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Sorption and Transport of Sulfur Dioxide in Polysulfone

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Introduction

The sorption and transport of sulfur dioxide (SO_2) in polymers is important in areas such as food packaging, polymer degradation, and sensors and monitoring devices.[1-3] Another possible application is in pollution control for exhaust gases from power plants. Polysulfone is a polymer that is widely used for commercial gas separations with membranes.[4] We have investigated the sorption and transport of SO_2 in a commercially available Bisphenol A polysulfone near room temperature. The results were interpreted using the dual-mode sorption model with partial immobilization.[5] Although similar data on other polymers have been published in the literature, we are not aware of any studies of sorption and transport of SO_2 in polysulfone.

Theory

The transport of small penetrant molecules through a dense polymer film below the glass transition temperature can be described by the solution-diffusion model (for a review, see ref 6). Under the conditions of a single penetrant permeating such a film with a constant upstream pressure and negligible downstream pressure, the permeability coefficient P can be calculated as:

$$P = DS \tag{1}$$

where P is the permeability coefficient in [cm^3(STP)·cm]/[cm^2·s·cmHg]. The solubility coefficient, S, equals the secant slope of the sorption isotherm, if the downstream pressure is negligible:

$$S = C/p \tag{2}$$

where p is the upstream pressure in cmHg and C is the equilibrium penetrant concentration in [cm^3(STP)]/[cm^3 of polymer] at the given upstream pressure p. The diffusion coefficient D in eq 1 is the average (mean) diffusion coefficient in cm^2/s. The average is taken across the film between its upstream and downstream faces. A diffusion coefficient D_{Sorp} can be determined from a kinetic sorption experiment according to ref 7, if Fickian behavior is assumed:

$$D_{\mathrm{Sorp}} = 0.04919 l^2/t_{1/2} \tag{3}$$

where l is the film thickness in centimeters and $t_{1/2}$ is the time in seconds required for uptake of half of the penetrant sorbed at equilibrium. Similarly, a diffusion coefficient D_{Desorp} can be determined from eq 3 by using the half time for desorption. However, the local diffusion coefficient usually depends on the penetrant concentration. An effective average diffusion coefficient can often be used to a good approximation:

$$D_{\mathrm{av}} = (D_{\mathrm{Sorp}} + D_{\mathrm{Desorp}})/2 \tag{4}$$

The average diffusion coefficient D_{av} is a good approximation for the D appearing in eq 1, when the sorption and desorption experiments are performed between the conditions at the upstream and downstream faces of the film. The dual-mode sorption model for a single penetrant species in a glassy polymer is given by the following equations:[8]

$$C = C_{\mathrm{D}} + C_{\mathrm{H}} \tag{5}$$

$$C = k_{\mathrm{D}}p + C'_{\mathrm{H}}bp/(1 + bp) \tag{6}$$

where p is the penetrant pressure in the gas phase in equilibrium with the polymer in cmHg, k_{D} is the Henry's law constant in [cm^3(STP)]/[cm^3 of polymer·cmHg], C'_{H} is the total sorption capacity of the polymer for the penetrant in the Langmuir mode in cm^3(STP)/cm^3 of polymer, and b is the affinity constant of the penetrant for the Langmuir sites in cmHg^{-1}. The dual-mode partial immobilization model predicts the following dependence of D_{av} on D_{D} (diffusivity of the Henry's mode penetrant population), D_{H} (diffusivity of the Langmuir mode population), and the dual mode parameters:[5]

$$D_{\mathrm{av}} = D_{\mathrm{D}}\frac{1 + FK/(1 + bp)}{1 + K/(1 + bp)} \tag{7}$$

with $K = C'_{\mathrm{H}}b/k_{\mathrm{D}}$ and $F = D_{\mathrm{H}}/D_{\mathrm{D}}$. A nonlinear regression of experimental data of D_{av} versus p according to eq 7 can be used to test the applicability of the dual-mode partial immobilization model and determine D_{D} and D_{H}.

Experimental Section

Equilibrium sorption and kinetic sorption/desorption experiments were carried out in a McBain-type sorption setup at 35 °C with a calibrated quartz spring (Ruska Laboratories, Houston, TX) of 100-mg capacity and a spring constant of 2 mm/mg load. A microscope with a resolution of 0.005 mm was focused on the spring to monitor the weight changes. We estimate the uncertainty of the equilibrium sorption values to be between 1.9% at the lowest applied pressure and 0.2% at the highest applied pressure. The absolute SO_2 pressure in the setup was measured with a Baratron pressure transducer. A liquid-nitrogen cooling trap was used to prevent backdiffusion of vacuum pump oil.

