of reagent grade. Nitrogen gas with a purity of 99.997% was obtained from Air Products.

Membrane Preparation. Membranes were prepared using the phase inversion method. The details of the preparation procedure have been reported elsewhere.[12] Four major steps, including casting, evaporation, gelation and solvent exchange, were involved in the membrane preparation, as summarized in Fig. 1. Briefly, membranes were cast from polymeric solutions, the compositions of which are summarized in Table 1. After partial evaporation of solvent the cast film was immersed in ice–cold water for gelation. Then, the membrane

was immersed in ethanol for solvent exchange before it was dried in air.

Apparatus and Procedures. The flow diagram of the experimental setup is shown schematically in Fig. 2. A mixture of organic vapour and nitrogen was produced by bubbling nitrogen gas from a porous sintered stainless steel ball immersed in a chosen organic liquid at room temperature. The permeation cell, whose structure is the same as that used in our earlier study,[12] was housed in an isothermal chamber whose temperature was controlled within ± 0.5°C. If necessary, the feed gas mixture was preheated to the experimental temperature in a heating coil before it was introduced to the feed side of the membrane. The permeate side of the membrane was connected to two cold traps, followed by a DuoSeal vacuum pump (Model 1400). The permeation of the organic vapour was induced by maintaining its partial pressure on the permeate side lower than the feed side. The membrane–permeated organic vapour was condensed and collected initially in one of the cold traps, and then the cold trap was switched to the other after the steady state was reached. The permeation rate was determined gravimetrically by weighing the sample collected for a predetermined period.

The feed gas stream was connected to a Varian gas chromatograph (Model 3400) both at the inlet and at the outlet of the feed chamber of the permeation cell through bypass valves to determine the composition of the feed mixture. The feed flow rate was so high that the concentration change from the inlet to the outlet of the feed chamber was negligible. In order to change the feed vapour concentration, nitrogen gas supplied from a cylinder was divided into two streams in such a way that only one stream was bubbled through organic liquid for being saturated by vapour, while the other was used to dilute the vapour saturated stream. By changing the flow rate ratio of the two nitrogen streams, different feed vapour concentrations were obtained.

The permeation rate of pure nitrogen was determined in the following way. A bubble flow meter was connected to the feed chamber outlet of the permeation cell and the inlet valve was closed as illustrated in Fig. 2(a). When the permeate side of the permeation cell was evacuated by a vacuum pump, nitrogen was sucked from the bottom of the bubble meter into the feed chamber, pushing a soap film in the buret upwards. The nitrogen flow rate was determined from the speed of the movement of the soap film.

RESULTS AND DISCUSSIONS

Permeability and Permselectivity. Some results from experiments with feed vapour concentrations corresponding to 97–99 % of saturation vapour pressures are illustrated in Fig. 3. The conditions of the membrane preparation are listed in Table I for all eleven membranes involved in the above experiments. The permeability, J_v (mol/m²·s·Pa), is plotted versus membrane selectivety, defined as the permeability ratio, J_v/J_N, of organic vapour and nitrogen, for five different organic vapours. Looking at data with the same symbol, for example (o) for n–pentane, there is a trend that J_v decreases with an increase in J_v/J_N ratio, indicating that there is a trade–off between permeability and selectivety. Some data, however, clearly show that it is possible to obtain one membrane that is higher both in permeability and selectivity than another by adjusting membrane preparation conditions properly.

Effects of Some Operating Variables. The permeabilities of five organic vapours are plotted versus temperature in Fig. 4 in the temperature range of 23–83°C with respect to the PEI–8 membrane. The permeability decreases with an increase in temperature except for toluene. The permeability change in the above temperature range is, however, below 50% in contrast to a sharp decrease reported in the literature with respect to silicone rubber.[7,8]

Figure 5 shows the effect of feed vapour concentration on the vapour permeation flux.

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The pressure on the permeate side was kept below 1.1 kPa throughout the experiments. The permeation flux increases with an increase in feed vapour concentration in nonlinear fashion as observed by Buys et al.[8]

The effect of permeate pressure on the vapour permeation flux is shown in Figure 6. ✓ The feed vapour concentration was kept between 97 and 99% of saturation vapour pressure throughout the experiments. The permeation flux decreases with an increase in the permeate pressure in nonlinear fashion and approaches zero as the permeate pressure approaches the saturation vapour pressure. For example, the flux for n-heptane and toluene approaches zero, when the permeate pressure approaches their respective saturation vapour pressure of 5.8 and 3.6 kPa.

