

Solubility and Diffusivity of Sulfur Dioxide in Latex Paint Films

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Synopsis

Sorption of SO₂ in latex paint films is measured as a function of time. This data is used to extract the solubility (*S*) and the diffusion coefficient (*D*) for SO₂ in these films. The solubility of SO₂ in each of the samples follows Henry's law behavior. Sorption occurs only in the polymer, with the inorganic pigment particles acting as impenetrable fillers. The diffusion of SO₂ is Fickian with an exponential dependence upon the concentration of SO₂. This data is used to calculate the permeabilities of the paint samples to SO₂, at levels typically found in the atmosphere.

INTRODUCTION

Over the last decade the problem of acid rain has grown from being the concern of small environmental groups to its present status near the top of governmental priorities. This acidified precipitation poses serious threats to the world's forest reserves and structural materials. In many cases the only protection offered to these structural materials comes from a few mils of paint. Paints protect a substrate, usually of wood or metal, by forming a barrier to harmful gases and vapors present in the environment. With the increasing tenacity of the attacking species in the atmosphere (such as SO₂ and NO_x gases from automobile emissions) questions are being raised about how successfully these paints are performing.¹⁻⁴

In assessing the possible deleterious effects of pollutant gases on paint films, it is of use to know how much gas dissolves in the paint film and how rapidly it moves through the paint film. The physical quantities of interest are the solubility (*S*), the diffusivity (*D*), and the permeability (*P*). For polymers above their glass transition temperature (*T_g*), solubility follows Henry's law,

$$C = Sp \quad (1)$$

where *C* represents concentration of dissolved species in equilibrium with a gas of partial pressure *p*. Diffusion in thin polymer films above their *T_g* along the thickness direction (*x*) generally follows Fick's law,

$$J = -D \frac{\partial C}{\partial x} \quad (2)$$

where J is the flux of penetrant through the film subject to a concentration gradient of $\partial C/\partial x$ and D represents the (concentration-independent) diffusion coefficient. These two quantities S and D can be deduced by measuring the mass of gas sorbed by a thin film of paint as a function of time.⁵⁻¹³ The permeability is defined as the product of S and D .

Many investigations of SO_2 solubility, diffusivity, and permeability in polymeric materials have been undertaken. Felder, Spence, and Ferrell have compiled some of the findings.¹⁴ Typical values for SO_2 permeability at 25°C are 1.32×10^{-9} and 4.32×10^{-8} ($\text{cm}^2 \text{ cc SO}_2$ (STP)/ cc sample cm Hg s) in poly(vinyl chloride) and poly(methyl methacrylate), respectively. Funke and Haagen¹⁵ report SO_2 as having a high diffusivity in many polymeric coatings for a molecule of its size. Keuhe and Friedlander¹⁶ found the solubility of SO_2 in polyacrylate to be very high. Davis and co-workers report high permeabilities for SO_2 in other commercial polymers^{17,18} such as 2.09×10^{-9} (same units as above) for polyethylene; 6.58×10^{-10} for polyamide; 2.24×10^{-9} for polycarbonate and 2.01×10^{-11} for the copolymer of vinylidene chloride and vinyl chloride.

Latex paints are composed of a latex base polymer with various additive extenders, emulsifiers, pigments, fungicides, and others. These paint additives may aid or hinder the solubility and diffusivity of an atmospheric component in the paint. Relatively little work regarding solubilities and diffusivities of pollutant gases in latex paints has appeared in the literature. In this work gravimetric determinations are made of the solubility and diffusivity of SO_2 in two latex paint formulas, and in the base polymer common to both.

EXPERIMENTAL

Samples. Two exterior grade latex paint formulations were prepared by and obtained from Union Carbide Coatings and Emulsions (Cary, NC). The base polymer, common to both paints, was also supplied. This latex was reported to be copolymer containing a 1 : 1 : 1 mole ratio of vinyl chloride, vinyl acetate, and butyl acrylate, with small amounts (less than 7 mol %, total) of methyl acrylate, methyl methacrylate, and acrylic acid. The two paints differed in that one contains a CaCO_3 extender while the other includes no CaCO_3 . The paint compositions are listed in Table I, and the approximate dry film compositions are listed in Table II. The values in Table II were obtained by assuming that all volatile paint components are removed in the drying process.

