

Anticipation of Anomalous Effects in Differential Sorption Experiments

J. S. VRENTAS, C. M. VRENTAS, W. J. HUANG

Department of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802 U.S.A.

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ABSTRACT: The concept of a diffusion Deborah number is used to anticipate the presence of anomalous effects in differential sorption experiments. The method is illustrated using sorption data for five experiments involving polymer–solvent mixtures. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2007–2013, 1997

Key words: differential sorption; Deborah number

INTRODUCTION

More than thirty years ago, Reiner¹ introduced a dimensionless group, which he called the Deborah number, as a convenient way of characterizing the flow behavior of viscoelastic materials. This group is simply the ratio of the characteristic relaxation time of a material to the characteristic time of the deformation process. This concept has been extended^{2–7} to the diffusion of solvents in polymers by introducing a diffusion Deborah number. This dimensionless group is also a ratio of two characteristic times, a characteristic relaxation time for the polymer–solvent system and a characteristic diffusion time. The diffusion Deborah number can be used to determine the character of the mass transfer for a given polymer–solvent system; hence, it can be used to anticipate conditions for which anomalous effects can be expected during a diffusion process. For example, differential sorption experiments are widely used as a means of measuring mutual diffusion coefficients for polymer–solvent systems, but this can be done only if the diffusion process is Fickian. Calculation of the diffusion Deborah number provides a simple method of determining whether a classical

diffusion process can be expected in a differential sorption experiment for a given set of conditions. In addition, the Deborah number concept can be used as a means of designing differential sorption experiments for which the diffusion process is Fickian.

The objective of this article is to illustrate how the diffusion Deborah number can be used to anticipate the presence of anomalous effects in differential sorption experiments. This is done by comparing calculated diffusion Deborah numbers with differential sorption data for five polymer–solvent sorption experiments. The basis of the diffusion Deborah number approach is presented in the second section of this article, and the differential sorption experiments are described in the third section. The experimental data are presented and discussed in the fourth section.

THE DIFFUSION DEBORAH NUMBER

In the absence of externally induced flow in a diffusion experiment, all deformations are the direct result of concentration gradients. For this case, a dimensionless group ($DEB)_D$, called the diffusion Deborah number, can be defined^{2–7} such that it provides a comparison of the rate of diffusion and the rate of rearrangement of polymer molecules as follows:

Correspondence to: J. S. Vrentas.

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$$(\text{DEB})_D = \frac{\lambda_m}{\theta_D} \quad (1)$$

In this equation, λ_m is the characteristic time of the fluid, and θ_D is the characteristic time of the diffusion process. Since λ_m is generally a strong function of concentration and temperature for a polymer–solvent mixture, it is clear that it is possible to define a single value of the Deborah number for an entire diffusion process only if the spatial and time variations of concentration and temperature are sufficiently small. For example, for a differential sorption experiment, the difference in the final and initial equilibrium concentrations is kept as small as possible so that a single value of the Deborah number can be calculated since it can be based on the temperature, polymer molecular weight, average pressure, and average concentration of the system.^{2–4} In an integral sorption experiment, large changes in concentration are imposed, and it is necessary to examine the nature of the diffusion process by calculating Deborah numbers at the initial and final conditions of the sorption process.^{2,4}

The characteristic time θ_D of the diffusion process is, of course, in general, different for each mass transfer operation. A step-change sorption experiment is an unsteady, one-dimensional mass transfer process; hence, an average characteristic diffusion time can be defined as follows:

$$\theta_D = \frac{L^2}{D^*} \quad (2)$$

Here, L is the initial thickness of the polymer film, and D^* is a diffusion coefficient, which is an appropriate measure of the diffusional transport in the system. The quantity D^* can be estimated, for example, by using predicted self-diffusion coefficients for the polymer and solvent.^{3,4} The above definition of the characteristic diffusion time of course represents an average value since a particle of fluid near the surface of the film has a different characteristic time than a particle located a significant distance from the surface. For an oscillatory sorption experiment,⁷ a single value of the characteristic diffusion time is applicable at every point in the diffusion field, and a more detailed Deborah number analysis is possible.⁷

