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Diffusion Control of Porous Membrane by Modifying the Nanopore Properties

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We have investigated the diffusion of various solvents on nanoporous membranes with various pore size and surface energy. We have modified the size of pore channel and surface energy of porous membrane through grafting different sized alkyl chain on inorganic membranes. Typically, disc type zirconia membranes with pore size of 3 nm and silica ones with 1 nm pore were purchased from Inocermic Co. Ltd. (Germany), and the surface and pore channel was modified by either octyltriethoxysilane (OTS) with chain length ~1 nm or pentyltriethoxysilane (PTS) with chain length ~0.5 nm. The water contact angles of both OTS and PTS grafted membrane were larger than 100° indicating the hydrophobically modified surface. Contact angles of hydrophilic and hydrophobic solvents were also examined to obtain exact surface energy (γ_{SV}) of grafted membrane, and the values were determined to be 56.3, 45.3, and 42.2 mN/m for ungrafted, PTS- and OTS-grafted membrane, respectively. The solvent diffusion patterns were evaluated by measuring the concentration gradient of small dye molecule, azobenzene. The diffusion coefficients of various solvents were measured on the basis of Fick's diffusion law. It was concluded that the diffusivity is dependent on the pore size for solvent with low surface tension and on the γ_{SV} value for solvent with high surface tension.

Keywords: Nanoporous Materials, Surface Modification, Nanopore, Diffusion.

1. INTRODUCTION

Researches on not only porous materials development but also pore size and property control in nanoporous materials are playing key roles in the development of various functional materials.[1–3] Those porous materials could be utilized as active molecule reservoirs,[4] drug delivery carriers,[5] adsorbents,[6,7] filters,[8] catalytic support,[9] nanoreactor[10] and etc. By manipulating the passage of target molecules across nanopores, controlled release in reservoirs or carrier systems, effective adsorption, and selective separation for filters can be achieved.

In this point of view, the development of pore modification methods and the study on pore characteristics are no less important than the invention of various nanoporous structures. Molecular passage rate across the channels can be intentionally controlled through attaching size-reducing groups on the nanopore entrance. On the other hand, the modification in surface energy of pore entrance prevents access of certain chemical species in liquid or gaseous phase.

In the previous report,[11] we carried out surface energy modification on a disc-type membrane in which a close packing of homogeneous ZrO_2 nanoparticles produces uniform nanopores of ~3 nm. Then we investigated the diffusion patterns of various solvents across the membrane utilizing small organic solute, azobenzene, and examined the relation between surface energy of solid substrate and diffusivity of solvents, and suggested that the higher the surface energy of nanoporous material is, the faster the solvent diffuses.

In the present study, we are going to demonstrate the effect of pore size on the diffusivity. In addition to the previous research, we prepared inorganic membranes with various sized nanopores by alkyl chain grafting method

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and compared the diffusion patterns of various solvents with respect to the pore size.

2. EXPERIMENTAL DETAILS

2.1. Preparation of Pore Size Controlled Membranes

The disc-type zirconia membranes with 3 nm pore and silica membranes with 1 nm pore was purchased from Inocermic Co. Ltd. (Germany). Silanes with various alkyl chains such as octyltrietholyxilane (OTS) and pentyltriethoxysilane (PTS) were purchased from Aldrich Co. Ltd. As described in our previous report,[11] silanes were grafted on the membrane by refluxing in toluene for 12 h. The resulting OTS-membrane and PTS-membranes were washed several times with toluene to remove unreacted silane moieties. Zirconia and silica membranes without grafting (pristine membrane) were also subjected to diffusion experiments for comparative study.

2.2. Measurement of Solvent Contact Angle

In order to evaluate surface property of each membrane, contact angles for various solvents such as water, formamide, ethyleneglycol, diiodomethane (DIM), dimethylformamide (DMF), toluene and ethanol was measured utilizing drop shape analysis system.

