

VOC vapor permeation through a liquid membrane using triethylene glycols

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Abstract

Supported-liquid membranes using four kinds of triethylene glycol (TEG) liquids were used for the VOC vapor removal from air. The supported-liquid membrane was a double-layer type, in which a liquid membrane was placed on a hydrophobic microporous membrane. This construction enabled the vacuum mode permeation of the VOC vapor through the TEG liquid membranes. In the experiments using a flat type membrane cell, the VOC vapors were effectively removed from the feed air. The TEG liquid membranes showed a comparable removal performance for VOC vapors to a silicone rubber membrane. The VOC removal performance of a liquid membrane was evaluated in terms of the vapor permeability. The resulting permeability of the VOC vapor and selectivity over air depended on the hydrophobic or hydrophilic property of the liquid membrane material. The hydrophobic TEG–dibutylether liquid membrane was effective for removing hydrocarbon vapors, benzene and toluene. On the other hand, the hydrophilic TEG liquid membrane had a selectivity for water-soluble vapors, methanol, acetone and ammonia. The selectivity for a VOC vapor of a TEG liquid membrane could be explained by the solubility or absorption of the vapor.

Keywords: Vapor permeation; VOC; Liquid membrane; Triethylene glycol

1. Introduction

The removal of volatile organic compounds (VOCs) from a waste gas stream or room air is needed to prevent air pollution and to maintain

human health. A membrane-based vapor permeation process has been expected to be used for the VOC vapor removal from air. The standard selection of a polymer membrane material for the VOC removal process is silicone rubber. Several VOC vapor removal processes have been

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developed using silicone rubber composite membranes and hollow-fiber membranes.

The liquid membrane is another promising membrane process for vapor separation besides polymer membranes. A liquid membrane may offer both a high permeability and high selectivity with a facilitated transport mechanism for gas or vapor separation. However, application of a liquid membrane for vapor and gas separation has not been developed due to the problem of durability. A supported-liquid membrane has not been able to be used under a transmembrane pressure condition. To solve this problem, a new type of liquid membranes, which is supported by another hydrophobic microporous membrane, was developed by the author [1]. The application of this double-layer liquid membrane using liquid triethylene glycol was reported for the separation of hydrocarbon vapor mixtures [2].

The permeabilities of air and VOC vapors through liquid membranes of triethylene glycol and related glycols were reported in this study.

The VOC removal performances from air by the liquid membranes were tested using a flat-type membrane cell. Resulted permeabilities were compared and were discussed in terms of solubility parameters, vapor absorption and liquid viscosity.

2. Liquid membrane and experiments

Fig. 1 shows the construction of a double-layer liquid membrane and the experimental setup for the vapor permeation experiments. The flat-type membrane cell had a 24 cm² permeation area. A liquid membrane, which had a double-layer construction, was placed on the porous stainless steel support. The top layer of the double-layer membrane was a conventional supported-liquid membrane. A hydrophilic treated polytetrafluoroethylene (PTFE) microporous membrane with a 1 μm pore size, 35 μm thickness and 83% porosity was soaked in a glycol liquid. The supported-liquid membrane was then placed on

