Sorption with Oscillations in Solid Polymers

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Introduction

Among the varieties of anomalous behaviors exhibited during the diffusion of vapors in polymers, sigmoidal sorption curves and case II diffusion are commonly cited. In previous work we have attempted to explain sigmoidal behavior as due to the elastic stresses experienced by polymers due to swelling by the penetrants (Kim and Neogi, 1984; Neogi et al., 1986). Case II, where the penetrant concentration front is nearly discontinuous and moves with a constant velocity, and the fractional mass uptake is linear with respect to time instead of the square root of time, has been explained through a model that introduces memory arising from the fact that glassy polymers are not at equilibrium or pointwise equilibrium is not attained during diffusion (Neogi, 1983). In addition the stress effects discussed earlier can themselves be memory-dependent. The expression for the flux is

$$j = -\int_o^t \mu(t - t')\nabla c(x, t')\, dt' \qquad (1)$$

where

$$\mu(t) = D_i\delta(t) + \frac{D_o - D_i}{\tau} e^{-t/\tau} \qquad (2)$$

where $\delta(t)$ is Dirac delta function, D_i and D_o are the initial and final diffusivities, and τ is the relaxation time. These continuum formalisms as yet contain no description of the molecular details.

In recent years a third type of behavior has been noted, in the form of decaying oscillations. Baird et al. (1971) observed an overshoot in sorption in case II. So did Peppas et al. (1984) later, but in their case the overshoots were jagged. Recently, Vrentas et al. (1984) showed that overshoots can also occur in systems showing classical diffusion. Further, Lyubimova and Frenkel (1984) have shown a wide variety of oscillations with decay in the sorption responses with a nearly classical overall behavior. (Here, an overshoot is being differentiated from oscillations-with-decay in that it shows one maximum followed by a decay.)

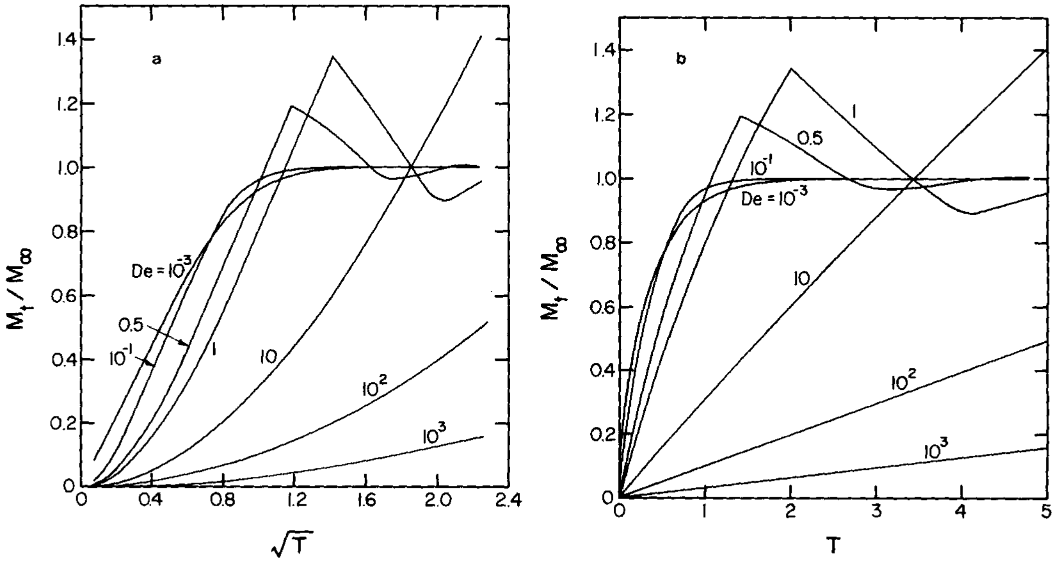

Figure 1. Equation 3 plotted for $\omega = 0$, $\theta = 0$ and various values of *De*.

We show below that Eqs. 1 and 2 do a reasonable job of unifying oscillations and overshoots in a wide variety of cases.