When the diffusion Deborah number is sufficiently small, molecular relaxation is much faster than the diffusive transport. The diffusion process thus involves what is effectively a purely viscous

binary mixture since conformational changes in polymer structure appear to take place instantaneously. The diffusion process at small values of $(\text{DEB})_D$ is Fickian diffusion in the classical sense, and it can be denoted as a viscous diffusion process. When the diffusion Deborah number is sufficiently large, there is a negligible time variation of the polymer structure during the diffusion process. Since a diffusing penetrant molecule moves in a material that effectively has the properties of an elastic solid, this type of diffusional transport can be denoted as elastic diffusion. Available data^{3,4} appear to indicate that diffusional transport for large Deborah numbers can be satisfactorily described by the classical theory of diffusion, even though the system is obviously not a purely viscous fluid mixture. Hence, Fickian diffusion should be observed at both low and high values of $(\text{DEB})_D$. When the diffusion Deborah number is of the order of unity, the molecular relaxation and diffusive transport processes occur in comparable time scales, and rearrangement of polymer chains and movement of solvent molecules take place simultaneously. This type of diffusional transport is denoted as viscoelastic diffusion. For differential sorption experiments, it is not possible to identify precise values of $(\text{DEB})_D$ for which viscous, elastic, and viscoelastic diffusion can be expected because eq. (2) represents only an estimated average value for the characteristic diffusion time. However, it seems reasonable to expect that viscous diffusion will be observed for $(\text{DEB})_D < 10^{-2}$, and elastic diffusion will be present for $(\text{DEB})_D > 10^2$. For $10^{-2} < (\text{DEB})_D < 10^2$, the possibility exists for the presence of viscoelastic diffusion and, hence, nonclassical, non-Fickian behavior.

Methods of calculating $(\text{DEB})_D$ for differential sorption experiments have been described elsewhere.^{3,4} These procedures will be used to compute $(\text{DEB})_D$ for the five polymer–solvent sorption experiments considered in this study. For a differential sorption experiment at normal pressures, the diffusion Deborah number will depend on the temperature, average solvent concentration, polymer molecular weight, and initial film thickness L . Hence, it is possible to study diffusion for a particular polymer at a given temperature and average solvent concentration by carrying out experiments using samples with different thicknesses. In effect, $(\text{DEB})_D$ can be varied conveniently by changing L , and the dependence of the measured sorption curve on L [and hence on $(\text{DEB})_D$] can be determined experimentally.

For a differential sorption experiment, it is possible to measure the quantity M ; the mass of solvent per unit area that has entered the polymer film at time t ; and the quantity M_∞ , the value of M at infinite time, where there is sorption equilibrium. For classical, Fickian diffusion, sorption data for films of different thicknesses must reduce to a single curve when M/M_∞ is plotted against $t^{1/2}/L$. Also, values of the mutual diffusion coefficient D calculated from such sorption curves must, of course, be independent of L since D is a material property of the polymer–solvent system. As noted above, it is possible to carry out differential sorption experiments over a range of diffusion Deborah numbers by using fixed polymer molecular weight, temperature, and average concentration and by varying only the sample thickness L . If $(\text{DEB})_D < 10^{-2}$ over the complete range of L , then the diffusion process will be a viscous, Fickian diffusion process; and curves of M/M_∞ versus $t^{1/2}/L$ and, hence, computed values of D , should be independent of L . Similarly, if $(\text{DEB})_D > 10^2$ over the range of L studied, then the diffusion process will be an elastic Fickian diffusion process. Again, for this case, curves of M/M_∞ versus $t^{1/2}/L$ and the values of D computed from such curves will be independent of L . If $10^{-2} < (\text{DEB})_D < 10^2$, then the possibility for anomalous, non-Fickian diffusion exists so that reduced sorption curves (M/M_∞ versus $t^{1/2}/L$) for films of different thicknesses may not yield a single curve as is required by the equations of the classical theory. Furthermore, computed, apparent values of the mutual diffusion coefficient D may depend on L . Valid mutual diffusion coefficients can be obtained in the intermediate Deborah number region [$10^{-2} < (\text{DEB})_D < 10^2$] only if it can be shown experimentally that the calculated D eventually becomes independent of L as L is increased or decreased.