TRANSPORT STUDY

Equations 3–5 were used to analyze experimental data obtained at 23°C. In particular, eqs. 3 and 6 assume that nitrogen gas permeability is unaffected by the presence of organic vapours in feed gas mixtures. The same assumption was made in our earlier work.[11,12] In order to test this assumption, the permeability of nitrogen gas saturated with methanol and n-pentane at 23°C was determined by experiments. Methanol and n-pentane were chosen for this test since the saturation vapour pressures of these organic compounds are the highest among all organic compounds involved in this study. Therefore, the strongest effect is expected from vapours of above two organic compounds. Compared with pure nitrogen, the permeability increase of 13% and 18.6% for methanol and n- pentane vapour, respectively, was obtained, indicating that eqs. 3 and 6 are valid approximations. Under the above assumption A in eq. 3 was evaluated to be 1.7313×10^{-11} mol/m^2·s·Pa using eqs. 2 and 6. This A value will be used throughout the rest of this paper.

All the data from permeation experiments were analyzed by using eqs. 3–5 and three unknown quantities, Q_N, B and Y_3 were calculated. Figures 7 and 8 illustrate the relationship between Q_v and $[(P_1 Y_1)^2 - (P_3 Y_3)^2]$. Note that eq. 4 implies that the relationship should be linear and the slope should be equal to the quantity B. The scatter of the data along the straight line measures the scatter in the numerical values of B. Thus, the straightline relationship presented in Figs. 7 and 8 justifies the use of eqs. 3–5 for the analysis of permeation data. The slopes of straight lines in the figure are listed in Table II as the parameter B. It is interesting to note that there is a strong correlation between the boiling point of hydrocarbons and the B value. Methanol B value is higher than expected from the boiling point probably due to a stronger interaction between alcohol and polyetherimide membrane material. Using the B values listed in Table II, instead of Q_v values, the vapour mole fraction in the permeate, Y_3, was recalculated by eqs. 3–5. The results are plotted versus feed vapour mole fraction, Y_1, as solid lines in Fig. 9. Solid lines of Fig. 10 illustrate similar plots but versus the permeate pressure, P_3. Symbols indicate Y_3 values obtained from calculations using experimental Q_v data. The agreement between the symbols and the lines indicates that average B values represent the experimental data reasonably well.

From Fig. 10 we claim the following conclusions. The vapour mole fraction in the permeate, Y_3, is above 0.87 for all experiments. The permeate pressure, P_3, has little effect on Y_3, when the liquid is as volatile as methanol and $n-$ heptane.

CONCLUSIONS

The following conclusions can be drawn from this work:

1. Dry asymmetric polyetherimide membranes prepared by the phase inversion technique and dried by the solvent exchange method can be used to separate organic vapours

from organic vapour/nitrogen gas mixtures.

2. The selectivity and the permeability of the membrane can be controlled by proper adjustment of membrane preparation conditions.

3. Membrane performance data are affected by operating conditions such as temperature, permeate pressure and feed concentration.

4. The proposed transport equations are applicable to analyze membrane permeation data. For a given temperature these equations involve only two adjustable parameters which are obtainable from one experiment for pure nitrogen permeation and one experiment under a single set of permeate pressure and feed vapour concentration. These parameters enable the prediction of the membrane performance for different permeate pressures and feed vapour concentrations.

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Table I

Membrane Preparation Conditions

	PI-1	PI-2	PEI-1	PEI-2	PEI-3	PEI-4	PEI-5	PEI-6	PEI-7	PEI-8	PEI-9
Casting solution compn, wt%											
polyimide (2080)	25	25	–	–	–	–	–	–	–	–	–
polyetherimide (1000)	–	–	30.95	30.95	30.95	30.95	25	25	25	25	25
dimethyl acetamide	72.5	72.5	69.05	69.05	69.05	69.05	74	74	75	74	74
lithium chloride	2.5	2.5	–	–	–	–	–	–	–	–	–
lithium nitrate	–	–	–	–	–	–	1	1	–	1	1
Temp of casting solun, °C	45	22.5	23	23	23	22.5	24	24	23	22.5	23
Casting atmosphere	a	a	a	a	a	a	a	a	a	a	a
Temp of casting atm, °C	22.5	22.5	23	23	23	22.5	24	24	23	22.5	23
Humidity of casting atm	b	b	b	b	b	b	b	b	b	b	b
Solvent evaporation temp, °C	95	70	23	100	100	100	100	100	23	110	24
Solvent evaporation temp, min	40	10	0.05	1.33	2	8	2	0.5	0.1	1.8	0.6
Gelation medium	c	c	c	c	c	c	c	c	c	c	c
Gelation period, min	20	20	20	20	20	20	20	20	20	24	20
Solvent for replacing water											
in the film	d	d	d	d	d	d	d	d	d	d	d
Solvent exchange time, hr	24	30	30	30	30	30	30	48	30	30	24
Drying of membrane	e	e	e	e	e	e	e	e	e	e	e

a: ambient air; b: 60-65%; c: ice cold water (1-3°C); d: ethanol; e: air dried.

