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Toluene Vapor Removal Using an Inorganic/organic Double-Network Ion Gel Membrane

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Abstract

Tough gel membrane composed of a large amount of an ionic liquid and an inorganic/organic composite double-network (inorganic/organic DN ion gel membrane) was examined to remove toluene vapor from toluene vapor/N_2 mixed gas. The DN ion gel membrane with 80 wt% of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide showed higher toluene vapor permeability (more than 30000 barrer) and toluene vapor/N_2 permselectivity (690) than the supported ionic liquid membrane. The toluene vapor permeability and toluene vapor/N_2 permselectivity were maintained under pressurized condition. It was confirmed that the toluene vapor permeation was limited by intra-membrane diffusion of the dissolved toluene vapor.

Keywords

Separation membrane, ionic liquid, gel, inorganic/organic double-network, toluene separation

1. Introduction

According to the World Health Organization (WHO), the volatile organic compounds (VOCs) are organic chemicals in the boiling point range of 50–260 °C.[1, 2] Most of VOCs are regarded as toxic compounds for the environment and human beings. The most important problem associated with VOCs is the formation of tropospheric ozone. In the presence of sunlight, VOCs readily react with airborne compounds such as nitrogen oxides (NO_x) and form tropospheric ozone. This tropospheric ozone can cause skin and respiratory tract irritation, genetic modification, and cancer.[1, 3] VOCs emissions are involved in the atmospheric discharge of many chemical industrial processes and daily life activities such as varnishes, paintings, and photocopying. To control environmental pollution and maintain human health, and also gain the opportunity to reuse these expensive chemicals, VOCs have to be removed from air, N_2, or other waste gas streams in industrial processes. The conventional separation processes to address this issue includes adsorption, absorption, condensation, and incineration.[4-6] However, these processes suffer from the large energy consumption and high operating cost. Industrially viable VOCs-recovery processes demand more efficient and less costly operations. Membrane process, which has high efficiency, small footprint, easy scale up, simple operation, and low environmental impacts, offers the opportunities of energy savings and reuse of the VOCs.[7-10] Therefore, membrane separation has gained significant attention as an alternative technology for the recovery of VOCs in many industrial processes. VOCs treatment through membranes is particularly promising at relatively high VOCs concentration of more than 5000 ppm and relatively low gas flow rate of less than 100 – 1000 scfm.[11-13]

To separate VOCs from air and N_2 streams, especially when VOCs are the minor components, VOC-selective membranes are preferred; thus to remove most of VOCs from the feed stream less gas has to permeate the membrane, requiring relatively small membrane areas. In a membrane separation process, the VOC/gas mixture is allowed to flow on one side of the membrane at the feed pressure, while vacuum is applied to the other side to provide for the driving force in terms of VOC partial pressure difference. The VOCs selectively permeate through the membrane, results in a permeate highly enriched in VOCs. The small permeated gas stream is later condensed to recover the VOCs.

The rubbery polymer membranes, which are more permeable to vapors, have favorable performance for the separation of VOCs from non-condensable gases. Among the rubbery membranes, poly(dimethylsiloxane) (PDMS), silicone rubber and polyurethane membranes are primarily studied for this application and exhibited high permeability and high selectivity for VOCs.[7, 13-19] The rubbery membranes used for such a process are usually in the form of composite, wherein a thin and nonporous selective layer is coated on an appropriate porous polymeric substrate.[7, 15, 20-22]

Cha *et al.* investigated the separation of VOCs from N_2 at atmospheric pressure using microporous polypropylene hollow fibers with an ultrathin plasma-polymerized nonporous silicone skin of approximately 1 μm thickness on the outside surface.[7] They found that the permeance of VOCs through silicon membranes were highly concentration dependent. The permeance of toluene varied exponentially as a function of toluene concentration. They reported toluene permeability of less than 2500 barrers.[7]

Utilizing liquid membrane which offers high permeability and high selectivity is considered as a promising alternative to polymer membranes for VOCs separation.[23] Recently, supported liquid membranes (SLMs), which are porous membranes whose pores are impregnated with liquids, have been studied extensively. SLMs combine the extraction and stripping processes, and require much lower amount of liquid compared to solvent extraction process. However, the instability of SLMs has limited their commercial application.[24, 25] To overcome the instability issue, the volatile organic solvents in SLMs were replaced by ionic liquids (ILs) to prepare supported ionic liquid membranes (SILMs).[26, 27] ILs, which are molten salts that are liquid at low temperature (< 100 °C), have gained great attention for VOCs separation processes, as they are green solvents with negligible vapor pressure which eliminate solvent loss through vaporization and improve the stability of the liquid membrane.[1, 27] Besides, their unique properties including high chemical stability as well as high solubility for VOCs compared to other light gases make them particularly attractive as a VOCs separation medium in a membrane.[1, 26, 28] Several studies have reported SILMs with selective separation performance for VOCs.[29-31]

Although the replacement of volatile organic solvents with ILs solved instability drawback in SLMs associated with solvent loss through evaporation, SILMs are still suffer from poor stability at moderate trans-membrane pressure difference. In other words, ILs retained in a porous support membrane by weak capillary forces are easily leaked out from the support at moderate trans-membrane pressure difference of more than 200 kPa and cause significant decline in the performance of SILMs.[32, 33] For ILs to take their place as industrial VOCs separation media, the development of stable IL-based membranes is required.

