Permeation of Nonaqueous Solution through Organic/Inorganic Hybrid Nanoporous Membranes

Toshinori Tsuru, Hiroyasu Kondo, Tomohisa Yoshioka, and Masashi Asaeda
Dept. of Chemical Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

DOI 10.1002/aic.10092

Keywords: nanofiltration, ultrafiltration, nanoporous membranes, inorganic membranes, organic–inorganic membranes, viscous flow

Introduction

Separation membranes have been developed for applications in aqueous systems such as desalination and drinking water treatment. It has recently been proposed that membrane separation could be expanded to a variety of applications such as the separation of nonaqueous solutions and the filtration of nonaqueous solutions. Several types of polymeric membranes have been investigated for possible use in the regeneration of a wide variety of solvents (Bhanushali et al., 2001; Machodo et al., 2000; Whu et al., 2000). However, such polymeric membranes do not cover all the potential applications. On the other hand, ceramic porous membranes, which have excellent resistance to most organic solvents and can be used over a wide temperature range, have the potential for use in the separation and filtration of nonaqueous solutions (Tsuru, 2001a; Tsuru et al., 2000a, 2001b).

From the perspective of surface chemistry, most ceramic membranes have hydrophilic properties because the surface of the metal oxide is hydrated, thus forming hydroxyl groups such as silanol (–SiOH) groups (Brinker and Scherer, 1990). On the other hand, organic materials have a wide variety of surface characteristics, although their thermal resistance is low. Therefore, it would be expected that the use of organic/inorganic hybrid materials could result in improved thermal and chemical resistance and that the surface chemistry could be well controlled. Several techniques have been proposed for preparing porous organic/inorganic hybrid membranes. In the sol–gel processes, organic/inorganic hybrid sols were prepared by hydrolysis and condensation of tetraethoxysilane (TEOS) and alkylsilane, including methyl-triethoxy-silane (Benes et al., 2000; Raman and Brinker, 1995), and coated and fired to produce porous hybrid membranes. The surface modification of porous inorganic membranes is another technique for producing organic/inorganic membranes; organic functional agents such as trimethylchlorosilane (TMCS) (Yazawa et al., 1988) and perfluorinated silanes (Miller and Koros, 1990) can be reacted in the gas or liquid phase.

Another issue that needs to be addressed is the mechanism by which molecules permeate through pores in the range of several nanometers. For microfiltration (MF; pore size: 100 nm–several micrometers) and ultrafiltration (UF; pore size: several nanometers–100 nm) membranes, the viscous flow mechanism satisfactorily explains the permeation of a liquid through a porous capillary. In the case of polymeric reverse-osmosis (RO) membranes, the pore size of which is thought to be <1 nm, the permeation mechanism has been explained by the solution–diffusion model where the solvent first dissolves in the membrane materials and then diffuses to the permeate stream along the chemical potential gradient. On the other hand, the mechanism of transport through nanofiltration membranes, which have pore sizes intermediate between UF and RO (that is, 1–2 nm) is not yet clear (Tsuru et al., 2001a; Tsuru et al., 2000b). It should be noted that several mechanisms for gaseous permeation, including the viscous flow, Knudsen flow, surface diffusion, and molecular sieving, have been proposed

---

Correspondence concerning this article should be addressed to T. Tsuru at tsuru@hiroshima-u.ac.jp.

as a function of Knudsen number, which is the pore size normalized with the gaseous mean free path (Xiao and Wei, 1992). On the other hand, the mechanism by which liquid is transported through porous materials with pore sizes of several nanometers has not yet been investigated in detail. Ceramic membranes have an advantage in that the swelling effect by solvents, which is unavoidable for polymeric porous membranes, is negligible. However, a limited number of articles have reported the effect of types of solvents on the permeabilities; the surface chemistry of porous membranes has been reported to affect the permeabilities of polar and nonpolar solvents not only for microporous membranes (Al_2O_3–ZrO_2, SiO_2–ZrO_2, SiO_2–TiO_2), with approximate pore sizes of 1 nm (Guizard et al., 2002), but also for commercial γ-alumina membranes with an average pore size of 10 nm (Dafinov et al., 2002; Font et al., 1996).

In this study, silica–zirconia porous membranes were fabricated by a sol–gel process, and modified with TMCS to produce organic–inorganic hybrid membranes in the nanometer scale. The effect of solvent types and temperatures on permeabilities through such nanoporous membranes was then investigated to discuss the mechanism of liquid permeation through porous membranes with a controlled surface chemistry.

Experimental

Silica–zirconia colloidal sol solutions, having a Si/Zr molar ratio of 9/1, were prepared by the hydrolysis and condensation of TEOS and zirconia-tetrabutoxide (ZrBT), and coated on α-alumina supports to give silica–zirconia porous membranes. The pore sizes of the porous silica–zirconia membranes were controlled in the range of 1–5 nm by an appropriate choice of colloidal diameters of sol solutions. Details of this preparation have been described elsewhere (Tsuru et al., 1998). The porous silica–zirconia membranes, the surface of which is covered with silanol groups, were modified at 20 and 100°C by a gas-phase reaction with TMCS, fed with nitrogen as a carrier gas. After a controlled reaction period, temperatures were increased up to 200°C to remove adsorbed TMCS and to allow for completion of the reaction.

