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GAS PERMEATION THROUGH GLASSY POLYMER MEMBRANES WITH HIGH GLASS-TRANSITION TEMPERATURE

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The sorption equilibria and permeation rates for carbon dioxide in such glassy polymer membranes with high glass-transition temperature as polyimide, polyetherimide, polysulfone and polyethersulfone membranes, were measured. The sorption isotherms for these systems can be described well by the dual-mode sorption model, whereas the pressure dependences of the mean permeability coefficients are simulated better by a modified dual-mode mobility model than the conventional dual-mode mobility model in which the Henry's law and Langmuir populations execute four kinds of diffusive movement.

1. Introduction

The sorption of gases and vapors in glassy polymers is generally more complex than in rubbery polymers. The sorption equilibria of gases in glassy polymers have been measured for many gas - glassy polymer systems, and have been described well in terms of a so-called dual-mode sorption model. In the dual-mode sorption model, sorbed molecules are retained in the polymer in two distinct ways, i.e., via Henry's law dissolution and Langmuir-type adsorption. Currently, it is no exaggeration to say that this dual-mode concept at sorption equilibrium has been well established. Two sorbed populations, which are termed Henry's law and Langmuir populations, respectively, can execute diffusive movements with different mobilities, while being at local equilibrium with each other. This parallel approach called dual-mode mobility model, has not been tested in many gas - glassy polymer systems, as opposed to the dual-mode sorption model, and the applicability of this model has not been confirmed yet. Besides, the two kinds of population should principally undergo movements with the two respective modes, but possibly execute jumps between the two modes. Basically four kinds of diffusion step are possible. The transport model

based on such a concept is called modified dual-mode mobility model. However, the applicability of this modified model has never examined satisfactorily.

By considering such a present situation, sorption equilibria and permeation rates for carbon dioxide in such glass polymer membranes with high glass-transition temperature as polyetherimide (PEI), polyimide (PI), polysulfone (PSF) and polyethersulfone (PES) membranes, were measured to especially discuss the mechanism of diffusion of a gas in glassy polymer membranes. In conjunction with the measured sorption equilibria, a gas diffusion mechanism was discussed by comparing it with the existing and newly proposed transport models; conventional and modified dual-mode mobility models.

2. Theoretical Background

The sorption of a gas in glassy polymers has been found to be described well by a so-called dual-mode sorption model (1):

$$C = C_D + C_H = k_D p + \frac{C_H' b p}{1 + b p} \quad (1)$$

This formula suggests two different modes of sorbed molecules, i.e., Henry's law dissolution mode (D) and Langmuir adsorption mode (H).

By assuming that two sorbed populations can execute diffusive movements with different mobilities while being at local equilibrium with each other, a dual-mode mobility model driven by gradients of concentration was proposed (2). On the basis of this dual-mode model, the mean permeability coefficient, defined by

$$\bar{P} = J_S L / (p_2 - p_1) \quad (2)$$

is given as

$$\bar{P} = k_D D_D + \frac{C_H' b D_H}{(1 + b p_1)(1 + b p_2)} \quad (3)$$

The above dual-mode mobility model, however, does not incorporate possible diffusive movements from Henry's law mode to Langmuir mode (D → H) and the reverse (H → D). Considering these two movements (3), the total diffusion flux should include four modes of diffusion, and the following modified dual-mode mobility model expression can be derived (4):

$$\bar{P} = k_D D_{DD} + \frac{2k_D D_{DH}}{b(p_2 - p_1)} \ln \frac{1 + b p_2}{1 + b p_1} + \frac{C_H' b (D_{HH} + D_{HD}) - k_D D_{DH}}{(1 + b p_1)(1 + b p_2)} \quad (4)$$

When the diffusive movement from Henry's law to Langmuir mode is neglected, that is, D_{DH} is taken to be zero, Eq.(4) reduces to

$$\bar{P} = k_D D_{DD} + \frac{C_H^b (D_{HH} + D_{HD})}{(1 + bP_1)(1 + bP_2)} \quad (5)$$

This agrees with Eq.(3) if $(D_{HH} + D_{HD})$ is set equal to D_H .

