

Combined Experimental and Computer Simulation Study of the Kinetics of Solute Release from a Relaxing Swellable Polymer Matrix. I. Characterization of Non-Fickian Solvent Uptake

K. G. Papadokostaki, J. K. Petrou

Institute of Physical Chemistry, Demokritos National Research Center, 15310 Aghia Paraskevi, Athens, Greece

Received 4 August 2003; accepted 7 January 2004

ABSTRACT: This article is concerned with a combined experimental and computer modeling study aimed at the characterization of the non-Fickian absorption of liquid water by cellulose acetate (CA) matrices (in the form of thin films) on the basis of a strictly limited number of parameters. The observed kinetics exhibited two distinct non-Fickian features, resulting from short-term and long-term viscous structural relaxations of the swelling glassy polymeric matrix. These relaxation processes were modeled by the extension of a previous model of micromolecular diffusion in a polymer subject to a single relaxation process. The successful simulation of the experimental kinetic curves then enabled the determination and cross-checking of the relevant

model parameter values. This work had the dual purpose of providing (1) input related to solvent absorption for the quantitative computer simulation (in part II of this series) of a model monolithic, solvent-activated, controlled-release device, consisting of a swellable glassy polymeric matrix (CA) loaded with an osmotically active solute (NaCl), and (2) an example of a general strategy of extracting meaningful values of micromolecular diffusivity in glassy polymers from non-Fickian absorption kinetic data. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2458–2467, 2004

Key words: diffusion; relaxation; computer modeling

INTRODUCTION

In previous works, we have studied experimentally^{1–3} various salient aspects of the kinetics of release of simple solutes of various osmotic activities from a swellable polymer matrix subject to viscous structural relaxation, and thus we have brought into evidence some practical advantages of such matrices, notably the preservation over longer periods of osmotically induced enhancement and relaxation-promoted constancy of the solute release rate.

We have also attempted to develop and study parametrically reasonably general, rigorous, and flexible model formulations of the salient features of the concurrent solvent uptake and solute release processes.^{4,5}

The objectives of this work are (1) to achieve deeper physical insights into these phenomena and (2) to provide the tools necessary for realistic computer simulations of the performance of solvent-activated monolithic controlled-release (MCR) devices. The

practical application of MCR devices, notably in the agrochemical and medical fields, is already well established and is expected to expand markedly. The attractiveness of such devices is due to their simplicity and resultant low cost. At the same time, their disadvantage of a generally nonconstant solute delivery rate has been shown to be largely allayable by proper design,^{6–8} which is likely to be greatly facilitated by the availability of reliable computer simulation tools.

The present capabilities of our modeling approach include the simulation of (1) the interactions that exist between the solvent and solute sorption and transport, (2) the presence of the solute in a finely dispersed form, (3) the osmotic action of the solute, and (4) the structural relaxation of the polymer matrix upon swelling (glassy polymers). The quantitative applicability of the model with respect to the second feature is limited in practice because of the coarseness of the solute dispersions normally used. Nevertheless, this model did provide a sound physical basis for the formulation² of a new more general mechanism of osmotically enhanced release in such cases, which has been experimentally demonstrated already.²

The aim of the work described in this and the following article was to apply a quantitative experimental test to the aforementioned modeling approach. The MCR system used for this purpose consisted of cellulose acetate (CA), NaCl as a solute, and water as a

Correspondence to: K. G. Papadokostaki (kpapadok@chem.demokritos.gr).

Contract grant sponsor: General Secretariat for Research and Technology, Greek Ministry of Development.

Contract grant sponsor: European Union.

solvent. This system is deceptively simple because it affords a critical test for the third and fourth features, which represent the most complex (and least amenable to simple or rigorous formulation) aspects of the model. The experimental conditions were formulated to avoid the presence of the relatively coarse solute particles used in previous work.² The values of the requisite input model parameters were determined from independent experimental studies of the solvent (as discussed later) and solute (see part II) sorption and diffusion properties.