The above discussion illustrates two aspects of the utility of the diffusion Deborah number in the design and interpretation of differential sorption experiments. First, it is clear that anomalous diffusion effects should be avoided if experiments are conducted with $(\text{DEB})_D > 10^2$ or $(\text{DEB})_D < 10^{-2}$. Hence, if experiments are designed (by appropriate choice of temperature, solvent concentration, and L) so that the diffusion Deborah number is either very small or very large, then it will be possible to use standard methods to compute valid mutual diffusion coefficients. Second, for a given set of conditions, calculation of the diffusion Deborah number immediately suggests whether anomalous

diffusion effects are possible. If a diffusion Deborah number for a given set of conditions is in the intermediate region [$10^{-2} < (\text{DEB})_D < 10^2$], then it is necessary to conduct differential sorption experiments at different values of L to establish the conditions for which D is independent of L . Only the values of D measured in the region where D becomes independent of L are valid mutual diffusion coefficients.

Finally, it is important to emphasize that the above discussion has been concerned with classification of the diffusion process inside the polymer film. For differential sorption experiments, it is possible that the surface concentration of the film does not instantaneously achieve the equilibrium value consistent with the solvent pressure in the gas phase.⁸ Hence, although the diffusion process in the bulk phase may be Fickian, the total mass transfer process may not exhibit classical behavior because of surface nonequilibrium effects. Consequently, a mass transfer process for polymer–solvent systems will exhibit classical behavior only if there is both a sufficiently high or low value of the diffusion Deborah number *and* attainment of instantaneous equilibrium at the phase boundary. In general, the presence of nonequilibrium surface effects will be evident from the shape of a single sorption curve.

If diffusional transport for a differential sorption experiment is described by the classical equations, the following behavior should be observed.

- 1) In the initial stages of the sorption process, a plot of M/M_∞ versus $t^{1/2}$ is linear.
- 2) The M/M_∞ versus $t^{1/2}$ plot is always concave with respect to the $t^{1/2}$ axis above the linear portion.
- 3) The sorption curves for all values of film thickness will form a single curve when plotted as fractional uptake versus $t^{1/2}/L$ for fixed initial and final penetrant concentrations.

In general, the first two criteria are not satisfied when the surface concentration does not instantaneously assume its equilibrium value. Hence, a single sorption curve will generally indicate the presence of surface nonequilibrium effects. On the other hand, the first two criteria are sometimes satisfied for a differential sorption experiment, but the third is not. This is a more subtle form of non-Fickian behavior since at least two sorption curves with different values of L are needed to test this thickness effect.

From the above discussion, it appears that the following procedure can be used to identify sorption data, which can be used to determine the mutual diffusion coefficient D from a standard diffusion analysis.

- 1) If the sorption curve does not satisfy the first two criteria, it cannot be used to determine D using a straightforward analysis.
- 2) If the sorption curve satisfies the first two criteria and either $(\text{DEB})_D < 10^{-2}$ or $(\text{DEB})_D > 10^2$, then the mass transfer process is described by the classical equations, and a standard diffusion analysis can be used to determine a valid mutual diffusion coefficient from this sorption curve.
- 3) If the sorption curve satisfies the first two criteria and $10^{-2} < (\text{DEB})_D < 10^2$, then sorption data must be obtained for different values of L to establish the conditions for which the third criterion is satisfied. Valid diffusion coefficients can then be obtained from sorption curves, which satisfy the third criterion.

DIFFERENTIAL SORPTION EXPERIMENTS

Differential step-change sorption experiments were carried out for polymer–solvent systems for five sets of conditions by introducing a sudden increase in the solvent pressure in the gas phase above a polymer sample. The experimental apparatus was a quartz spring sorption balance. The cylindrical sorption column was 1.2 m in length with an inside diameter of 10 cm. The temperature of the experiment was controlled by circulating heat-transfer fluid in a jacket surrounding the sorption balance. The solvent pressure was supplied to the column by a computer-controlled solvent boiler. The quartz springs and quartz buckets used in the column were provided by Worden Quartz Products, Inc., and the spring extension was measured using a cathetometer. All experiments reported here are absorption experiments.