3. Experimental Section

Equilibrium sorption of a gas by a polymer film sample was measured by a pressure decay method. The sorption cell is similar to one designed by Koros et al. (5). The apparatus for permeability measurements is similar to a variable-volume method employed by Stern et al. (6). The gas to be permeated was fed into the high-pressure compartment, while the low-pressure compartment was filled with the same gas at an atmospheric pressure. The volumetric flow rate through the membrane to the low-pressure side was measured by observing the displacement of a small amount of 1-propanol in a capillary tube connected to the low-pressure side. The mean permeability coefficient was determined from this steady-state permeation rate. The permeation area of the cell is 19.6 cm^2 .

Carbon dioxide, methane, oxygen and nitrogen were used for sorbate or penetrant gas, and homogeneous dense membranes of polyetherimide (PEI, FS-1400, $T_g = 216^\circ\text{C}$, Sumitomo Bakelite), polyimide (PI, Upilex R, $T_g = 285^\circ\text{C}$, Ube Industries), polysulfone (PSF, Trayslon-PS, $T_g = 190^\circ\text{C}$, Toray) and polyethersulfone (PES, TALPA 1000, $T_g = 225^\circ\text{C}$, Mitsui Toatsu Chemicals) were used for glassy polymer membrane with high glass-transition temperature (T_g).

4. Experimental Results and Discussion

4.1 Sorption equilibria

Typical examples of measured sorption isotherms are shown in Figure 1, which represents the sorption isotherms for CO_2 and CH_4 in PSF membranes. Each isotherm exhibits a similar downward concave pattern, characteristic of glassy polymers. The sorption behavior can be simulated by the dual-mode sorption

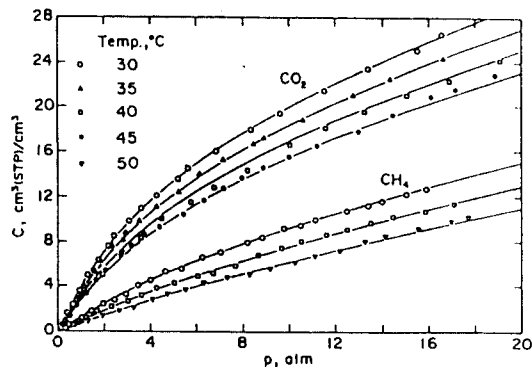


Fig.1. Sorption isotherms for CO_2 and CH_4 in PSF membranes at different temperatures.

model, viz. Eq.(1). The values of the dual-mode sorption parameters in Eq. (1) were estimated by using the Marquardt method (7), and for CO₂ they are listed in Table 1. The solid

Table 1 Dual-mode sorption parameters for CO₂ in different membranes

Polymer	Temp. [°C]	k _D [m ³ (STP)/(m ³ MPa)]	b [MPa ⁻¹]	C _H [m ³ (STP)/m ³]
PSF	30	6.38	1.92	20.5
	35	5.87	1.75	19.4
	40	5.40	1.66	18.3
	45	5.01	1.53	17.1
PEI	25	6.89	4.16	18.3
	30	5.92	3.42	17.9
	40	4.73	2.58	15.0
PES	30	7.91	5.13	17.2
PI	30	12.2	16.8	7.39
	40	10.3	12.1	5.67
	50	8.07	8.54	4.27
	60	6.83	6.27	3.34

represent the sorption isotherms calculated using Eq.(1) with these estimates. Sorption isotherms for CO₂, O₂ and N₂ in PEI and PES membranes and for CO₂ in PI membrane at various temperatures also exhibit similar non-linear patterns simulated well by the dual-mode sorption model. In Table 1, the values of the dual-mode sorption parameters for CO₂ in PEI, PES and PI membranes are also listed.