Density measurements of the three samples were carried out using an Archimedes apparatus and are as follows: 1.287 g/cm^3 for the base latex; 2.112 g/cm^3 for the latex with CaCO_3 ; and 2.122 g/cm^3 for the latex without CaCO_3 .

Paint Film Preparation. Films of uniform thickness were prepared from the samples by casting with a draw bar on clean glass plates. The films remained on the plates in a dust-free environment under room conditions for 16 h. The samples were then placed in a freezer for 3-6 h and removed to room temperature for 10 min in order to aid in removing the films from the glass plates. The films were then stored in a desiccator over anhydrous CaSO_4 for a minimum of 3 days. Determination of film thickness was achieved through the use of a micrometer having a precision of $\pm 1.2 \mu\text{m}$. Film thickness for this study was on the order of 5 mils ($127 \mu\text{m}$).

TABLE I
Acrylic Latex Paint Composition

Components	Wt %	
	Latex w/CaCO ₃	Latex w/o CaCO ₃
Water	20.5	20.5
UCAR 516 (acrylic terpolymer)	35.0	35.0
RCL 9 TiO ₂ (pigment)	21.2	25.4
Genstar camel white (CaCO ₃ extender)	12.7	0.0
Optiwhite P (china clay extender)	4.2	12.7
Aqualon H ₄ Br (bioresistant thickener)	0.2	0.2
BYK 155 (dispersant)	0.8	0.8
TKPP (codispersant)	0.1	0.1
Triton N101 (nonionic surfactant)	0.2	0.2
Nalco 2315 (foam reduction)	0.3	0.3
Ethylene glycol	2.4	2.4
Texanol (coalescent)	1.4	1.4
Trysan polyphase (biocide)	0.8	0.8
Ammonium hydroxide	0.2	0.2

Sorption-Desorption Measurements. A McBain¹³ balance with quartz springs (spring constants = 0.51 and 0.332 mg/mm) were used to perform mass uptake measurements of SO₂ as a function of time. The deflection of the sample suspended on the end of the spring was recorded through the use of an optical reader traveling vertically on a calibrated shaft (cathetometer). The ultimate sensitivity of this system is 0.026 mg and 0.017 mg for the two springs mentioned above. Anhydrous grade SO₂ was purchased from Union Carbide and was reported to be 99.98% pure. This gas was used as received and the system pressures reported are as read from a mercury manometer with a readability of ± 1 mm. A mechanical vacuum pump was used to evacuate the system and degas the sample; it could achieve vacuum of 1 mtorr. Temperature control was maintained to ± 1°C by circulating water through a jacket surrounding the sorption cell.

RESULTS AND DISCUSSION

The treatment of the sorption (or desorption) data is represented in Figure 1, where M_t is the mass of SO₂ sorbed (or desorbed) at time t and M_∞ is the

TABLE II
Approximate Dry Film Composition

Component	Latex paint (w/CaCO ₃)		Latex paint (w/o CaCO ₃)	
	(wt %)	(vol %)	(wt %)	(vol %)
Latex base polymer	37	61.6	37	63.6
CaCO ₃	21	16.1	0	0.0
TiO ₂	35	17.6	42	22.0
China clay	7	4.7	21	14.4