The pore size distribution of the porous membranes was estimated, using water and carbon tetrachloride vapor, based on nanopermporometry (Tsuru et al., 2001c), which is also referred to as permporometry or dynamic flow-weighted porometry (Fain, 1989; Katz and Baruch, 1986). In the case of nanopermporometry, where a mixture of a noncondensable gas such as N_2 and a condensable gas (vapor) such as H_2O is fed to the porous membranes and the permeability of the noncondensable gas is measured, the vapor is assumed to be capillary-condensed in membrane pores that are smaller than the following Kelvin diameter d_K, thus blocking the permeation of the noncondensable gas.

$$d_K = -4\bar{v}\sigma \cos\theta / [RT \ln(P/P_s)] \tag{1}$$

where θ is the contact angle, σ is the surface tension, $\bar{v}$ is the molar volume, P is the vapor pressure, and P_s is the saturation vapor pressure. The Kelvin diameters increase with the vapor pressure of a condensable gas in the feed. By measuring the permeability of the noncondensable gas as a function of relative pressure P/P_s, it is possible to estimate the pore size distribution. Details of the experimental apparatus can be found in our previous article (Tsuru et al., 2001c).

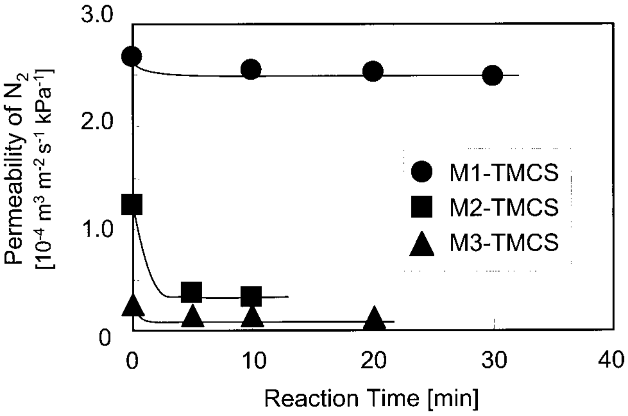


Figure 1. Time course of N_2 permeability as a function of reaction time [M1-TMCS (average pore size, d_p ~ 3 nm), M2-TMCS (d_p ~ 1.5 NM), M3-TMCS (d_p ~ 1 nm); N_2 permeability was measured at 200°C].

Permeation experiments using pure solvents (hexane, methanol, ethanol, toluene) were carried out in a stainless-steel cell under conditions of continuous stirring. The feed solution was pressurized up to 1.0 MPa using a plunger pump and recycled to the feed tank, while the permeate stream was maintained at atmospheric pressure. The permeation temperature ranged from 30 to 60°C. The water concentration of 10–100 ppm was determined by injecting several-10 μL of hexane into a TCD gas chromatograph (Shimadzu GC14BT).

Results and Discussion

Characterization of silica–zirconia membranes by nanopermporometry

The silanol groups on the surface of silica–zirconia membranes were reacted with TMCS, resulting in a monolayer modification, which resulted in a hydrophobic surface. Reactions using silica–zirconia membranes having different pore sizes (average pores sizes before modification: 1–3 nm) was investigated by monitoring nitrogen permeabilities, which were measured at 200°C after purging TMCS with nitrogen, as a function of reaction time. As shown in Figure 1, nitrogen permeability decreased with reaction time, suggesting that TMCS reacted with silanol groups on the membrane surface or on the inner surface of the membranes pores, resulting in a reduction in the effective pore size for the permeation of nitrogen. After a short reaction time (<30 min), the nitrogen permeability reached a steady state. The introduction of methyl groups into the membranes was confirmed by infrared spectrophotometry using the specular reflection mode (Shimadzu FTIR-8600).

Figures 2 and 3 show the pore-size distribution based on nanopermporometry in terms of the dimensionless permeability of nitrogen (DPN), which was normalized with the permeability of pure nitrogen, for membrane M4 before and after modification with TMCS, using H_2O and CCl_4 as condensable vapors, respectively. It should be noted that the Kelvin diameters were calculated assuming a contact angle of zero (com-

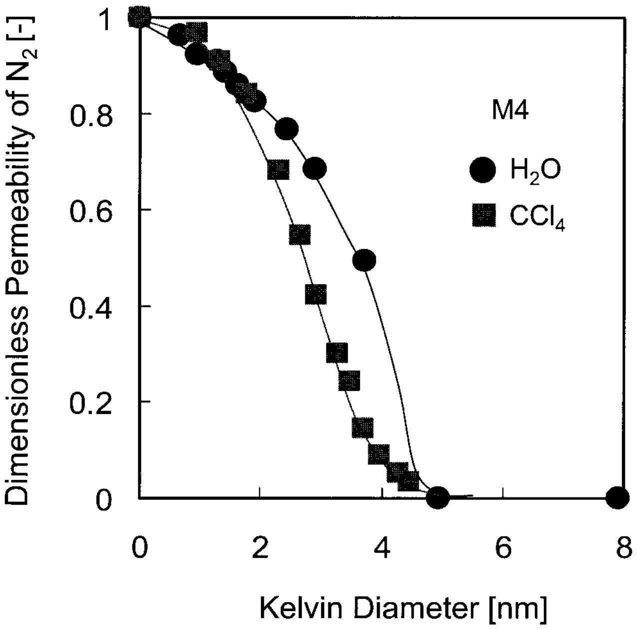


Figure 2. Dimensionless permeability of nitrogen curves by H_2O and CCl_4 for an unmodified membrane, M4.