Table II

Boiling Point of Organic Vapor and its B Value for

Permeation through PEI-8 Membrane at 23°C

Organic Vapor	Boiling Point[a], °C	B, mol/m^2.s.Pa^2
Methanol	64.7	1.142×10^{-12}
n-Pentane	36.3	1.874×10^{-14}
Cyclohexane	80.5	5.990×10^{-13}
n-Heptane	98.4	2.812×10^{-12}
Toluene	110.8	6.647×10^{-12}

[a] From Reference 13.

FIGURE CAPTIONS:

1. Membrane preparation sequence.

2. Schematic diagram of experimental setup.

3. Permeability vs. selectivity for organic vapours through PI and PEI membranes. Feed: nitrogen + organic vapour (97–99% saturated); Temperature: 23°C; Permeate pressure: 0.18–1.1 kPa depending on the membrane permeability.

4. Temperature dependence of permeability of organic vapours. Membrane: PEI-8; Feed: nitrogen + organic vapour (97–99% saturated); Permeate pressure: 0.18–1.1 kPa.

5. Effect of feed vapour concentration on vapour permeation flux. Membrane: PEI-8; Temperature: 23°C; Permeate pressure: 0.18–1.1 kPa.

6. Effect of permeate pressure on vapour permeation flux. Membrane: PEI-8; Feed: Nitrogen + organic vapour (97–99 % saturated); Temperature: 23°C.

7. Linear relationship between Q_v and $[(P_1Y_1)^2 - (P_3Y_3)^2]$ for n-pentane.

8. Linear relationship between Q_v and $[(P_1Y_1)^2 - (P_3Y_3)^2]$ for methanol, cyclohexane, n-heptane and toluene.

9. Permeate vapour concentration, Y_3, as a function of feed vapour concentration, Y_1. Solid lines correspond to Y_3 values calculated by using average B: Symbols correspond to Y_3 values calculated by using experimental Q_v.

10. Permeate vapour concentration, Y_3, as a function of permeate pressure, P_3. Lines and symbols have the same meaning as in Fig. 9.

PRESSURE GAUGE

GC

ISOTHERMAL CHAMBER

COLD TRAP

HEATER

PRESSURE REGULATOR

N₂

HEATING BATH

BUBBLER

MEMBRANE

VACUUM GAUGE

COLD TRAPS

VACUUM PUMP

VACUUM REGULATOR

MEMBRANE

(a)

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┌─────────────────────────────────────────────┐
│   Solution of Polymer and Additive in Solvent │
└─────────────────────────────────────────────┘
                      │
         ┌────────────────────────────────┐
         │   Casting at Ambient Temperature │
         └────────────────────────────────┘
                      │
          ┌──────────────────────────────┐
          │   Partial Evaporation of Solvent │
          └──────────────────────────────┘
                      │
           ┌────────────────────────────┐
           │   Gelation in Ice Cold Water │
           └────────────────────────────┘
                      │
       ┌──────────────────────────────────────┐
       │   Solvent Exchange to Replace the Water │
       │            Within the Membrane          │
       └──────────────────────────────────────┘
                      │
              ┌──────────────────┐
              │   Drying in Air   │
              └──────────────────┘
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Figure showing J_v, mol/m²·s·Pa versus Selectivity, J_v/J_N

Legend:
- □ = Methanol
- ○ = n-Pentane
- △ = Cyclohexane
- + = n-Heptane
- × = Toluene

Data series labeled: PEI-1, PEI-7, PI-2, PEI-6, PEI-9, PEI-2, PEI-3, PI-1, PEI-8, PEI-4, PEI-5

10^{-7}

J_v, mol/m^2.s.Pa

10^{-8}

10^{-9}

O = toluene
□ = methanol
△ = n-heptane
● = cyclohexane
■ = .n-pentene

10^{-10}

0   20   40   60   80   100

Temperature, °C

4

Permeation flux $\times 10^n$, mol/m^2.s

Feed vapor concentration, mol%

n=5

○ = toluene
□ = n-heptane
▽ = cyclohexane

n=4

methanol

n=5

n-pentane

5

Figure showing Permeation flux, mol/m².s versus Permeate pressure, kPa

Legend:
+ = methanol
O = n-pentane
□ = cyclohexane
△ = n-heptane
× = toluene

6

n-Pentane

$Q_v \times 10^5$, mol/m^2.s

$[(P_1Y_1)^2 - (P_3Y_3)^2]/10^9$, Pa^2

$Q_v \times 10^4$, mol/m^2.s

□ = methanol
○ = cyclohexane
△ = n-heptane
◇ = toluene

$[(P_1Y_1)^2-(P_3Y_3)^2]/10^8$, Pa^2

8

1, ● = methanol
2, ○ = n-pentane
3, □ = cyclohexane
4, △ = n-heptane
5, ✕ = toluene

(Y-axis: Permeate vapor mole fraction; X-axis: Permeate pressure, kPa)

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