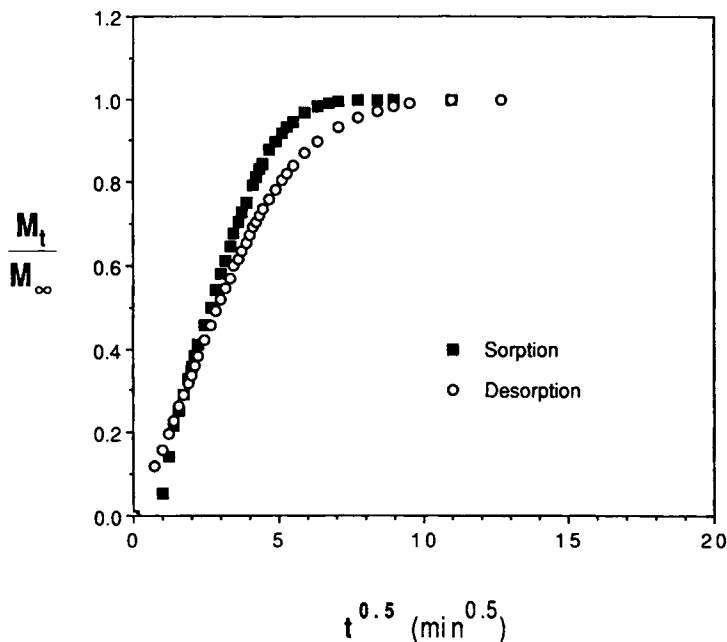


Fig. 1. A typical plot showing the treatment of the sorption and desorption data. The data shown is for the base polymer at 28°C and 161 torr of SO₂.

mass of SO₂ sorbed (or desorbed) at equilibrium. The data is plotted for convenient use of

$$\frac{M_t}{M_\infty} = \frac{4}{l} \left(\frac{Dt}{\pi} \right)^{0.5} \quad (3)$$

which describes Fickian diffusion in a thin film at short times. In eq. (3), l represents the film thickness while D is the diffusion coefficient. The slope of the initial linear region from plots such as Figure 1 is used with eq. (3) to determine D .

Sorption isotherms are obtained by plotting M_∞ vs. pressure. Sorption isotherms acquired at 28°C for SO₂ in the two paint samples and the base polymer are displayed in Figure 2. All samples exhibit the expected Henry's law behavior for a polymer above its T_g . In accordance with previous work with SO₂ in other polymers,¹⁴ the solubility is quite high; the polymer base absorbs about 13% by weight at 1 atm of SO₂. The isotherms nearly superimpose when the amount of SO₂ sorbed by the paint samples is normalized to the amount of polymer in the paint (37%, from Table II). This is shown by the dashed lines in Figure 2, and indicates that sorption occurs only in the polymer, with the inorganic additives in the paint samples acting simply as impenetrable fillers. The small differences in the normalized isotherms for the three samples could be due to the uncertainty in the amount of polymer contained in each paint. Adjustments to this number of less than 4% will cause the isotherms for all three samples to superimpose perfectly. The solubilities are listed in Table III for these iso-

