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SHORT COMMUNICATION

CO_2, N_2 GAS SORPTION AND PERMEATION BEHAVIOR OF CHITOSAN MEMBRANE

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Abstract – The sorption equilibria for CO_2 and N_2 in dry chitosan membrane at 20 and 30 °C were measured by a pressure decay method. The steady-state permeation rates for CO_2 and N_2 in dry and wet (swollen with water vapor) chitosan membranes at 20 and 30 °C were measured by a variable volume method. The sorption equilibrium for N_2 obeyed Henry's law, whereas that for CO_2 was described apparently by a dual-mode sorption model. This non-linear sorption equilibrium for CO_2 could be interpreted by the interaction of sorbed CO_2 with the chitosan matrix expressed as a reversible reaction. The logarithm of the mean permeability coefficient for CO_2 in dry chitosan membrane increased linearly with upstream gas pressure. A linear increase of the logarithmic mean permeability coefficient for CO_2 with the pressure could be interpreted in terms of a modified free-volume model. The mean permeability coefficient for N_2 in dry chitosan membrane only slightly increased with upstream gas pressure. The permeabilities for CO_2 and N_2 in wet chitosan membrane increased by 15 to 17 times and 11 to 15 times, respectively, as compared to those in the dry membrane.

Key words: Sorption, Permeation, Chitosan, Membrane, CO_2, N_2

INTRODUCTION

The membrane gas separation process is based on selective permeation, by which a specific gas can be separated from a mixture containing the gas. The membrane should possess large permeability as well as high permselectivity. Currently, intensive studies are being made on gas sorption and permeation behavior in various synthetic polymer membranes. One of the promising membrane materials is believed to be a glassy polymer with a high glass-transition temperature in view of its high thermal and chemical stability. A dual-mode model has commonly been applied to describing gas sorption and permeation behavior in glassy polymer membranes. However, concentration-dependent diffusivities in the polymer phase and the depression of glass-transition temperature owing to plasticization action of sorbed gas have often been observed [Bae et al., 1994; Kumazawa and Bae, 1996].

The biopolymer membrane may also be attractive from the standpoint of selective permeation. In fact, the chitosan membrane may possibly be used as a water permeable membrane in pervaporation of aqueous ethanol solution [Won et al., 1996]. Chitosan, which is a basic biopolymer, seems to be an attractive membrane material for separating an acidic gas, CO_2, from a gas mixture containing CO_2.

In the present work, the possibility of separating CO_2 for CO_2-N_2 mixtures with the chitosan membrane was investigated. This was done by measuring sorption equilibria and pressure dependencies of permeabilities for the relevant gases. The sorption and permeation mechanisms were discussed in the dry and wet states of the membrane.

EXPERIMENTAL

1. Membrane Preparation

Chitin was dried for 48 hours at 60 °C. The dried particles were weighed, and 3 grams was mixed and solubilized in 200 ml of 2 wt% acetic acid solution for 24 hours at room temperature, thus producing a chitosan solution. Undissolved chitin and any impurities were filtered through a glass filter, and any solvents from chitosan solution were evaporated at room temperature. The chitosan solution was casted, that was followed by 12 hours drying in a drier at 60 °C. The remaining acetic acid from the chitosan membrane was neutralized in 1 N NaOH for 30 minutes. The membrane was dried for 12 hours at 60 °C to produce chitosan membrane. The density for the membrane is approximately 1.408 g/cm^3 and the average thickness of the membrane that was used in the experiments was 0.05 mm.

2. Sorption and Permeation Experiment

Sorption equilibria and permeabilities for a gas in a chitosan membrane were measured at 20 °C and 30 °C. CO_2 and N_2 were used as a penetrant or sorbate. Sorption isotherms for a gas were determined by the pressure decay method. The sorption cell is of a dual-chamber type, similar to one designed by Koros et al. [1976]. The pressure in the sorption chamber was determined with a pressure transducer. The apparatus for gas permeability measurement is similar to the variable volume

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method employed by Stern et al. [1963]. The procedure for the permeation experiment method has been described in detail elsewere [Sada et al., 1987]. After permeating moisture gas by using the saturator for 50 hours, we measured the permeation rate of the gas through the wet membrane at the experimental temperature. The low pressure side of the permeation cell was filled with the same penetrant gas at 1.101 MPa.