Recently, ion gel membranes composed of polymer networks inside ILs, have gained considerable attention for gas separation applications, owing to their excellent stability.[34, 35] The polymer network of the ion gel with a volume concentration of a few percent acts like a sponge immobilizing the ionic liquids within the voids of 10 to 100 nm.[36] During last years, different kinds of ion gel membranes with high stability for gas separation applications have been developed.[33, 35, 37-

41] For VOC separation, some kinds of IL-based gel membrane including IL/polymer blend were developed.[42, 43] In spite of stable performance, most of the ion gel membranes showed gas separation performance much lower than the corresponding SILMs with the same IL.[35, 37-41, 44]

A straightforward approach to enhance the separation performance of ion gel membranes, is to increase the IL content in the gel. However, mechanical strength is generally significantly reduced by decreasing the network composition. A promising approach to overcome the trade-off between mechanical strength and solute diffusivity is to utilize tough gels.

Recently, we fabricated a novel ion gel with excellent mechanical strength.[45] The tough ion gel, termed double-network ion gel (DN ion gel), was consisted of an inorganic/organic composite network with a large amount of ILs. Because the DN ion gel can be prepared via a single-pot preparation process, the shape of the DN ion gel can be designed; i.e. a DN ion gel membrane can be easily prepared. The developed DN ion gel membranes consisted of the specific network and a large amount of an IL exhibited gas permeability and separation performance higher than SILMs with the same IL.[46, 47] To synthesize the DN ion gel membrane, the inorganic component was formed by thermally induced polycondensation of tetraethylorthosilicate (TEOS), and the polymer network was formed by UV-initiated free-radical polymerization of N,N-dimethylacrylamide (DMAAm). TEOS polycondensation resulted in the formation of silica nanoparticles which were inter-connected by weak physical interactions like hydrogen bonding and van der Waals forces to form a three-dimensional

(3D) silica particle network in the IL.[48-51] Since the fragile silica particle network acts as the sacrificial bond, it could dissipate the loaded energy by destruction during the application of a force. The excellent mechanical strength of the DN ion gel membrane overcomes the trade-off limitation on the increase of IL content and the decrease of mechanical strength. The toughness allows to increase the content of an IL in the DN ion gel membrane. In this work, we examined the potential of the tough ion gel membrane for toluene vapor removal from toluene vapor/N_2 mixed gas.

2. Experimental

2.1 Reagents

The chemicals used for the preparation of the DN ion gel membrane were summarized in Table 1. As an IL, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_4mim][Tf_2N]$) was used. It was purchased from Sigma-Aldrich Co. (St Louis, MO, USA). TEOS, purchased from Sigma-Aldrich Co. (St Louis, MO, USA) was used as a precursor of the inorganic network. For the polycondensation reaction of TEOS, formic acid was used as a solvolytic agent. Formic acid was purchased from Wako Pure Chemicals Industry Ltd. (Osaka, Japan). As the organic network monomer, cross-linker and photo-initiator, DMAAm, N,N'-methylenebis(acrylamide) (MBAA) and 2-oxoglutaric acid were used, respectively. DMAAm and 2-oxoglutaric acid were purchased from Tokyo

Chemical Industry Co. (Tokyo, Japan). MBAA was purchased from Wako Pure Chemicals Industry Ltd. (Osaka, Japan). All chemicals were used as received.

2.2 Preparation of inorganic/organic DN ion gel membrane

The inorganic/organic DN ion gel membrane was prepared based on the procedure written in elsewhere.[45, 47] The DN ion gel membrane was prepared by one-pot/two-step process. A certain amount of TEOS and formic acid for inorganic network formation was added in [C_4mim][Tf_2N] and agitated for more than 2 hours to dissolve them completely. DMAAm, MBAA, and 2-oxoglutaric acid for organic network formation were added in the TEOS/[C_4mim][Tf_2N] solution and agitated for several minutes to dissolve them. The given precursor solution was injected into a mold, which was consisted of two glass plates and PTFE spacer with a certain thickness. After sealing the mold, it was heated at 323 K for 48 hours to complete the hydrolysis followed by polycondensation reaction of TEOS to form the inorganic silica particle network. After 48 h heating, the mold was set under 365 nm UV light for more than 9 hours to form the PDMAAm network throughout the gel membrane via photo-initiated free radical polymerization. The given DN ion gel membrane was peeled off from the mold and heated at 373 K for more than 3 hours under vacuum to remove the remaining formic acid and generated ethanol through the polycondensation of TEOS. To check the ionic liquid holding property of the prepared DN ion gel membrane in toluene, we immersed the DN ion gel in liquid toluene for 24 hours and measured its weight after drying to remove the distributed toluene in the sample. The weight change of the ion gel membrane was calculated and it was found that the weight of the sample was hardly changed (less than 1 wt%). From the result it was found that the ionic liquid would hardly leaked from the gel matrix in toluene environment.

2.3 Preparation of inorganic/organic μ-DN ion gel membrane

In our previous paper, we developed two kinds of tough ion gel; one is a DN ion gel with higher toughness and the other is μ-DN ion gel. The μ-DN ion gel has completely different network from the DN ion gel. Although silica particles were percolated to form silica particle network in the DN ion gel, they were completely dispersed and no silica particle network was formed in μ-DN ion gel. To investigate the effect of inorganic silica particle network on the toluene permeability, we prepared the μ-DN ion gel membrane and evaluated its toluene permeation property. The μ-DN ion gel membrane was also prepared based on the procedure written in elsewhere.[45] The chemicals used for the preparation of μ-DN ion gel membrane was same as those for DN ion gel membrane preparation, which were shown in Table 1. The precursor solution consisted of [C_4mim][Tf_2N], TEOS, formic acid, DMAAm, MBAA and 2-oxoglutaric acid were injected in the mold. For the μ-DN ion gel membrane preparation, the PDMAAm network formation was firstly conducted by irradiation of 365 nm UV light for 9 hours. After UV light irradiation, the mold was heated at 323 K for 48 hours to complete the inorganic/organic composite network formation. The obtained μ-DN ion gel membrane was removed from the mold and heated at 373 K for more than 3 hours under vacuum to remove the remaining formic acid and generated ethanol through the polycondensation of TEOS.