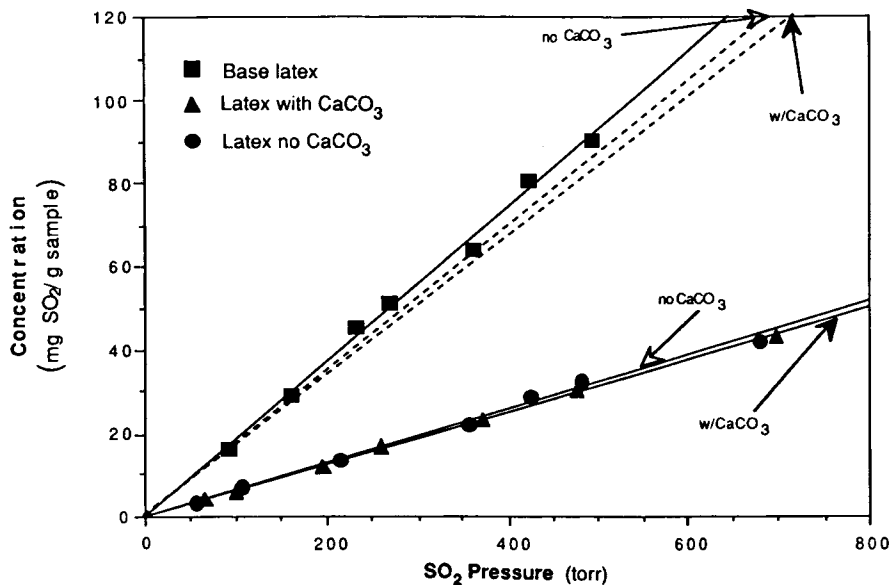


Fig. 2. Isotherms for several paint samples taken at 28°C: (—) least-squares fit to data; (---) isotherms for the paint samples normalized to the mass of polymer base contained in each sample using a factor of 0.37 g polymer base/g sample.

therms (run 2), as well as for a second set of samples (run 1) to illustrate the degree of reproducibility. In the worst case (latex without CaCO_3), the solubilities from the two runs differ by about 11%. Also listed in Table III are the unnormalized solubilities for the paints, in terms of grams of sample.

The diffusion coefficient was calculated from plots such as Figure 1 at each pressure, and was found to be pressure (concentration)-dependent. This is not surprising for high-solubility penetrants (such as SO_2) that are likely to plasticize the polymer. In cases where D is concentration-dependent, an average diffusion coefficient D_{ave} is usually defined, which describes transport over some small concentration range C_1 - C_2 :

$$D_{\text{ave}} = \frac{1}{C_2 - C_1} \int_{C_1}^{C_2} D(C) dc \quad (4)$$

TABLE III
Solubilities (S) for Sulfur Dioxide in Paint Samples

Sample	S (mg SO_2 /g sample torr)		S (mg SO_2 /g polymer torr)	
	Run #1	Run #2	Run #1	Run #2
Latex base	0.192	0.186	0.192	0.186
Latex w/o CaCO_3	0.0720	0.0641	0.194	0.173
Latex w/ CaCO_3	0.0620	0.0623	0.168	0.168

An approximation to D_{ave} is obtained by performing integral sorption and desorption experiments at each pressure, calculating the sorption and desorption diffusion coefficients from eq. (3) and averaging these two numbers. In integral sorption $C_1 = 0$ for sorption and $C_2 = 0$ for desorption.

For Fickian diffusion in polymers above T_g , for which the sorbed penetrant concentration does not exceed approximately 10 wt % of polymer, an exponential dependence of D on concentration is common, i.e.,

$$D_{ave} = D_0 \exp(AC) \quad (5)$$

Here D_0 is the penetrant diffusivity at infinite dilution, and A is a "plasticization parameter."²⁰⁻²⁴ A plot of $\ln D_{ave}$ as a function of pressure is presented in Figure 3. The fit to the data for the latex base is reasonably good, while the data for the paints show considerably more scatter. The values of D_{ave} for the base polymer are consistently higher than for the two paint samples, which seem to have the same D_{ave} at a given pressure. This is as expected since the diffusing molecules are not hindered in their motion through the polymer network by the presence of the filler particles in the base latex while these obstacles are present in the two paints. The lower values for the diffusion coefficient in the two paints is very likely due to the increase in the diffusion path for a penetrant molecule which must travel around these filler particles.

In spite of the scatter in the data for the paints, the slope of all three lines in Figure 3 are essentially equal, indicating that the polymer phase in each

