

대기중의 휘발성 유기물 제거용 분리막

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Membrane for the Removal of Volatile Organic Compounds from Air

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Abstract: Porous asymmetric membranes were prepared from polyetherimide polymer by the phase-inversion technique under different conditions. The performance of the membranes was tested for the removal of acetone vapour from nitrogen. A membrane which showed a high acetone permeability and a high selectivity was chosen and tested further for the separation of different organic vapours from nitrogen. The molecular structure of organic vapours and the selectivity were correlated. A strong correlation was also found between the chromatographic retention time of the organic vapour and the selectivity. These experimental results led to the conclusion that the sorption is the factor governing the separation of volatile organic compounds from nitrogen. A membrane was also prepared by coating the surface of a porous polyetherimide membrane with silicone rubber. The performance of membranes with and without silicone rubber coating was compared.

1. Introduction

In recent years air pollution has become the most serious especially in advanced countries. In these countries, many industrial processes handling organic solvents produce solvent containing exhaust streams. These streams cause not only severe air pollution problems but also a significant economic loss. From an environmental point of view, it is necessary to limit and control organic vapour emissions because they affect the composition of the ozone layer, the change of climate, the growth and decay

of plants, and the health of human beings and all animals. For example, the release of chlorofluoromethanes and other chlorine containing compounds in the atmosphere increases the absorption and emission of infrared radiation[1]. The heat loss from the earth is retarded and thus the earth's temperature and climate are affected. Studies on carcinogenicity of certain classes of hydrocarbons indicate that some cancers appear to be caused by exposure to aromatic hydrocarbons found in soot and tars. Hydrocarbons, in combination with NO_x, in the presence of sunlight, undergo photochemical

oxidation, producing a photochemical smog that is environmentally hazardous[2]. Therefore, regulations on the controlling of organic vapour pollutants in air have been issued worldwide. In the Ambient Air Quality Standards, produced by the U.S. Environmental Protection Agency, the maximum 3-hour concentration (from 6 to 9 am) of hydrocarbon content (corrected for methane) is $160\mu\text{g}/\text{m}^3$ (0.24 ppm), not to be exceeded more than once a year [3]. From an economic point of view, it is desirable to recover and reuse the organic solvents that are released to the air. The amount of solvents emitted to the atmosphere is extremely large. It is estimated that solvent emissions in the U.S. are in the order of 10 to 15 million tons per year, which represents an annual loss of two billion dollars, based on their fuel value alone[4]. The organic vapour pollutants include almost all of organic compounds which have low boiling points and high vapour pressures. Some typical examples of organic pollutants in the gas or vapour state are hydrocarbons, aldehydes, ketones, alcohols, organic halides, organic acids, organic sulfides and organic peroxides[3].

Two types of conventional organic emission control techniques are still used[2, 3]. They are : (1) processes to recover organic vapours, including adsorption, absorption and condensation; and (2) processes to destroy organic vapours, including direct flame incineration, thermal incineration and catalytic incineration. Each of these techniques has advantages and disadvantages, in regards to safety, performance, operating costs and space facilities. A direct condensation technique is unfavourable when the concentration of organic vapour in the waste stream is too low. Adsorption and absorption techniques require a regeneration step which causes new disposal problems. Energy is required and new hazardous substances may be produced when organic vapour emission control is attempted by incineration processes. In the recent decades, a significant achievement was made in many applications of membrane separation techniques. The separation and recovery of organic vapours by a membrane

process may have great economic potential[5, 6]. Most of the published research work on organic vapour permeation by membranes was performed using composite, silicone rubber membranes supported on a porous polymer substrate[4-9]. Polysulfone membranes were usually used as substrates. The resistance of silicone rubber to hydrocarbons and gasoline is however poor[10]. Therefore, attempts were made to use some glassy polymers without coating. Ilinitich et al. used polyphenylene oxide (PPO) and some PPO-based copolymer membranes for separation of hydrocarbons[11]. Aromatic polyimide (PI) and polyetherimide (PEI) membranes were employed for recovering various organic vapours from nitrogen by Feng et al.[12, 13] and Deng et al.[14].

