

# Transient Sorption of Sulfur Dioxide in Epoxy Resin of Aliphatic Diglycidyl Ether

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## Synopsis

Diffusion of sulfur dioxide in epoxy resin of aliphatic diglycidyl ether was studied performing differential sorption kinetic measurements at temperatures ranging from 1°C to 45°C and activities varying from 0.12 to 0.55. The diffusion of sulfur dioxide appears to be Fickian over the entire temperature range studied. There is a marginal increase in the diffusion coefficient with increase in concentration. The diffusion coefficients evaluated from both "small times" data and "large times" data are in reasonable agreement.

## INTRODUCTION

The understanding of the transport phenomena governing a particular penetrant-polymer system is extremely important for barrier applications of the polymer. Sorption kinetic studies are commonly used to study the diffusion of a gas into polymers.<sup>1</sup> The data obtained from these studies can be used to evaluate the diffusion coefficient. Sorption kinetic data are also helpful to decide if the diffusion coefficient is concentration-dependent or to detect any non-Fickian processes occurring during the process of transient sorption.<sup>2</sup> Knowing the diffusion coefficient and the equilibrium solubility of the gas in the polymer, an estimate of permeability of the gas can be readily obtained.<sup>3</sup> Koros et al. studied the kinetics of sorption and equilibrium solubility of sulfur dioxide in Kapton™ polyimide.<sup>4</sup> Felder et al. have given extensive permeability data and some diffusion data for sulfur dioxide transport through polymers.<sup>5</sup> Davis and Rooney studied the diffusion of sulfur dioxide in polyethylene, polycarbonate, and polyamide.<sup>6</sup>

A major problem facing ancient marble structures is deterioration due to exposure to various degrading gases present in the polluted atmosphere.<sup>7</sup> The damage caused by natural weathering processes has been accelerated due to increased air pollution in recent years. In particular, sulfur dioxide is a major degrading component in highly industrialized areas. Several different types of epoxy resins were tried in order to evaluate their effectiveness as a protection for marble.<sup>7</sup> It was found that there were major differences in the amount of protection provided by different epoxy resins.

These differences can be understood only by a systematic study of sulfur

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dioxide transport through these epoxy resins. A suitable epoxy resin coating for protection against degrading atmospheric gases should have good barrier properties along with excellent weatherability, crack resistance, and stability. Kim studied the equilibrium sorption of sulfur dioxide in different epoxy resins.<sup>8</sup> The present study deals with transient sorption of sulfur dioxide in epoxy resin of aliphatic diglycidyl ether. It was expected that this study would provide an understanding of the general mechanism of transport of sulfur dioxide in similar epoxy resins and would be useful in predicting epoxy resin performance for protective barrier applications. The energetics and temperature dependence of equilibrium solubility for this sulfur dioxide-epoxy resin system will be discussed in a later publication.<sup>9</sup>

### EXPERIMENTAL

The experimental setup consisted of a McBain quartz spring balance provided with a water jacket. The temperature of the chamber was controlled to a  $\pm 0.1^\circ\text{C}$  using a circulating bath. The extension of the quartz spring could be measured by an Eberbach cathetometer with a least count of 0.005 cm. The gas pressure in the sorption chamber was measured using a manometer. The temperature of the water jacket was adjusted to the desired value before the start of a differential sorption kinetic experiment. The polymer film was completely degassed before beginning the differential sorption measurements. Sulfur dioxide was then introduced in the sorption chamber and its pressure was adjusted to a desired value ( $P_1$ ). The film was allowed to achieve equilibrium with the gas. After the achievement of equilibrium, the pressure of sulfur dioxide in the sorption chamber was increased to a higher value ( $P_2$ ). The extension of the spring and also the pressure in the sorption chamber was monitored after the pressure change was made. The experiment continued until equilibrium was achieved again. The pressure of sulfur dioxide in the chamber when equilibrium was achieved ( $P_\infty$ ) was also recorded. The change in pressure from  $P_2$  to  $P_\infty$  was due to gas sorption by the polymer film. The values of  $P_1$ ,  $P_2$ , and  $P_\infty$  are shown in Table I. Further details of the experimental procedure are given by Nadgir.<sup>10</sup> Epi-Rez 502 (Celanese Chemical Co.) is an aliphatic diglycidyl ether which can be cured using diethylene triamine (DETA). The amount of DETA curing agent

TABLE I  
Comparison of Diffusion Coefficients Obtained by Different Methods

Temp (°C)	Pressure (cm Hg)			Diffusion coefficient ( $\times 10^9$ cm <sup>2</sup> /s)	
	$P_1$	$P_2$	$P_\infty$	$D$ (C <sub>0</sub> )	Apparent $D_a$
1	21	68.9	66.8	7.5	7.6
6	12.7	30.5	28.8	7.9	6.5
	28.8	62.5	60.5	8.1	7.6
20	7.3	29.8	28.8	12.7	13.1
	28.8	71.7	70.6	12.7	13.1
33	26.2	50.5	50	19.3	30.3
	64.6	99.3	98.7	20.0	30.3
45	74.8	93.2	92.6	28.8	28.0

used in the present study for complete curing was 6.86 phr. A polymer film of thickness of 0.0076 cm was prepared using a Bird film applicator. The epoxy resin film is expected to be in a rubbery state at room temperature due to its low glass transition temperature.