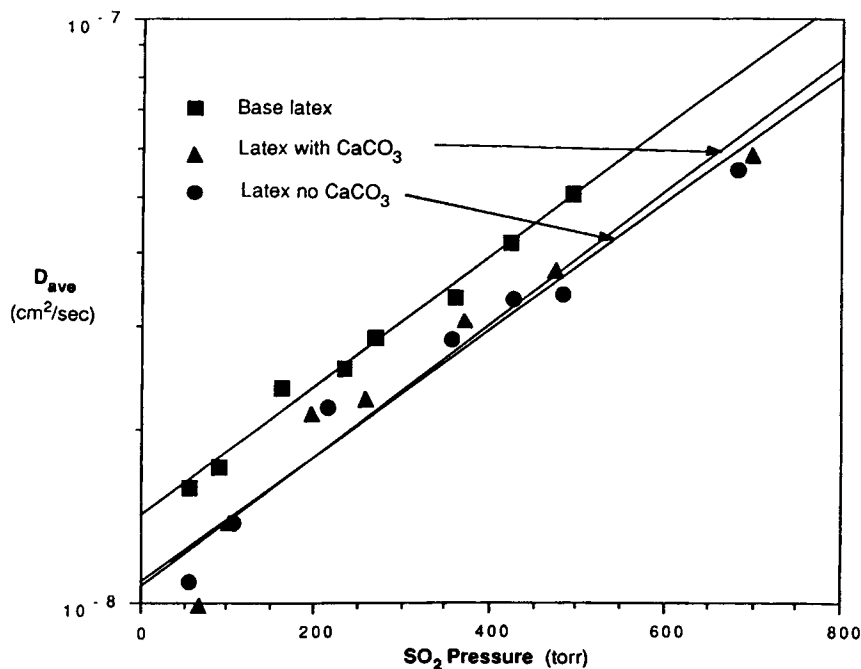


Fig. 3. A semilog plot of the average diffusion coefficients for the three samples against SO_2 pressure. The lines are least-square fits to the data, showing an exponential dependence of the diffusion coefficients on pressure.

sample undergoes the same amount of plasticization when the concentration of SO_2 in the polymer phase is the same (i.e., at equal pressures). However, the overall concentration of SO_2 in the paints (per gram sample) is less than it is in the base polymer for a given pressure, as shown in Figure 1. This leads to higher diffusivities in the paint samples when the data is plotted versus concentration instead of pressure (except when C approaches 0). The net effect is to make the paint samples appear more plasticizable than the unfilled base polymer. This is manifested in the plasticization parameter A , which has been calculated from the slopes in Figure 3 and

$$\ln(D_{\text{ave}}) = \ln(D_0) + ASp \quad (6)$$

where C in eq. (5) has been replaced by Sp . The values of S used to obtain A were the two-run averages of the unnormalized solubilities (per gram sample) from Table III. The results are listed in Table IV, along with values for D_0 .

Permeability is defined as the product of the solubility and the diffusivity. Predicted permeabilities based on the diffusivities in Figure 3 and the average unnormalized solubilities (per gram sample) from Table III are plotted against pressure in Figure 4. Standard units for permeability have been used. The permeability curves follow the same trends with pressure as the diffusivity; semilog plots yield reasonably good straight lines. It should be emphasized that experiments designed to directly measure permeability from the steady-state flux of penetrant through the samples may not produce the same values as obtained here. This is due to the fact that the diffusion coefficient D is concentration-dependent, and experiments designed to directly measure P produce a constant concentration gradient across the sample. Therefore, permeability varies throughout the sample, and the value obtained is an integral average of the concentration-dependent permeability across the thickness of the sample. In our experiments for measuring D , a concentration gradient exists at the beginning of the experiment, but eventually disappears as the sorption of penetrant approaches its equilibrium value. Thus, D varies not only with position in the sample, but with time as well. The boundary conditions are clearly different for the two types of experiments, and results for the pressure dependence of the permeability cannot be directly translated from one to the other.

In any case, the permeability in the infinite dilution regime, where concentration dependence vanishes, should be comparable for both types of experiments. This quantity, $P_0 = D_0S$, has been listed in the last column of Table IV. Maximum atmospheric levels of SO_2 seldom exceed 10 ppb (7.6×10^{-6} torr), so that these P_0 values should produce reasonable practical estimates of