Discussion

The solution to conservation equations for sorption subject to Eqs. 1 and 2, with minor corrections from Neogi (1983), is given by

$$\frac{M_t}{M_\infty} = 1 - \theta e^{-T/De} - \sum_{m=1}^{2} \sum_{k=0}^{\infty} \frac{\left(1 - \frac{y_k}{y_k + De^{-1}}\theta\right) e^{-y_k T/(De^{-1} + \omega\xi_k^2)}}{\xi_k^2/2 - \frac{De\xi_k}{2}\frac{(1-\omega)}{(Dey_k + 1)^2}} \tag{3}$$

where

$$y_k = -\frac{1}{2}(De^{-1} + \omega\xi_K^2) \pm \frac{1}{2}\left[(De^{-1} + \omega\xi_k^2)^2 - \frac{4\xi_k^2}{De}\right]^{1/2}$$

and $m = 1$ and 2 refer to the two values of y_k, and

$$\xi_k = (2k + 1)\,\pi/2, \quad k = 0, 1, 2, \ldots$$

Here $T = 4\,D_o t/L^2$, $\omega = D_i/D_o$, and $\theta = (c_{sf} - c_{si})/(c_{sf} - c_i)$, and c_{sf} and c_{si} are the final and initial solubilities and c_i is the initial concentration in the system. Further, $De = \tau/(L^2/4D_o)$.

The Deborah number De, the ratio between relaxation time and the macroscopic diffusion time, has been used as suggested by Vrentas et al. (1975). In Figure 1a and 1b, the fractional

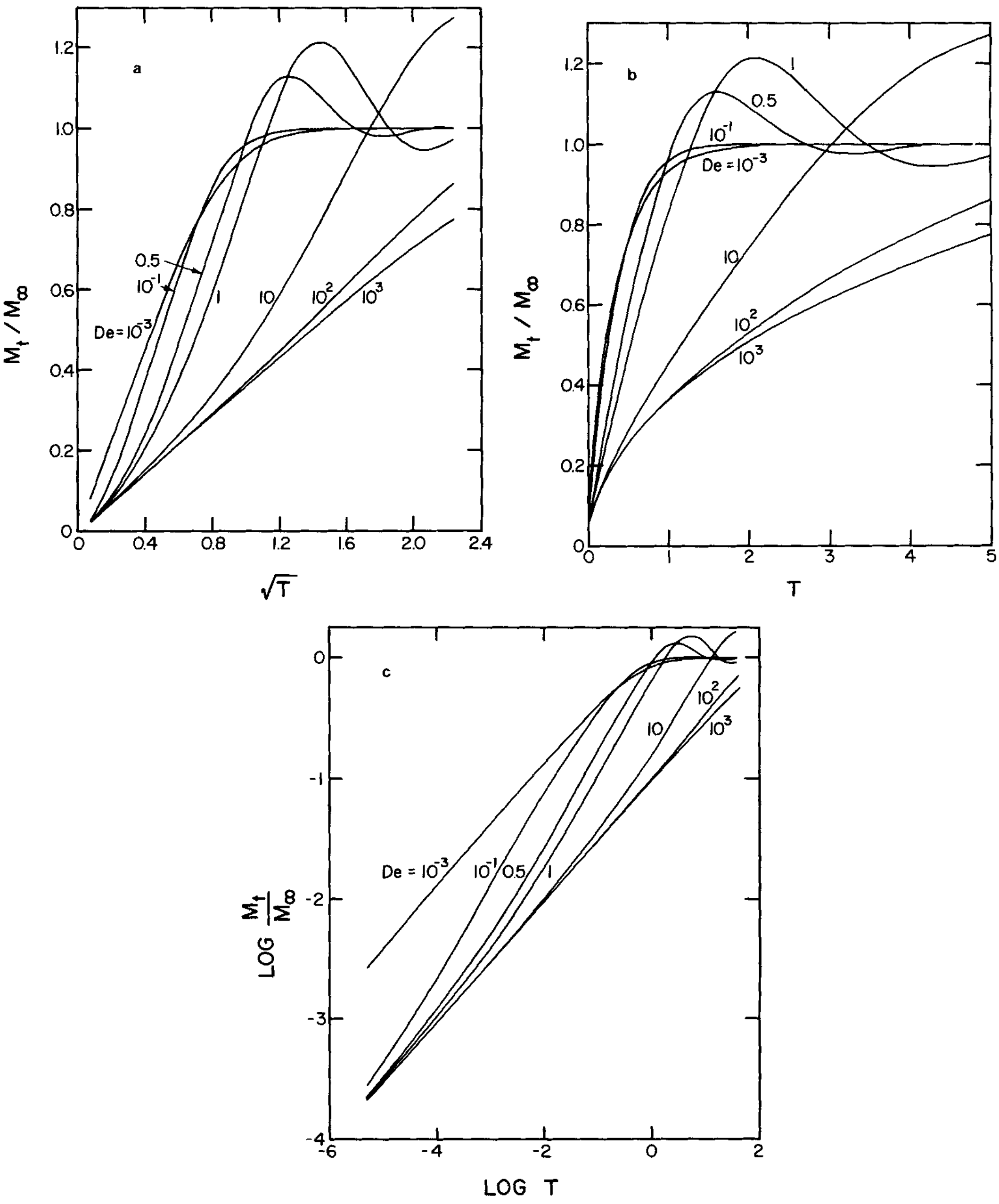

Figure 2. Eq. 3 plotted for $\omega = 0.1$, $\theta = 0$ and various values of De.