2.4 Preparation of supported IL membrane (SILM) containing [C_4mim][Tf_2N]

To compare the toluene vapor permeabilities of the DN ion gel membrane and SILM, we prepared SILM by the following procedure. The commercially available hydrophilic PTFE membrane was used as a support. It was purchased from Toyo Roshi Kaisha (Japan). The support membrane had 0.1 μm of nominal pore size, 27 μm of thickness and 71% of porosity. The support membrane was immersed in [C_4mim][Tf_2N]. The air in the support was completely removed by vacuum for more than 1 hour. The membrane was then removed from [C_4mim][Tf_2N] and the remaining IL on the surface was carefully wiped off. As prepared SILM was used to measure the permeabilities of toluene vapor and N_2 at 303 K under atmospheric pressure condition.

2.5 Permeabilities of toluene vapor and N_2

The schematic diagram of the apparatus used to measure the permeabilities of toluene vapor and N_2 is shown in Figure 1. The membrane was sealed in a stainless steel permeation cell with the effective membrane area of 9.62 cm^2. The permeation cell was equipped in a thermostat oven in which temperature was maintained at 303 K. Into the upper side of the permeation cell, N_2 gas with a certain partial pressure of toluene was introduced at a constant N_2 flow rate of 200 cm^3/min. The toluene concentration in the stream was controlled by mixing N_2 flows with and without toluene vapor. The N_2 without toluene vapor was used as a diluent. The N_2 with toluene vapor was prepared by bubbling a certain flow rate of N_2 through the toluene tank. The temperature of the toluene tank was maintained at 280 K. The toluene was continuously stirred to accelerate toluene vaporization. We measured the toluene concentration in the mixed N_2 flow and made calibration curve. The calibration curve showed linear relationship, which indicated that the toluene partial pressure could be controlled by changing the flow rates of N_2 for bubbling and that used as a diluent. The N_2 flow rates were controlled with mass flow controllers (Hemmi Slide Rule Co., Ltd., Japan). In addition, in every experiment, the toluene composition in the feed gas was checked by a gas chromatograph (GC-2014, Shimadzu Co.) equipped with a flame ionization detector (GC-FID). On the other hand, into the lower side of the permeation cell, pure helium was introduced as a sweep gas. Some of the toluene vapor and N_2 permeated through the membrane were swept by the sweep gas flow and introduced to a gas chromatograph (GC-8A, Shimadzu Co.) equipped with a thermal conductivity detector (GC-TCD) to analyze the N_2 composition and then introduced to the GC-FID to measure the toluene composition. For each measurement, the N_2 and toluene peak area were continuously measured. It was confirmed that the steady state was achieved within 100 min.

The experimental conditions of the toluene vapor and N_2 permeation test are summarized in Table 2.

3. Results and discussion

3.1 Toluene vapor permeability of SILM containing [C_4mim][Tf_2N]

The toluene vapor permeability of the SILM containing [C_4mim][Tf_2N] was measured at 303 K under atmospheric pressure condition. The partial pressure of toluene vapor was maintained at 0.5 kPa. The permeabilities of toluene vapor and N_2 through the SILM were 8277±109 barrer and 42±7 barrer, respectively. The toluene vapor/N_2 permselectivity was 197. It was reported that the SILM consisted of 127 μm polyvinylidene fluoride membrane as the support and 1-butyl-3-methylimidazolium triflate ([C_4mim][OTf]) as the IL showed about 5×10^{-9} mol/(m^2sPa) of benzene vapor permeance,[31] which is correspond to about 2000 barrer of permeability. The order of the reported benzene vapor permeabilities was same as the toluene vapor permeability of the SILM we prepared. In addition, regarding N_2 permeability, we previously reported the N_2 permeability of an SILM containing [C_4mim][Tf_2N] for CO_2/N_2 binary system at 303 K under atmospheric pressure condition[46, 47] and the obtained N_2 permeability was 35 barrer. This is almost same to that obtained for the SILM prepared in this work. From these comparison, it can be said that the permeabilities of toluene vapor and N_2 for the SILM prepared in this work were believable and [C_4mim][Tf_2N] is promising IL as a separation medium of an aromatic hydrocarbon from light gases.

3.2 Permeabilities of toluene vapor and N_2 through the inorganic/organic DN ion gel membranes

3.2.1 Effect of toluene vapor partial pressure on toluene vapor permeability

To confirm the permeation mechanism of toluene vapor across the inorganic/organic DN ion gel membrane, the effect of toluene vapor partial pressure on the toluene vapor permeability was investigated. When gas and vapor permeate across the membrane based on solution-diffusion mechanism, the permeability can be expressed by the product of the diffusion coefficient and the concentration gradient of the dissolved gases and vapors. If the IL absorb the gas and vapor based on Henry's law, the permeability should be independent on the partial pressure of the gas and vapor in the feed stream. It is reported that toluene was absorbed in an imidazolium-type IL, decyl-3-Methyl-Imidazolium bis(trifluoromethylsulfonyl)imide, according to Henry's law.[52] Therefore, it was expected that the toluene vapor would permeate through the DN ion gel membrane according to solution-diffusion mechanism; i.e. the toluene vapor permeability would be independent on the toluene vapor partial pressure. As clearly shown in Figure 2, the toluene vapor permeability as well as the N_2 permeability was not dependent on the toluene vapor partial pressure. This result indicated that the toluene vapor was permeated through the DN ion gel membrane based on solution-diffusion mechanism. Comparing the permeation performances of the DN ion gel membrane and the SILM, the toluene vapor permeability and toluene vapor/N_2 selectivity of the DN ion gel membrane with 80 wt% of [C_4mim][Tf_2N] were much higher than those of the SILM. An interesting result is shown in the permselectivity of toluene vapor/N_2. Although the SILM showed about 200 of toluene vapor/N_2 permselectivity, the inorganic/organic DN ion gel membrane indicated about 450 of the permselectivity. In general, the permselectivity of light gases through an IL-base membrane was governed by the solubility selectivity because the viscosity of an IL is high and diffusion coefficient of dissolved gases in an IL is almost same.[44] The trend is also confirmed in ion gel membranes; i.e. the permselectivities of CO_2/N_2 for ion gel membranes were almost the same as that for the SILMs with the same IL.[46, 47] However, in the case of toluene vapor/N_2 separation, the permselectivities of toluene vapor/N_2 for the ion gel membrane was more than twice of that for the SILM. Because the DN ion gel membrane and the SILM had same IL and used under same condition, the concentration of toluene absorbed in the two types of membranes would be the same. Therefore, it is considered that the diffusivity of toluene in the DN ion gel membrane would become higher than that in the SILM. It could be considered that a specific pathway for toluene permeation would be in the DN ion gel membrane. In the investigation on the effect of the composition of DN ion gel membrane, we discuss about the toluene pathway.