Thus, this article is concerned with an experimental kinetic study of liquid water absorption by the neat CA matrix (as well as the proper quantitative characterization of the observed deviations from simple Fickian kinetics induced by viscous structural relaxation of the swelling polymer), providing input related to the solvent properties for the MCR simulation indicated previously.

We also hope, however, that the kinetic features reported here and the ensuing method of data analysis will also serve as an example of a generally applicable strategy of correcting for the effect of structural relaxation in studies of micromolecular diffusion behavior in glassy polymers.

Previous kinetic studies of the CA–water system were mostly devoted to absorption from the vapor phase, and they showed inconsistent results. In particular, the practical or Fickian diffusion coefficient (D_{WP}) commonly measured has been variously reported^{9–15} as exhibiting positive, negative, or insignificant dependence on the imbibed water concentration (C_W). Physically, all these possibilities are admissible, on the basis of the interplay of two different mechanisms, namely, the plasticization of the polymer by monomeric sorbed water molecules and the clustering of these sorbed molecules, which tend to promote positive or negative dependence of the diffusivity on C_W , respectively.^{13–15} Accordingly, the aforementioned inconsistency is attributable to variations in the CA film structure and properties (reflecting differences in the film preparation and subsequent history) and possibly also in the chemical composition or even in the method of measurement or data analysis. The last factor becomes important in the presence of deviations from Fickian kinetics because there are, at present, no established methods of accounting for the effects of such deviations. A detailed kinetic analysis^{13,14} has shown that substantial deviations from Fickian kinetics can occur during water vapor uptake by CA as a result of complications caused by viscous structural relaxation of the swelling polymer leading to an enhancement of its capacity for the uptake of the penetrant. Under suitable conditions, more than one relaxation process can be detected.^{13,14}

EXPERIMENTAL

Materials and film preparation

CA in a powder form (type CA-398-30; acetyl content = 39.8 wt %) was kindly provided by Eastman Chemicals (Zug, Switzerland) with the following specifications: melting range = 230–250°C, glass-transition temperature = 189°C, density = 1.31 g/cm³, and viscosity (measured according to ASTM D 871 and D 1343) = 114 P (30 s).

The films normally used (here and in part II) were prepared by the casting of 20% solutions of the polymer in acetone on a glass plate with a doctor knife. The solvent was eliminated by evaporation in the atmosphere, and this was followed by evacuation for 2–3 days. The resulting films (of thickness $2\ell = 120 \mu\text{m}$) were kept in water until needed, at which stage their original degree of hydration (C_W^0 ; g/g of dry film) was measured.

Films of reduced or enhanced water uptake capacity were also prepared to help elucidate the nature of the observed non-Fickian kinetic features. The former compacted films were produced by the treatment of normal films with boiling water for about 2 h. The latter expanded films were prepared by the addition of solid NaCl particles (ca. 5 μm) to the CA–acetone dope,² which were subsequently completely leached out by water, leaving the film in a superhydrated state.

Equilibrium vapor sorption isotherm

Films of a normal degree of hydration were hung over suitable saturated salt solutions in specially designed bottles, thermostated at 25°C, and degassed so that faster equilibration could be achieved. Equilibrium water regain was determined gravimetrically. The ascending and descending branches of the sorption isotherm were determined by the exposure of the films to increasing (after prior evacuation to dryness) or decreasing (after prior blotting of the fully hydrated film) values of the relative humidity [equated here with the activity of water (a_W)], respectively.

Liquid water absorption kinetics

Films previously dried by evacuation and then equilibrated with a given relative humidity were immersed in a thermostated water bath and were periodically taken out, blotted, and weighed. For as accurate a determination of the final weight gain as possible, measurements were continued during the following few days.

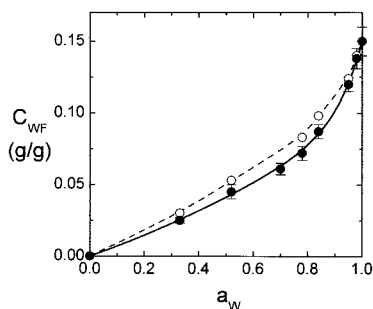


Figure 1 Water regain of neat CA films equilibrated with various relative humidities (a_w) by (●) absorption or (○) desorption. The solid line was calculated with eqs. (2) and (12) with $s = 11$, $K_{W1F} = 0.0675$, $K_{W2F} = 0.030$, and $K_{WSF} = 0.0525$ g/g.