The surface energy of each membrane was then calculated according to Lifshitz-Van der Waals and Lewis Acid–base theory.[12]

2.3. Diffusion Experiment

Following our previous work,[11] we obtained diffusion patterns with respect to time and diffusion coefficients for each membrane using home-made Teflon lined diffusion apparatus. Typically, azobenzene solutions were prepared with various solvents and the diffusion of solvent across the membrane was checked by measuring molecular passage of azobenzene dye with UV-Vis spectroscopy.

Table I. Contact angle measurement results.

		Contact angle (°)		
Solvent	γ_{LV} (mN/m)	Pristine membrane (ZrO_2 and SiO_2)	PTS-grafted membrane	OTS-grafted membrane
Distilled water	72.8	20.5	124.4	101
Formamide	58.2	13	83.8	77.4
Ethylene-glycol	47.7	N.D.	84.1	71.8
DIM	50.8	17.8	35.1	30.0
DMF	37.1	N.D.	28.4	29.4
Toluene	28.4	N.D.	N.D.	N.D.
Ethanol	22.1	N.D.	N.D..	N.D.

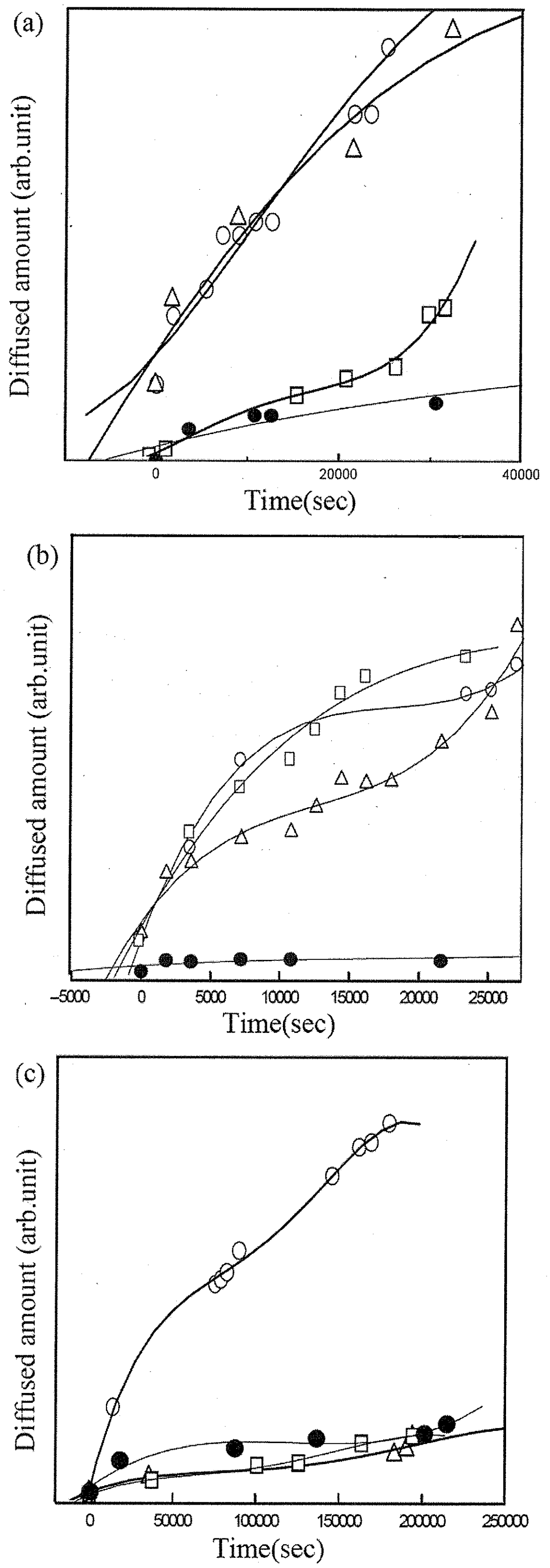

Fig. 1. (a), (b) and (c) indicate the diffusion patterns of ethanol, toluene, and formamide, respectively, on 3 nm-pristine (○), PTS-grafted membrane (△), OTS-grafted membrane (□) and 1 nm-pristime membrane (●).