3.2.2 Effect of the component in the DN ion gel membrane

The permeation test of toluene vapor and N_2 through the inorganic/organic DN ion gel membranes containing different amount of [C_4mim][Tf_2N] was conducted. The results are shown in Figure 3. The permeabilities of toluene vapor and N_2 were monotonically increased with the increase of the IL content of the inorganic/organic DN ion gel membranes. The increase of the IL content means the decrease of the network composition of the gel membrane. Because the gel network becomes a significant diffusion resistance of the gas molecules in the gel membrane, the permeabilities of toluene vapor and N_2 were increased with the increase of the IL content. On the other hand, regarding the toluene vapor/N_2 selectivity, the selectivity was also monotonically increased up to 550 with the increase of the [C_4mim][Tf_2N] content in the DN ion gel membrane. This enhancement of the toluene vapor/N_2 selectivity indicated that the enhancement degree of the permeabilities of toluene vapor and N_2 was different. Comparing the enhancement degree of the permeabilities of toluene vapor and N_2 of the DN ion gel membranes containing 50 wt% and 80 wt% of [C_4mim][Tf_2N], the enhancement degree of toluene vapor permeability was about 800% although that of N_2 permeability was only 300%. The slight increase of the N_2 permeability would be due to the enhancement of diffusivity of the dissolved N_2 in the gel membrane. On the other hand, the increase of the toluene vapor permeability would be caused by an additional enhancement of diffusivity of dissolved toluene in the DN ion gel membrane. One possibility is the formation of diffusion path for toluene in the DN ion gel membrane, as described above. There are three possible diffusion paths of toluene in the DN ion gel; (1) microstructure in [C$_4$mim][Tf$_2$N], (2) silica particle network, and (3) PDMAAm chain. The reasonable diffusion pathway for toluene permeation in the DN ion gel membrane was investigated by changing the inorganic/organic network structure of the DN ion gel membrane.

Firstly, the effect of cross-linking degree of the PDMAAm network in the DN ion gel membrane was investigated. In general, the gas permeability is affected by the cross-linking degree of the gel membrane; i.e. the highly cross-linked gel membrane shows lower gas permeability and vice versa.[53] As reported in our previous work,[47] the permeability of light gases through the DN ion gel membrane was also clearly affected by the cross-linking degree of the PDMAAm network; i.e. the CO_2 and N_2 permeabilities were monotonically decreased with the increase of cross-linking degree of the PDMAAm network. The enhancement of the cross-linking degree of PDMAAm network leads to the decrease of the diffusivity of the dissolved gas species in the DN ion gel membrane. If the toluene vapor permeation also affected simply by diffusivity in the DN ion gel membrane, the permeability would be also decreased with the increase of the cross-linking degree of the PDMAAm network. The effect of cross-linking degree on the toluene vapor and N_2 permeabilities are shown in Figure 4. As shown in Figure 4, although the N_2 permeability was slightly decreased with the increase of the cross-linking degree of PDMAAm, the toluene vapor permeability was independent on the cross-linking degree of PDMAAm network (32417±1919 barrer). As the result, the toluene vapor/N_2 permselectivity was increased with the increase of cross-linking degree of PDMAAm network. Because the IL content in the DN ion gel membrane used in this investigation was constant at 80 wt%, the absorption amount of toluene vapor in the DN ion gel membranes is not affected by cross-linking degree.

The independence of the toluene vapor permeability suggested that the toluene diffusivity in the ion gel membrane was hardly affected by the PDMAAm network. In other words, it could be suggested that the inorganic silica particle network would be a diffusion pathway for the toluene dissolved in the ion gel membrane. To confirm the possibility of inorganic pathway for toluene vapor permeation, we examined the toluene vapor permeation using a μ-DN ion gel membrane. In our previous research, it was confirmed that the inorganic/organic DN ion gel and the inorganic/organic μ-DN ion gel have completely different networks.[45] The silica particles in the DN ion gel were percolated and formed network. On the other hand, in the μ-DN ion gel, the silica particles were almost completely dispersed and formed no network structure. If the silica particle network became the permeation pathway of toluene in the ion gel, the toluene vapor permeability of the μ-DN ion gel membrane would be lower than the DN ion gel membrane. We prepared the μ-DN ion gel membrane containing 80 wt% of [C_4mim][Tf_2N]. The composition of the TEOS/DMAAm was 5 mol/mol and the MBAA concentration was 0.5 mol% in DMAAm basis. The toluene vapor permeability of the μ-DN ion gel membrane was 32960 barrer, which was almost same as that of the DN ion gel membrane with the same [C_4mim][Tf_2N] content and network composition (ca. 32000 barrer). From this result, it was suggested that the silica particle network would not be a pathway of toluene permeation in the DN ion gel membrane.