plete wetting), irrespective of the types of vapors. As shown in Figure 2, before modification with TMCS, the DPN using H_2O as a condensable gas decreased to zero with an increase in vapor pressure in the feed stream, that is, an increase in Kelvin diameter. Concerning the effect of the type of vapor, nitrogen permeation through an unmodified silica–zirconia membrane was reduced to zero by condensed vapors for both H_2O and CCl_4. It should be noted that the DPN curves for H_2O shifted to a slightly larger distribution, compared to CCl_4, probably because of an insufficient assumption of a contact angle of zero for both condensed vapors. The physical properties needed to calculate the Kelvin diameter are the contact angle θ and the surface tension σ. The applicability of these physical properties, which were measured in a bulk solution, for the calculation in nanopores is not yet clear, but it should be noted that we reported that pore sizes down to 0. 5 nm showed a reasonable agreement with the separation properties (Tsuru et al., 1998, 2001c). On the other hand, as shown in Figure 3, after TMCS modification, nitrogen permeation was blocked for CCl_4 as a condensable vapor, whereas the DPN did not decrease to zero, when H_2O was used. Inside the hydrophobic pores, produced by TMCS modification of the hydrophilic pores covered with silanol groups, it is possible that CCl_4 could capillary-condense, whereas H_2O might not. Therefore, application of the nanopermporometry technique verified that the inner surface of the membrane pores with diameters of several nanometers can be successfully modified with TMCS.

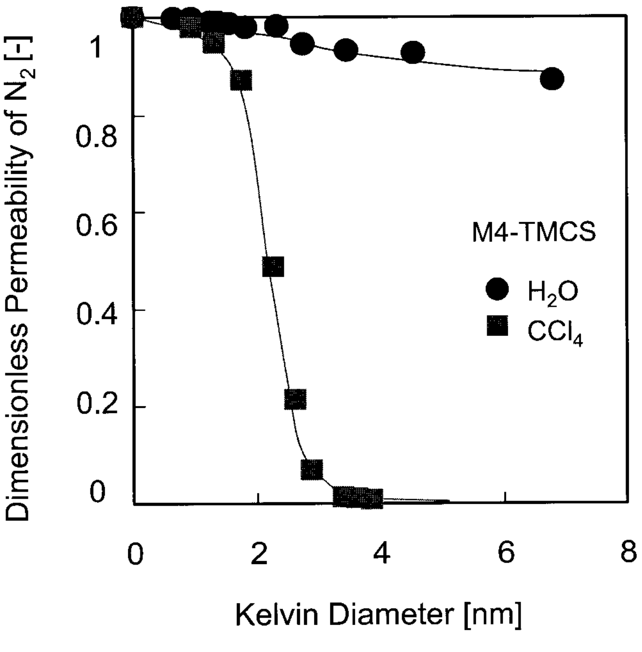


Figure 3. Dimensionless permeability of nitrogen curves by H_2O and CCl_4 for a membrane modified with TMCS (M4-TMCS, which was prepared by modifying M4 with TMCS).

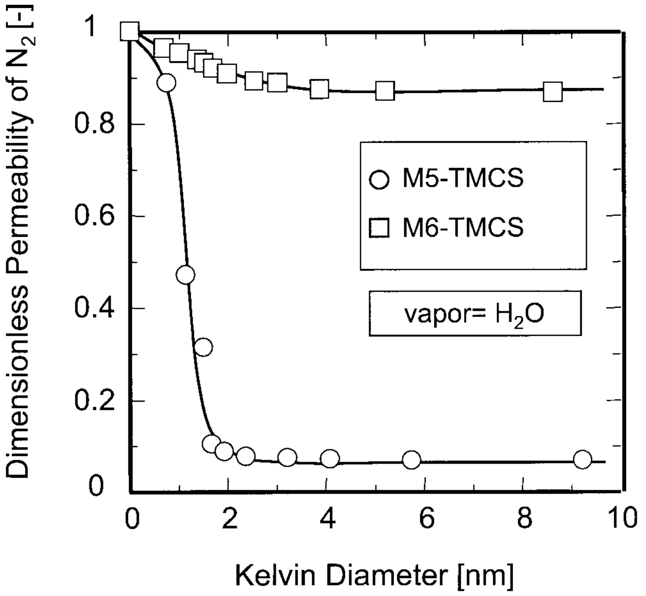


Figure 4. Dimensionless permeability of nitrogen curves by H_2O for membranes modified with TMCS (M5-TMCS, M6-TMCS).

Figure 4 shows DPN curves for TMCS-modified silica–zirconia membranes with different pore sizes using water as a condensable vapor. The DPN decreased in the range of 0 to 2 nm, becoming constant for Kelvin diameters larger than approximately 2 nm for the two membranes. This indicates that capillary condensation or the adsorption of water vapor occurred at a Kelvin diameter < 2 nm, which corresponds to a relative vapor pressure P/P_s of 0.38, probably because of the hydrophilic property of the pores. This suggests that the inner surface of the pores < 2 nm was not completely modified with TMCS because of steric hindrance to TMCS penetration and reactions inside pores < 2 nm.

The TMCS-modified membranes were fired in air to remove methyl groups, leaving only silicone atoms as the silica layer.