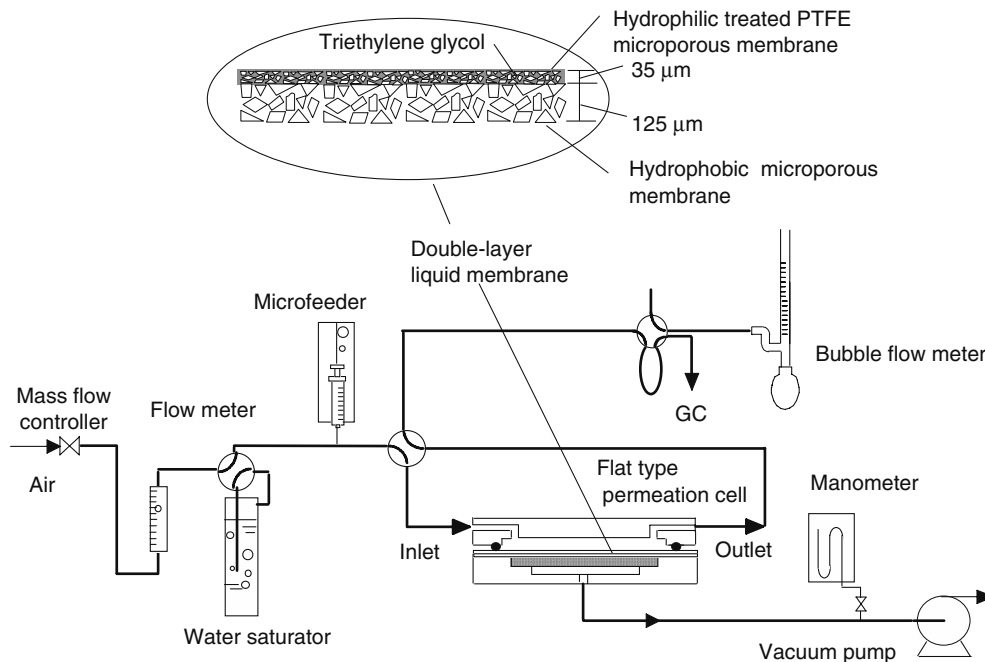


Fig. 1. Experimental setup for vapor permeation through TEG liquid membranes.

another hydrophobic microporous membrane, i.e., a Durapel membrane (Millipore). For the hydrophobic–hydrophilic interaction between a liquid and the Durapel membrane surface, the permeate side of the liquid membrane is able to be maintained under vacuum conditions. Under the transmembrane pressure condition, the VOC vapors absorbed on the surface of liquid membrane could be removed from the feed air.

The materials for the liquid membrane used in this study were hydrophilic and non-volatile liquids, which were triethylene glycol (TEG, $\text{CH}_2(\text{OH})\text{CH}_2\text{O}(\text{CH}_2\text{O})_2(\text{CH}_2)_2\text{OH}$), triethylene glycol monobutylether (TEG–MBE, $\text{CH}_3(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_2(\text{CH}_2)_2\text{OH}$), triethylene glycol dimethylether (TEG–DME, $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_3$), and triethylene glycol dibutylether (TEG–DBE, $\text{CH}_3(\text{CH}_2)_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_3\text{O}(\text{CH}_2)_3\text{CH}_3$).

A silicone rubber membrane ($\delta = 72 \mu\text{m}$) was also tested as a reference. The volatile organic compounds for the permeation experiments were methanol, acetone, benzene, toluene, ammonia and acetaldehyde.

For the permeation experiments, the feed air flow rate was constant at $180 \text{ cm}^3/\text{min}$. A micro-feeder for the VOC liquid feed was used to make air containing 0.05–2 mol% of the VOC vapor. Under several conditions, the feed air was also saturated by water vapor. The permeate side of the membrane cell was evacuated by a vacuum pump and its pressure was monitored by a manometer. The downstream pressure was maintained at 0.4 kPa. The vapor concentration in the inlet and outlet feed air of the membrane cell was analyzed by an FID gas-chromatograph.

After the experiments, a piece of the liquid membrane was weighed to estimate the thickness of the liquid layer. The thickness of the liquid membrane was 12–85 μm , which was varied by soaking.

The membrane VOC removal performance was measured from the difference between the inlet and outlet vapor concentrations of the

membrane cell. Permeability of a vapor through a liquid membrane was defined as follows:

$$Q_v = \frac{(\text{Permeation flux}) \delta}{(\text{Driving force}) A} = \frac{F_{\text{air}}(P_{\text{in}}/P_0 - P_{\text{out}}/P_0) \delta}{(P_{\text{in}} - P_{\text{out}})/\ln(P_{\text{in}}/P_{\text{out}}) A} \quad (1)$$

where δ is the liquid membrane thickness, A is the permeation area, F_{air} is the feed air flow rate, and P_0 , P_{in} , and P_{out} are the total pressure (atmospheric pressure), inlet vapor partial pressure and outlet vapor partial pressure, respectively. The driving force for the vapor is calculated using the logarithmic average of the inlet and outlet vapor partial pressure, while the partial pressure in the permeate is negligible.

The permeation rate of air through the liquid membrane was measured in other permeation modes, in which the feed-side pressure was elevated to 250 kPa and the permeate-side was opened to the atmosphere. The permeability of air was calculated from the permeation rate and the membrane thickness.

Additional measurements were also done regarding the properties of the membrane liquids. The vapor sorption amount of a glycol liquid was measured by weight increase of the liquid in air with a VOC vapor at atmospheric pressure. The sample weight was measured by a magnetic suspension balance (RUBOTHERM, Germany). The viscosity of the liquid was measured using a capillary viscometer.

All experiments and measurements were done at the room temperature, 293–296 K.