It is well known that the ILs make microstructure and form nanoscale segmentation.[54-56] It is also reported that when small amount of water was co-existed in an IL, the water molecule could be mainly distributed in a polar domain in the IL.[56] Because the imidazolium ring in the [C_4mim][Tf_2N] interacts with toluene though the C-H···π type of hydrogen bonding,[57, 58] the nanoscale domain of the imidazolium ring might be the pathway of toluene. As the result, the toluene vapor permeability was increased with the increase of the [C_4mim][Tf_2N] content in the gel. On the other hand, the toluene vapor permeability would be independent on the cross-linking degree of PDMAAm network because the [C_4mim][Tf_2N] content in the DN ion gel membranes used in this investigation was constant. On the other hand, N_2 would randomly diffuse in the gel matrix because N_2 has no interaction with the gel networks. In this case, the cross-linked PDMAAm network prevented the N_2 diffusion. Therefore, the N_2 permeability was dependent on the cross-linking degree of PDMAAm network. Because of the decrease of N_2 permeability, the toluene vapor/N_2 selectivity was increased with the increase of cross-linking degree of the DN ion gel membrane. As the result, the DN ion gel membrane marked about 690 of toluene vapor/N_2 selectivity while maintaining the high toluene vapor permeability of ca. 32000 barrer.

In the previous work, we also indicated that the light gas permeabilities of the DN ion gel membrane was dependent on the composition of inorganic and organic networks.[47] The CO_2 and N_2 permeabilities were increased with the increase of the inorganic network composition in the DN ion gel membrane with a constant IL content. The results indicated that the PDMAAm network became a significant diffusion resistance of the light gases in the gel membrane. Furthermore, it could be said that the inorganic silica particle network becomes no diffusion resistance for the light gas molecules in the DN ion gel membrane. In this study, we also examined the effect of the inorganic/organic network composition on the toluene permeability. As shown in Figure 5, although the N_2 permeability was monotonically increased with the decrease of the organic/inorganic network composition, the toluene vapor permeability indicated almost same value. This result again suggested that the toluene would mainly permeate through the diffusion path formed in $[C_4mim][Tf_2N]$ and independent on the gel network in the DN ion gel membrane. Because the N_2 permeability was decreased with the increase of organic/inorganic network composition, the toluene vapor/N_2 selectivity reached about 680 by increasing the organic/inorganic network composition up to 9 mol/mol. Regarding the diffusion path formed in $[C_4mim][Tf_2N]$, the obvious evidence is not yet obtained. Further detailed investigation is necessary to clarify this path more details.

In terms of toluene permeability and toluene/N_2 selectivity, ion gel membrane with high ionic liquid content and crosslinking degree and the larger amount of inorganic network is desirable while the mechanical strength of ion gel membrane decreases. This means lower ionic liquid content, crosslinking degree and inorganic give rise to the better mechanical strength of ion gel membrane. According to obtained experimental results, an ion gel membrane consisting of 80 wt% of ionic liquid, 1.5 mol% of crosslinker, and DMAAm/TEOS ratio of 7 is a desirable network structure that not only possesses high toluene/N_2 separation performance but also good mechanical strength.

Comparing the performances of toluene vapor separation between the inorganic/organic DN ion gel membrane and previously reported membranes is summarized in Table 3. The maximum performance of the inorganic/organic DN ion gel membrane containing investigated in this study showed about 32000 barrer of toluene vapor permeability and 690 of toluene vapor/N_2 selectivity. The 32000 barrer of toluene permeability was higher than the other ionic liquid-based VOC separation membranes and the 690 of toluene vapor/N_2 selectivity was higher than the polymer membranes. From the comparison, it could be said that the inorganic/organic DN ion gel would be a promising material for toluene vapor separation.

In addition, we surveyed the Henry's constants for the absorption of toluene and N_2 into [C_4mim][Tf_2N]. Bedia *et al.* reported that the Henry's constant of toluene at 298 K, which was estimated by the COSMO-RS method, was 0.0073 MPa.[52] Carlisle *et al.* reported that the Henry's constant of N_2 at 313 K, which was determined by group contribution approach, was 970 atm.[59] According to Bedia *et al.*, the density of [C_4mim][Tf_2N] at 303 K was 1432 kg/m^3.[47] From these values, the solubilities of toluene and N_2 in [C_4mim][Tf_2N] could be calculated as about 470 mol/(m^3kPa) and about 0.035 mol/(m^3kPa), respectively. On the other hand, the diffusion coefficients of toluene and N_2 in [C_4mim][Tf_2N], which were calculated using the Wilke-Chang equation were about 7.1×10^{-11} m^2/s and about 1.6×10^{-10} m^2/s, respectively. Based on the solubilities and diffusion coefficients, the ideal permeabilities of toluene and N_2 of [C_4mim][Tf_2N]-based membrane could be estimated as ca. 100000 barrer and ca. 17 barrer, respectively. The ideal toluene/N_2 permselectivity estimated from the permeabilities was about 6000. These ideal toluene permeability and toluene/N_2 selectivity are greater than those of DN ion gel membranes obtained in this work. Thus, it was expected that enhancement of the toluene permeability and toluene/N_2 selectivity could be achieved by further optimization of the DN ion gel membrane.

3.3 Pressure resistance of the inorganic/organic DN ion gel membrane

The most important feature of the inorganic/organic DN ion gel was the extraordinary high mechanical strength. Because the mechanical strength of the DN ion gel was very high (compressive fracture stress was more than 25 MPa), the DN ion gel membrane had good pressure resistance. Figure 6 shows the effect of trans-membrane pressure difference on the toluene vapor and N_2 permeabilities and toluene vapor/N_2 permselectivity of the DN ion gel membrane. The high toluene vapor permeability and the N_2 barrier property were maintained under high trans-membrane pressure condition of 400 kPa. As the result, the DN ion gel membrane sustained high toluene vapor/N_2 selectivity under high trans-membrane pressure condition. Owing to the excellent mechanical strength and the good IL holding property of the DN ion gel, the DN ion gel membrane was not broken under pressurized condition at all. This robustness allows us to use the DN ion gel membrane in wide industrial application.