4.2 permeabilities

The experimental results of mean permeability coefficients for CO₂, O₂ and N₂ in PEI membranes and for CO₂ in PI membranes are shown as a function of upstream gas pressure in Figures 2 and 3, respectively. The mean permeability coefficients to CO₂ at each temperature exhibited pressure dependence,

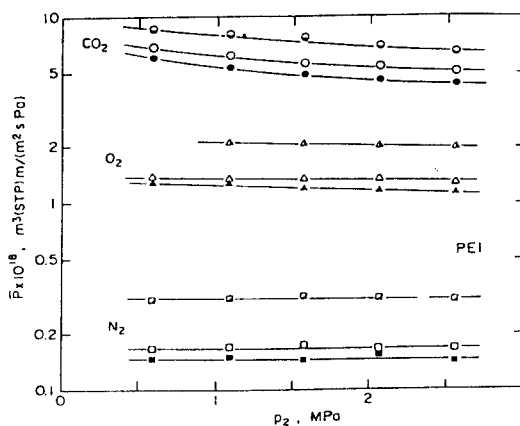


Fig.2. Mean permeability coefficients for CO₂, O₂ and N₂ in PEI membrane at 25°C (filled keys), 30°C (open keys) and 40°C (half filled keys) as a function of upstream pressure.

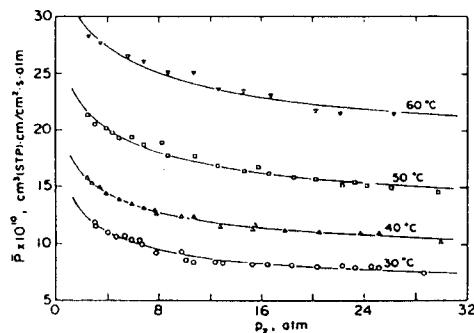


Fig.3. Mean permeability coefficients for CO₂ in PI membrane as a function of upstream pressure at different temperatures.

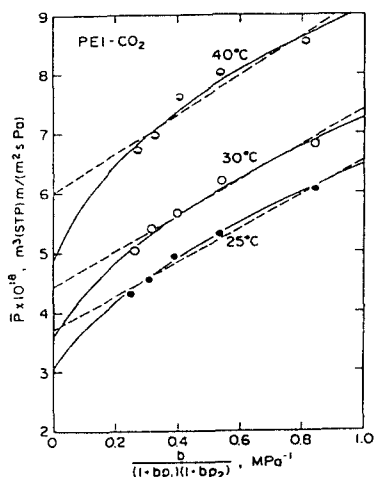


Fig.4. Test of dual-mode mobility model and comparison with a modified dual-mode mobility model for permeabilities of PEI to CO₂.

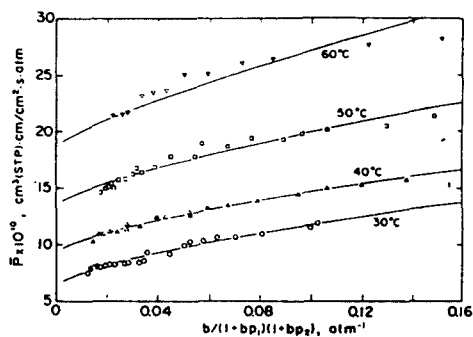


Fig.5. Test of dual-mode mobility model and comparison with a modified dual-mode mobility model for permeabilities of PI to CO₂.

characteristic of glassy polymer membranes, whereas those to O₂ and N₂ were almost independent of gas pressure. The permeability coefficients for CO₂ and CH₄ in PSF and for CO₂ in PES exhibited also similar pressure dependence. Then, it was checked whether the dual-mode mobility model is applicable or not to the observed pressure dependences of the mean permeability coefficients to CO₂.

The mean permeability coefficient data for CO₂ in PEI membrane at 25, 30 and 40°C were plotted on the basis of Eq.(3) in Figure 4. The plots do not conform to Eq.(3), i.e., conventional dual-mode mobility model as depicted by broken lines. Similarly, the mean permeability coefficient data for CO₂ in PI and PES and for CO₂ and CH₄ in PSF at different temperatures were plotted on the basis of Eq.(3). The plots are not also on the straight lines at all. The deviation from a straight line becomes especially large at higher applied gas pressures. Figure 5 indicates a typical example of these plots.

