

STUDIES ON THE SELF-DIFFUSION OF WATER ETHANOL MIXTURE IN CHITOSAN PERVAPORATION MEMBRANE WITH PULSED FIELD GRADIENT NMR DATA

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Abstract The self-diffusion of water, ethanol and water-ethanol mixtures in chitosan (CS) membranes crosslinked by aqueous H₂SO₄ solution and uncrosslinked membrane was measured using pulsed-field gradient (PFG) nuclear magnetic resonance (NMR) spectroscopy to obtain the partial solubilities and self-diffusion coefficients. An attempt was made to explain the transport properties of water and ethanol through the CS membrane. It was concluded that there are two types of channel water and ethanol diffusate transfer. The water was localized in the hydrophilic ionic region formed by the ionized groups, and the ethanol was localized in the hydrophobic amorphous network of the polymer. There was a good agreement between the separation factors estimated from PFG-NMR data and those obtained by pervaporation testing.

Keywords Chitosan membrane, Pervaporation, Pulsed-field gradient NMR

INTRODUCTION

The magnetic resonance methods, such as electron spin resonance (ESR), electron nuclear double resonance (ENDOR), and pulsed-field gradient nuclear magnetic resonance (PFG-NMR) are widely applied in the investigation of membrane polymeric matrix structure diffusion state and diffusion mobility on the microscopic level. The PFG-NMR method can directly observe the diffusion motion of molecules^[1, 2]. Now, the PFG-NMR method has been used to investigate the molecular diffusion in various systems, such as gels, zeolite crystallinity, water-in oil emulsions, polymers, solid foods and biological systems^[3–5].

Only recently in Russia and Japan, PFG-NMR has been used in the membrane field to study the submicron-structure of membrane transport channels with dimensions from 0.3 to 5.0 nm^[3–6]. PFG-NMR is a direct method for measuring the molecular and ionic self-diffusion coefficients in membranes. The main advantages of PFG-NMR are that it can not only investigate the self-diffusion processes in a range from 10^{–7} to 10^{–3} m, but also permits separation of the partial self-diffusion coefficients and solubilities in the case of complicated self-diffusion processes.

For pervaporation (PV), PFG-NMR is an ideal method to measure the interaction between the permeants and the polymer matrix and to determine their state of interaction. Therefore, the direct thermodynamic factors, which control the pervaporation process, can be understood. This information can help us to understand the transport mechanism of the permeants, and to design suitable polymer membrane for the separation of mixtures.

The application of chitosan (CS) to PV membrane materials has received much attention from many researchers since 1980s^[7]. Chitosan PV membrane showed excellent permselectivity in the separation of ethanol-water mixture^[7, 8]. The interactions occurring between the membrane and the polar solvents strongly affected the membrane separation properties^[8, 9].

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In this paper, the self-diffusion of water, ethanol and water-ethanol mixtures in chitosan membrane crosslinked by aqueous H_2SO_4 solution and uncrosslinked membrane was measured by PFG-NMR spectroscopy.

EXPERIMENTS

Self-diffusion Coefficient Measurement

PFG-NMR measurements were carried out on a spectrometer which was constructed by the Molecular Physical Department of Kazan State University, Russia^[10, 11]. The NMR frequency for the proton was 100MHz. The measurements were performed in a stimulated spin-echo mode. The spin-echo signal of ^1H nuclear of diffusate molecules was obtained if spin-spin T_2 proton magnetic relaxation times of diffusate molecules was not shorter than 10^{-3} s, the maximum value of pulse gradient amplitude g and the pulse duration were 40 T/m and 4×10^{-3} s, respectively. It gives us the opportunity to measure the diffusion coefficient from 10^{-8} to 10^{-14} m^2/s and to observe the amplitude echo signal changing over the four orders of magnitude. The latter is very important when the echo signal is non-exponential. The process of measurement was largely computerized. The temperature varied from -60°C to 100°C and was kept within ± 0.1 K. For molecules of diffusate undergoing unhindered isotropic Brownian motion, the evolution of spin-echo amplitude is described by the following equation.

$$A(2\tau, \tau_1, g) = A(2\tau, \tau_1, 0) \exp(-\gamma^2 g^2 \delta^2 t_d D_s)$$

where γ is the proton geomagnetic (or magnetogyric) ratio, $t_d = (\Delta - \delta)/3$ is the diffusion time. Δ is the interval between the gradient pulses. D_s is the self-diffusion coefficient of diffusion in the i -th phase (or channel), details of the calculation procedure of self-diffusion coefficients from the amplitude echo signal changing against g is already described in our previous paper^[6].