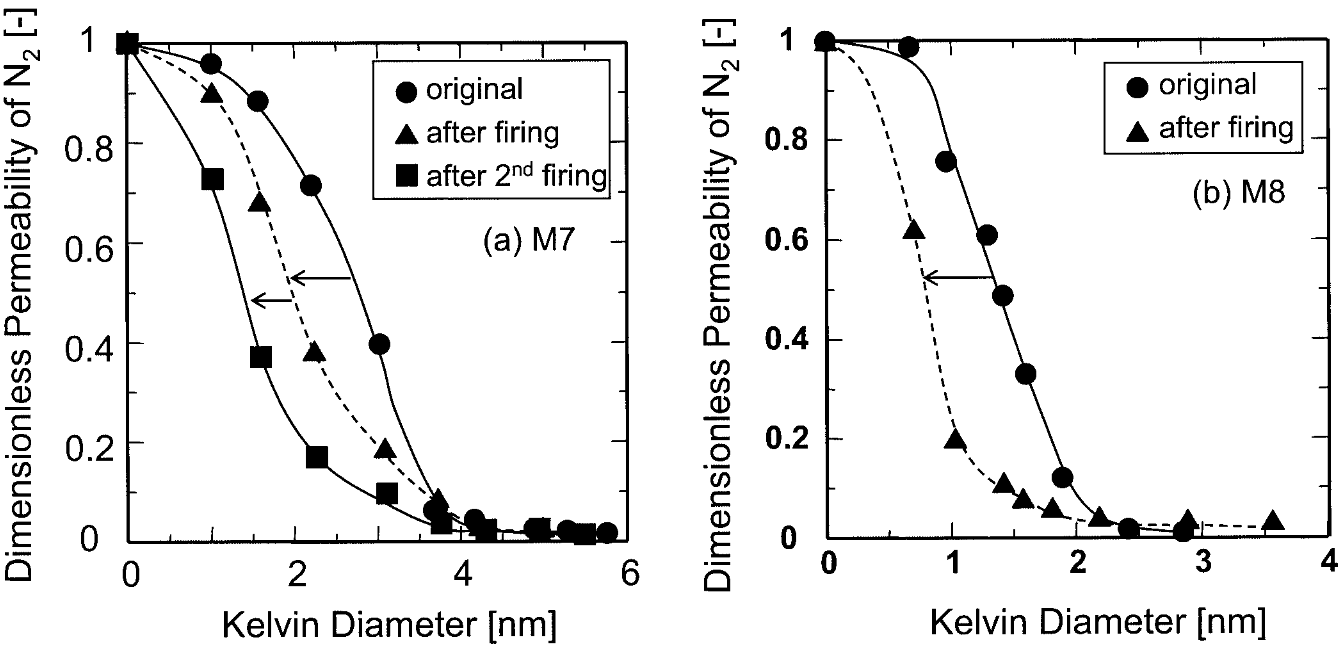


Figure 5. Dimensionless permeability of nitrogen curves before TMCS modification and after firing of the modified membranes [(a) M7; (b) M8; vapor: CCl_4].

A comparison of DPN curves of silica–zirconia membranes before TMCS modification and DPN curves after firing the TMCS-modified membranes provides information in terms of the sites where the TMCS reaction occurred. As shown in Figure 5(a), the average pore size of M7, which was approximately 3 nm, decreased to 2 nm after the TMCS modification-firing process. The pore size would be reduced at the thickness of –Si—O from the original pore wall (~ 0.5 nm), as shown schematically in Figure 6. The subsequent TMCS modification-firing process shifted the average pore size by 0.5 nm, from 2 to 1.5 nm. As shown in Figure 5(b), the average pore of 1.5 nm, using membrane M8, was also shifted by 0.5 nm to 1.0 nm after the modification-firing process. By considering DNP curves measured using water and CCl_4, we conclude that pores > 2 nm, which showed a reduction in average pore sizes of approximately 1 nm, were nearly completely modified, whereas pores from 1 to 2 nm, which decreased by 0.5 nm, were partially modified, probably because no spatial freedom was available after reaction of one molecule of TMCS inside pores with diameters of several nanometers. Therefore, membranes having pore sizes > 2 nm would be preferable to discuss the effect of the surface chemistry (hydrophilicity and hydrophobicity) on liquid permeation.

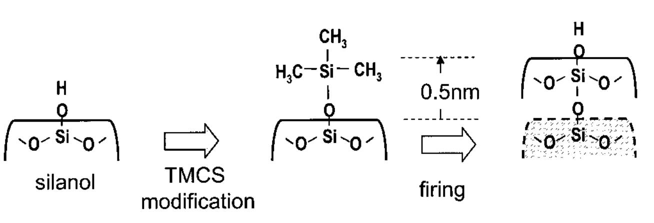


Figure 6. Change in surface structure by a TMCS reaction and firing process. (Silica surface grows approximately by 0.5 nm by TMCS modification and firing process.)

Permeation of pure hexane

Figure 7 shows the time course for the permeabilities of pure hexane L_p, through unmodified and modified silica–zirconia membranes, the average pore size of which was controlled at 3 nm, as shown in Figure 8. Hexane was chosen as a representative nonpolar solvent, and has no significant interaction with unmodified membranes or TMCS-modified membranes. The unmodified membrane shows a gradual decrease in hexane permeability, whereas the modified membrane showed approximately a constant permeability. Because the difference between the two membranes was their surface chemistry (hydrophobicity and hydrophilicity), the reason for this is likely

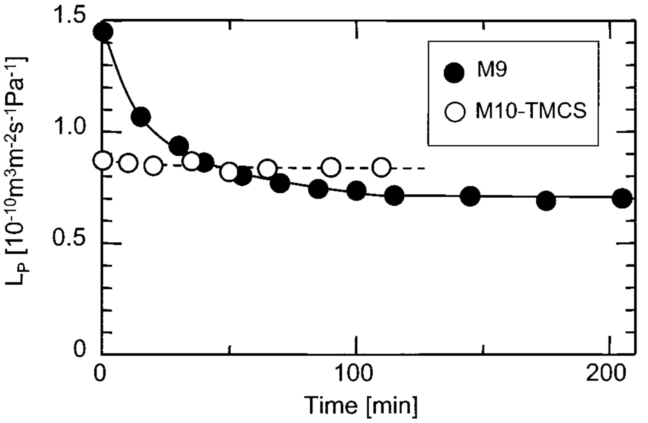


Figure 7. L_p as a function of time for pure hexane using M9 (unmodified) and M10-TMCS (modified).