The anhydrous grade SO_2 was 99.98% pure. All samples were cast from a 5 wt % solution of polysulfone (Udel P 1700 NT 11, Amoco, Ridgefield, CT) in chloroform (Mallinckrodt, 99.9% pure) under ambient conditions into a steel ring on a glass plate. The films were removed from the glass plate and dried at ambient conditions for at least 10 days and then in a vacuum oven for 24 h at 200 °C. The samples were then cooled to room temperature at a rate of about 1 °C/min by turning the oven off.

Results and Discussion

Equilibrium Sorption. Figure 1 shows the equilibrium sorption isotherm for SO_2 in polysulfone. The isotherm shows a shape typical for the dual-mode sorption behavior for gases in glassy polymers. Table I shows the dual-mode parameters (obtained by nonlinear regression) in comparison with values for N_2 and CO_2.

The Henry's law constant k_{D} and the Langmuir affinity constant b for SO_2 are significantly larger than those for CO_2 or N_2. This reflects the fact that SO_2 at 35 °C is much below its critical temperature of 157.6 °C. The high overall sorption capacity of SO_2 has implications for the permselectivity that will be discussed later.

Sorption Kinetics. Figure 2 shows a representative sorption/desorption run at the highest SO_2 pressure that was used. Also shown is a curve that is calculated using D_{av} from eq 4 and the Fickian model with a constant diffusion coefficient.[7] This curve is reasonably close to the sorption data for all sorption/desorption runs, but the desorption data lag somewhat behind.

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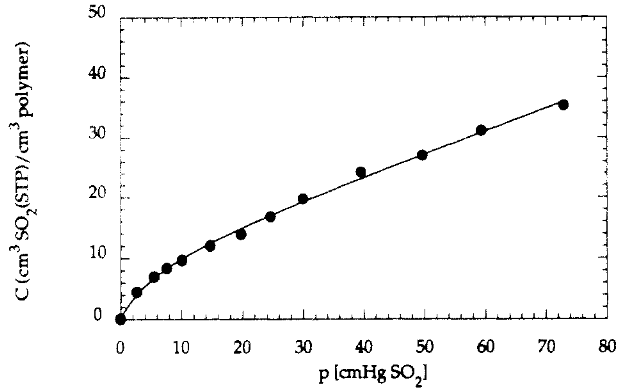

Figure 1. Equilibrium sorption isotherm of SO_2 in polysulfone at 35 °C. The curve has been plotted using eq 6 and the dual-mode parameters from Table I.

Table I. Dual-Mode Sorption Parameters for SO_2, CO_2, and N_2 at 35 °C in Polysulfone

gas	k_D (cm^3 (STP)/cm^3 of polymer·cmHg)	C'_H (cm^3 (STP)/ cm^3 of polymer)	b (cmHg^{-1})	$K = C'_H b/k_D$
SO_2	0.37	9.82	0.17	4.51
CO_2[a]	9.61×10^{-3}	19.6	3.42×10^{-3}	6.98
N_2[a]	2.24×10^{-3}	0.96	1.32×10^{-3}	0.57

[a] McHattie, J. S. Ph.D. Thesis, The University of Texas at Austin, Austin, TX, 1990.

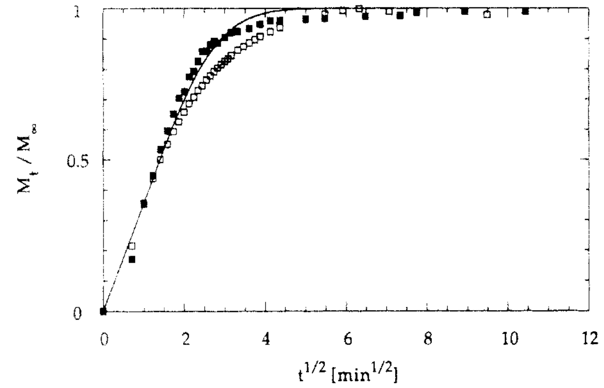

Figure 2. Sorption/desorption of SO_2 in polysulfone (35 °C, 0.92-mil thickness; sorption, 66.2 cmHg SO_2): (■) Sorption, $D_{Sorp} = 2.4 \times 10^{-9}$ cm^2/s; (□) Desorption, $D_{Desorp} = 2.4 \times 10^{-9}$ cm^2/s. The curve has been calculated using the Fickian model with D_{av} according to eq 4.