Membrane Preparation

Chitosan (CS) was supplied by Toko Kasei Co. Ltd (Japan) with a molecular weight of 8.0×10^4 – 1.0×10^5 . Its deacetylation degree is 87 mol% and 75 mol%, respectively.

CS membrane was prepared as reported in the previous paper^[8]. The thickness of the membrane is about 20 μm .

The CS membranes were equilibrated with water or absolute ethanol or water-ethanol mixtures for three days; the films and some feed solution were placed in glass NMR sample tubes (outside diameter was 7 mm) which were sealed.

RESULTS AND DISCUSSION

Self-Diffusion of Water in Membrane

The CS films equilibrated with different water content in the feed solution were investigated. The effects of the amount of water in the membrane on the self-diffusion coefficients of water for the crosslinked and uncrosslinked CS membranes are shown in Fig. 1. The results indicated that only one self-diffusion coefficient for moving water was obtained and the self-diffusion coefficient of water in the crosslinked membrane was higher than that in the uncrosslinked membranes. This is attributable to the existence of a crosslinking structure of $-\text{NH}_3^+ \dots \text{SO}_4^- \dots \text{H}_3\text{N}^+$. This structure has two effects. One is the formation of a three-dimensional structure, which limits the degree of swelling and improves the mobility. The other is the existence of ionized amino groups, which cause the preferential interaction with water. For crosslinked membrane, the sites of the preferential interaction are formed and water permeates through the sites more readily. Therefore, water could be preferentially bound to the ionized amino groups by hydrogen-bonding force or by forming hydration shells and transport through the hydrophilic region by involving a high exchange rate between the free water and ionized water in the hydration shells.

Figure 1 also shows that the self-diffusion coefficient of water increases with increasing water content in the membrane, when the content of water was lower than 50%. This is because with increasing water content in the membrane, the degree of swelling of the membrane increases, the channel for water diffusion becomes wider and

the water mobility is enhanced. However, when the water content is higher than 50%, the self-diffusion coefficient remains the same. The activation energy of the self-diffusion obtained in 50 wt% water content was 21 kJ/mol, which is close to the bulk water self-diffusion activation energy. This indicates that the channel of the membrane at this water content level is large enough for water to diffuse freely. Only one self-diffusion coefficient of water was obtained. It indicates that there is only one type of channel to be occupied by the water molecules, or the water molecules in the channels are of different types but the exchange rates of the water molecules between these channels are high as compared with the diffusion time (10^{-3} s).

Sorption and Self-Diffusion of Ethanol

CS membranes were equilibrated with absolute ethanol (99.5 wt%). The swelling degree of the membrane was found to be 7 wt%–10 wt% only, so the mobility of ethanol molecules was very low. Therefore, the spin-spin relaxation time was too low (near 400 μ s at room temperature) in order to measure the self-diffusion coefficient of ethanol.

Self-diffusion of Water-Ethanol Mixtures in the CS Membrane

Figure 2 shows the results of self-diffusion of water and ethanol in the CS membranes, which have been equilibrated with water-ethanol mixtures. These results indicate that there are two self-diffusion coefficients. The one with lower self-diffusion coefficient is in the range of 10^{-12} – 10^{-11} m^2/s . The population of this component accounts for 1/3 of the total amount of diffusate. The one with higher self-diffusion coefficient is above 10^{-9} m^2/s which was close to the self-diffusion coefficient of the whole of the water (2.1×10^{-9} m^2/s at room temperature). The activation energy for the lower self-diffusion coefficients is 46 kJ/mol, but for the higher one is 21 kJ/mol.