## RESULTS AND DISCUSSION

Differential sorption kinetic data were collected at temperatures of 1°C, 6°C, 20°C, 33°C, and 45°C to investigate the processes occurring during transient sorption. The activities for these sorption experiments varied from 0.12 to 0.55. The values of  $M_t$ , the amount of SO<sub>2</sub> sorbed in time  $t$ , were corrected by subtracting the amount due to surface adsorption. This type of correction is common for sorption kinetic data and is also mentioned by Huvard.<sup>11</sup> Figures 1 and 2 show the plots of  $M_t/M_\infty$  vs.  $t^{1/2}$ , where  $M_\infty$  is the amount of penetrant sorbed when equilibrium is achieved.  $P_1$  and  $P_\infty$  are the initial and final pressures of sulfur dioxide to which the polymer film was exposed.  $P_0$  is the vapor pressure of sulfur dioxide at that temperature.

An initial linear portion which extends up to at least 60% of  $M_\infty$ , for each of these curves at different pressure intervals, indicates that Fickian diffusion is obeyed.<sup>1</sup> The pertinent equation for Fickian diffusion at small times is given by Crank and Park<sup>1</sup>:

$$M_t/M_\infty = 4(Dt/\pi l^2)^{1/2} \quad (1)$$

where  $D$  = constant diffusion coefficient (cm<sup>2</sup>/s),  $l$  = polymer film thickness (cm), and  $t$  = time (s).

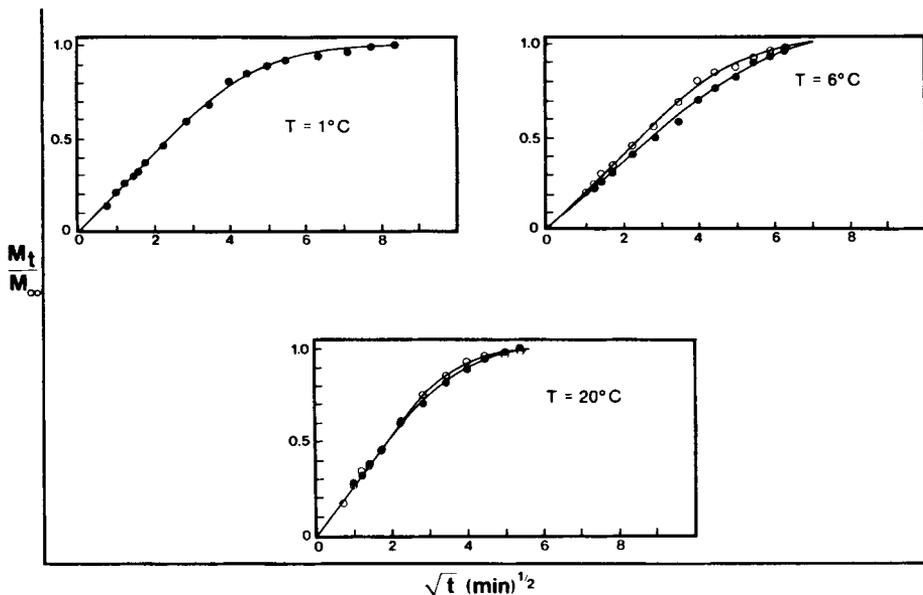


Fig. 1. Sorption kinetic plots for sulfur dioxide in epoxy resin film at 1°C, 6°C, and 20°C. Note the initial linear portions of all plots. At 1°C (cm Hg):  $P_1 = 21$ ;  $P_\infty = 66.8$ ;  $P_0 = 121.3$ . At 6°C: (●)  $P_1 = 12.7$ ,  $P_\infty = 28.8$ ; (○)  $P_1 = 28.8$ ,  $P_\infty = 60.5$ ;  $P_0 = 147.9$ . At 20°C: (●)  $P_1 = 7.3$ ,  $P_\infty = 28.8$ ; (○)  $P_1 = 28.8$ ,  $P_\infty = 70.6$ ;  $P_0 = 247.7$ .

