

Sorption and Desorption Kinetics of Carbon Tetrachloride Vapor on Wheat Kernels

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ABSTRACT

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Kinetic data for the sorption and desorption of carbon tetrachloride vapor on wheat kernels containing 12% moisture have been obtained at 86°F. Both whole kernels and pearled kernels were studied. In all cases an internal diffusion model adequately represented the data; however, with whole ker-

nels the diffusivity for desorption was found to be approximately one-third that found for the sorption process. The data for pearled wheat produced essentially equal diffusivities for the sorption and desorption processes. A seed coat resistance mechanism is used to explain these results.

In order that modeling techniques successfully applied to fixed-bed adsorption-desorption operations in the chemical and petroleum industries find applicability to fumigation and aeration operations, it is first necessary to understand and be able to mathematically represent the single particle behavior. A step in this direction was taken by Park and Kyle (1975), who studied the sorption kinetics of carbon tetrachloride vapor in wheat kernels. They found that an internal diffusion model adequately represented their data with a diffusion coefficient that was physically realistic. The purpose of our study was to investigate the desorption kinetics of sorbed carbon tetrachloride from wheat kernels.

MATERIALS AND METHODS

In an earlier study in this laboratory (Park and Kyle 1975), the sorption rate of carbon tetrachloride vapor by wheat was determined by measuring weight changes of a sample of wheat where the temperature, relative humidity, and partial pressure of carbon tetrachloride were controlled. An extremely long time was required to obtain kinetic data suitable for analysis. Additionally, because the moisture content of the wheat was very large (about 12% by weight) compared with the small amount of carbon tetrachloride sorbed (about 0.5 to 1% by weight), a slight change in moisture content could give rise to a weight change of the same order of magnitude as that due to sorption of carbon tetrachloride. Furthermore, the accuracy of the previous technique relied on the questionable assumption that sorbed carbon tetrachloride molecules do not replace sorbed water molecules and that the recorded weight change represented the amount of carbon tetrachloride sorbed. Because of these disadvantages, a new experimental technique relying on the direct determination of the carbon tetrachloride content of wheat was developed for this study. Details of the equipment and procedure are given by Chang (1977).

Hard red winter wheat harvested in 1975 was used for this study. Prior to use in the experiments the wheat was stored for one month in a desiccator at room temperature over a saturated solution of potassium carbonate. The relative humidity provided by this saturated salt solution was 42%, the equilibrium value (Anonymous 1970) corresponding to a wheat moisture content of 12 wt %. A moisture determination of this conditioned wheat showed a value of 12.27 wt % (dry basis).

The carbon tetrachloride used in this study was Fisher Scientific Company A.C.S. reagent grade of a stated purity of 99%.

Sorption Rate Experiments

The sorption rate experiments consisted of placing wheat samples in stoppered glass flasks containing known concentrations of carbon tetrachloride and water vapor, maintaining the temperature constant, and removing the wheat sample at the desired time and analyzing for carbon tetrachloride content. Initially the relative

humidity of the air in the flask was adjusted to 46.8% by purging the flask with air that passed through a saturator containing saturated calcium nitrate solution. At the temperature at which all experiments were performed, 86°F, this is the relative humidity in equilibrium with wheat containing 12% moisture (Anonymous 1970). Next, the carbon tetrachloride vapor concentration within the flask was established by adding with a micrometer syringe a predetermined volume of liquid carbon tetrachloride. This volume could be measured to within ± 0.001 ml. After introduction of the liquid carbon tetrachloride, the flask was stoppered and allowed to stand until evaporation was ensured. Then the flask was opened and the wheat sample introduced and the flask restoppered. At a predetermined time, the wheat sample was removed from the flask and analyzed for its carbon tetrachloride content. The wheat sample size and amount of carbon tetrachloride were adjusted to precalculated values for each flask so that during the time sorption was occurring the carbon tetrachloride partial pressure did not change by more than 5%.

For the determination of the carbon tetrachloride content of the wheat, a wet aeration and colorimetric determination method described by Ramsey (1957) was used; colorimetric determination was made with a Bausch and Lomb Spectronic 600 spectrophotometer.