RESULTS

Equilibrium sorption isotherm

The results of the equilibrium vapor sorption measurements (Fig. 1) are in good agreement with those previously reported by others,^{13,16} however, the absorption–desorption hysteresis loop shown in Figure 1 is narrower than that reported in ref. 13. This result is, in all likelihood, attributable to the longer equilibration times (extending over several days) used in this work and points to very slow structural relaxation during desorption as the primary cause of the observed hysteresis.

Sorption kinetics

Kinetic absorption experiments were performed with films of a normal degree of hydration conditioned to different initial concentrations of imbibed water (C_{W0}) by previous equilibration at the appropriate initial water activity (or relative humidity; a_{W0}). The reproducibility of the results obtained is illustrated, for $a_{W0} = 0.10$, in Figure 2 in the form of plots of the mean concentration of imbibed water at time t (\bar{C}_{Wt}) versus \sqrt{t} . In the course of this work, it became apparent that an important factor contributing to the observed spread of the kinetic data was the variability of C_{W0} . Accordingly, care was taken to use film specimens with C_{W0} values as similar as possible for a detailed comparison of the absorption kinetic curves pertaining to different a_{W0} values (cf. the examples in Fig. 3).

The aforementioned kinetic curves exhibit, as shown most clearly at the lowest C_{W0} value (Fig. 2), two distinct kinds of deviation from Fickian absorption kinetics:^{13,17} (1) a sigmoid shape and (2) an unusually protracted approach to the final absorption equilibrium. These non-Fickian kinetic features are attributable, respectively,^{13,17} to (1) relatively short-range viscous structural relaxations occurring in the swelling polymer at a rate comparable to that of the

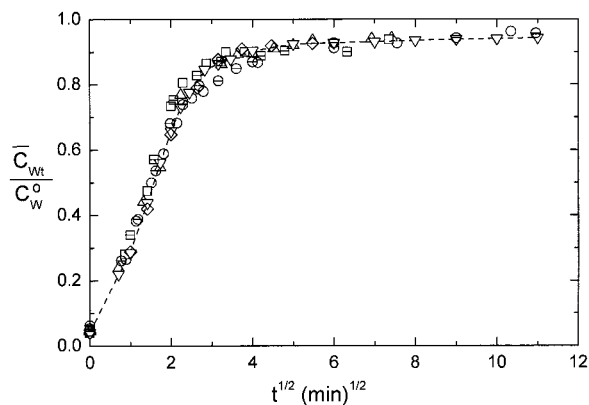


Figure 2 Experimental kinetic curves of \bar{C}_{Wt} (normalized with respect to C_{W0}^0) in CA films ($C_{W0}^0 = 0.14$ – 0.17 g/g) during absorption after preequilibration at $a_{W0} = 0.10$.

diffusion of sorbed water molecules and (2) slower similar relaxations involving larger polymer segments presumably made possible by some looseness of polymer chain packing in the amorphous regions of normal CA films.

Strong supporting evidence for this picture is provided by the corresponding kinetic behavior exhibited by compacted and expanded films (prepared as indicated in the previous section). In the latter case (shown as squares in Fig. 4), the second effect is intensified, and this agrees with the expected looser chain packing in expanded films. The relaxation responsible for the first effect, however, is accelerated up to the point that the said effect is no longer detectable. In the former