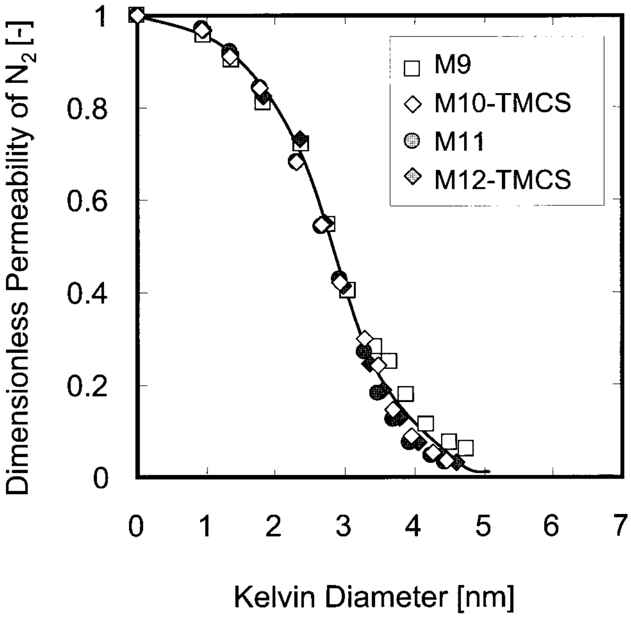


Figure 8. Dimensionless permeability of nitrogen curves for four silica–zirconia membranes used for permeation experiments (M9, M10-TMCS, M11, M12-TMCS; DPN curves were obtained before modification, vapor: CCl_4).

attributable to the adsorption of a small amount of water dissolved in the hexane.

The effect of small amounts of water in the hexane was investigated by adding a small amount of water in hexane in the range of 10 to 100 ppm, and the permeation properties in terms of permeability L_p and $L_p\mu$ through the hydrophilic (unmodified) and hydrophobic (modified) silica–zirconia membranes are summarized in Figure 9a and 9b, respectively. M10-TMCS, a modified silica–zirconia membrane, shows approximately the same permeability L_p, irrespective of the water concentration in the hexane. On the other hand, M9, an unmodified membrane, shows a decrease in L_p with an increase in water concentration, and this tendency was pronounced at low temperature. Negligible permeation occurred for the case of a water concentration of 100 ppm and at a permeation temperature of 30°C. This can be explained as follows. A preferential adsorption of water occurred on the inner surface of the hydrophilic membrane pores, resulting in a reduction in the effective pore sizes for hexane permeation. It should be noted that the amount of adsorption is usually larger at low temperature and high concentrations, and this is consistent with the permeation property as shown in Figure 9(a). Another explanation is the formation of a meniscus by the adsorbed water. This might be formed after a certain adsorption amount of water accumulates inside the micropores, thus blocking the permeation of hexane. Once a meniscus is formed in the nanopores, the mechanical force required to expel the meniscus can be estimated by applying the Kelvin–Laplace equation:

$$\Delta P = \frac{4\rho \cos \theta}{d} \tag{2}$$

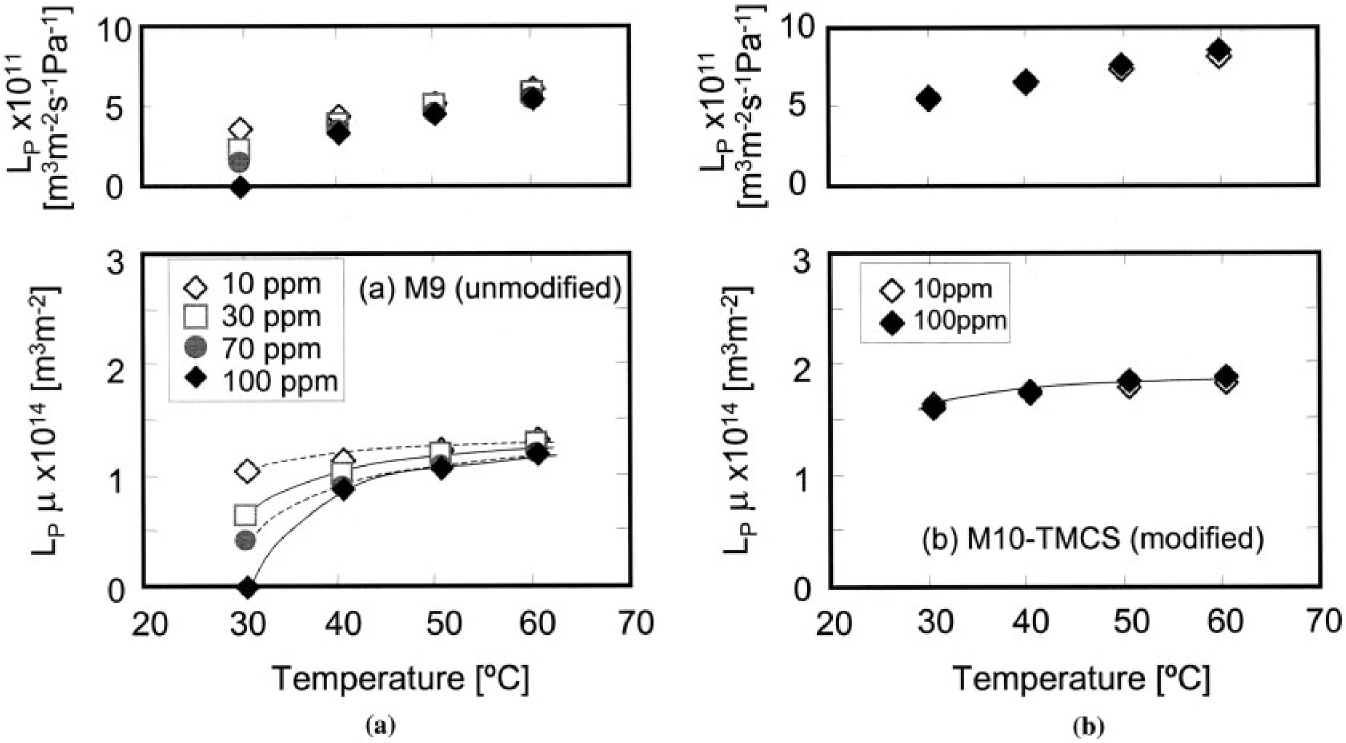
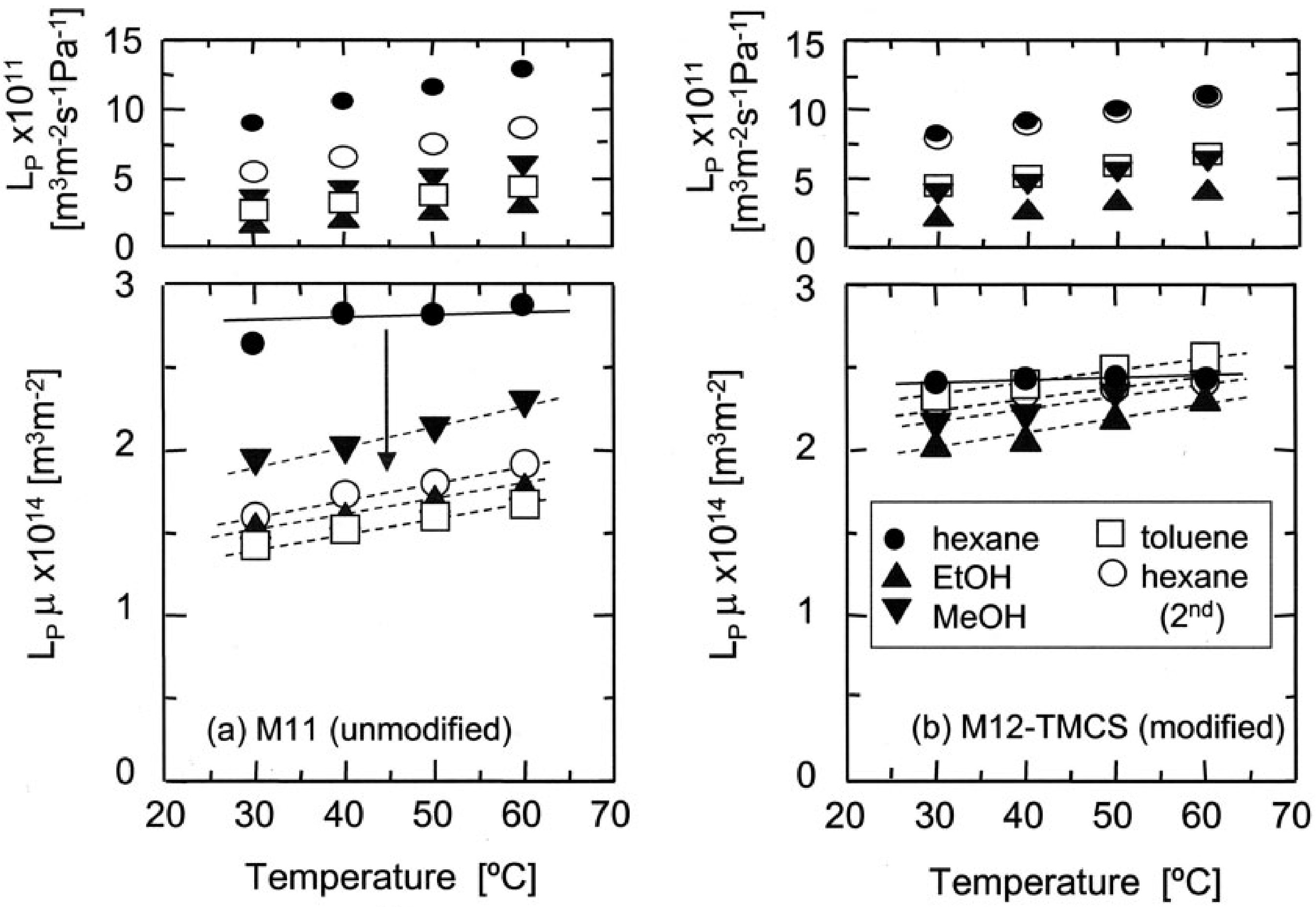


Figure 9. L_p and $L_p\mu$ of hexane with a small amount of water as a function of temperature for unmodified (M9) and modified (M10-TMCS) membranes.



(a)

(b)

Figure 10. L_p and $L_p\mu$ of several types of pure solvents through unmodified (M11) and modified (M12-TMCS) membranes.

By assuming an interfacial tension ρ between water and hexane inside micropores 2 nm in diameter to be 50×10^{-3} Nm^{-1}, although the physicochemical properties inside nanopores might be different from those in bulk solutions, the pressure difference across a membrane was 100 MPa, indicating that hexane permeation was completely blocked. Because water in a nonpolar solvent such as hexane was found to affect the solvent permeability through hydrophilic porous membranes, even in the range of 10–100 ppm, the water concentration needs to be reduced $<$10 ppm.