Two polymers were used in this study: polystyrene (PS) and poly(vinyl acetate) (PVAc). The PS and PVAc were additive-free, commercial polymer samples with weight-average molecular weights of 2.75×10^5 and 2.3×10^5 , respectively. The polymer samples were prepared directly in quartz buckets with a diameter of 1.7 cm using a solvent-casting technique. Additional details of the exper-

imental apparatus and procedure are given elsewhere.⁹

RESULTS AND DISCUSSION

The characteristics of the five polymer–solvent sorption experiments carried out in this study are summarized in Table I. The diffusion Deborah number for these experiments was varied by changing the initial sample thickness L , and the ranges of $(\text{DEB})_D$ and L are presented in the last two columns of this table. For all five step-change absorption experiments, the reduced sorption curves (plots of M/M_∞ versus $t^{1/2}/L$) satisfy the first two criteria presented above. Hence, it does not appear likely that surface nonequilibrium effects are important for these experiments. Furthermore, for the first experiment in Table I, $(\text{DEB})_D > 10^2$ so that the sorption process should be an elastic, Fickian diffusion process. Also, for the second, third, and fourth experiments, $(\text{DEB})_D$ is effectively less than 10^{-2} since the upper limit in the third experiment is only slightly greater than 10^{-2} . In these three cases, the sorption processes should be viscous, Fickian diffusion processes. Consequently, for the first four experiments listed in Table I, the Deborah number analysis predicts that the reduced sorption curves will form a single curve when plotted versus $t^{1/2}/L$. Also, the calculated mutual diffusion coefficient D for each experiment should be independent of L and, hence, should be a valid material property. The data for the first four experiments indeed show that the third criterion listed above is clearly satisfied and that the calculated values of D are independent of L . The sorption curves for the first four experiments are not presented here, but the D versus L data for these four cases are presented in Figures 1 and 2. Clearly, the diffusion Deborah number analysis has correctly identified experiments from which valid mutual diffusion coefficients can be derived.

For the fifth experiment, part of the Deborah range extends into the intermediate region [$10^{-2} < (\text{DEB})_D < 10^2$] so that anomalous diffusion effects can be expected. The experiments for the PVAc–water system at 45°C do indeed show that the reduced sorption curves do not form a single curve, and the third criterion is, hence, not satisfied. Also, as is evident from Figure 3, the calculated mutual diffusion coefficients depend on L and, hence, are not valid material properties for all values of L . The D values appear to level off

Table I Summary of Sorption Experiments

Polymer	Solvent	Temperature (°C)	Average Solvent Weight Percent	Range of $(DEB)_D$	Range of L (cm)
PS	Methanol	70	0.25	1.0×10^{24} – 3.3×10^{24}	0.028–0.051
PVAc	Toluene	90	16.8	1.2×10^{-7} – 2.2×10^{-7}	0.047–0.063
PVAc	Methanol	60	4.6	1.1×10^{-3} – 1.2×10^{-2}	0.014–0.047
PVAc	Water	90	0.35	1.7×10^{-4} – 3.8×10^{-3}	0.072–0.34
PVAc	Water	45	0.53	3.4×10^1 – 2.5×10^3	0.0088–0.075

at high and low values of L , and these values of D can be tentatively identified as being material properties that are representative of two distinct Fickian diffusion regions. However, the values of D calculated for intermediate values of L are clearly not meaningful material properties. It is clear that a diffusion Deborah number analysis has correctly anticipated anomalous diffusion effects.

From the above results and discussion, it is fair to conclude that the concept of a diffusion Deborah number is very useful in the design and analysis of differential sorption experiments. As noted previously, calculation of the diffusion Deborah number for a particular set of experimental variables provides a relatively simple way of anticipating conditions for which anomalous effects can be expected during a differential sorption experiment.

This was illustrated above for the PVAc–water system at 45°C. In addition, since calculation of a Deborah number identifies a Fickian diffusion process, the diffusion Deborah number analysis can be useful in the design of differential sorption experiments. The first four experiments in Table I are examples of how the calculated Deborah number can be used to identify differential sorption experiments that can be analyzed using the classical Fickian approach.