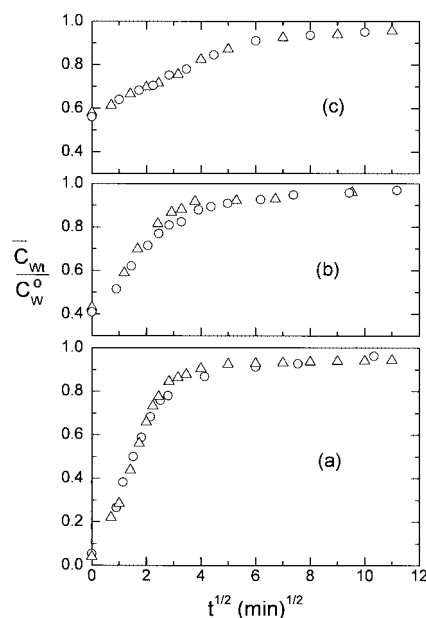


Figure 3 Experimental kinetic curves of \bar{C}_{Wt} in two CA films ($C_{W0}^0 = 0.17$ g/g) during absorption after preequilibration at various a_{W0} values: (a) 0.10, (b) 0.70, and (c) 0.85.

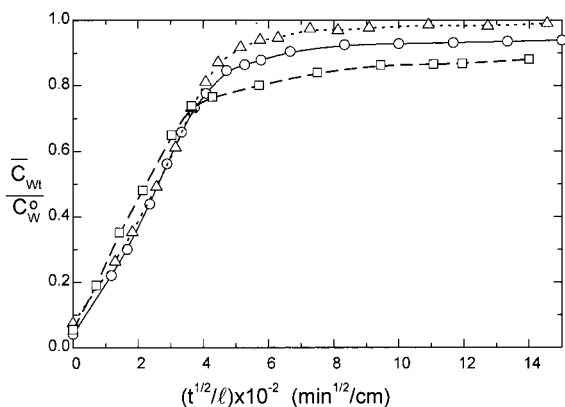


Figure 4 Typical experimental kinetic curves of \bar{C}_{wI} in (○) normal ($C_w^0 = 0.16$ g/g), (△) compacted ($C_w^0 = 0.125$ g/g), and (□) expanded ($C_w^0 = 0.198$ g/g) CA films during absorption after preequilibration at $a_{w0} = 0.10$.

case (shown as triangles in Fig. 4), the first effect persists, whereas the second effect disappears, and this indicates the absence of the aforementioned looseness of chain packing in the compacted film. This is consistent with the appearance of a second small endotherm (preceding the main melting endotherm) in the DSC thermogram of the compacted film, which is indicative of more ordered chain packing than in the normal film (Fig. 5).

THEORETICAL MODEL

The general model description of non-Fickian water uptake kinetics previously presented⁵ was extended

(as described later) to allow for the presence of more than one distinct structural relaxation process. The extended model was then specialized, as needed, to take into account significant specific features of the particular experimental system under study.

General model of solvent uptake kinetics in a polymer subject to multiple relaxations

In the model description of solvent uptake adopted in ref. 5, two extreme states of the solvent-imbibing matrix are recognized:¹⁸ (1) the unrelaxed matrix, the sorptive capacity of which, when maintained at a given solvent activity a_w , permits solvent uptake up to a concentration $C_w = C_{wI}$, and (2) the fully relaxed polymer matrix, which, under the same conditions, can imbibe the solvent up to a concentration $C_w = C_{wF} > C_{wI}$. Thus, for a polymer matrix relaxing in contact with a penetrant, under conditions of a constant and uniform a_w value, the concentration of the absorbed solvent (C_w) will vary from C_{wI} to C_{wF} . The difference ($C_{wF} - C_{wI}$) represents the extra sorptive capacity, which can be generated by the structural relaxation process at a_w . The relaxation process is assumed to follow first-order kinetics:

$$\frac{\partial C_w}{\partial t} = \beta_w(C_{wF} - C_w) \quad (1)$$

where β_w is the relaxation rate constant (or relaxation frequency because it is the reciprocal of the commonly used relaxation time).