Then, from the comparison of the present permeability data with Eq.(4), plausible values of diffusivities D_{DD} , D_{DH} and $(D_{HH} + D_{HD})$ were determined. They are listed in Table 2. The values of $(D_{HH} + D_{HD})$ were evaluated, because D_{HH} cannot be distinguished from D_{HD} using Eq.(4). The solid curves in Figures 4 and 5 represent the calculated relations using Eq.(4) with the

Table 2 Diffusion parameters for CO₂ in different membranes via a modified dual-mode mobility model

Polymer	Temp. [°C]	D _{DD} × 10 ¹³ [m ² /s]	D _{DH} × 10 ¹³ [m ² /s]	(D _{HH} + D _{HD}) × 10 ¹³ [m ² /s]
PEI	25	4.4	4.1	0.78
	30	6.0	5.0	0.80
	40	10.2	7.6	0.83
PI	30	0.518	0.645	0.275
	40	0.896	0.672	0.355
	50	1.66	0.674	0.785
	60	2.69	0.740	1.60
PSF	30	39.5	26.8	4.53
	35	51.2	29.1	5.55
	40	62.8	30.4	7.25
	45	75.1	33.9	8.85
PES	30	11.5	9.94	4.96

estimates listed in Table 2. At every temperature, they are found to be in reasonable agreement with experimental points over the whole range of applied gas pressures for the five systems. Of course, it should be kept in mind that the good data-theory fits based on Eq.(4) are at least partially due to that fact that Eq.(4) has one more parameter than the conventional dual-mode mobility model.

4.3 Deviation from the conventional dual-mode mobility model

When the temperature for permeation runs is much lower than the glass-transition temperature (T_g) of the polymer, that is, T_g of the polymer is very high as compared to the experimental temperature, the pressure dependence of the mean permeability coefficient to CO₂ is apt to deviate from the prediction by the conventional dual-mode mobility model, and to be predicted by the modified dual-mode mobility model. This has been confirmed in the systems of CO₂ - PEI ($T_g = 216^\circ\text{C}$), CO₂ - PI ($T_g = 285^\circ\text{C}$), CO₂, CH₄ - PSF ($T_g = 190^\circ\text{C}$) and CO₂ - PES ($T_g = 225^\circ\text{C}$).

On the other hand, when the experimental temperature is not so much lower than T_g of the polymer, also, the pressure dependence of the mean permeability coefficient is apt to deviate from the prediction by the conventional dual-mode mobility model, and to obey a dual-mode mobility model with concentration-dependent diffusivities proposed by Zhou and Stern (8). This has been met in the systems of CO₂ - Cellulose triacetate (9), CO₂ - Methylmethacrylate/n-butyl acrylate copolymer (9), CO₂ - Polystyrene and CO₂ - Poly-4-methylpentene-1 (10). The pressure dependence of diffusivities of Henry's law and Langmuir populations can be regarded as the

result of the plasticization action of sorbed CO₂ in the polymer.

5. Conclusion

The sorption isotherms of gases in glassy polymers with high glass-transition temperature can be described well by the dual-mode sorption model. The pressure dependences of the mean permeability coefficients to CO₂ in glassy polymer membranes with high T_g are simulated better by the modified dual-mode mobility model than the conventional dual-mode mobility model in which the Henry's law and Langmuir populations execute four kinds of diffusive movement.

Nomenclature

b = Langmuir affinity constant, pa
 C = total sorbed concentration, m³ (STP)/m³
 C_D = concentration of Henry's law population, m³ (STP)/m³
 C_H = concentration of Langmuir population, m³ (STP)/m³
 C_H' = Langmuir capacity constant, m³ (STP)/m³
 D = diffusion coefficient in polymer membrane, m²/s
 J_s = steady-state permeation flux, m³ (STP)/(m² s)
 k_D = Henry's law constant, m³ (STP)/(m³ pa)
 L = thickness of membrane, m or μ m
 \bar{P} = mean permeability coefficient, m³ (STP) m/(m² s pa)
 p = gas pressure, pa or MPa

Subscripts

D = Henry's law mode
DD = within Henry's law mode
DH = from Henry's law mode to Langmuir mode
H = Langmuir mode
HD = from Langmuir mode to Henry's law mode
HH = within Langmuir mode
1 = downstream surface
2 = upstream surface

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