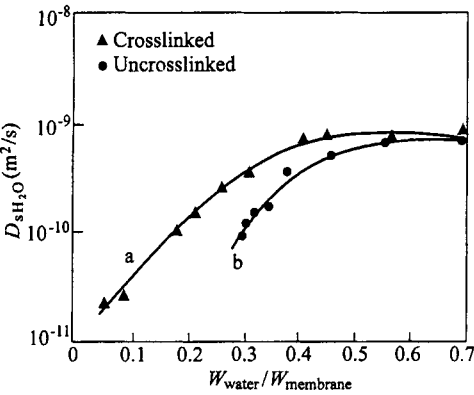


Fig. 1 The effects of water content in the membrane on the self diffusion coefficients of water
The maximum value of $W_{water}/W_{membrane}$ is 50 wt%.

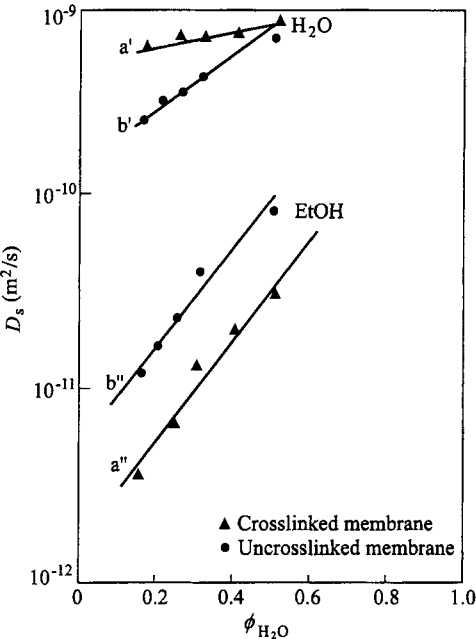


Fig. 2 The effects of water contents in ethanol-water feed solution on partial self-diffusion coefficients of water (a', b') and ethanol (a'', b'')
a'), a'') The membrane crosslinked by pH = 0.5 aqueous H_2SO_4 solution
b'), b'') The uncrosslinked membrane

In order to confirm whether the higher self-diffusion coefficients belonged to the self-diffusion of water or not, D_2O was used instead of ordinary water in the water-ethanol mixture. The relative amount of water and ethanol in the membrane was determined and found to be in good agreement with their relative populations by

PFG-NMR. Thus it is concluded that in the CS membrane the higher self-diffusion coefficient belongs to water while the lower one belongs to ethanol.

Figure 2 also displays the effects of water contents in feed solution on the partial self-diffusion coefficients of water (Fig. 2a', b') and ethanol (Fig. 2a'', b'') for the crosslinked and uncrosslinked CS membranes. The data indicate that the values of the self-diffusion coefficient of water (D_{sH_2O}) for the crosslinked membrane are higher than for the uncrosslinked one. However, for ethanol, the situation is reversed, the values of the self-diffusion coefficient of ethanol (D_{sEtOH}) for the crosslinked membrane are lower than for the uncrosslinked one. On the other hand, the self-diffusion coefficient of ethanol increases with increasing water contents in the feed solution more rapidly than the self-diffusion coefficient of water. This could be explained as following: For the ethanol component, the ethanol diffusion transports through the hydrophobic amorphous network, so the ethanol diffusion strongly depends on the mobility of the polymer chain segment. For crosslinked membrane or at low water content the polymer chain segment becomes less mobile, and the channel for ethanol diffusion also becomes smaller, so the self-diffusion coefficient of the ethanol is decreased. Increasing the content of water in the membrane could improve the plasticization of polymer chain and increase its mobility, resulting in a rapid increase of ethanol diffusion. In the case of the water, it is mainly transport easily through the hydrophilic ionic part region in CS membrane by high speed exchange between the ionized water in hydration shells and the free water. Therefore, for crosslinked membrane, water diffusion becomes high, and the mobility of the polymer chain segment exerts a smaller effect on the water transport than on ethanol. This is the main reason why the separation factor ($\alpha_{w/e}$) for the crosslinked membrane is higher than that of the uncrosslinked one.