The first experimental results showed considerable variation in carbon tetrachloride content among triplicate analyses of a given wheat sample. To determine the accuracy of the analytical method, four analyses were performed using known quantities of carbon tetrachloride. In these tests the recovery of carbon tetrachloride was found to range between 94 and 107% thus confirming the reliability of the analytical method. A wheat sample size of 1g had been used and it was found that the variability between samples could be decreased by increasing the sample size. Because of space considerations, however, we were limited to performing triplicate analyses with sample sizes in the range of 1 to 2g and thus the precision of the data is less than desirable. To reflect this nonuniformity of wheat samples, we have shown data points corresponding to each of the triplicate analyses rather than a single average value in our graphical representations.

Desorption Rate Experiments

Desorption rate data were obtained by placing wheat samples of known carbon tetrachloride content into flasks through which a continuous stream of pure air flowed. The previously mentioned analytical method was used to determine the carbon tetrachloride content of the wheat prior to and after a specified aeration time. The temperature was maintained constant at 86°F and again the proper relative humidity of the air stream was provided by saturated calcium nitrate solution. Before being used in these experiments, wheat previously conditioned to a moisture content of 12% was exposed to carbon tetrachloride vapor for several days. After this exposure, the wheat was placed in a stoppered flask and maintained at 86°F for approximately one month in order that the sorbed carbon tetrachloride might be uniformly distributed within each kernel.

Pearled Wheat

The second part of this study was conducted using pearled wheat samples to investigate the effect of seed coat on the rates of sorption and desorption. Hard red winter wheat harvested in 1976 was treated in a barley pearler for 40 sec and No. 6 and No. 7 screens were used to obtain kernels with an average spherical radius of 0.153 cm. Both sorption and desorption experiments with pearled wheat were conducted as previously described.

RESULTS AND DISCUSSION

The internal diffusion model for a sphere (Wicke 1939) was previously found to represent the sorption kinetics of carbon tetrachloride vapor in wheat kernels (Park and Kyle 1975). This model can be adapted (Chang 1977) for either sorption or desorption. For sorption it is

$$\frac{Q_t}{Q_{es}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{\pi^2 n^2 D t}{r^2}\right) \quad (1)$$

and for desorption it is

$$\frac{Q_t}{Q_o} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{\pi^2 n^2 D t}{r^2}\right) \quad (2)$$

where D = diffusivity,
 n = summation index,
 Q_{es} = equilibrium value, or the amount sorbed after infinite time,
 Q_o = initial sorbate content of wheat,
 Q_t = sorbate content at time t,
 r = radius of spherical particle,
 t = time,
 π = 3.1416.

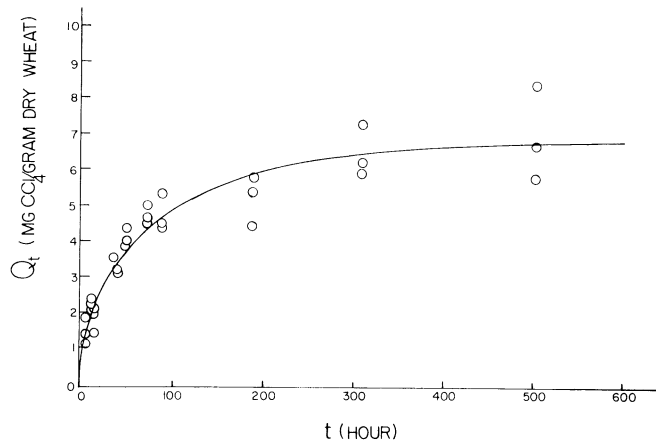


Fig. 1. Sorption of carbon tetrachloride by whole wheat kernels.

Inherent in this model is the requirement that the temperature and fluid-phase composition remain constant and that the initial solute content be uniform throughout the particle. The experiments were designed so that these conditions would be closely approximated.

The sorption and desorption rate data were fitted to this model using Bard's (1967) nonlinear parameter estimation method. The summation was evaluated up to n=100 or up to a term for which the contribution to the entire summation was less than 0.01%. When fitting the sorption rate data, the equilibrium sorption quantity, Q_{es}, was treated as an unknown parameter instead of determining its value directly from wheat samples allowed to equilibrate over a very long time. The results of the parameter estimation are summarized in Table I along with previously published results.