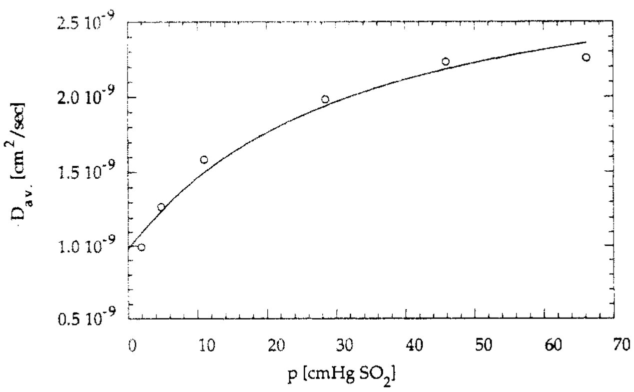

Figure 3. Average diffusion coefficient D_{av} of SO_2 in polysulfone at 35 °C. The nonlinear regression to determine D_D and D_H according to eq 7 is shown ($D_D = 3.0 \times 10^{-9}$ cm^2/s, $D_H = 5.2 \times 10^{-10}$ cm^2/s).

Table II. Solubility and Diffusivity Contributions to the Estimated SO_2/N_2 Permselectivity of Polysulfone at 35 °C[a]

P_{N_2} (barrer)[b]	$\alpha^*_{SO_2/N_2} = P_{SO_2}/P_{N_2}$	S_{N_2} [cm^3(STP)/ cm^3 of polymer·cmHg]	S_{SO_2}/S_{N_2}	D_{N_2} (10^{-8} cm^2/s)	D_{SO_2}/D_{N_2}
0.25	83.30	1.97×10^{-3}	694.13	1.22	0.12

[a] Assumed conditions: upstream 1% SO_2 in N_2, total pressure 5.05 atm, downstream pressure negligible, no strong penetrant interactions present. N_2 data at 35 °C and 5 atm from: McHattie, J. S. Ph.D. Thesis, The University of Texas at Austin, Austin, TX, 1990. [b] 1 barrer = 1×10^{-10} cm^3(STP)·cm/cm^2·cmHg·s.

Figure 3 shows the D determined from eq 4 as a function of SO_2 pressure. Typical for glassy polymers in the absence of plasticization, the diffusion coefficient increases first with pressure and then levels off at higher pressures. The curve shown in Figure 3 is a nonlinear regression of eq 7 to fit the data. The good fit shows the applicability of the dual-mode partial immobilization model. The diffusion coefficient of the Henry's mode population D_D is almost an order of magnitude higher than that of the Langmuir population, D_H.

Estimation of the Behavior of SO_2/N_2 Mixtures. We have chosen a dilute mixture of 1% SO_2 in N_2 as an example, since the dilute case often occurs in practical problems. The ideal gas selectivity α^* can be factored into a diffusivity (mobility) selectivity and a solubility (thermodynamic) selectivity:[6]

$$\alpha^*_{A,B} = P_A/P_B = (D_A/D_B)(S_A/S_B) \qquad (8)$$

where A and B denote the components of a mixture. In this calculation it is assumed that no strong interactions between the penetrants are present, so that single penetrant data can be used to approximate mixture data. Table II shows the result for a SO_2/N_2 mixture.

The very large solubility selectivity for SO_2 is counteracted by the fact that the diffusivity selectivity favors the smaller N_2 molecule.

Conclusions

The single gas sorption and diffusion of SO_2 in polysulfone were investigated at SO_2 pressures up to about 1 atm and 35 °C. The dual-mode partial immobilization model was applicable and described the data reasonably well. The sorption capacities for SO_2 were extremely high, compared to N_2 and CO_2. The estimated selectivity for SO_2 over N_2 in a dilute mixture is caused mainly by the very high solubility selectivity which is counteracted by a diffusivity selectivity favoring the smaller N_2 molecule.

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References and Notes

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