The objective of this paper is to prepare asymmetric porous polyetherimide membranes under different conditions to find an optimum condition of membrane formation. The membrane is then subjected to the test for the separation of different organic vapours to find the correlation between the molecular structure of the organic vapour and the permeability and selectivity. To find the possible mechanism of the gas and vapour transport is another objective of the work.

2. Experimental

2.1. Membrane preparation

Polyetherimide (PEI, Ultem 1000/2000) powder supplied by General Electric Co. was dried at 150°C for 4 hours in an oven with forced air circulation. Reagent grade N, N-dimethyl acetamide (DMAc), supplied by BDH Chemicals, was used as solvent without any further treatment. Lithium nitrate from Fisher Scientific Co. was dried at 150°C for four hours before use as a nonsolvent additive to the polymer solution. In order to prepare a casting solution, lithium nitrate was dissolved in DMAc, into which dry polyetherimide powder was added. The mixture of solvent, additive and polymer powder was then stirred at room temperature for 24 hours

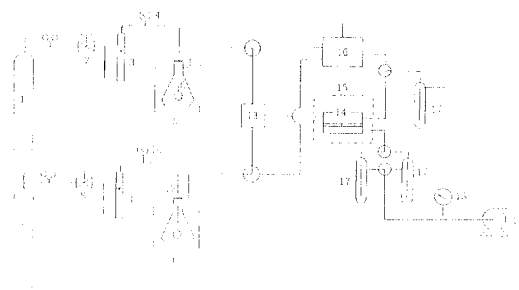
and further kept in an oven overnight at 55°C to ensure the complete dissolution of polymer. The polymer solution was then cooled to room temperature and centrifuged at 5000 rpm for about an hour to remove undissolved solid particles.

The solution was cast on a clean glass plate to a thickness of 250 μ m. Both casting solution temperature and the temperature of the casting atmosphere were ambient. The cast polymer solution film, together with the glass plate, was placed in an oven at a predetermined temperature for two minutes to partially evaporate the solvent. Then, the film, together with the glass plate, was immersed into ice-cold water for 40 minutes, during which period gelation took place and the film stood apart from the glass plate. The membranes were kept in water for another 20~24 hours before they were immersed into ethanol for 24 hours to replace the water in the membrane with ethanol. Then, the membranes were dried in air at room temperature for at least three days.

The coating of a porous PEI membrane (membrane 26 in Table 1 and 2) was done in the following way. Sylgard supplied by Dow Corning Corp. was mixed with three parts of the curing agent, also supplied by Dow Corning Corp., and the mixture was diluted with an equal amount of hexane. A 50/50% mixture of hexane/ethanol solution was also prepared for the pretreatment of the top surface layer of the porous PEI membrane. A small amount of the hexane/ethanol mixture was spread over the surface and dried. Then, a thin layer of Sylgard solution was cast on the surface using a glass bar and the coated layer was dried at room temperature for 24 hours.

2.2. Permeation Experiment

The flow diagram of the experimental apparatus is shown in Fig. 1. A mixture of a chosen organic vapour and nitrogen was produced by a saturator in which nitrogen stream was saturated with the organic vapour while nitrogen gas bubbles were passing through a layer of organic liquid. The tempera-



1,7-nitrogen cylinder	13-mixer
2,8-valve	14-membrane cell
3,9-flowmeter	15-isothermal chamber
4,10-pressure gauge	16-GC
5, 11-bath	17-cold trap
6-organic bubbler	18-vacuum gauge
12-water bubbler	19-vacuum pump

Fig. 1. Schematic diagram of vapour permeation system.

ture of the saturator was maintained between 15 and 17°C. The permeation cell was housed in an isothermal chamber whose temperature could be controlled within $\pm 0.5^\circ\text{C}$. The permeate side of the permeation cell was connected to two cold traps immersed in liquid nitrogen, which were followed by a Duoseal vacuum pump (Model 400). 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 by-path valves to determine the composition of the feed mixtures.