The diffusion coefficients were calculated on the basis of Fick's diffusion law below.

$$D = J \cdot \Delta X/\Delta C = [(dC_2(t)/dt) \cdot (V(t))]/[S(t)] \cdot [\Delta X/\Delta C]$$

(J: flux, D: diffusion coefficient, ΔC: difference between C_1 (azobenzene concentration in reservoir chamber) and C_2 (azobenzene concentration in receiving chamber), ΔX: thickness of membrane, S: surface area of membrane, V: chamber volume, t: time).

3. RESULTS AND DISCUSSION

3.1. Characterization of Membranes

The surface modification was confirmed by Fourier transform infrared spectroscopy as reported previously.[11] The contact angles of various solvents with different surface energies (γ_{LV}: surface energy between liquid and vapor) on the membranes were measured in order to calculate the surface energy of membrane. The enhanced contact angles in both PTS and OTS grafted membranes compared to the pristine ones obviously showed that the hydrophobic alkyl chains were well grafted (Table I). We also calculated the membrane surface energy (γ_{SV}) according to Lifshitz-Van der Waals and Lewis Acid–base theory.[12] According to this theory, γ_{SV} can be calculated from the contact angle values of hydrophobic and hydrophilic solvents such as diiodomethane and formamide along with contact angle of water. The γ_{SV} were determined to be 56.3, 45.3 and 42.2 mN/m for pristine membrane, PTS and OTS-grafted membranes, respectively, showing considerable decrease in surface tension upon alkyl chain modification. Supposing that the grafting occurs homogeneously through the membrane surface and pores, γ_{SV} of membrane surface could be considered as that of pore entrance.

Similarly, the pore size of grafted membrane can be calculated considering the chain length of octyl and pentyl group, assuming the homogenous grafting of alkyl chain throughout the pore. Since pentyl and octyl has length of 5.1 and 9.0 Å, PTS grafted membrane is thought to have reduced pore size of ~2 nm and OTS grafted one has pore size of ~1 nm (Fig. 2). In a word, both PTS and OTS-grafted membranes have not only decreased wettability but also reduced pore accessibility as to solvent.

3.2. Diffusion Behavior of Solvent Across Porous Membranes

In order to investigate the effect of pore property like size and surface energy on the solvent passage through pore channel, diffusion coefficients of various solvents for each membrane were determined. Three solvents with different surface energy (γ_{LV}) and polarity (ability of solvent to interact as a proton donor, acceptor or dipole) such as ethanol, toluene and formamide were selected (Table II). Following our previous work, we selected azobenzene molecule to check the solvent diffusivity as it is easily visualized. Generally, The solvents with higher surface energy less penetrate the membrane pore. Not surprisingly, the diffusion of ethanol and toluene, which are low γ_{LV} solvents, showed fast and time-dependent diffusion patterns while formamide with high γ_{LV} showed suppressed diffusion behavior (Fig. 1). All the diffusion patterns of three solvents for 1 nm, 3 nm-pristine, PTS and OTS-grafted membranes were investigated, and showed similar patterns (Figs. 1(a–c)).

It was determined that the diffusion rates for PTS and OTS-grafted membranes are lower than those for pristine membrane. It is because that both reduced pore size and decreased surface energy of membrane prevents the smooth passage of solvents through pore channel. In a solvent with low γ_{LV} like ethanol ($\gamma_{LV} = 22.1$ mN/m), the reduced pore size is considered to play an important role in diffusivity. The diffusion coefficient of ethanol decreases as the pore size reduces; 3 nm-ZrO_2 (3 nm pore) > PTS-3 nm ZrO_2 (2 nm pore) > OTS-3 nm ZrO_2 (1 nm pore) ≈ 1 nm-SiO_2 (1 nm pore) (Table II and Fig. 2). On the other hand, in a solvent with high γ_{LV} like formamide, the diffusion is more dependent on γ_{SV} than pore size. The diffusion coefficient in PTS and OTS-grafted membranes was determined to be lower than 1 nm SiO_2 membrane although their pore sizes are slightly higher than 1 nm SiO_2 membrane.