RESULTS AND DISCUSSION

1. Sorption Equilibria

Measured sorption isotherms for CO_2 and N_2 in dry chitosan membrane at 20 °C and 30 °C are plotted in Fig. 1. The isotherms for N_2 can be described by Henry's law,

$$C=k_D p \tag{1}$$

whereas the isotherms for CO_2 exhibit a downward concave pattern. Apparently, the sorption behavior can be expressed in terms of a dual-mode sorption model described mathematically by

$$C=k_D p+\frac{C'_H bp}{1+bp} \tag{2}$$

The values of the sorption parameters in Eq. (1) for N_2 and Eq. (2) for CO_2 are listed in Table 1. The solid lines and curves in Fig. 1 represent the calculated sorption isotherms by Eqs. (1) and (2). The sorption process for N_2 is controlled by the dissolution into the matrix of the chitosan structure, whereas that for CO_2 is not completely controlled by the dissolution only. The reason why the sorption equilibrium for CO_2 in the chitosan membrane can apparently be simulated by the dual-mode model will be considered in the following.

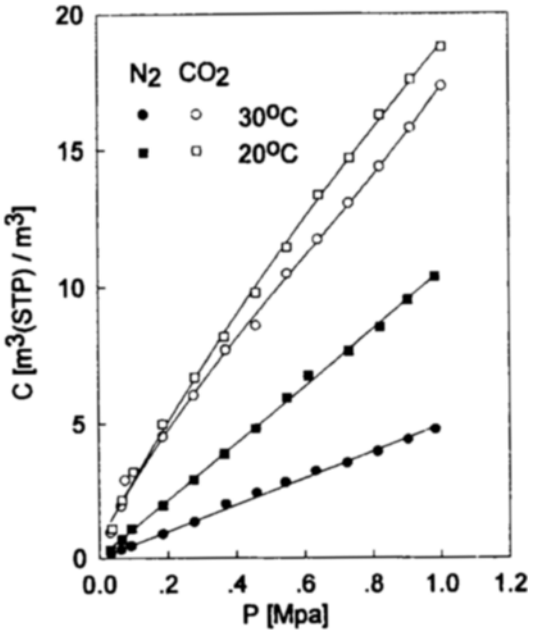

Fig. 1. Sorption isotherms for CO_2 and N_2 in dry chitosan membrane at 20 °C and 30 °C.

Table 1. Sorption parameters for CO_2 and N_2 in dry chitosan membrane

Temp.[°C]	Gas	k_D [m^3(STP)/$m^3 \cdot$MPa]	b [MPa^{-1}]	C'_H [m^3(STP)/m^3]
20	CO_2	17.0	28.0	3.00
	N_2	10.5	-	-
30	CO_2	15.3	25.0	2.82
	N_2	4.89	-	-

The interaction of sorbed CO_2 (A) with the chitosan matrix (B) will be assumed to be expressed as a reversible reaction

$$A+B \rightleftarrows AB \tag{3}$$

with the equilibrium constant K. At an equilibrium, the following relation holds.

$$K=\frac{[AB]_e}{[A]_e[B]_e}=\frac{[B]_o-[B]_e}{[A]_e[B]_e} \tag{4}$$

Here, the subscript "e" refers to the concentration at an equilibrium, and the subscript "o" refers to the initial value. The total concentration of sorbed CO_2 at the equilibrium, $[A]_{tot}$, is given by

$$[A]_{tot}=[A]_e+[AB]_e \tag{5}$$

Combining Eq. (5) with Eq. (4) yields

$$[A]_{tot}=[A]_e+\frac{K[B]_o[A]_e}{1+K[A]_e} \tag{6}$$

If the physical dissolution obeys Henry's law, $[A]_e$ is written as

$$[A]_e=k_D p \tag{7}$$

As the total concentration of sorbed CO_2, $[A]_{tot}$, is also C, Eq. (6) reduces to

$$C=k_D p+\frac{K[B]_o k_D p}{1+Kk_D p} \tag{8}$$

The above equation is of the same form as Eq. (2). It also coincides with Eq. (2), when Kk_D and $Kk_D[B]_o$ are replaced by b and C'_H, respectively.

2. Permeabilities

The experimental results for the mean permeability coefficients for CO_2 and N_2 in dry chitosan membrane at 20 °C and 30 °C are shown in Fig. 2. The logarithmic mean permeability coefficients for CO_2 at both temperatures are shown to increase linearly with upstream pressure, whereas those for N_2 increase only slightly with the pressure.