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. When the permeate side of the permeation cell was evacuated by a vacuum pump the nitrogen in the feed chamber was sucked through the membrane, drawing the soap film in the burette of the bubble flow meter downwards. The permeability of pure nitrogen gas through the membrane, J_v (mol/s m^2 pa), is obtained by the following relationship :

Table 1. Conditions of Membrane Preparation

Membrane No.	Polymer (wt %)	Nonsolvent additive, LiNO ₃ (wt%)	Evaporation temperature (°C)
1	25	0.0	25
2	25	1.0	25
3	25	1.5	25
4	25	2.0	25
5	25	2.5	25
6	25	2.91	25
7	25	0.0	50
8	25	1.0	50
9	25	1.5	50
10	25	2.0	50
11	25	2.5	50
12	25	2.91	50
13	25	0.0	75
14	25	1.0	75
15	25	1.5	75
16	25	2.0	75
17	25	2.5	75
18	25	0.0	105
19	25	1.0	105
20	25	1.5	105
21	25	2.0	105
22	25	2.5	105
23	23	1.0	75
24	27	1.0	75
25	29	1.0	75
26 ^a	25	1.5	25

^a No solvent evaporation was involved.

$$J_N = \frac{1}{6 \times 10^7} \frac{VP_0}{ART(P_0 - P_3)} \quad (1)$$

where V is the volumetric permeation rate (mL/min) of nitrogen through the membrane measured by the bubble flowmeter; A is the effective membrane area (m²); T is the absolute temperature (K); P₀ is the feed pressure (Pa); P₃ is the downstream pressure (Pa); and R is gas constant, 8.314 (J/K Pa). It has to be noted that the residual solvent in the membrane was removed completely by letting nitrogen gas permeate through the mem-

Table 2. Nitrogen and Acetone Permeability Data

Membrane NO.	J _N × 10 ⁹ (mol/s m ² Pa)	J _A × 10 ⁹ (mol/s m ² Pa)	J _A /J _N
1	97.6	67.2	0.69
2	82.5	66.8	0.81
3	66.4	65.4	0.98
4	1.45	4.81	3.32
5	1.34	5.07	3.78
6	4.31	10.7	2.48
7	23.8	22.6	0.95
8	9.87	15.7	1.59
9	2.35	11.0	4.68
10	7.81	31.1	3.98
11	11.3	39.6	3.50
12	14.7	22.1	1.50
13	2.26	14.9	6.59
14	0.783	7.85	10.0
15	n.d.	2.26	-
16	n.d.	3.20	-
17	n.d.	3.75	-
18	0.93	29.6	31.8
19	0.112	6.69	60.0
20	0.232	10.3	44.4
21	0.98	9.12	9.31
22	n.d.	5.08	-
23	n.d.	2.80	-
24	n.d.	3.32	-
25	n.d.	3.53	-
26	135.3	78.5	0.58

n.d. = not detectable

brane for two hours before the nitrogen permeability test.

Assuming that the permeability of nitrogen, J_N, is unaffected by the presence of an organic vapour, which was confirmed by our earlier work[13], the organic vapour permeability (mol/s m² pa), is obtained by solving the following set of equations.

$$Q_N = J_N [P_1(1 - \sum Y_{i,1}) - P_3(1 - \sum Y_{i,3})] \quad (2)$$

$$Q_i = J_i [(P_1 Y_{i,1}) - (P_3 Y_{i,3})] \quad (3)$$

$$Y_{i,3} = \frac{Q_i}{\sum Q_i + Q_N} \quad (4)$$

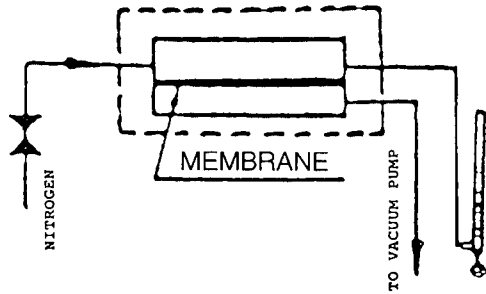


Fig. 2. Schematic diagram of the system for the measurement of nitrogen permeation rate.

where Q 's are permeation fluxes (mol/s m^2); P 's are pressures (pa); Y 's are mole fractions of the organic vapour; the subscripts N and i represent nitrogen gas and organic vapour, respectively; and respectively. Considering equations (2) to (4), Q , P_i , P_N , $Y_{i,1}$, and J_N are quantities known from the permeation experiments. Consequently, the three unknowns, J_i , Q_N , and $Y_{i,3}$ can be calculated from the above three equations.