It can be explained that very low surface energy of alkyl grafted membranes effectively blocks the accessibility of formamide, therefore the diffusivity became very low regardless of pore size. This phenomenon is observed when the surface energy of solvent is much higher than that of solid surface ($\gamma_{LV} > \gamma_{SV}$). It is therefore concluded

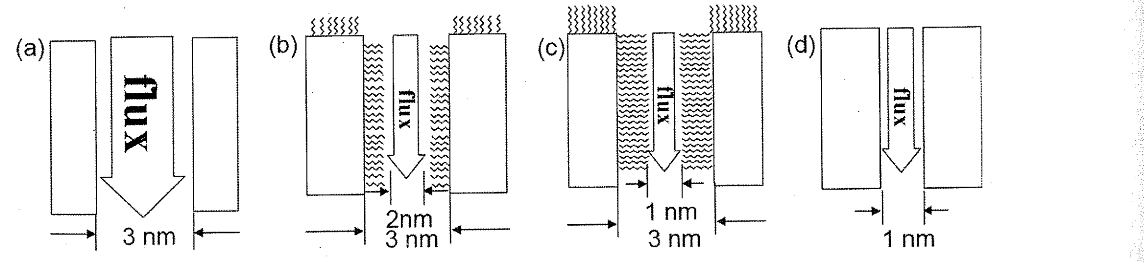

Fig. 2. Schematic illustrations for controlled pore size membranes. (a), (b), (c) and (d) indicate 3-nm pristine, PTS, OTS-grafted, and 1 nm-pristine membranes, respectively.

Table II. Diffusion coefficient of various solvents for size controlled membrane. The values in the parenthesis represent the relative diffusion coefficient values.

		Diffusion coefficient (m^2/s)			
Solvent	γ_{LV} (mN/m)	3 nm-ZrO_2 (3 nm pore)	PTS-3 nm ZrO_2 (2 nm pore)	OTS-3 nm ZrO_2 (1 nm pore)	1 nm-SiO_2 (1 nm pore)
Ethanol	22.1	5.51×10^{-9} (100)	3.21×10^{-9} (58.3)	2.86×10^{-9} (51.9)	2.61×10^{-9} (47.4)
Toluene	28.4	4.81×10^{-9} (87.3)	4.22×10^{-9} (76.6)	4.39×10^{-9} (79.6)	1.41×10^{-9} (25.6)
Formamide	58.2	4.52×10^{-10} (8.2)	6.06×10^{-11} (1.1)	5.68×10^{-11} (1.0)	1.32×10^{-10} (2.4)

that the diffusivity generally depends on the pore size except the solvent has unusually high surface energy.

It is notable that the diffusion rate in toluene was not affected by the alkyl chain grafting (Fig. 1(b)). Toluene is well known solvent to dissolve alkane moiety compared to ethanol or formamide, therefore the pore size decrease by alkyl chain does not effectively take place for toluene. Consequently, the original pore size of inorganic membrane became a major factor in the passage of toluene across the membrane.

4. CONCLUSION

We have successfully modified nanoporous membranes and investigated the solvent diffusivity based on pore size, surface energy (γ_{SV}) and surface energy of solvent (γ_{LV}). The alkyl chain grafting reduced the pore size and surface energy (γ_{SV}). The pore sizes of each membrane are as follow; 3 nm-ZrO_2 ($\sim$3 nm) > PTS-3 nm ZrO_2 ($\sim$2 nm) > OTS-3 nm ZrO_2 ($\sim$1 nm) $\approx$ 1 nm-SiO_2 ($\sim$1 nm) (Fig. 2). This order is well corresponding with that of decreasing diffusion coefficient in a solvent with low surface energy like ethanol ($\gamma_{LV} = 22.1$ mN/m). On the other hand, the solvent with unusually high surface energy ($\gamma_{LV} > \gamma_{SV}$) like formamide ($\gamma_{LV} = 58.2$ mN/m) induces surface energy dependent diffusion behavior rather than pore size.

Therefore, it is concluded that the solvent diffusivity could be controlled by modifying the pore size and surface energy of porous materials and by selecting appropriate solvents.

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