A linear relation of the logarithm of the mean permeability coefficient to upstream pressure, which might be attributed to the plasticization action of sorbed CO_2, can be interpreted in terms of a modified free volume model [Kumazawa and Bae, 1996]. According to the modified free-volume model, the diffusion coefficient of penetrant gas in a polymer can be written as

$$D_T=RTA_d \exp(-B_d/\Phi_a v_f) \tag{9}$$

where Φ_a refers to an amorphous fraction of the polymer. The

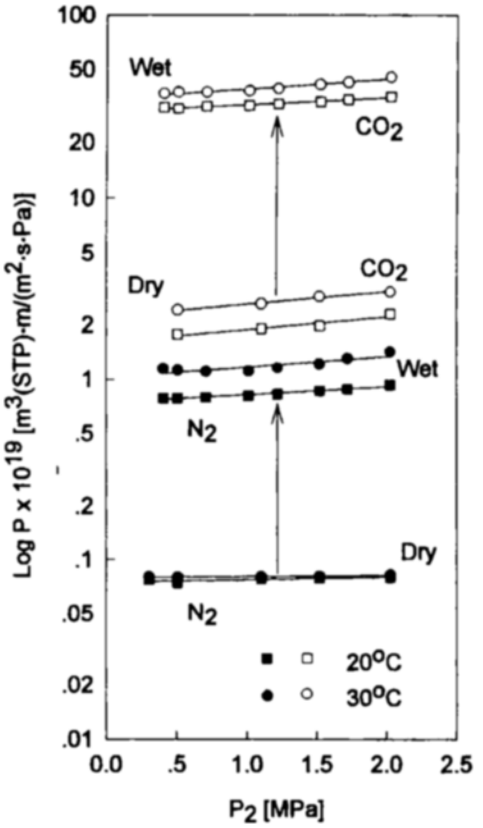

Fig. 2. Pressure dependencies of permeabilities for CO_2 and N_2 through dry and wet chitosan membranes at 20 °C and 30 °C.

fractional free volume (v_f) is a function of the temperature, the hydrostatic pressure applied to the system and the penetrant concentration by fractional volume, v. If the reference state for the free volume is taken as being the pure polymer (v=0) at some reference temperature, T_s, and pressure, p_s, the free volume near this reference state can be written as

$$v_f = v_{fs}(T_s, p_s, 0) + \alpha(T - T_s) - \beta(p - p_s) + \gamma v \qquad (10)$$

where α is the thermal expansion coefficient, β is the compressibility and γ is a concentration coefficient which defines the effectiveness of the penetrant as a plasticizer. The above equation can also be written in the form

$$v_f = v_f^o + \gamma v \qquad (11)$$

where

$$v_f^o = v_{fs}(T_{\text{fonti}}s,\ p_s,\ 0) + \alpha(T - T_s) - \beta(p - p_s) \qquad (12)$$

The steady-state permeation rate can be expressed as

$$J_s = \frac{1}{\delta}\int_{v1}^{v2} D_T\ dv = \frac{RTA_d}{\delta}\int_{v1}^{v2}\exp\left(-\frac{B_d}{\Phi_a v_f}\right)dv \qquad (13)$$

Then, the mean permeability coefficient can be given as

$$P = \frac{J_s\delta}{p_2 - p_1} = \frac{RTA_d}{p_2 - p_1}\int_{v1}^{v2}\exp\left(-\frac{B_d}{\Phi_a v_f}\right)dv \qquad (14)$$

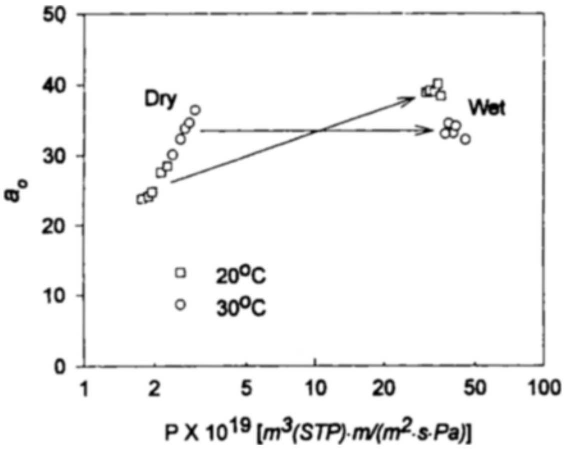

Fig. 3. Ideal separation factor of CO_2 relative to N_2 versus permeability for CO_2 through dry and wet chitosan membranes at 20 °C and 30 °C.

