CORRECTIONS

Juchen Guo and Timothy A. Barbari*,† A Dual Mode, Local Equilibrium Relaxation Model for Small Molecule Diffusion in a Glassy Polymer.

In a recent paper [Guo, J.; Barbari, T. A. *Macromolecules* **2008**, *41*, 238−245], we relaxed the local equilibrium assumption often employed in the development of transport models that are based on dual mode sorption of small molecules in glassy polymers. The resulting model was then used to fit sorption kinetics data measured by Fourier transform infrared attenuated total reflectance (FTIR-ATR) spectroscopy for acetonitrile in glassy cellulose acetate. The motivation for relaxing this assumption was twofold: (1) while a simple Fickian framework could fit mass uptake (integral) data for this system, it could not capture the lag in the FTIR-ATR (local) data, suggesting a mechanism in addition to diffusion (such as hole filling in the dual mode model) that could slow the transport process, and (2) incorporation of the dual mode sorption model with local equilibrium, while an improvement over the simple Fickian model, did not fully capture the lag in the FTIR-ATR data. Recently, we discovered an error in the equation used to test the local equilibrium assumption in the dual mode framework. Using the correct expression, the dual mode model assuming local equilibrium is able to describe the local concentration data obtained from the spectroscopic technique, negating the need to relax this assumption and introduce an additional parameter.

The dual mode, local equilibrium relaxation model used to fit the data in the original paper was developed and used correctly. Therefore, we feel it is worthwhile to use this opportunity to explain the relevance of the additional kinetic parameter that results from the full model in the context of the local equilibrium assumption and to illustrate the importance of carefully assessing results from optimization tools for fitting purposes.

DUAL MODE SORPTION AND TRANSPORT

The development that follows is a summary of that found in the original paper, and the reader should refer to that source for complete details. The dual mode sorption model assumes that there are two populations of molecules sorbed into a glassy polymer: (1) one dissolved in the dense portion of the polymer (the Henry's law population) and (2) one residing in pre-existing excess free volume or "holes" (the Langmuir population). According to this model, the total concentration, C_T, of sorbed penetrant is given by

$$C_T = C_D + C_H = k_D a + C'_H \frac{ba}{1 + ba} \tag{1}$$

where k_D is the Henry's law constant, a is the penetrant activity in the gas or vapor phase, C'_H is the Langmuir capacity constant, and b is the Langmuir affinity constant.

At low concentrations, the diffusion of each population is represented as Fickian, and one interpretation takes the two penetrant populations as mobile, with a fraction, F, of the "hole" population immobilized. The resulting dual mode transport model, in its most general form to account for the hole filling mechanism, is

$$\frac{\partial C_D}{\partial t} = \frac{\partial}{\partial z}\left(D_D \frac{\partial C_D}{\partial z}\right) - k_f C_D (C'_H - C_H) + k_r C_H \tag{2}$$

where D_D is the diffusion coefficient, k_f is the rate constant for

$$\frac{\partial C_H}{\partial t} = \frac{\partial}{\partial z}\left(F D_D \frac{\partial C_H}{\partial z}\right) + k_f C_D (C'_H - C_H) - k_r C_H \tag{3}$$

hole filling, and k_r is the rate constant for hole emptying.

Assuming local equilibrium between the two populations, the model reduces to

$$\frac{\partial C_T}{\partial t} = \frac{\partial}{\partial z}\left(D_D \frac{\partial C_D}{\partial z} + F D_D \frac{\partial C_H}{\partial z}\right) \tag{4}$$

and

$$k_f C_D (C'_H - C_H) = k_r C_H \tag{5}$$

Eliminating C_H, the model can be written, assuming D_D constant or concentration averaged, as

$$\frac{\partial C_T}{\partial t} = D_D \frac{\partial}{\partial z}\left[\frac{1 + \dfrac{FK}{(1 + \alpha C_D)^2}}{1 + \dfrac{K}{(1 + \alpha C_D)^2}} \frac{\partial C_T}{\partial z}\right] \tag{6}$$

where

$$C_D = \frac{-(1 + K - \alpha C_T) + [(1 + K - \alpha C_T)^2 + 4\alpha C_T]^{1/2}}{2\alpha} \tag{7}$$

In the original paper, eq 7 was incorrectly written as

$$\alpha = \frac{b}{k_D} = \frac{k_f}{k_r} \tag{8}$$

$$K = \frac{C'_H b}{k_D} \tag{9}$$

$$C_D = \frac{-(1 + K) + [(1 + K)^2 + 4\alpha C_T]^{1/2}}{2\alpha} \tag{10}$$

which was the expression inadvertently used to test the local equilibrium assumption with the FTIR-ATR data for acetonitrile in cellulose acetate, leading to the conclusion that the full

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* Corresponding author. E-mail: tab53@georgetown.edu.