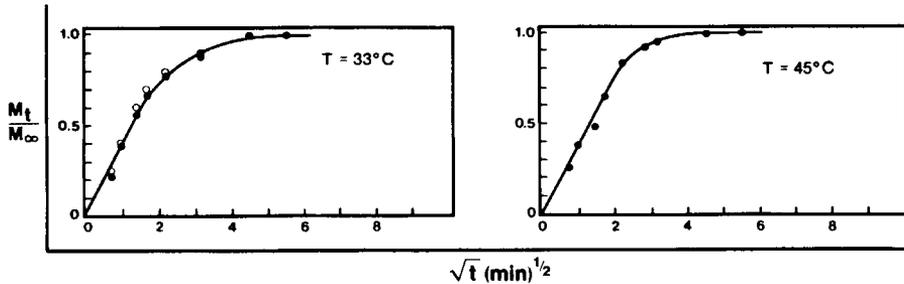


Fig. 2. Sorption kinetic plots for sulfur dioxide in epoxy resin at 33°C and 45°C. Note that at 33°C sorption curves for different final pressures overlap. At 33°C (cm Hg): (●)  $P_1 = 26.2$ ,  $P_\infty = 50$ ; (○)  $P_1 = 64.6$ ,  $P_\infty = 98.7$ ;  $P_0 = 381.3$ . At 45°C:  $P_1 = 74.8$ ;  $P_\infty = 92.6$ ;  $P_0 = 548.2$ .

The initial linear portion is present at all temperatures varying from 1°C to 45°C. This indicates that the diffusion of sulfur dioxide in the epoxy resin is Fickian at these temperatures.

Equation (1) can be used to obtain the value of the diffusion coefficient if it is independent of concentration. In the case of a concentration-dependent diffusion coefficient, the slope of the initial linear portion of the sorption curve would give an apparent diffusion coefficient  $D_a$ , which is some integral average value of the diffusion coefficient over the concentration range involved.<sup>12</sup> If the diffusion coefficient increases with increase in concentration, the initial linear portion of  $M_t/M_\infty$  vs.  $t$  curve may extend to more than 60% of  $M_\infty$ , depending on the relative change in the diffusion coefficient in the concentration range involved.<sup>2</sup>

At a temperature of 33°C, the two sorption curves for different pressure intervals overlap. At 20°C, the initial linear portions of sorption curves for the final  $\text{SO}_2$  pressures ( $P_\infty$ ) of 28.8 cm Hg and 70.6 cm Hg have essentially the same slope. At 6°C, the sorption curve for a final pressure of 28.8 cm Hg lies below the corresponding curve for 60.5 cm Hg, though the divergence between the curves is rather small.

The above data indicate that the diffusion coefficient increases with increase in penetrant concentration in the polymer because of higher slopes of the initial linear portions of the sorption curves at higher pressures.<sup>12</sup> The divergence between the sorption curves indicates the relative change in the magnitude of diffusion coefficient.<sup>12</sup> It is apparent that the increase in the diffusion coefficient is only marginal as the divergence between the curves at any given temperature is very small, and, in other cases, the sorption curves actually overlap. The values of apparent diffusion coefficients  $D_a$  were calculated using the slopes of initial linear portions of the sorption curves. The values of  $D_a$  at different temperatures and pressures are listed in Table I.

For a constant diffusion coefficient, Fickian diffusion, the governing equation at large times is

$$\ln(1 - M_t/M_\infty) = \ln(8/\pi^2) - D\pi^2 t/l^2 \quad (2)$$

The  $\ln(1 - M_t/M_\infty)$  vs.  $t$  plot of large times data has an intercept of  $\ln(8/\pi^2)$  on the ordinate and the constant diffusion coefficient can be obtained from the slope of the plot knowing the film thickness. For a concentration-dependent

diffusion coefficient  $D(C)$  this plot will asymptotically approach a straight line, the slope of which will yield a diffusion coefficient  $D(C_0)$ , where  $C_0$  is the saturation concentration.<sup>1</sup>

Figure 3 shows the large times  $\ln(1 - M_t/M_\infty)$  vs.  $t$  plots at 1°C and 45°C. The plots are linear throughout indicating that the diffusion coefficient is essentially constant. The values of  $D(C_0)$  at different pressure ranges and temperatures are listed in Table I. These values confirm the earlier conclusion that the diffusion coefficient increases with an increase in concentration, even through the variation in  $D(C_0)$  is very slight. It can also be noted that  $D(C_0)$  values are not very different from  $D_a$ , the apparent diffusion coefficient. This is likely only in the case of marginal variation in the diffusion coefficient with change in concentration. The reason for the discrepancy between the  $D(C_0)$  and  $D_a$  values at 33°C is not quite clear.