Solubility Selectivity, Diffusion Selectivity and Separation Factor of the Membrane from the Self-Diffusion Coefficient

Permeation of liquid across the pervaporation membranes was usually interpreted by a solution-diffusion mechanism. It has been pointed out that the separation factor could be calculated from the solubility selectivity and the diffusion selectivity. Spitzen *et al.*^[12] defined the separation factor of pervaporation as follows:

$$\alpha = \alpha_s \alpha_m$$

$$\alpha_m = D_s^m H_2O / D_s^m EtOH$$

$$\alpha_s = (c^m_{H_2O} / c^m_{EtOH}) (c^f_{H_2O} / c^f_{EtOH})$$

where $c^m_{H_2O}$, c^m_{EtOH} , $c^f_{H_2O}$, c^f_{EtOH} are the concentrations of water and ethanol in membrane and in the feed, respectively. Using the water diffusion coefficient (D_{sH_2O}), water population in water channel (P_{H_2O}), ethanol diffusion coefficient (D_{sEtOH}), and ethanol population (P_{EtOH}), the separation factor could be calculated. The results of solubility selectivity, diffusion selectivity and the separation factor dependence on water contents in feed solution for crosslinked and uncrosslinked membranes are shown in Figs. 3, 4 and 5. The separation factor increases with the increase of ethanol content in the feed. The separation factor which is calculated from the data of self-diffusion coefficients and populations are very close to the separation factor of pervaporation experiments as shown in our previous paper^[8]. From Figs. 3, 4 and 5, it is clear that the separation of water-ethanol mixture could be achieved due to the preferential sorption and diffusion of water. Because of the existence of preferential interaction between ionized amino group in chitosan and water, the determination of the self-diffusion by the PFG-NMR gives us a good result to verify the permeation mechanism of water-ethanol in chitosan membrane.

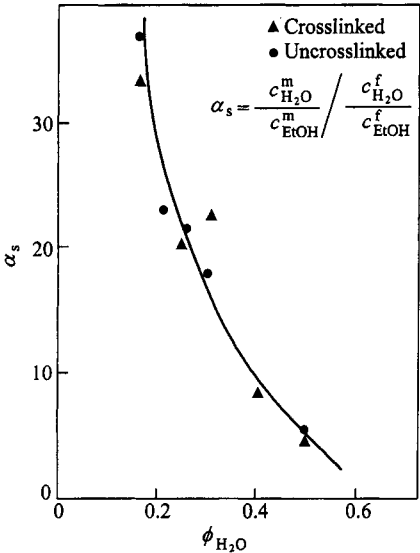


Fig. 3 The effects of water contents in ethanol-water feed solution on the solubility selectivity for crosslinked and uncrosslinked membranes

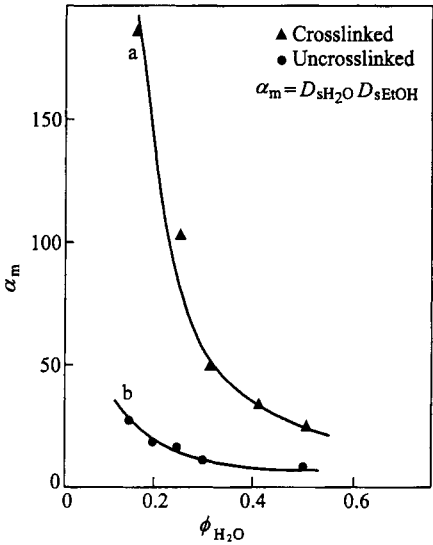


Fig. 4 The effects of the water contents in ethanol-water feed solution on diffusion selectivity for crosslinked and uncrosslinked membrane

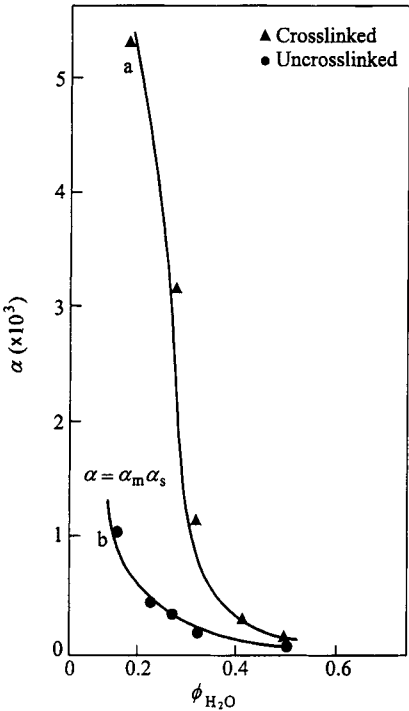


Fig. 5 The effects of water contents in ethanol-water feed solution on separation factor for crosslinked and uncrosslinked membrane