3.4 Effect of membrane thickness

To confirm the rate-determining step of toluene vapor permeation, the effect of the thickness of the DN ion gel membrane on the toluene vapor permeance was investigated. Figure 7 shows the relationship between the toluene vapor permeance and the inversed membrane thickness. The results for N_2 permeation was also shown in this figure. As clearly shown in this figure, the permeance of toluene vapor as well as N_2 showed proportional relationship with the inversed membrane thickness. These results indicated that the rate-determining step of both toluene vapor and N_2 permeations was trans-membrane diffusion. Therefore, it is expected that the toluene vapor permeance of the DN ion gel membrane could be increased by using the ion gel membrane with thinner thickness.

5. Conclusions

An inorganic/organic DN ion gel membrane was used for removal of toluene vapor in N_2 stream as an example of VOC separation application. Because of the good affinity of the imidazolium type cation with toluene, the DN ion gel membrane with a large amount of [C_4mim][Tf_2N] showed high toluene vapor permeability and good toluene vapor/N_2 permselectivity. The toluene vapor permeability of the DN ion gel membrane was higher than that of SILM with the same IL ([C_4mim][Tf_2N]) while the N_2 permeability was maintained low level. The permselectivity of toluene vapor/N_2 reached up to 690 by optimization of the inorganic silica particle network and the organic PDMAAm network. Owing to the excellent mechanical strength and the good IL holding property of the DN ion gel, the DN ion gel membrane maintained the high toluene vapor permeability and good toluene vapor/N_2 permselectivity under pressurized condition. Because the rate-determining step of the toluene vapor permeation was diffusion of the dissolved toluene vapor across the gel membrane, it can be expected that the higher toluene vapor permeance can be achieved using thinner DN ion gel membrane. The reduction of the thickness of the DN ion gel membrane is our next challenge.

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Figure captions

Figure 1 Schematic diagram of the toluene vapor permeation setup

Figure 2 Toluene vapor partial pressure dependence on toluene vapor and N_2 permeabilities of the inorganic/organic DN ion gel membrane. The DN ion gel membrane was prepared with 5 mol/mol of DMAAm/TEOS network composition and 0.5 mol% MBAA in DMAAm basis. The $[C_4mim][Tf_2N]$ content in the DN ion gel membrane was 80 wt%. The thickness was 139 μm.

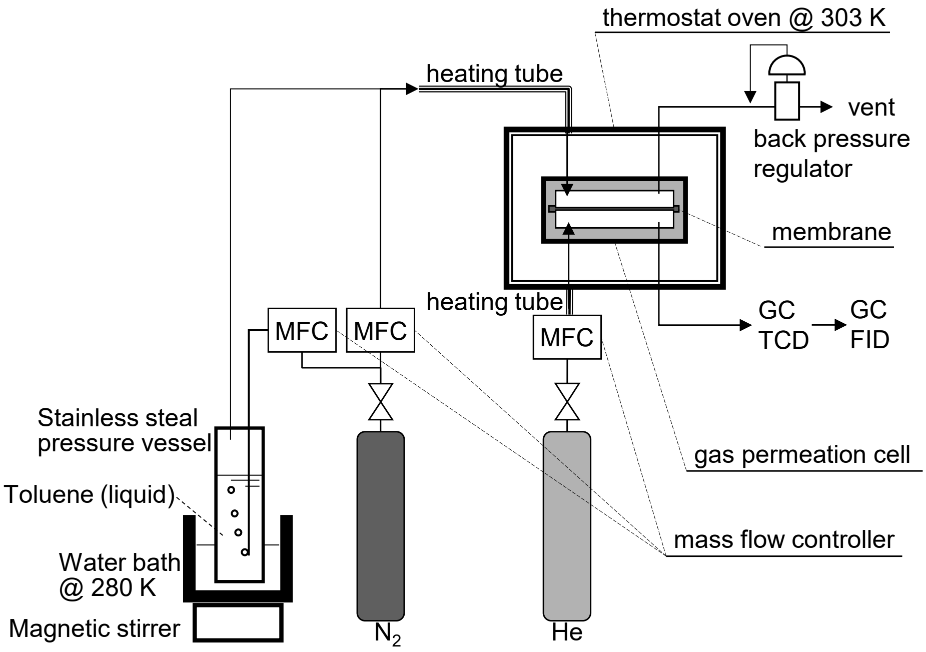
Figure 3 Effect of IL content in inorganic/organic DN ion gel membrane on toluene and N_2 permeabilities. The DN ion gel membranes with different IL contents were prepared with 5 mol/mol of DMAAm/TEOS network composition and 1.0 mol% MBAA in DMAAm basis. The thickness of the DN ion gel membranes were about 150 μm.

Figure 4 Effect of cross-linker (MBAA) composition of the inorganic/organic DN ion gel membrane on toluene and N_2 permeabilities. The ion gel membranes with different cross-linking degrees were prepared with 5 mol/mol of DMAAm/TEOS network composition. The IL content in the membrane was 80 wt%. The thickness of the DN ion gel membranes were about 200 μm.

Figure 5 Effect of monomer (DMAAm) composition of the inorganic/organic DN ion gel membrane on toluene and N_2 permeabilities. The ion gel membranes with different inorganic/organic network compositions were prepared with 1 mol% MBAA in DMAAm basis. The IL content in the membrane was 80 wt%. The thickness of the DN ion gel membranes were about 200 μm.

