Self-diffusion of 2-Propanol and Acetone Molecules in Surface-modified and Unmodified Controlled-pore Glasses Studied by the Pulsed Field Gradient NMR Technique and Their Permeation Characteristics for Associated Glass Membranes*¹

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Self-diffusion coefficients were determined for organic adsorbates (2-propanol and acetone) in triamine-modified and unmodified controlled-pore glasses, using the pulsed field gradient NMR technique. Saturated amounts of adsorption were decreased considerably by the surface modification, indicating the reduction of free space for adsorption. With modified surface, both diffusivity and permeability were increased irrespective of the state of adsorption (unmixed or mixed). With unmodified surface, the order of diffusivity was reversed for 2-propanol and acetone by changing the state of adsorption; the same reversal was also observed for permeability. This common characteristic feature is interpreted in terms of preferential adsorption of acetone (*vs.* 2-propanol) on hydroxyl (acidic) adsorption sites on the glass surface. Modification of surface acidity by treating with aqueous aluminium nitrate (or sodium acetate) supports this view.

Together with the common trend in diffusivity and permeability for the triamine-modified surface, importance of diffusivity in determining the permeation property is suggested.

Key words : Glass membrane, Surface modification, Self diffusion, NMR

Introduction

We have been interested in the chemical heat-pump system¹⁾ based on the reaction, $(\text{CH}_3)_2\text{CHOH} \rightarrow (\text{CH}_3)_2\text{CO} + \text{H}_2$; waste heat ($\sim 80^\circ\text{C}$) is absorbed

by the forward (endothermic) reaction in the liquid phase, and the absorbed heat is recovered at higher temperatures ($\sim 200^\circ\text{C}$) by the backward (exothermic) reaction conducted in the gas phase. The separation of 2-propanol (IPA) and acetone is essential in this system, and from the viewpoint of energetic economy, it is more advantageous to use membrane (permeation or pervaporation) for this process than to use fractional distillation.

We consider that controlled-pore glass (C.P.G.) membranes are promising for this purpose in view of their favorable properties (no swelling in con-

*¹ 表面修飾および非修飾均一細孔多孔質ガラスに吸着した 2-プロパノールおよびアセトン分子の NMR パルス磁場勾配法による自己拡散性と関連ガラス膜への透過性
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tact with organic compounds, high thermal and mechanical stability, high pressure applications, etc.). In the present work, we investigated the self diffusion of these two molecules within the pores of C.P.G. granules using the pulsed field gradient NMR technique²⁾. Wherein surface modification with a silane-coupling reagent (diethylenetriamine functionality) was employed so as to affect the diffusional characteristics of the adsorbed molecules. The results are compared with permeation coefficients determined for the corresponding unmodified and surface-modified C.P.G. tubes.

Experimental

The used C.P.G. was supplied by the Inorganic Section of the Government Industrial Research Institute, Osaka, Japan. It was a leached borosilicate glass, ground and sieved. The 35-48 mesh (0.417-0.295 mm) fraction was used in these experiments. The glass was characterized by a large pore diameter of 4 nm (by mercury intrusion), and a specific pore volume of $0.34 \text{ cm}^3 \text{ g}^{-1}$. The fixation of silylpropyldiethylenetriamine groups to C.P.G. was effected by use of trimethoxysilylpropyldiethylenetriamine (Petrarch Systems, Inc.). The amount of the fixed organofunctional group was evaluated from the carbon and nitrogen analyses. In the evaluation, the two values, coinciding within 1% deviation by the neglect of methoxyl carbons, were averaged.

NMR samples were made up in the following way. Approximately 0.5 g of C.P.G. granules was placed in a standard 10 mm NMR sample tube equipped with a stopcock and joints, which was connected to a vacuum and gas-handling system, and then outgassed at 25°C and 10^{-3} Torr for 4 d. The constant temperature adsorption (25°C) of an adsorbate (IPA or acetone) into the pores of C.P.G. was accomplished by exposing the adsorbent to the vapor of the adsorbate liquid, whose temperature was maintained constant to control the amount of adsorption. During the adsorption procedure, the adsorbed amount was monitored separately with a

sorption balance (quartz spiral). NMR (H-1) experiments were carried out at 25°C using a Fourier-transform pulsed spectrometer operating at 60 MHz (JEOL JNM FX-60Q) or 270 MHz (JEOL JNM GX-270) with an equipment which generates magnetic field gradient pulses (JEOL JNM PL-35). G was calibrated using a water sample ($D=2.266 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 25°C)³⁾. The samples were thermostatted in a stream of nitrogen issuing from a liquid nitrogen bath ($\pm 1^\circ \text{C}$).

Permeation coefficients were determined with a double cylindrical cell module, where the inner cylinder was made of Corning porous Vycor glass (# 7930, 10mm-O.D., 1 mm-thick) which also possessed average pore diameter of 4 nm. Permeating vapor was feeded to the outer portion of the cell with constant evacuation of the inner portion, and permeated gas was condensed with a liquid nitrogen trap. Compositions of feeded and permeated gases were analyzed by GLC.

Surface modification with aluminium nitrate was done by immersing the Vycor glass tube in an aqueous aluminium nitrate solution (2.2 N) for 3 d, followed by calcination at 500°C for 2 h. For modification with sodium acetate, the Vycor glass was immersed in an aqueous sodium acetate solution (2.0 N) for 3 d, and then calcined (400°C, 2 h).

Results and Discussion

The saturated amounts of adsorption are shown in Table 1. It is apparent that the amounts were reduced considerably by surface modification with triamine groups. This would be simply explained in terms of the decrease of free space for adsorption due to surface modification. Based on this Table, the amount of adsorption for NMR measurement was commonly chosen as 0.02 g/g-glass, which is enough below saturation but still gives sufficient signal-to-noise ratio in the NMR spectra.