We conclude by commenting on two interesting aspects of the above results. The first involves the characteristics of the polymer sample, and the second is concerned with the effect of changing the sample thickness L . The PS-methanol experiment was conducted 30°C below the glass transition temperature of the pure polymer, whereas the PVAc–solvent experiments were conducted about

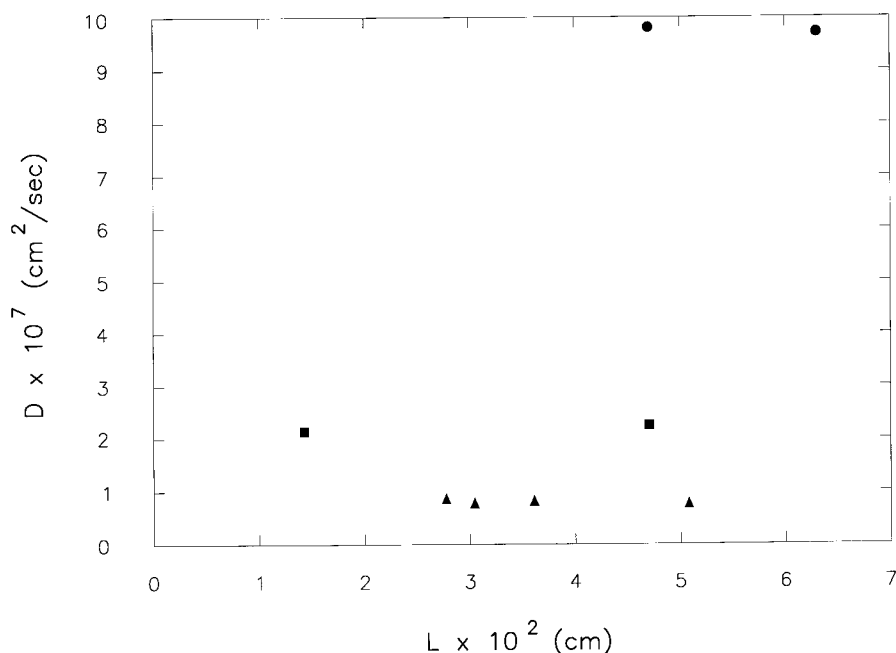


Figure 1 Dependence of D on L for three polymer–solvent systems: PS–methanol at 70°C, ▲; PVAc–toluene at 90°C, ●; PVAc–methanol at 60°C, ■.

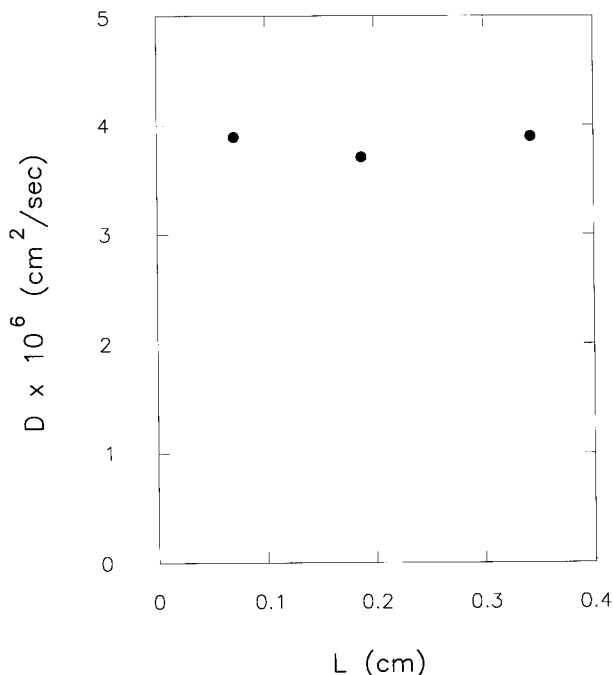


Figure 2 Dependence of D on L for PVAc–water system at 90°C.

15–60°C above the pure polymer glass transition temperature. The presence of a Fickian diffusion process for sorption in the glassy PS–methanol system provides further evidence to that noted previously^{3,4} that diffusional transport for large diffusion Deborah numbers can be satisfactorily described by the equations of the classical, Fickian theory. The presence of Fickian diffusion for

the sorption of solvents in PVAc at temperatures 30°C or more above the pure polymer glass transition temperature (the second, third, and fourth experiments in Table I) indicates that the classical form of viscous, Fickian diffusion can be expected for temperatures sufficiently far above the polymer glass temperature. Also, the possibility of Fickian diffusion is enhanced if the solvent concentration is sufficiently high. The results for the PVAc–water system at 45°C clearly indicate that anomalous diffusion can be present in rubbery polymer–solvent systems if the temperature is only slightly above the glass temperature of the pure polymer and if the solvent concentration is kept low. The anomalous diffusion for the PVAc–water system at 45°C is in the form of a film thickness effect, and it is similar to the film thickness anomaly reported previously by Odani¹⁰ for a rubbery polymer–solvent system.