3. Results and discussion

3.1. VOC removal efficiency of the TEG liquid membranes

Fig. 2(a) shows the benzene vapor removal efficiency of TEG, TEG–dibutylether liquid membrane and silicone rubber membrane. The

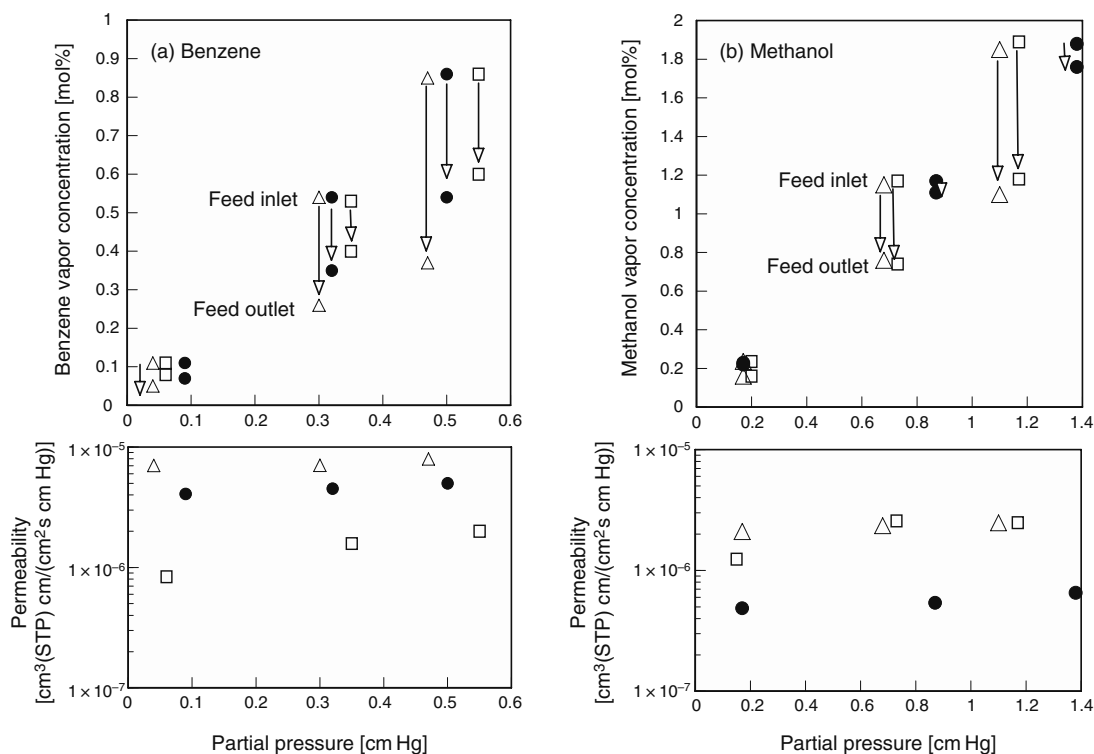


Fig. 2. Removing of VOC vapor in air by liquid membranes: (a) benzene vapor and (b) methanol. \square : TEG liquid membrane ($\delta = 21\text{--}35 \mu\text{m}$), Δ : TEG-DBE liquid membrane ($\delta = 35\text{--}64 \mu\text{m}$), \bullet : Silicone rubber ($\delta = 72 \mu\text{m}$).

decreasing vapor concentration on the feed air is indicated vs. average vapor partial pressure in the feed side. For example, the TEG liquid membrane reduced the benzene vapor concentration from 0.86% to 0.55% at the mean vapor partial pressure of 0.55 cm Hg in the feed air flow. The bottom figure shows the permeabilities evaluated from the decreasing the vapor concentration on the feed side.

The silicone rubber (SR) membrane effectively removes benzene vapor from air, while the removal performance of the TEG liquid membrane is lower than that of the SR membrane. When the membrane material is changed to TEG-DBE, the benzene removal efficiency increased when compared to that for the TEG liquid membrane. In the term of permeability, the silicone rubber has a higher permeability

than the TEG liquid membrane. On the other hand, the TEG-DBE liquid membrane had a higher permeability for the benzene vapor than the silicone rubber.

For the TEG liquid membrane materials, the dependence of the permeability on the partial pressure was low in the measured partial pressure range. Generally, the vapor permeability of polymer membranes increases depended on the vapor partial pressure, because the state of polymer changes from a dry state to a swelling state. Since the liquid membrane is originally in the swelling state, the dependency of the permeability is low, which is one feature of the liquid membrane.