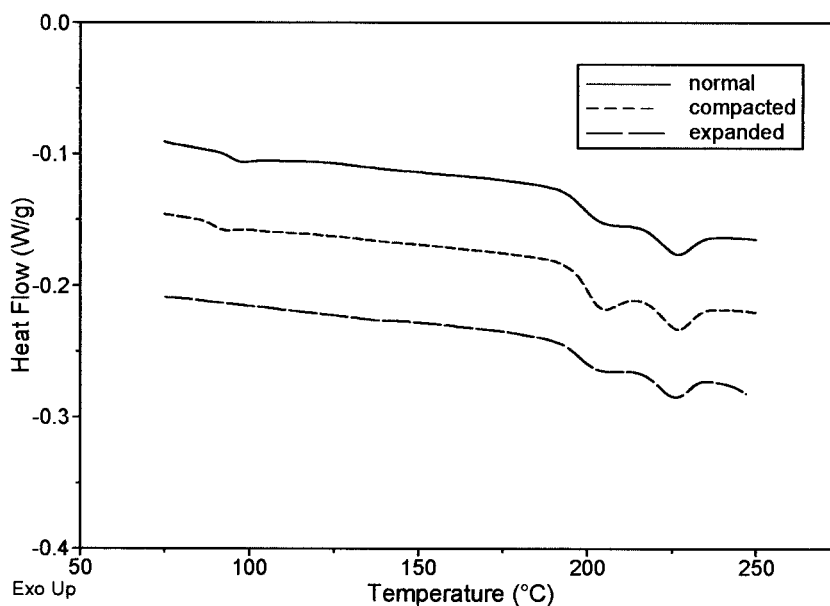


Figure 5 Typical DSC thermograms of (—) normal, (- - -) compacted, and (- · -) expanded CA films (model 2920 MDSC, TA Instruments; heating rate = 5°C/min).

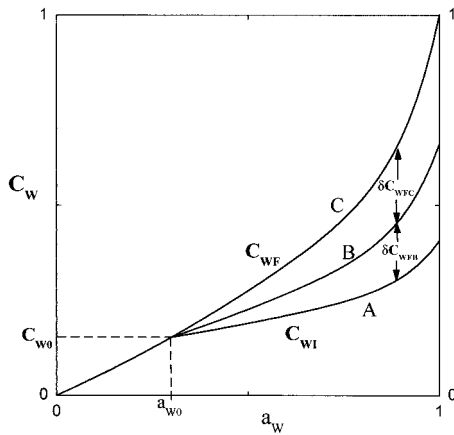


Figure 6 Schematic representation of the absorption isotherms applicable to the (A) unrelaxed, (B) partly relaxed, and (C) fully relaxed states of a polymeric matrix subject to two relaxation processes (i.e., for $N_R = 2$, which is representative of the CA–water system under consideration here) in an absorption experiment covering the activity range of $a_W = a_{W0}$ to $a_W = 1$ (see the text).

We consider a polymer monolith, in the form of a thin polymer film (of thickness 2ℓ), preequilibrated with a relative humidity corresponding to $a_W = a_{W0}$ and immersed at time $t = 0$ in liquid water ($a_W = 1$). Under these conditions, water diffusion into the matrix is effectively one-dimensional.

The sorptive capacity of the relaxed polymeric matrix as a function of $0 \leq a_W \leq 1$ is described by the usual equilibrium absorption isotherm (because the final attainment of equilibrium presupposes full relaxation of the polymer by definition), illustrated schematically by curve C in Figure 6. We have

$$C_{WF} = F_F(a_W) \quad (2)$$

where $F_F(a_W)$ may be any chosen function that can represent the relevant experimental data adequately. The sorptive capacity of the unrelaxed polymer may similarly be described by an instantaneous absorption isotherm (illustrated by curve A in Fig. 6). In this connection,⁵ it is important to bear in mind that the isotherm in question (1) is defined in the experimental range $a_{W0} \leq a_W \leq 1$ and (2) must coincide with the final isotherm at $a_W = a_{W0}$, that is, $C_{WI}(a_W = a_{W0}) = C_{WF}(a_W = a_{W0}) = C_{W0}$. The instantaneous isotherm may be conveniently formulated as a function of the new variable, $\delta a_W = a_W - a_{W0}$ ($0 \leq \delta a_W \leq 1 - a_{W0}$):⁵