Activation Energies of E_{H_2O} and E_{EtOH} in CS Membrane Crosslinked with Different Amount of Aqueous H_2SO_4 Solution and the Uncrosslinked Membrane

E_{H_2O} and E_{EtOH} in CS membrane crosslinked with different amount of aqueous H_2SO_4 solution and the

uncrosslinked membrane are listed in Table 1. The data indicate that the values of $D_s^m{}_{\text{H}_2\text{O}}$, $D_s^m{}_{\text{EtOH}}$ and the activation energy of $E_{\text{H}_2\text{O}}$ and E_{EtOH} are quite different, E_{EtOH} is always higher than $E_{\text{H}_2\text{O}}$. This is the reason why water and ethanol are localized in different parts of CS membrane. Water is localized in the hydrophilic ionic moiety region which is formed by the ionized groups, while the ethanol is localized in the hydrophobic amorphous network of the polymer. The difference of E_{EtOH} and $E_{\text{H}_2\text{O}}$ is the lowest for the uncrosslinked membrane. Because an increase of the content of aqueous H_2SO_4 in solution could decrease the flexibility of the polymer, and diffusion of EtOH molecules become difficult. $E_{\text{EtOH}} - E_{\text{H}_2\text{O}}$ increase with increase of the amount of H_2SO_4 . These results are in good agreement with the data which were obtained from pervaporation experiment. This is the main reason that the chitosan membrane could transport water preferentially to ethanol, and separate the water from the water-ethanol mixtures feed solution.

Table 1. The self-diffusion coefficient of water $D_{\text{sH}_2\text{O}}$ and ethanol D_{sEtOH} and their activation energies $E_{\text{H}_2\text{O}}$ and E_{EtOH} in CS membranes crosslinked with different amount of H_2SO_4 and for uncrosslinked membrane

pH	D_{sEtOH} (m^2/s)	E_{EtOH} (kJ/mol)	$D_{\text{sH}_2\text{O}}$ (m^2/s)	$E_{\text{H}_2\text{O}}$ (kJ/mol)	$E_{\text{EtOH}} - E_{\text{H}_2\text{O}}$ (kJ/mol)
0.5	1.3×10^{-11}	48.5	6.2×10^{-10}	21.0	27.6
1.0	1.5×10^{-11}	46	6.1×10^{-10}	20.1	26.0
3.0	1.3×10^{-11}	45.1	5.5×10^{-10}	21.7	23.4
Uncrosslinked	4.0×10^{-11}	44.0	4.1×10^{-10}	23.0	18.8

CONCLUSIONS

The self-diffusion of water, ethanol and water-ethanol mixture in chitosan membrane was investigated with the help of PFG-NMR spectroscopy. The partial self-diffusion coefficients and the population of water and ethanol in different channels of membrane were obtained.

The self-diffusion of water and ethanol for CS membrane equilibrated with water-ethanol mixtures were calculated. The results indicate that there are two self-diffusion coefficients, the higher one belonging to water and the lower one to ethanol. The self-diffusion of water ($D_{\text{sH}_2\text{O}}$) for the crosslinked membrane is higher than for the uncrosslinked one. However, for ethanol the situation is reversed.

The solubility selectivity, diffusion selectivity and the separation factor dependence on water contents in feed solution for crosslinked and uncrosslinked membrane were obtained. The separation factor calculated from the data of self-diffusion coefficients and populations is very close to the separation factor obtained from pervaporation experiments. The determination of self-diffusion from PFG-NMR gives us a good result to verify the permeation mechanism of water-ethanol in chitosan membrane.

The values of $D_{\text{sH}_2\text{O}}$ and D_{sEtOH} , $E_{\text{H}_2\text{O}}$ and E_{EtOH} are quite different, E_{EtOH} is always higher than $E_{\text{H}_2\text{O}}$. This is the reason why water and ethanol are localized in different parts of the CS membrane.

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