Fig. 2(b) indicates the vapor removal efficiency for methanol vapor. In this case, silicone rubber shows a small removal effect for methanol vapor. On the other hand, the TEG liquid

membrane had a higher removal effect. The permeabilities of the methanol vapor through the liquid membranes are greater than that through the silicone rubber membrane.

The silicone rubber has a hydrophobic property, and the TEG is hydrophilic, while benzene is hydrophobic component and methanol is the hydrophilic component. These results suggest that the VOC removing efficiency may depend on a combination of the hydrophobic/hydrophilic nature between the membrane material and permeate vapor. Based on the above result, the TEG liquid membrane is effective for removing the hydrophilic vapor, methanol, from the air, and the TEG–DBE liquid membrane is effective for the hydrophobic vapor, benzene.

All the permeability data are shown in Fig. 3(a), which are evaluated from the vapor removal experiments by many combinations of the liquid membrane materials and vapors. The vapor permeability for the indicated components in the figure are shown vs. the molecular weight of the vapor components. The abscissa is only for convenience.

For the case of ammonia and acetaldehyde, which both have a lower molecular weight and hydrophilic VOC, a high permeability was obtained in the hydrophilic liquid membrane, such as TEG. For the benzene and toluene, which are both higher molecular weight and hydrophobic VOC compounds, a high permeability was obtained by the hydrophobic liquid membrane, such as the TEG–dibutylether, etc. In addition, the benzene permeability of the TEG–dibutylether is higher than that of the silicone rubber. After all, the combination of the hydrophilic and hydrophobic properties of the liquid membrane and vapor has a significant influence on the permeability.

For the application of a membrane for VOC removal from room air or exhaust air, it is important to know the effect of the water vapor in the air on the vapor permeation, because the TEG liquid membrane has a high water-vapor permeability

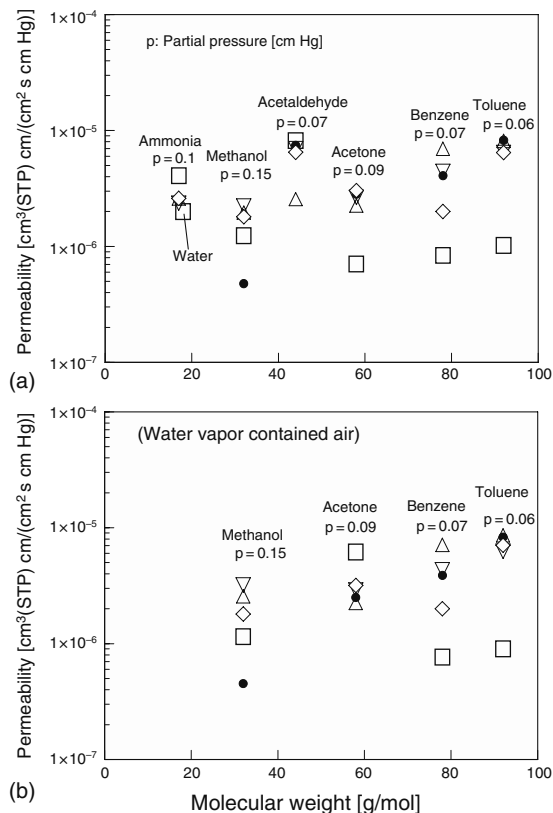


Fig. 3. Permeabilities of VOC vapors through TEG liquid membranes and silicone rubber. □: TEG liquid membrane ($\delta = 21\text{--}53 \mu\text{m}$), \triangle : TEG–DBE liquid membrane ($\delta = 12\text{--}85 \mu\text{m}$), ∇ : TEG–DME liquid membrane, ($\delta = 34\text{--}79 \mu\text{m}$), \diamond : TEG–MBE liquid membrane ($\delta = 23\text{--}35 \mu\text{m}$), ●: silicone rubber ($\delta = 72 \mu\text{m}$).

of water vapor and is applicable to a dehumidification process [1]. Fig. 3(b) shows the VOC permeability results by using the humidified air. The humidity of the feed air was 83–96%RH. The results show that there is little effect of the water vapor in air on the VOC permeation through the TEG and other liquid membranes.

3.2. Relation among vapor permeability, solubility and viscosity

Based on a solution-diffusion model, the gas or vapor permeability of a membrane will

depends on two factors, i.e., the solubility and diffusivity. Since a VOC vapor is condensable, its permeability mainly depends on the solubility in a membrane material. The solubility of both the vapor and liquid membrane material can be illustrated using the Hansen solubility parameters [3]. In this 3-D plot, the closer pair of a solvent and a polymer material is expected to have a higher solubility.