† Current address: Georgetown University, Washington, DC 20057

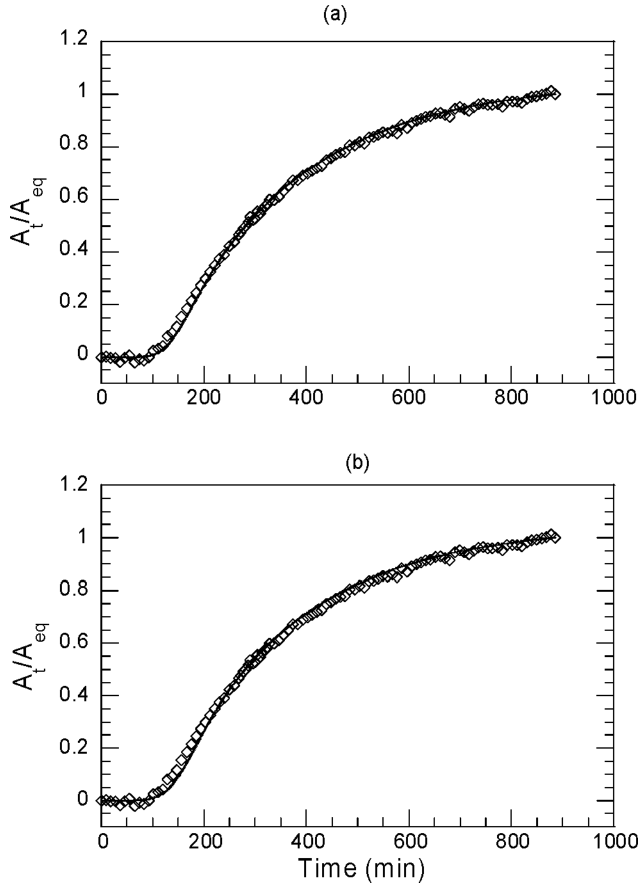

Figure 1. FTIR-ATR absorbance data of acetonitrile in cellulose acetate at activity 0.2 and $T = 25$ °C with (a) the best fit using the dual mode model under local equilibrium assumption ($D_D = 6.67 \times 10^{-10}$ cm^2/s) and (b) the best fit using the dual mode model with the local equilibrium assumption relaxed ($D_D = 6.34 \times 10^{-10}$ cm^2/s and $k_r = 4.48 \times 10^{-3}$ s^{-1}). $L = 49.2$ μm.

Table 1. Diffusion Coefficients Assuming Local Equilibrium (Eqs 6 and 7) and Those Relaxing Local Equilibrium (Eqs 2 and 3) with $k_r = 4.85 \times 10^{-3}$ s^{-1}

	$D_D \times 10^{10}$ cm^2/s	
activity	local equilibrium	local equilibrium relaxed
0.25	7.38 ± 0.90	7.04 ± 0.11
0.20	6.46 ± 0.18	6.38 ± 0.04
0.15	4.58 ± 0.24	4.66 ± 0.01
0.10	2.94 ± 0.13	2.96 ± 0.02
0.06	1.86 ± 0.10	1.91 ± 0.03

expressions given in eqs 2 and 3 should be used instead, introducing k_r as an additional parameter to fit the data.

MODEL COMPARISON: LOCAL EQUILIBRIUM VS LOCAL EQUILIBRIUM RELAXATION

Application of the dual mode sorption model, eq 1, to the sorption isotherm for acetonitrile in cellulose acetate resulted in dual mode sorption parameters of $k_D = 0.282$ $g_{nitrile}/g_{polymer}$, $C'_H = 0.030$ $g_{nitrile}/g_{polymer}$, and $b = 38.1$ (see original paper). Assuming local equilibrium, eqs 6 and 7 were used to fit the FTIR-ATR absorbance data for sorption kinetics from triplicate experiments, using D_D as the only adjustable parameter and F set equal to zero. The result for one experiment at activity 0.2 is shown in Figure 1a. The diffusion coefficients are listed in Table 1 for all activities. For the purposes of comparison, the full model with local equilibrium relaxed, applied to the same experiment at activity 0.2, is shown in Figure 1b, and the resulting diffusion coefficients are also listed in Table 1 (k_r fixed at the average value obtained from activity 0.2). More details on how the fits were obtained are given in the original paper.