2.3. Determination of Retention Time of Organic Vapours by Gas Chromatography Experiments

The chromatography experiments were carried out by a Varian Gas Chromatograph (Model 1400). PEI polymer powder, the diameter of which was controlled within 53 to 63 μm by sieving was packed into a 1/8th inch stainless steel column with a length of 56cm. One μL of organic liquid was injected into the helium stream which was flowing through the chromatography column. The vapour was detected by a thermal conductivity detector at the column outlet and the retention time was recorded.

3. Results and Discussion

Twenty six membranes were prepared under different conditions. The details of the membrane preparation conditions are summarized in Table 1. The performance of the membranes was tested by determining nitrogen permeability, J_N , and acetone va-

Table 3. Vapour Permeation Results (for membrane 19, $J_A/J_N = 60.0$)

Organic vapour	Feed mole fraction	Vapour permeability ($\text{mol/s. m}^2 \text{ Pa}$)	Selectivity
Pentane	0.464	2.60E-9	23.28
Hexane	0.171	4.19E-9	37.60
Heptane	0.0391	5.54E-9	49.72
c-Hexane	0.0865	4.03E-9	36.18
Toluene	0.0231	1.18E-8	106.2
MeOH	0.108	3.59E-8	321.9
EtOH	0.0402	1.96E-8	175.6
PrOH-1	0.0166	1.79E-8	160.3
BuOH-1	0.00402	4.38E-8	392.7
PeOH-1	0.00132	5.96E-8	534.8
PrOH-2	0.0296	1.40E-8	125.9
BuOH-2	0.142	2.38E-8	254.2
2-Me-PrOH-1	0.0069	3.58E-8	321.3
PeOH-2	0.00744	4.82E-8	432.2
Acetone	0.213	6.69E-9	59.99
Me-Et-ketone	0.0813	7.75E-9	69.56
Et-Et-ketone	0.0298	8.50E-9	76.24
Methyl acetate	0.193	1.75E-9	15.71
Ethyl acetate	0.0815	3.08E-9	27.64
Propyl acetate	0.0261	5.11E-9	45.82
Chloroform	0.165	1.21E-9	10.89
Dichloromethane	0.396	1.43E-9	128.3
1, 1, 1-Trichloroethane	0.195	1.80E-9	17.01
1, 2-Dichloropropane	0.0371	6.60E-9	59.18
Water	0.00950	3.61E-7	3237.3

$$\text{Selectivity} = J_i/J_N$$

pour permeability, J_A . The data on J_N , J_A and their ratio J_A/J_N are summarized in Table 2. For membranes 15~17 and 22~25 the nitrogen permeation rate was below the lowest permeation rate detectable by the bubble flow meter, 0.05 cm^3/min , therefore J_N is recorded accordingly. Comparing Tables 1 and 2, it is difficult to find a general rule for the effect of membrane preparation conditions on its performance.

Membrane 19 was chosen to study different organic vapours and water for their separation from nitrogen, since this membrane showed sufficiently

high selectivity and permeability. The organic vapours included aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, alcohols, ketones and esters. The experimental results are summarized in Table 3. The table includes mole fraction of organic vapour in the feed, permeability of organic vapour, J_o , and the selectivity defined as J_o/J_w . Comparing oxygen containing organic compounds, the order in selectivity is water \gg alcohols $>$ ketones $>$ esters.

This is exactly the order of the hydrogen bonding capacity of the functional groups involved.

The order in selectivity in hydrocarbons is aromatic hydrocarbon $>$ aliphatic hydrocarbon.

This is the order in the sorption capacity of the polymer to hydrocarbon molecules.