TABLE IV
Zero-Pressure Diffusivities and Permeabilities of SO_2

Sample	A (g sample/mg SO_2)	D_0 (cm^2/s)	P_0 ($\text{cm}^2 \text{ cc SO}_2$ (STP)/ cc sample cm Hg s)
Latex base	0.0135	1.42×10^{-8}	1.21×10^{-8}
Latex w/o CaCO_3	0.0366	1.09×10^{-8}	5.52×10^{-9}
Latex w/ CaCO_3	0.0420	1.06×10^{-8}	4.88×10^{-9}

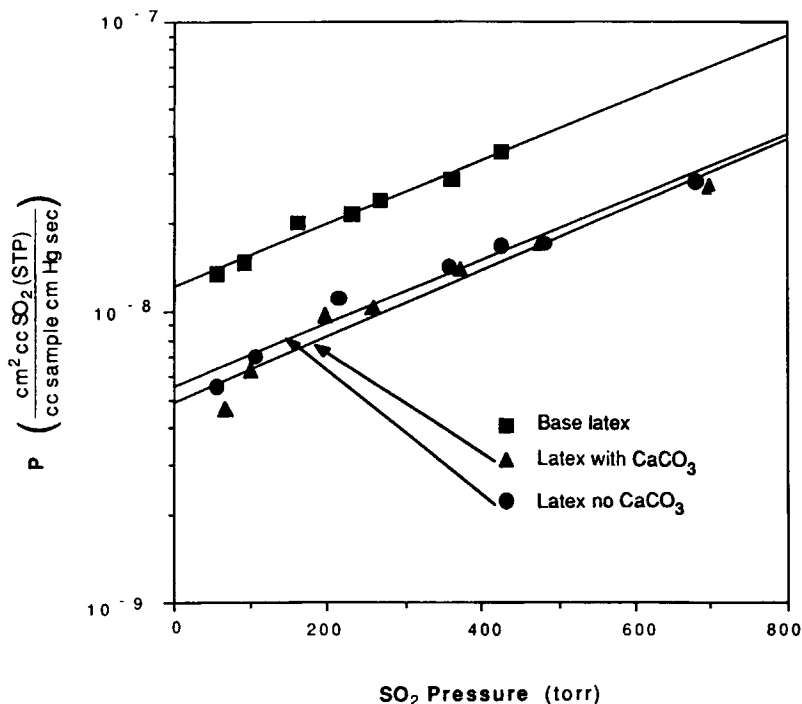


Fig. 4. Calculated permeabilities for the three samples using diffusivities from Figure 3 and average solubilities from Table III. The lines are least-square fits to the data.

the atmospheric SO₂ flux through these paint films at 28°C. Comparison of the *S*, *D*, and *P* values reported here with values for other polymers is hard to make since very little work with acrylic latex films has been reported; however, comparisons of SO₂ solubilities, diffusivities, and permeabilities in other amorphous polymers of similar *T_g* (≈ 10°C) show good agreement.¹⁴

CONCLUSIONS

Sorption and diffusivity measurements for SO₂ in representative acrylic latex paints and the base polymer at 28°C have indicated that SO₂ is very soluble in the base polymer. The presence of impenetrable inorganic additive particles in the paints lowers the effective solubility of SO₂ in these samples proportionately. Henry's law describes the sorption process in all three samples over a pressure range of 50–700 torr. The diffusivity decreases exponentially with decreasing pressure (concentration) over this pressure range, falling to within 5% of its limiting (infinite dilution) value at about 20 torr. At a given pressure, the diffusivity of SO₂ in the base polymer is slightly higher than in the paints, due to the presence of additive particles in the paints. The limiting permeabilities expected to be applicable at typical atmospheric levels of SO₂ (< 10 ppb) are calculated to be 1.21×10^{-8} , 5.52×10^{-9} , and 4.88×10^{-9} cm² cc SO₂ (STP) / cc sample cm Hg s, for the polymer base, the latex without CaCO₃, and the latex with CaCO₃, respectively.

The authors gratefully acknowledge the support of this work by the U.S. Environmental Protection Agency through Cooperative Agreement #CR-814166-01-0.

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Received September 19, 1988

Accepted April 17, 1989