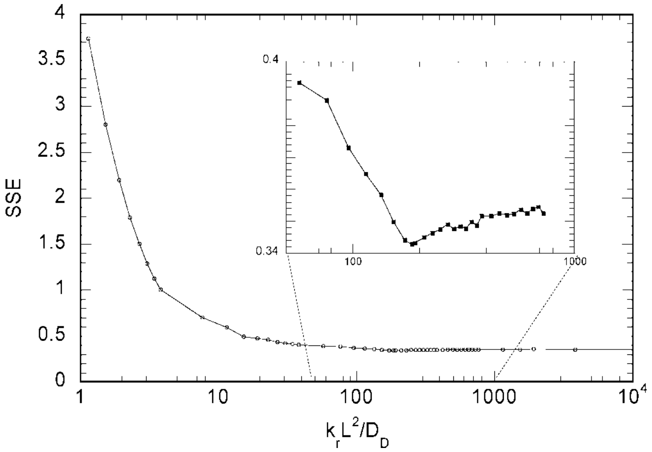

Figure 2. Sum of squared error (SSE) as a function of the ratio of diffusion time to hole emptying time ($k_r L^2/D_D$) for the dual mode, local equilibrium relaxation model applied to the experimental data in Figure 1. $D_D = 6.34 \times 10^{-10}$ cm^2/s. $L = 49.2$ μm.

Given that the diffusion coefficients at a particular activity for the two models are nearly identical, it is worth examining the parameters from local equilibrium relaxation in terms of time scales for diffusion and hole filling (or emptying). The dimensionless grouping, $k_r L^2/D_D$, represents the ratio of diffusion time to hole emptying time. If this group is very large (approaching infinity), then the kinetics of hole filling and emptying can be taken as instantaneous and local equilibrium is approximated. For the experiment shown in Figure 1, $k_r L^2/D_D$ is equal to 184. For all of the experiments, this ratio varied from 64 to 225. In other words, diffusion is roughly 2 orders of magnitude slower than hole emptying, and local equilibrium would likely be a reasonable assumption within experimental error. Although we determined the ratio of time scales during the writing of the original paper and thought it high, we erroneously concluded that it was of a magnitude that was necessary to capture the lag in the FTIR-ATR data, given that the incorrect expression for local equilibrium could not.

OPTIMIZATION TOOLS

When the dual mode, local equilibrium relaxation model is applied to the FTIR-ATR absorbance data for activity 0.2, there are two adjustable parameters, D_D and k_r. The fitting program was written with MATLAB Optimization Toolbox. In the program, each parameter is given an initial guess, a lower limit value (very low) and a higher limit value (very high). The values of the two adjustable parameters are used to calculate the absorbance values at each time point, which is then compared to the corresponding experimental values and the sum of squared error (SSE) is calculated. This process was repeated until the SSE was minimized. Since we had convinced ourselves that the local equilibrium assumption needed to be relaxed to describe this system, we did not question the resulting values of the parameters that emerged and also did not carefully examine the SSE as the values of the parameters are varied. Figure 2 plots the SSE as a function of $k_r L^2/D_D$ at a fixed value of D_D (the value obtained from the optimization routine). In the larger plot, it is clear that above a certain value of $k_r L^2/D_D$ (~100), the SSE does not change significantly, consistent with the physical interpretation inherent with local equilibrium. However, expanding the plot (see inset) shows that a mathematical minimum in SSE exists, which led to the erroneous conclusion that the resulting parameter value had physical relevance.

CONCLUSION

FTIR-ATR spectroscopy remains a powerful tool for studying diffusion in polymers. In glassy polymers, it is able to illustrate that simple Fickian diffusion cannot describe local concentration data as a function of time even though mass uptake can be described with the simpler approach. Introducing dual mode sorption into the transport model captures the anomaly, and the technique can be used to validate critical assumptions introduced, such as local equilibrium.

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