The diffusion Deborah number for the differential sorption experiments was varied in this study by changing the initial sample thickness L , and different types of diffusional behavior were observed. This does not constitute an artificial dependence of the diffusion process on sample size. The film thickness L simply determines the time scale for a step-change sorption experiment. It is the relationship between this time scale and the time scale for the rearrangement of polymer molecules that determines the nature of the diffusional behavior for a particular system. In addition, changing the sample thickness L will often not change the nature of the diffusion process since

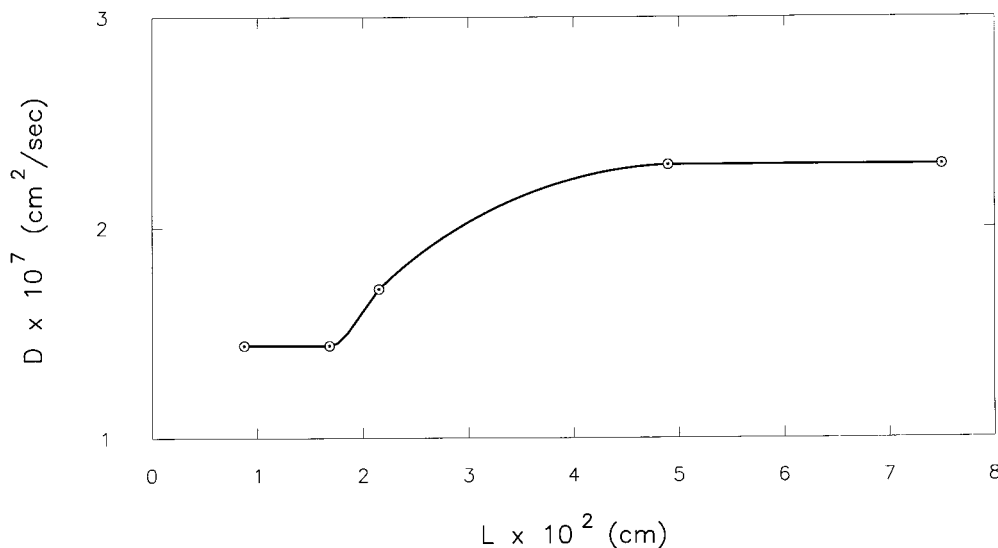


Figure 3 Dependence of D on L for PVAc–water system at 45°C.

it is not possible to carry out reasonable sorption experiments over a very large range of sample thicknesses. For example, $(DEB)_D$ for the glassy PS–methanol system at 70°C is so large that an elastic, Fickian diffusion process will be observed for all reasonable values of L . Similarly, $(DEB)_D$ for the rubbery PVAc–toluene system at 90°C is so small that a viscous, Fickian diffusion process will be observed for all physically reasonable values of the sample thickness. In general, changes in the nature of the diffusion process can be effected by changing the sample thickness only if the diffusion Deborah number is not too far removed from unity [$10^{-2} < (DEB)_D < 10^2$]. For Deborah numbers in this intermediate range, it is possible to change the sample thickness so that an anomalous diffusion process is changed to an elastic or viscous Fickian diffusion process. It appears that this was the case for the PVAc–water system at 45°C. Finally, we note that it is highly unlikely that a case II diffusion process¹¹ can be changed to a Fickian diffusion process by changing the initial thickness of the polymer sample. Case II diffusion is characterized by an initial solvent uptake in an absorption experiment, which is linear in time, rather than an initial uptake, which is proportional to $t^{1/2}$, as is the case for Fickian diffusion. Case II diffusion is observed in an absorption experiment when a relatively high surface concentration of solvent is imposed on a pure, glassy polymer sample. The initial value of $(DEB)_D$ is generally very high (because of the

properties of the glassy polymer), and it will not be possible to lower this value significantly by increasing the sample thickness L . Indeed, the sample thickness required to change the initial Deborah number from a very high value to a very low value (and, hence, change the case II diffusion process to a Fickian diffusion process) could easily lead to a sorption experiment, which would take more than 1000 years to complete.

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