mass uptakes M_t/M_∞ have been plotted against $T^{1/2}$ and T, for values of De between 10^{-3} and 10^3, for $\theta = 0$ and $\omega = 0$. The classical diffusion shows up in M_t/M_∞ vs. $T^{1/2}$ plots as linear at short times, and case II shows up in M_t/M_∞ vs. T as linear. For $De = 10^{-3}$ the diffusion is classical. For De near 1, overshoots and oscillations are clearly seen. The overshoots are sharp and jagged, much like those observed by Peppas et al. (1984). Systems with very large De do not show classical behavior for this case where $\omega = 0$.

The cases where $\omega = 0.1$ and $\theta = 0$ have been plotted in Figure 2a as fractional mass uptake against time, in Figure 2b against square root of time, and in log-log form in Figure 2c. The overshoots are clearly seen near $De \sim 1$. Oscillations appear even for the largest values of $De = 10^3$ shown there. For De 10^5 and 10^7, we have determined that there are no oscillations. As is apparent in the figures, in cases of both large and small De the response is classical.

We have also calculated the fraction uptakes for values of θ up to 0.5. No qualitative differences were observed.

Lastly, we note that all oscillations decay, sometimes so rapidly that only an overshoot is observed.

Quantitative comparison with theory is difficult because y_k's are complex. Rough estimates of parameters were sought using the method of moments, up to the third moment. None of the cases showing case II diffusion yielded reasonable results. The reason was found to be that assumed values for equilibrium concentrations were not correct. It is expected that for case II where $De \sim 1$, the relaxation effects are not damped quickly compared to the cases of nearly classical diffusion. (In fact in case II the investigators do not claim the apparent saturation values as the true equilibrium values.) Such complications are not expected in the data of Vrentas et al. (1984), where the data show large damping. The estimated values are $D_o \sim 10^{-10}$ cm²/s, $De \sim 0.1$, that is $\tau \sim 10^5$ s, $\theta \sim 0.1$, and $\omega \approx 0$. As noted in Figure 2, for $De \sim 0.1$ only an overshoot can be observed.

Conclusion

It has been shown earlier that Eqs. 1 and 2 represent a general form capable of predicting case II as well as classical diffusion (Neogi, 1983). It has been shown here that they are also capable of showing oscillations with decay.

Literature cited

Baird, B. R., H. B. Hopfenberg, and V. Stannett, "The Effect of Molecular Weight and Orientation on Sorption of *n*-Pentane in Glassy Polystyrene," *Polym. Eng. Sci.*, **11,** 274 (1971).

Kim, M., and P. Neogi, "Concentration-Induced Stress Effects in Diffusion of Vapors through Polymer Membranes," *J. Appl. Polym. Sci.*, **29,** 731 (1984).

Lyubimova, V. A., and S. Frenkel, "Auto-oscillating Regime of Sorption of Low Molecular Solvent by Inomers," *Polym. Bull.*, **12,** 229 (1984).

Neogi, P., "Anomalous Diffusion of Vapors through Solid Polymers. I, II," *AIChE J.*, **29,** 829, 833 (1983).

Neogi, P., M. Kim, and Y. Yang, "Diffusion in Solids Under Strain, with Emphasis on Polymer Membranes," *AIChE J.*, **32**(7) 1146 (1986).

Peppas, N. A., J. L. Sinclair, M. J. Smith, and J. G. Mounts, "Relaxation-Controlled Transport of Penetrants in Glassy Polymers," *Proc. 9th Int. Cong. Rheology*, **3,** *Polymers*, B. Mena, A. Garcia-Rejon and C. Rangel-Nafile, eds., Universidad Nacional Autunoma de Mexico (1984).

Vrentas, J. S., J. L. Duda, and A.-C. Hou, "Anomalous Sorption in Poly (Ethyl) Methacrylate," *J. Appl. Polym. Sci.*, **29,** 399 (1984).

Vrentas, J. S., C. M. Jarzebski, and J. L. Duda, "A Deborah Number of Diffusion in Polymer-Solvent Systems," *AIChE J.*, **21,** 894 (1975).

Manuscript received Jan. 15, 1986, and revision received April 21, 1986.