Another point that should be addressed is the temperature dependency of L_p. L_p, which is defined as a volumetric permeability in the dimension of m^3 m^{-2} s^{-1} Pa^{-1}, increased with temperature for the both membranes. To discuss the permeation mechanism of solvents through nanopores, the viscous flow mechanism should be examined as the first priority in consideration. If the permeation mechanism obeys the viscous flow mechanism $L_p\mu$, permeability L_p multiplied by the viscosity μ should be constant, irrespective of the types of solvents used and the permeation temperature, as shown in the following Hagen–Poiseuille equation:

$$L_p = \frac{J_v}{\Delta P} = \frac{\pi r_p}{8\Delta x} \cdot \frac{N}{\mu} \tag{3}$$

where r_p is the effective pore radius Δx is the effective membrane thickness, and N is the number of pores.

$L_p\mu$ for the unmodified membranes increased drastically with temperature, especially in the case of high concentrations of water, whereas $L_p\mu$ for the modified membrane increased slightly with temperature. It can be concluded that hexane permeation through the modified membrane is consistent with the viscous flow mechanism.

Permeation of various types of pure solvents

Figure 10(a) shows L_p and $L_p\mu$ for polar and nonpolar solvents through the M11 membrane (unmodified hydrophilic membrane). The water content of hexane was reduced to $<$5 ppm by distillation and this solvent was used in a permeation experiment immediately after membrane preparation. A large $L_p\mu$, which was nearly independent of permeation temperature, was obtained; therefore, the viscous flow seems to be a probable permeation mechanism for the case of hexane and unmodified hydrophilic porous membranes.

However, the following repeated permeation experiments of alcohols showed a lower $L_p\mu$ than the case for hexane, and the $L_p\mu$ of methanol was larger than that of ethanol, a larger molecule. The present result was consistent with our previous data, which showed the permeability ratio of methanol over ethanol increased with a decrease in pore diameter (Tsuru et al., 2000a). In terms of the temperature dependency of $L_p\mu$ for alcohols (methanol, ethanol), $L_p\mu$ increased with temperature. There are several possible explanations for this tendency, including the effects of molecular sieving, adsorption, and viscosity (Tsuru et al., 2000a,b). In terms of the effect of molecular sieving, molecules receive friction forces (energy potential) from pore walls, and the friction force can be considered to be larger for large molecules, resulting in a larger permeability for small molecules, as was the case of methanol and ethanol in Figure 10(a). The permeating molecules, which have larger kinetic energy at elevated temperature, show an increased permeability with temperature; this is similar to an activated process for molecular sieving membranes for gas separation (Yoshioka et al., 2001).

Another explanation could be possible based on the viscosity in a small pore. Viscosity near the surface might have a different value as well as a different dependency on temperature from bulk solution (Ternan, 1987), given that molecules receive potential from the wall. This could be simply interpreted as the change of adsorption thickness on the surface. Alcohols, which are hydrophilic polar molecules, become adsorbed to the surface of silica–zirconia membranes covered with silanol groups by hydrogen bonding. The adsorbed molecules are tightly bound to the surface and could be a source of hydrodynamic resistance to the permeation of the permeating molecules, resulting in increased viscosity (Assabumrungat and White, 1996; Tsuru et al., 2000a). The number of adsorbed molecules decreased with temperature and consequently the effective pore diameter available for solvent permeation increased. The $L_p\mu$ of hexane, after repeated permeation experiments with ethanol and methanol, showed a smaller value than that of hexane in the first permeation experiment, probably because of the reduction in effective pore sizes for permeation by the adsorbed alcohols. For the case of γ-alumina membranes having an average pore size of 10 nm, the adsorption of alcohol was suggested to explain a lower permeability of cyclohexane than that of ethanol (Font et al., 1996).

$L_p\mu$ through a modified membrane, M12-TMCS, the pore size of which before TMCS modification was also approximately 3.0 nm as shown in Figure 8, is demonstrated in Figure 10(b). The surface of M12-TMCS was covered with methyl groups and hydrophobic, and thus the interaction between solvents and pore surface would be small in comparison with M11. Similar to M11, the $L_p\mu$ of hexane is independent of permeation temperature. Moreover, the differences in $L_p\mu$ among the various types of solvents were relatively small, and the values for hexane before and after repeated permeation of alcohols were nearly the same. Another point that should be addressed is that $L_p\mu$ was nearly constant, irrespective of permeation temperature. By considering the permeation performance through unmodified and modified membranes, the effect of adsorption on permeation performance appears to be a more likely explanation, given that molecular sieving effect was not observed for the modified membrane M12-TMS, which should have smaller pore sizes than those of the unmodified membrane M11.

It can be concluded that the mechanism of permeation through pores several nanometers in diameter does not obey the viscous flow mechanism for a system having the interactions between the pore surface and solvents. On the other hand, the mechanism of permeation is consistent with the viscous flow for a system where the interactions are small for porous membranes approximately several nanometers in diameter, indicating the interactions between solvent molecules were significant in comparison to the interaction between solvent molecules and pore walls.

Conclusions

Silica/zirconia (SZ; Si/Zr molar ratio = 9/1) membranes having pore sizes in the range of 1–5 nm were prepared by the sol–gel process. Organic/inorganic hybrid membranes were developed by modifying the surface of the SZ porous membranes by a gas-phase reaction with trimethylchlorosilane (TMCS) to give a surface that was modified with a monolayer of TMCS. Using nanopermporometry, where the vapor is assumed to be capillary-condensed in membrane pores that were smaller than the Kelvin diameter and block the permeation of noncondensable gas, it was found that the inner surface of membrane pores with diameters larger than several nanometers were successfully modified with TMCS.