Fig. 4 is the 3-D plot of the Hansen solubility parameters for the VOC-components and liquid membrane materials in this study. The solubility parameters of the liquid membrane components in this study change from hydrophilic to hydrophobic in the order of TEG, TEG–dimethylether and TEG–dibutylether. The hydrophilic VOCs, such as methanol and acetone, are placed close to the hydrophilic liquid, TEG. The hydrophobic VOCs, such as benzene and toluene, are placed

close to the hydrophobic liquid, TEG–dibutylether. The solubility of a VOC vapor to a liquid membrane material is inversely proportional to the distance between them on this 3-D plot. The closer pair of the vapor and membrane liquid is expected to have a high solubility or absorption.

For the permeation of a condensable vapor, a high solubility means a high permeability. So, for example, it is expected to the benzene vapor that the permeability is high through the TEG–DBE liquid membrane and low through the TEG liquid membrane. This discussion may coincide with the result shown in Fig. 2(a). The results for the permeability of other vapors shown in Fig. 3 also show a general trend that the hydrophilic TEG liquid membrane has a high permeability for the water soluble vapors, and the hydrophobic TEG–DBE and TEG–DME liquid membrane have a high permeability for the hydrocarbon vapors.

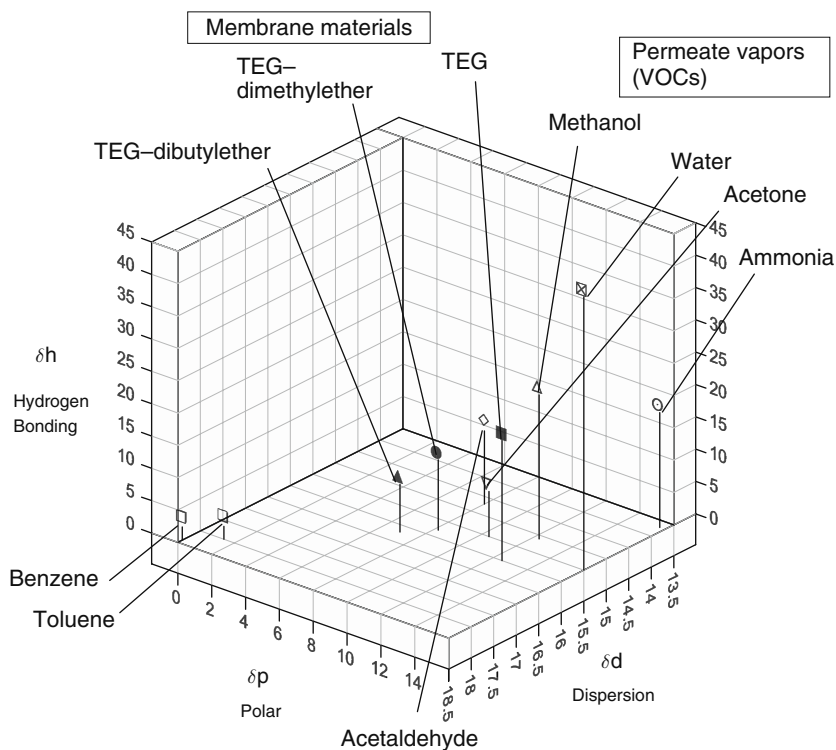


Fig. 4. Hansen solubility parameters of VOCs and the liquid membrane materials.

To examine the above discussion in detail, the permeability, separation factor, vapor absorption and viscosity are compared in Fig. 5 for selected vapors, i.e., benzene, methanol and water [1], and liquid membrane materials, TEG, TEG–MBE and TEG–DBE.

TEG has a higher viscosity than TEG–DBE which is indicated at the bottom of the figure. Since the liquid viscosity determines the diffusion coefficient of permeate in the liquid, the main trend of permeabilities of air and vapors are in inverse proportion to the liquid viscosity. For example, TEG of the highest viscosity has smallest air and vapor permeabilities among the liquid membrane materials.