It can be concluded that the sorption capacity which can be enhanced either by hydrogen bonding capacity or aromaticity of organic vapours is the governing factor of the selectivity.

Comparing organic compounds in a homologous group, the increase in the molecular size increases the selectivity in the case of ketones, esters and straight chain hydrocarbons. As for straight chain alcohols, the selectivity changes in the following way methanol $>$ ethanol $>$ propanol-1 and propanol-1 $<$ butanol-1 $<$ pentanol-1.

The decreasing selectivity from methanol to propanol-1 is due to the decreasing hydrogen bonding capacity while the increasing selectivity from propanol-1 to pentanol-1 is due to increasing interaction between the vapour and the membrane polymer by dispersion force. The branching of the chain lowers the selectivity as can be seen by the selectivity change from propanol-1 to propanol-2, from butanol-1 to butanol-2 or 2-methyl propanol-1, and from pentanol-1 to pentanol-2.

It should specially noted that the selectivity of water is far greater than any organic vapours.

The selectivity and the solubility parameter of organic and water vapours are correlated in Fig. 3. It can be concluded from the figure that the selectivity increases with an increase in solubility parameter,

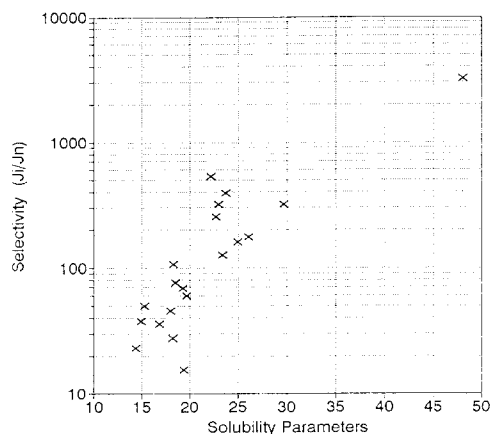


Fig. 3. Selectivity versus solubility parameter for vapours listed in Table 4.

although a large scatter is found in the correlation.

The retention time of the organic vapour obtained from chromatographic experiments is considered to represent the strength of the interaction force working between an organic vapour and the polymer packed in the column. A longer retention time corresponds to a stronger interaction force. The similarity and difference between the interaction forces involved in the chromatography and membrane experiments were discussed by Tam[15] in detail.

Table 4 summarizes the chromatography data. When organic compounds involving two or three carbon atoms are chosen from each homologous group for comparison, the order in retention time (min) is acetic acid (23.0) $>$ (water) (20.5) $>$ ethanol (13.5) $>$ acetone (1.75) $>$ methyl acetate (1.68) $>$ (pentane) (0.47).

Water and pentane are bracketed since these molecules contain less than two or more than three carbon atoms.

The above order is the same as that in the solubility parameter ($\text{cal}^{1/2}\text{cm}^{-3/2}$) with few exceptions (water) (23.5) $>$ acetic acid (12.9) $>$ ethanol (12.7) $>$ acetone (9.6) \geq methyl acetate (9.5) $>$ pentane (7.0).

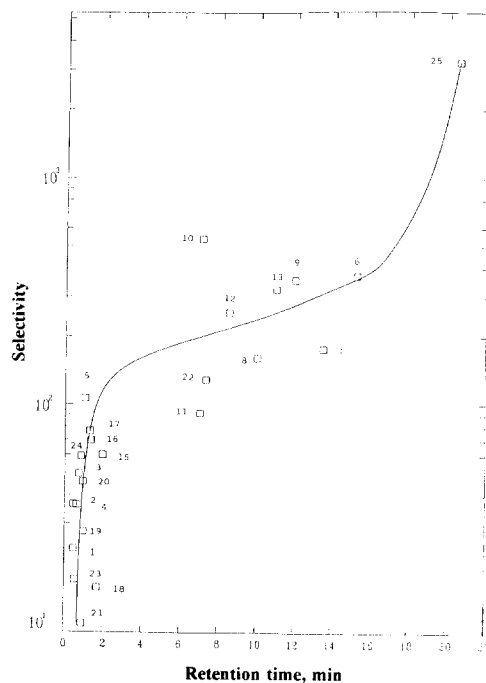
The following order is known to be the hydrogen bonding capacities of oxygen containing functional