Sorption rate data for whole kernels of wheat taken at 86°F and at a carbon tetrachloride partial pressure of 95 mm Hg are plotted in Fig. 1. The solid curve on this figure represents equation 1 with the parameters Q_{es} and D obtained from the parameter estimation. Within the limitations of the data, a reasonably good fit is observed. Table I shows a comparison of these parameters with those obtained by Park and Kyle (1975) using 1971 harvested hard red winter wheat under identical conditions. Uncertainty in the method of parameter determination and variability of wheat samples might be invoked to explain the 34% discrepancy in the diffusivity values; however, one would expect better agreement between the equilibrium sorption quantity. A possible explanation for this discrepancy might be due to the assumption in the previous work that the sorbed carbon tetrachloride did not displace any previously sorbed molecules. Because the quantity sorbed was determined by weight change, this assumption would lead to sorption quantities being too low if displacement occurred. If the equilibrium sorption capacity found in the present study is correct, then the previously reported value could be explained in terms of every sorbed carbon tetrachloride molecule displacing three water molecules, a ratio that is not unreasonable in light of relative molecular sizes. It should be noted that such an error would not have affected the value of D obtained

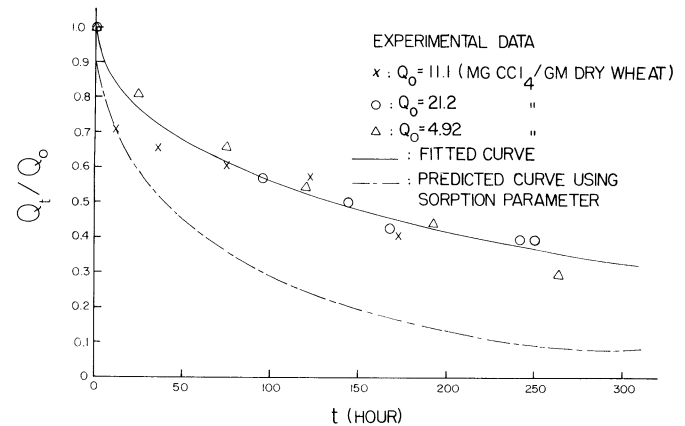


Fig. 2. Desorption of carbon tetrachloride from whole wheat kernels.

TABLE I
 Parameters Determined for the Intraparticle Diffusion Model for Sorption and Desorption of Carbon Tetrachloride on Wheat Kernels at 86°F

Process	Reference	Kernel Radius (cm)	Kernel Condition	P _{CCl₄} (mm Hg)	Q _{es} or Q _o (mg CCl ₄ /g dry wheat)	D × 10 ⁹ (cm ² /sec)
Sorption	Park & Kyle (1975)	0.165	Sound	95	4.25	4.38
	Present study	0.165	Sound	95	6.91	5.84
		0.159	Combined	95	6.81	6.01
Desorption	Present study	0.165	Sound	0	11.1	1.69
					21.3	
					4.92	
					5.88	4.64

previously because that parameter depends on Q_t/Q_{es} , the relative quantity sorbed.

Fig. 2 shows the desorption kinetics for whole wheat kernels at 86°F. These data were taken for several initial carbon tetrachloride levels within the kernel and it is seen all data can be represented reasonably well by equation 2 using a single parameter, D . One would normally expect this diffusivity to be essentially the same as that obtained from the sorption kinetic data. Table I reveals that this is not the case and, in fact, is only about one-third the value obtained for sorption. This result is illustrated graphically on Fig. 2 where the desorption curve predicted from equation 2 and the sorption-obtained diffusivity are also shown.

A possible explanation for this large difference in sorption and desorption diffusion coefficients can be offered in terms of seed coat resistance. There is no doubt that the resistance to diffusion during desorption is greater than that for sorption. A difference in seed coat resistance might be explained in terms of equilibrium at the solid-gas interface, an assumption commonly used in interphase mass transfer and a boundary condition used in the derivation of

the internal diffusion model. During sorption the particle surface, or seed coat, would be in equilibrium with air containing considerable carbon tetrachloride vapor and thus some carbon tetrachloride would be dissolved in the surface layer (seed coat). This dissolved carbon tetrachloride might swell or distort the seed coat sufficiently to render it more permeable to diffusing carbon tetrachloride molecules. For the desorption process, there is no carbon tetrachloride vapor in the air and hence none dissolved in the surface layer, thus the seed coat could be tighter and considerably less permeable to diffusing carbon tetrachloride molecules. This may explain why the diffusion coefficient of sorption is almost three to four times as large as the diffusion coefficient of desorption.