Figure 6 Effect of trans-membrane pressure difference on toluene vapor and N_2 permeabilities of the inorganic/organic DN ion gel membrane. The DN ion gel membrane was prepared with 5 mol/mol of DMAAm/TEOS network composition and 0.5 mol% MBAA in DMAAm basis. The thickness of the DN ion gel membranes were about 200 μm.

Figure 7 Effect of thickness of the inorganic/organic DN ion gel membrane on toluene and N_2 permeances. The ion gel membranes containing 80 wt% of $[C_4mim][Tf_2N]$ with different thicknesses were prepared with 5 mol% of TEOS/DMAAm network composition and 0.5 mol% of MBAA in DMAAm basis.



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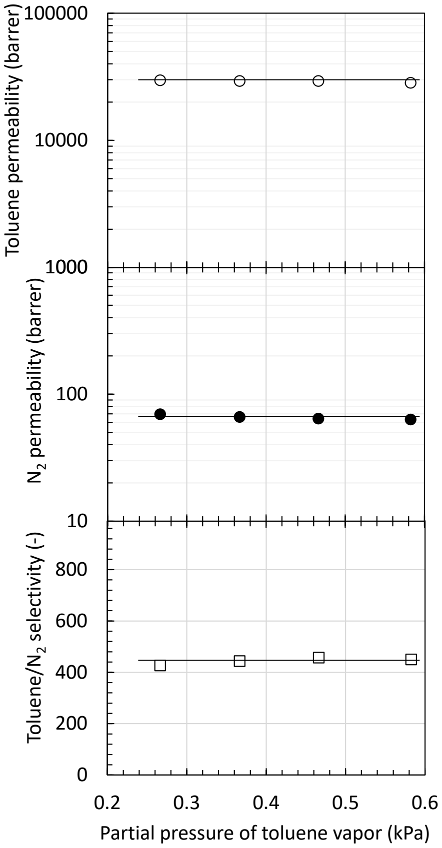

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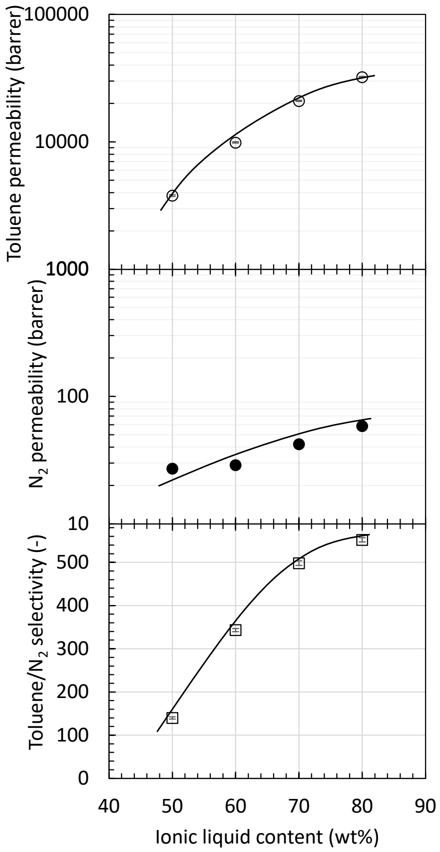

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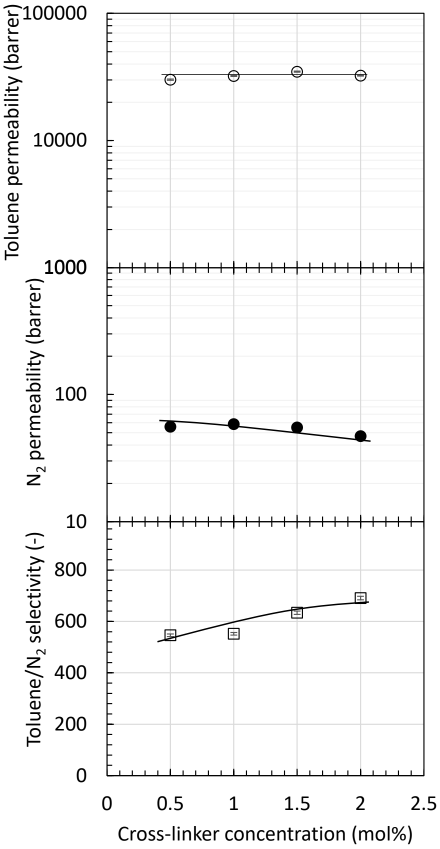

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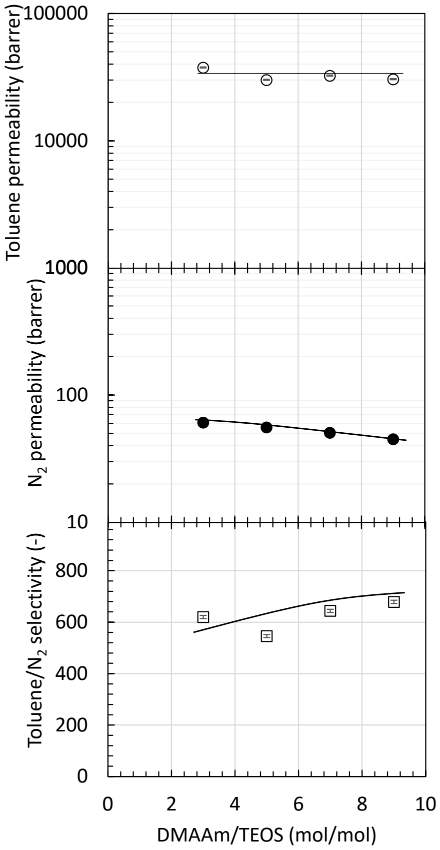