The above equation can be approximately written as

$$\ln P \fallingdotseq \ln p_o + \frac{B_d}{2\Phi_a(v_f^*)^2}(-2\beta + \gamma S)p_2 + \frac{B_d\gamma S}{2\Phi_a(v_f^*)^2}p_1 \qquad (15)$$

where

$$p_o = RTA_dS\ \exp(-B_d/\Phi_a v_f^*) \qquad (16)$$

$$v_f^* = v_{fs}(T_s, p_s, 0) + \alpha(T - T_s) + \beta p_2 \qquad (17)$$

Eq. (15) shows that the logarithm of the mean permeability coefficient should be linear to upstream gas pressure, consistent with experimental results depicted in Fig. 2.

Fig. 2 also shows the permeability results of the wet chitosan membrane swollen by the saturated water vapor. The permeabilities for CO_2 at 20 and 30 °C increase on average by 17 and 15 times, respectively. Those for N_2 at 20 and 30 °C also increase by 11 and 15 times, respectively. The increased permeability in a swollen chitosan membrane may arise from the fact that the diffusivity rather than the solubility was increased in a swollen state. The ratio of the permeability for CO_2 to that for N_2, i.e., the ideal separation factor for CO_2 relative to N_2, at 30 °C remains constant, while the permeability for CO_2 increases by 15 times. At 20 °C, both the permeability for CO_2 and the separation factor increase. Fig. 3 shows the experimental data plotted in Fig. 2 as the relationship between the permeability for CO_2 relative and the ideal separation factor for CO_2 to N_2.

Actually, the exhaust gas usually contains saturated water vapor. The chitosan membrane, whose permeability and separation factor for CO_2 can be increased by coexisting with water vapor, seems to be desirable from the practical point of view.

CONCLUSION

The sorption equilibrium for CO_2 in dry chitosan membrane at 20 °C and 30 °C can apparently be described in terms of a dual-mode sorption model, characteristic of glassy polymers, whereas that for N_2 obeys Henry's law. The non-linear sorption equilibrium for CO_2 could be interpreted by the concept that the interaction of sorbed CO_2 with the chitosan matrix is expressed as a reversible reaction. The logarithmic mean permeability coefficient for CO_2 in dry chitosan membrane at 20 °C and 30 °C increases linearly with upstream gas pressure, while the mean permeability coefficient for N_2 only slightly increases with the pressure. The mean permeability coefficients for CO_2 and N_2 in the wet chitosan membrane swollen with the water vapor increase by 15 to 17 times and 11 to 15 times, respectively, as compared to those in the dry membrane. The linear increase in the logarithmic mean permeability coefficient for CO_2 with the upstream gas pressure, which is attributed to the plasticization action of sorbed CO_2, can be interpreted in terms of a modified free-volume model.

NOMENCLATURE

A_d : characteristic parameter in Eq. (9) [mol·s/kg]
a_o : ideal separation factor (P_{CO_2}/P_{N_2}) [-]
b : Langmuir affinity constant $[Pa^{-1}]$
B_d : characteristic parameter in Eq. (9) [mol·s/kg]
C : total sorbed concentration $[m^3(STP)/m^3]$
C'_H : Langmuir capacity constant $[m^3(STP)/m^3]$
D_T : thermodynamic diffusion coefficient in membrane $[m^2/s]$
J : permeation flux through membrane $[m^3(STP)/m^2 \cdot s]$
K : equilibrium constant of reaction A+B=AB[Eq. (3)] $[m^3/m^3(STP)]$
k_D : Henry's law constant $[m^3(STP)/m^3 \cdot Pa]$
$\underline{p}$: pressure of penetrant gas [Pa or MPa]
P : mean permeability coefficient $[m^3(STP)/m^2 \cdot s \cdot Pa]$
R : gas constant [J/mol·k]
S : solubility coefficient $[m^3(STP)/m^3 \cdot Pa]$
T : temperature [K]
v : volume fraction concentration of penetrant gas in membrane $[m^3(STP)/m^3]$
v_f : volume fraction of free volume in membrane
α : thermal expansion coefficient of free volume defined by $(\partial v_f/\partial T)_s$
β : free volume defined by $(\partial v_f/\partial p)_s$
γ : concentration coefficient of free volume defined by $(\partial v_f/\partial v)_s$
δ : thickness of homogeneous membrane [m or μm]
Φ_a : armorphous volume fraction of polymer membrane

Subscripts

D : Henry's law mode
e : equilibrium state
H : Langmuir mode
s : steady state or reference state
tot : total
0 : zero concentration state
1 : downstream side
2 : upstream side

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