The second part of this study was conducted using pearled wheat samples to investigate the effect of seed coat on the rates of sorption and desorption. Both sorption and desorption experiments for pearled wheat were conducted under the same operating conditions as for whole wheat. Fig. 3 shows little difference between the experimental sorption data for both whole and pearled wheat.

Parameters obtained by applying the estimation method to the combined whole and pearled wheat sorption data are shown in Table I where it is observed that these parameters are essentially the same as those obtained for whole wheat. This would imply that during sorption no major resistance to diffusion is offered by the seed coat.

Desorption rate data with pearled wheat are plotted in Fig. 4 along with the curve of equation 2 fitted to these data by the parameter estimation method. Also shown in Fig. 4 are the desorption curve fitted to the whole wheat desorption data and previously shown on Fig. 2, and the desorption curve predicted from equation 2 using the diffusivity obtained from the sorption experiment with whole and pearled wheat. It is observed that the desorption rate for pearled wheat is much higher than that of whole wheat and is close to that predicted from the sorption behavior of whole and pearled wheat. This can also be seen from Table I where the diffusivities are compared. These experiments with pearled wheat show that removal of the seed coat greatly increases the rate of desorption, but has little effect on sorption rates.

It can be concluded that both sorption and desorption rates of carbon tetrachloride vapor in whole wheat kernels can be represented by the diffusion model, but that the diffusion coefficient for desorption is only about one-third as large as for sorption. The explanation of this phenomena by means of seed coat resistance seems reasonable. Cognizance of this effect should be essential to the design of fumigation and aeration systems and could be instrumental in selection of fumigant compounds.

ACKNOWLEDGMENT

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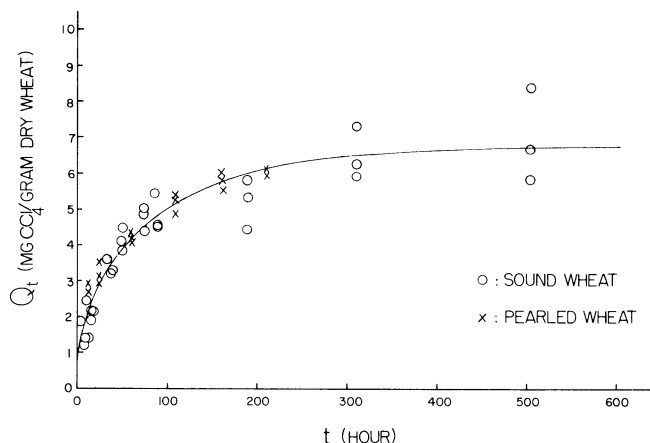


Fig. 3. Sorption of carbon tetrachloride by whole and pearled wheat kernels.

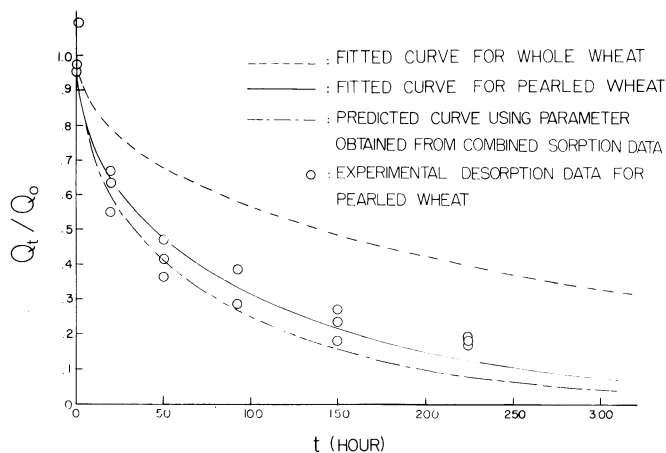


Fig. 4. Desorption of carbon tetrachloride from pearled wheat kernels.

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