Fickian diffusion of gases in various rubbery polymers was observed by several workers and is very common.<sup>3,12,13,14</sup> Koros et al. studied the diffusion of sulfur dioxide in glassy Kapton™ polyimide and found that the diffusion coefficient increased with an increase in concentration.<sup>4</sup> Davis and Rooney studied the permeation of sulfur dioxide in polyethylene, polycarbonate, and polyamide.<sup>6</sup> Fickian diffusion was obeyed for all SO<sub>2</sub>-polymer systems studied by them except at high sulfur dioxide pressures. Also, the diffusion coefficient increased with an increase in sulfur dioxide concentration in the polymers. The increase in diffusion coefficient with an increase in sulfur dioxide concentration in the present study can be explained to be due to a plasticizing effect of high concentrations of penetrant. The diffusion coefficients were also calculated using a more rigorous procedure which corrected for the slight pressure decrease in the sorption chamber.<sup>1,10</sup> These diffusion coefficients were within 5% of the values calculated from eq. (3), indicating no significant error was introduced in the

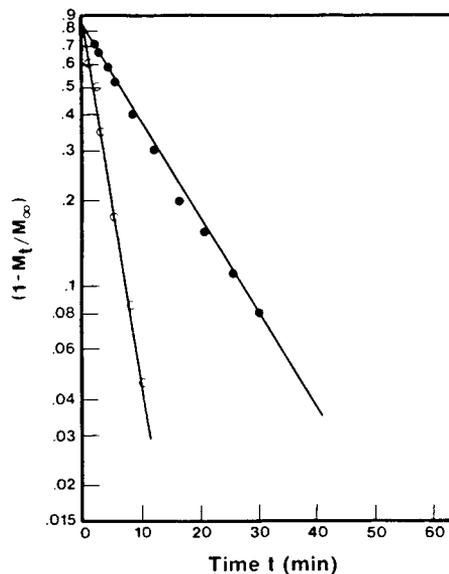


Fig. 3. Large times  $\ln(1 - M_t/M_\infty)$  vs.  $t$  plot at 1°C (●) and 45°C (○). Note the linearity of plot throughout.

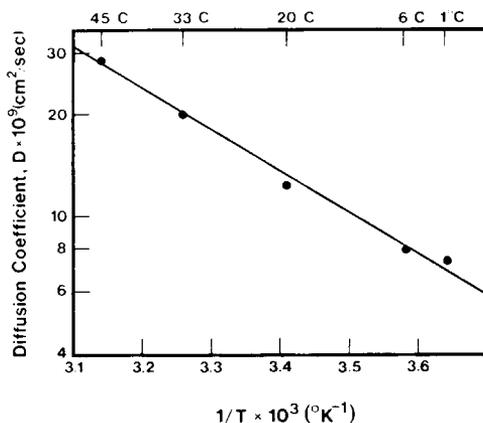


Fig. 4. Arrhenius plot of the diffusion coefficient for sulfur dioxide epoxy resin system.

calculation of diffusion coefficients due to slight pressure decrease in the sorption chamber.

Figure 4 shows an Arrhenius plot for the diffusion coefficient. Because the dependence of the diffusion coefficient on concentration was very small, an average value was used at each temperature. The Arrhenius plot is linear and the activation energy for diffusion is  $23 \text{ kJ}\cdot\text{mol}^{-1}$ . ( $5.5 \text{ kcal/g}\cdot\text{mol}$ ). Table II lists the diffusion coefficients of sulfur dioxide in various polymers for the purpose of comparison.<sup>5,4</sup>

## CONCLUSIONS

A study of transient sorption of sulfur dioxide in epoxy resin of aliphatic diglycidyl ether indicated Fickian diffusion over the temperature range of  $1^\circ\text{C}$  to  $45^\circ\text{C}$ . In this temperature range, the diffusion coefficient varied from  $7.5 \times 10^{-9} \text{ cm}^2/\text{s}$  to  $28.8 \times 10^{-9} \text{ cm}^2/\text{s}$ . The diffusion coefficient was seen to increase with increase in concentration; however, the small change ( $<4\%$ ) over the concentration ranges studied justifies the use of an essentially constant value at each temperature for describing the sorption kinetics. This slight increase in the diffusion coefficient is presumably due to plasticization of the polymer matrix. The diffusion coefficient exhibited an Arrhenius temperature dependency with an activation energy of  $5.5 \text{ kcal/g}\cdot\text{mol}$ .

TABLE II  
Sulfur Dioxide Diffusion Coefficients in Various Polymers<sup>5,4</sup>

Polymer	Temp (°C)	Diffusion Coefficient $D \times 10^{-10}$ $\text{cm}^2/\text{s}$
Vulcanized natural rubber	22	10,000
TFE Teflon	25	1,300
Ethyl cellulose	25	530
Epi-Rez 502 epoxy resin	20	127 (present study)
	45	288 (present study)
Poly(methyl methacrylate)	25	6.2
Kapton™ polyimide	25	1.25

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