TMCS-modified membranes showed approximately the same permeability L_p, irrespective of water concentration (10 and 100 ppm) in hexane. In contrast, an unmodified membrane showed a decrease in L_p with increasing water concentration, which was pronounced at low permeation temperatures. This suggests that small amounts of water adsorbed to the inner surface of unmodified SZ membranes and blocked the permeation of hexane.

The permeation of various types of pure solvents in the temperatures range of 20–60°C was examined. The collected data show that the transport mechanism of pure solvents through the unmodified membranes does not obey the viscous flow mechanism, given that pure solvent permeabilities multiplied by the viscosity $L_p\mu$, which should be constant in the case of the viscous-flow mechanism, increased with temperature. On the other hand, SZ membranes modified with TMCS showed a relatively constant $L_p\mu$ for nonpolar solvents (hexane and toluene) as well as polar solvents (methanol and ethanol), suggesting that the viscous flow mechanism holds for porous membranes in which the pore diameter is several nanometers.

Literature Cited

Assabumrungrat, S., and D. A. White, "Permeation of Ethanol and Methanol Vapours through a Porous Alumina Membrane," *Chem. Eng. Sci.*, **51**, 5241 (1996).

Benes, N., A. Nijmeijer, and H. Verweij, "Microporous Silica Membranes," *Recent Advances in Gas Separation by Microporous Ceramic Membranes*, N. K. Kanellopoulos, ed., Elsevier Science, Amsterdam, pp. 335–372 (2000).

Bhanushali, D., S. Kloos, C. Kurth, and D. Bhattacharyya, "Performance of Solvent-Resistant Membranes for Non-Aqueous Systems: Solvent Permeation Results and Modeling," *J. Membr. Sci.*, **189**, 1 (2001).

Brinker, C. J., and G. W. Scherer, *Sol-Gel Science*, Academic Press, San Diego, CA (1990).

Dafinov, A., R. Garcia-Valls, and J. Font, "Modification of Ceramic Membranes by Alcohol Adsorption," *J. Membr. Sci.*, **196**, 69 (2002).

Fain, D. E., "A Dynamic Flow-Weighted Pore Size Distribution," Proc. 1st Int. Conf. on Inorg. Membr., Montpelier, France, 1989, pp. 199–205.

Font, J., R. P. Castro, and Y. Cohen, "On the Loss of Hydraulic Permeability in Ceramic Membranes," *J. Colloid Interface Sci.*, **181**, 347 (1996).

Guizard, C., A. Ayral, and A. Julbe, "Potentiality of Organic Solvents

Filtration with Ceramic Membranes. A Comparison with Polymer Membranes," *Desalination,* **147**, 275 (2002).
Katz, M. G., and G. Baruch, "New Insights into the Structure of Microporous Membranes Obtained Using a New Pore Size Evaluation Method," *J. Membr. Sci*., **58**, 199 (1986).
Machado, D. R., D. Hasson, and R. Semiat, "Effect of Solvent Properties on Permeate Flow through Nanofiltration Membranes," *J. Membr. Sci*., **166**, 63 (2000).
Miller, J. R., and W. J. Koros, "The Formation of Chemically Modified γ-Alumina Microporous Membranes," *Sep. Sci. Technol*., **25**, 1257 (1990).
Raman N. K., and C. J. Brinker, "Organic 'Template' Approach to Molecular Sieving Silica Membranes," *J. Membr. Sci.*, **105**, 273 (1995).
Ternan, M., "The Diffusion of Liquid in Pores," *Can. J. Chem. Eng.*, **60**, 244 (1987).
Tsuru, T., "Inorganic Porous Membranes for Liquid Phase Separation," *Sep. Purif. Methods*, **30**, 191 (2001a).
Tsuru, T., T. Hino, T. Yoshioka, and M. Asaeda, "Permporometry Characterization of Microporous Ceramic Membranes," *J. Membr. Sci.*, **186**, 257 (2001c).
Tsuru, T., S. Izumi, T. Yoshioka, and M. Asaeda, "Temperature Effect on Transport Performance by Inorganic Nanofiltration Membranes," *AIChE J.*, **46**, 565 (2000b).
Tsuru, T., T. Sudoh, S. Kawahara, T. Yoshioka, and M. Asaeda, "Permeation of Liquids through Inorganic Nanofiltration Membranes," *J. Colloid Interface Sci*., **228**, 292 (2000a).
Tsuru, T., T. Sudoh, T. Yoshioka, and M. Asaeda, "Nanofiltration in Non-Aqueous Solutions by Porous Silica-Zirconia Membranes,"*J. Membr. Sci.*, **185**, 253 (2001b).
Tsuru, T., S. Wada, S. Izumi, and M. Asaeda, "Preparation of Microporous Silica–Zirconia Membranes for Nanofiltration," *J. Membr. Sci*., **149**, 127 (1998).
Whu, J. A., B. C. Baltzis, and K. K. Sirkar, "Nanofiltration Studies of Larger Organic Microsolutes in Methanol Solutions," *J. Membr. Sci.*, **170**, 159 (2000).
Xiao, J., and J. Wei, "Diffusion Mechanism of Hydrocarbon in Zeolites. 1. Theory," *Chem. Eng. Sci.,* **47**, 1123 (1992).
Yazawa, T., H. Nakamichi, H. Tanaka, and K. Eguchi, "Permeation of Liquid through Porous Glass Membrane with Surface Modification," *J. Ceramic Soc. Japan*, **96**, 18 (1988).
Yoshioka, T., E. Nakanishi, T. Tsuru, and M. Asaeda, "Experimental Studies of Gas Permeation through Microporous Silica Membranes," *AIChE J.*, **47**, 2052 (2001).

Manuscript received Dec. 25, 2002, and revision received Aug. 20, 2003.