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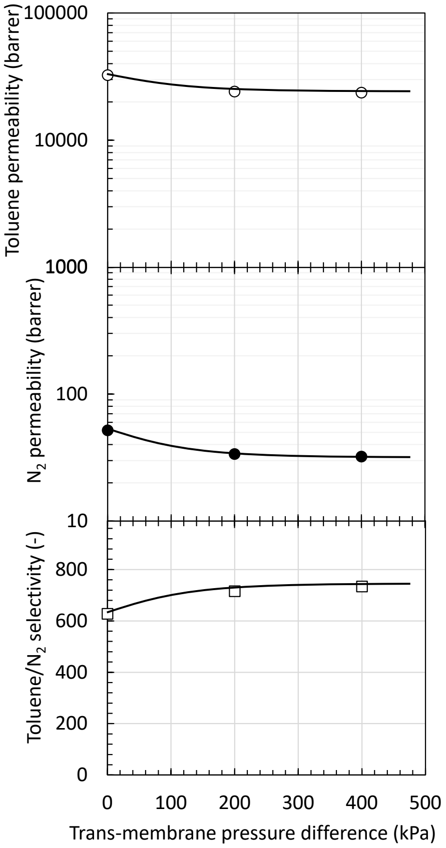

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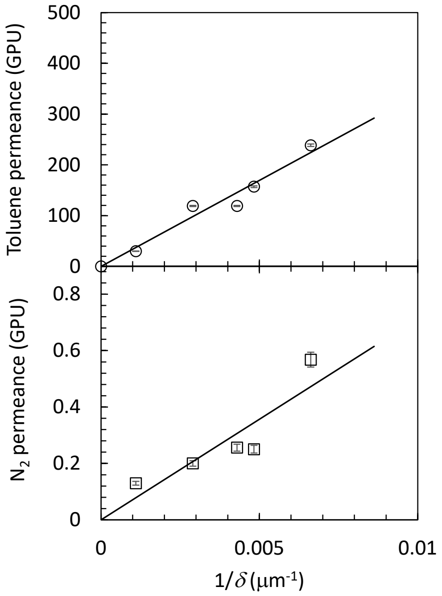

Figure 7 Effect of thickness of the inorganic/organic DN ion gel membrane on toluene and N_2 permeances. The ion gel membranes containing 80 wt% of [C_4mim][Tf_2N] with different thicknesses were prepared with 5 mol% of TEOS/DMAAm network composition and 0.5 mol% of MBAA in DMAAm basis.

Table 1 Reagents and the amount used for preparation of the inorganic/organic DN and μ-DN ion gel membranes composed of 5 mol/mol of the inorganic/organic network composition, 0.5 mol% of cross-linker for the organic network and 80 wt% of [C_4mim][Tf_2N]

Reagent	Amount
[C_4mim][Tf_2N]	8.0 g
TEOS	0.59 g
Formic acid	7.8 mol/mol-TEOS
DMAAm	1.41 g
MBAA	0.4 mol% in DMAAm basis
2-oxoglutaric acid	0.1 mol% in DMAAm basis

Table 2 Experimental conditions for toluene vapor permeation test

Conditions	Standard condition	Partial pressure dependence	Total pressure dependence
Temperature	303 K	303 K	303 K
Feed side			
Feed gas	Toluene/N_2 mixture	Toluene/N_2 mixture	Toluene/N_2 mixture
Total pressure at feed side	atmospheric	atmospheric	100, 300, 500 kPa
Partial pressure			
Toluene	0.5 kPa	0.3, 0.4, 0.5, 0.6 kPa	0.5 kPa
N_2	100 kPa	100 kPa	100, 300, 500 kPa
Flow rate of N_2	Total 200 sccm	Total 200 sccm	Total 200 sccm
for toluene bubbling	66 sccm	40, 53, 66, 79, 92 sccm	66, 52, 50 sccm
for diluent	134 sccm	balance	balance
Permeate side			
Sweep gas	helium	helium	helium
Total pressure at permeate side	atmospheric	atmospheric	atmospheric
Flow rate of helium	40 sccm	40 sccm	40 sccm

Table 3 Comparison of the performances of toluene vapor separation between the inorganic/organic DN ion gel membrane and previously reported membranes

Aromatic VOC/ light gas	VOC permeability (barrer)	VOC/light gas selectivity	Membrane	Reference
Toluene/N_2	32000	690	DN ion gel membrane	This work
Toluene/N_2	3500	194	IL/polymer blend	[42]
Benzene/N_2	18000	4700	SILM	[31]
Toluene/N_2	53100	16	PDMS membrane (PDMS made with 10:1 prepolymer/cross-linker ratio)	[18]
Toluene/N_2	49000	110	PDMS membrane (PDMS made with 10:2.5 prepolymer/cross-linker ratio)	[18]
Toluene/N_2	2000	ca 250	PEO-PPO-PEO based polyurethane membrane (sample code: PU-71-0.25)	[19]
Toluene/N_2	4000	ca 270	PEO-PPO-PEO based polyurethane membrane (sample code: PU-52-0.75)	[19]
Toluene/N_2	4000	ca 275	PEO-PPO-PEO based polyurethane membrane (sample code: PU-62-0.50)	[19]
Toluene/N_2	8000	ca 50	PTMO/PDMS based polyurethane urea membrane (sample code: PUU-54-1.00)	[19]
Toluene/N_2	8000	ca 65	PTMO/PDMS based polyurethane urea membrane (sample code: PUU-51-0.58)	[19]
Toluene/N_2	5000	ca 75	PTMO/PDMS based polyurethane urea membrane (sample code: PUU-50-0.28)	[19]
Toluene/N_2	4000	ca 80	PTMO/PDMS based polyurethane urea membrane (sample code: PUU-49-0.10)	[19]