Diffusion and permeation characteristics are tabulated in Table 2, where diffusivity for the mixed state was obtained using a perdueterated adsorbate for one of a pair to mask the NMR signal

therefrom. It can be seen that surface modification with triamine groups increased the diffusivity of both adsorbates irrespective of their state of adsorption (unmixed or mixed). This would be reconciled with the hydrogen bonding interaction of 2-propanol or acetone molecules with surface hydroxyl groups⁴⁾; it was pointed out that the diffusivity of adsorbed benzene on the methylated silica surface was distinctly greater than that on the hydroxylated one⁵⁾.

It is often observed that the order of permeability for two compounds is reversed when they are feeded in the mixed state. This is also the case here for 2-propanol and acetone with unmodified porous glass membrane (acetone (18.61) > 2-propanol (6.21) for

unmixed state, 2-propanol (3.83) > acetone (2.69) for mixed state). It is of interest that the reversal in the same direction is also observed for diffusivity (acetone (0.82) > 2-propanol (0.60) for unmixed state, 2-propanol (0.80) > acetone (0.69) for mixed state). This may be a phenomenon caused by the coupling of vaporization and adsorption, *i.e.*, while the vaporization of acetone from an upper adsorption layer is easier than that of 2-propanol, acetone is adsorbed preferentially on the hydroxyl (acidic) adsorption site.

In order to examine this hypothesis (acetone (stronger base) interacts more strongly with acidic sites than 2-propanol (weaker base)), surface acidity was modified by treating the porous-glass membrane with aqueous aluminium nitrate (to enhance acidity)⁶⁾ or aqueous sodium acetate (to reduce acidity); by these treatments Brønsted-acid sites (as present on silica-alumina) and neutralized silanol groups (Si-ONa) are expected to form, respectively. Results are shown in Table 3. Following can be concluded from this Table. (1) The characteristic reversal of permeability in the mixed and unmixed states holds for all the cases irrespective of the surface modification. (2) In the unmixed state, acetone permeates more easily than 2-propanol for every case. (3) However, the permeability of acetone is decreased in the increasing order of acidity

Table 1 Amounts of Saturated Adsorption of 2-Propanol and Acetone on Surface-modified and Unmodified Porous Glass*

Adsorbate	Amount (g/glass-g)	
	Unmodified	Triamine-mod.**
2-Propanol***	0.133	0.056
Acetone****	0.125	0.034

*) Adsorption at 25°C with the temperature of adsorbate liquid kept constant (22°C). **) Fixed amount of 0.578 mmol g⁻¹. ***) Vapor pressure of 5.0 kPa. ****) Vapor pressure of 27.2 kPa.

Table 2 Diffusion and Permeation of 2-Propanol and Acetone in Porous Glass with and without Surface Modification

State	Compound	Diffusivity* (10 ⁻⁴ m ² s ⁻¹)		Permeability (10 ⁻⁹ gm ⁻¹ s ⁻¹ Pa ⁻¹)	
		Unmodified	Triamine-mod.**	Unmodified	Triamine-mod.***
Unmixed	2-Propanol	0.60	0.99	6.21	20.25
	Acetone	0.82	0.88	18.61	11.71
Mixed	2-Propanol	0.80	1.04	3.83****	4.71****
	Acetone	0.69	0.75	2.69****	2.65****

*) Self-diffusion constants for the adsorbed amount of 0.02 g/g-glass with (mixed) and without (unmixed) the same amount of perdeuterated coadsorbate. Desorption of preadsorbed hydrogenated molecules during adsorption of perdeuterated ones was negligible as confirmed by NMR signal intensities. Self-diffusion constants were obtained by varying δ (0.1–0.2 ms) at constant Δ (1.5 ms) and G (4.45 G cm⁻¹). **) Fixed amount of 0.578 mmol g⁻¹. ***) Fixed amount of 0.055 mmol g⁻¹. ****) Mole ratio of feed gas: 49/51 (2-propanol/acetone).

Table 3 Effect of Surface Treatment (Acidity Change) of Porous Glass on Permeability of 2-Propanol and Acetone

State	Compound	Permeability ($10^{-9} \text{ gm}^{-1} \text{ s}^{-1} \text{ Pa}^{-1}$)		
		Unmodified	Al(NO ₃) ₃ -treated	NaOAc-treated
Unmixed	2-Propanol	6.21	12.33	3.85
	Acetone	18.61	13.79	22.92
Mixed	2-Propanol	3.83*	3.63**	3.69***
	Acetone	2.69*	2.35**	2.54***

*) Mole ratio of feed gas: 49/51 (2-propanol/acetone). **) Mole ratio of feed gas: 44/56 (2-propanol/acetone). ***) Mole ratio of feed gas: 36/64 (2-propanol/acetone).

(22.92 > 18.61 > 13.79). Clearly the last feature supports the hypothesis.

In the case of triamine-modified surface (Table 2), 2-propanol is somewhat more diffusive than acetone for both states (2-propanol (0.99) > acetone (0.88) for unmixed state, 2-propanol (1.04) > acetone (0.75) for mixed state). The correspondence between the diffusivity and permeability also sets up here (2-propanol (20.25) > acetone (11.71) for unmixed state, 2-propanol (4.71) > acetone (2.65) for mixed state).

Taking into account the observed correlation between the diffusivity and permeability, importance of diffusivity in determining the permeation property is obvious. We consider that measurement of diffusivity with pulsed field gradient NMR technique offers a simple and readily accessible criterion for selective permeation, and may give a promising clue to understanding this complicating phe-

nomena physico-chemically.

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