The middle figures show the ideal separation factors and the vapor absorption of the liquids. The ideal separation factors of the membrane liquids are that for the methanol vapor over air and the benzene vapor over air. The vapor absorption into a liquid material at a partial vapor pressure is identical to the vapor solubility. One can see that the variation of vapor absorption for each vapor agrees with distance of solubility parameter between a vapor and a liquid membrane material as shown in Fig. 5. For example, as the TEG–DBE liquid is closest to benzene, its benzene absorption is highest among TEG liquids. On the other hand, the TEG liquid has a higher absorption for ethanol vapor than for benzene vapor. The separation factors of the liquid membranes for the ethanol and benzene vapor over air show a trend similar to the vapor absorption behavior. The higher separation factors are shown for the both hydrophobic benzene/TEG–DBE and the both hydrophilic methanol/TEG. These pairs also show higher vapor absorption. The ideal separation factor for vapor is normalized by the air permeability, the effect of diffusivity do not concern the separation factor. The solubility or absorption of the permeate

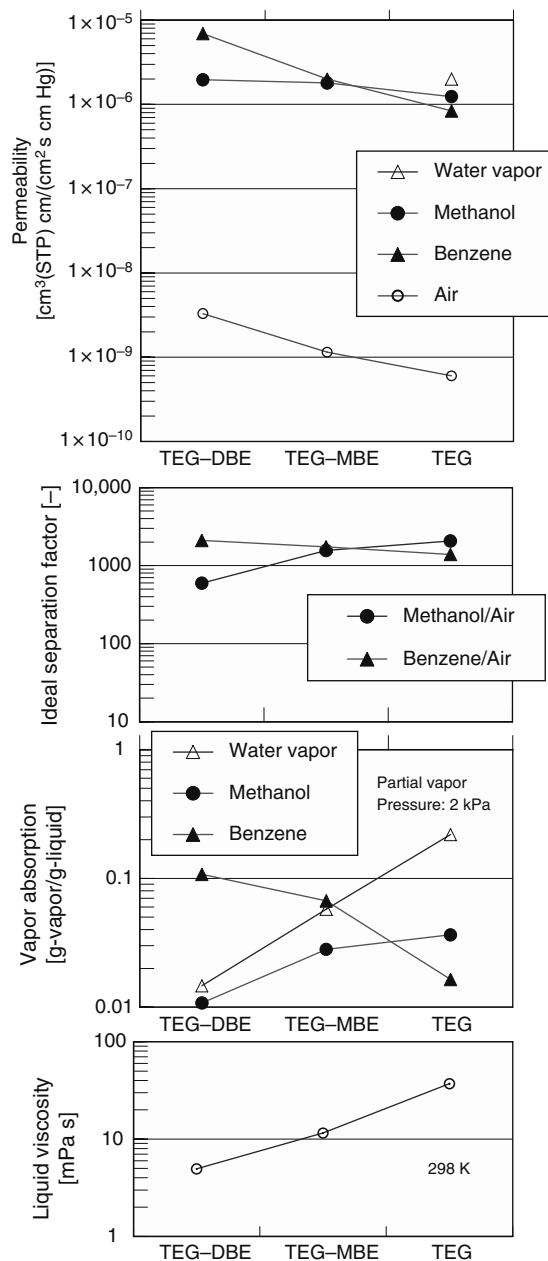


Fig. 5. Relation among vapor permeabilities, separation factors and vapor absorption of benzene, methanol and water vapor for TEG liquid membranes, and liquid viscosity.

component will govern the separation factor for the vapor over air.

4. Conclusions

Supported-liquid membranes using four kinds of triethylene glycol (TEG) liquids were used for the VOC vapor removal from air. The supported-liquid membrane was a double-layer type, in which a liquid membrane was placed on a hydrophobic microporous membrane. This construction enabled the vacuum mode permeation of the VOC vapor through the TEG liquid membranes. In the experiments using a flat type membrane cell, the VOC vapors were effectively removed from the feed air. The TEG liquid membranes showed comparable removing performance with a silicone rubber membrane for VOC vapors, benzene, acetone, methanol, etc. The VOC permeability and selectivity over air depended on the hydrophobic or hydrophilic property of the liquid membrane material. The TEG–dibutylether liquid membrane of hydrophobic was effective for removing hydrocarbon vapors, benzene and toluene. On the other hand

the hydrophilic TEG liquid membrane had selectivity for water-soluble vapors, methanol, acetone and ammonia. The selectivity for a VOC vapor of a TEG liquid membrane could be explained by the solubility or absorption of the vapor. The magnitude of the permeability for air and the VOC vapors was related to the viscosity of the liquid membrane materials. If one can make the appropriate material selection for a particular VOC component to be removed, a TEG liquid membrane will be applicable as a new VOC removal process.

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