Table 4. Chromatography Retention Time Data

Organic Vapour No.	Organic Vapour	Retention time (min)
1	Pentane	0.47
2	Hexane	0.52
3	Heptane	0.72
4	c-Hexane	0.61
5	Toluene	1.03
6	MeOH	15.73
7	EtOH	13.5
8	PrOH-1	10.1
9	BuOH-1	12.0
10	PeOH-1	7.07
11	PrOH-2	7.0
12	BuOH-2	8.5
13	2-Me-PrOH-1	10.9
14	PeOH-2	-
15	Acetone	1.75
16	Me-Et-ketone	1.33
17	Et-Et-ketone	1.20
18	Methyl acetate	1.68
19	Ethyl acetate	0.96
20	Propyl acetate	0.93
21	Chloroform	0.90
22	Dichloromethane	3.77
23	1, 1, 1-Trichloro-ethane	0.54
24	1, 2-Dichloropropane	0.78
25	Water	20.5
26	Formic acid	19.72
27	Acetic acid	23.0
28	Propionic acid	23.5
29	Butyric acid	24.0
30	Butanediol	23.0
31	Ethylene glycol	17.79
32	Diethylene glycol	24.0

groups, carboxyl > hydroxyl > carbonyl > ester.

Therefore, the orders found in selectivity, retention time and solubility parameter are precisely that of the hydrogen bonding capacity amongst functional groups. Branching of the hydrocarbon backbone in alcoholic molecules lowers the retention time as can be seen by comparison of propanol-1 and propanol-2, butanol-1 and butanol-2 or 2-methyl pro-

**Fig. 4.** Selectivity versus retention time for vapours listed in Table 4.

panol-1, and pentanol-1 and pentanol-2. Thus, the molecular structure of organic vapours affects the chromatography retention time and the membrane selectivity in a similar fashion. As shown in Fig. 4, the correlation between retention time and selectivity is excellent except few points which include several alcohols.

The experimental data for a silicone coated membrane are summarized in Table 5. The data include the feed mole fraction and the permeability for each organic (and water) vapour. Comparing Tables 3 and 5, the vapour permeability increased without exception from Table 3 to Table 5, meaning that the permeability of vapours from higher for the silicone coated membrane than the membrane without silicone coating. It is also interesting to note that the nitrogen permeation rate was below detectable limit with respect to the silicone coated membrane. Therefore, silicone coating enhanced both the permeability of vapours and the selectivity.

Table 5. Permeability Data for Silicone Coated Membrane

Organic vapour	Mole fraction (-)	$J_i \times 10^9$ (mol/s m ² Pa)
Pentane	0.455	5.40
Toluene	0.023	25.8
MeOH	0.093	54.5
EtOH	0.050	22.9
Acetone	0.169	10.1
Methyl acetate	0.137	14.7
Chloroform	0.173	6.25
Water	0.011	593

4. Conclusions

The following conclusions can be drawn from the experimental data.

(1) Membranes can be prepared from polyetherimide polymer by the phase-inversion technique to remove organic and water vapours from nitrogen stream. These membranes should have sufficiently small pore sizes but do not require silicone rubber coating.

(2) The transport of organic (and water) vapours through such membranes is governed by the sorption of the vapour to the membrane.

(3) The sorption is further governed by the hydrogen bonding capacity and the dispersion force.

(4) A membrane prepared by coating silicone rubber on a polyetherimide membrane of a relatively large pore size enhanced both vapour permeability and selectivity.

Acknowledgement

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Nomenclature

A : effective membrane area, m²
 J : permeability, mol/s m² Pa
 P : pressure, Pa
 Q : permeation flux, mol/s m²
 R : gas constant, 8.314 J/K Pa
 T : absolute temperature, K
 V : volumetric permeation rate, mL/min
 Y : mole fraction

Subscript

1 : feed
 3 : permeate
 A : acetone
 N : nitrogen
 i : vapour

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