$$C_{WI} = C_{W0} + f_I(\delta a_W) = F_F(a_{W0}) + f_I(\delta a_W) \quad (3)$$

The final absorption isotherm may be reformulated similarly:⁵

$$C_{WF} = C_{W0} + f_F(\delta a_W) = F_F(a_{W0}) + f_F(\delta a_W) \quad (2a)$$

Note that $f_I(\delta a_W = 0) = f_F(\delta a_W = 0) = 0$. It is also worth noting that the direct measurement of the instantaneous absorption isotherm presupposes sufficiently rapid diffusion into the polymer or use of a sufficiently thin film to permit the establishment of a reasonably uniform concentration across the film before any significant relaxation has occurred. Because direct experimental information of this kind is not usually available, it is simplest to assign to $f_I(\delta a_W)$ the same functional form as $f_F(\delta a_W)$, subject, of course, to the condition $f_I(\delta a_W) \leq f_F(\delta a_W)$.

In the presence of more than one distinct structural relaxation processes, we consider that (1) the said processes proceed independently and in parallel and (2) their effect on the sorptive capacity is additive. Thus, in the presence of a number, N_R , of relaxation processes (which are numbered for convenience in the order of descending values of β_{Wi}), we recognize $N_R - 1$ notional intermediate states of the polymer and write for a given value of a_W

$$C_{WF} - C_{WI} = \sum_{i=1}^{N_R} \delta C_{WFi} \quad (4)$$

where δC_{WFi} represents (for the given value of a_W) the increment in the absorptive capacity produced by the i th relaxation process. The i th state is the state attained in the hypothetical case in which all relaxation processes from $j = 1$ to $j = i$ are complete, whereas those from $j = i + 1$ to $j = N_R$ are frozen; thus, the states denoted by $i = 0$ and $i = N_R$ correspond to the instantaneous and final absorption equilibrium, respectively. The case of CA–water under consideration here, for which N_R is 2, is illustrated in Figure 6. The relevant incremental absorption isotherms may be expressed in terms of δa_W :

$$\delta C_{WFi} = f_i(\delta a_W) \quad (5)$$

where it should be taken into account that $\delta C_{WFi}(a_W = a_{W0}) = 0$. $f_i(\delta a_W)$ may conveniently be assigned the same functional form as $f_F(\delta a_W)$, subject, of course, to the condition embodied in eq. (4). The corresponding kinetic equations are analogous to eq. (1):

$$\frac{\partial(\delta C_{Wi})}{\partial t} = \beta_{Wi}(\delta C_{WFi} - \delta C_{Wi}) \quad (6)$$

where δC_{Wi} is 0 at $t = 0$. Thus, the concentration of the absorbed solvent in a relaxing matrix, maintained at any given constant value of a_W , is

$$C_W(t) = C_{WI} + \sum_{i=1}^{N_R} \delta C_{Wi}(t) \quad (7)$$

During an absorption experiment, eqs. (6) and (7) provide an adequate description of the evolution of $C_W(t)$ at either of the surfaces of the film, located at $x = 0$ and $x = 2\ell$ (with $x = \ell$ at the midplane of the film), exposed to the liquid solvent. Here, the extra sorptive capacity generated by the relaxation process is satisfied by immediate uptake from the liquid, thus maintaining $a_W(x = 0, t > 0) = 1$ throughout the experiment. At any location in the interior of matrix x (because of symmetry, we restrict our attention to the half-space $0 < x \leq \ell$), however, the rate at which solvent molecules are transported to that location by diffusion must be considered. The relevant equations are⁵

$$\frac{\partial C_W}{\partial t} = \frac{\partial}{\partial x} \left(D_W S_W \frac{\partial a_W}{\partial x} \right) \quad (8)$$

$$\begin{aligned} \frac{\partial C_W}{\partial t} &= \frac{dC_{W1}}{da_W} \frac{\partial a_W}{\partial t} + \sum_{i=1}^{N_R} \frac{\partial(\delta C_{Wi})}{\partial t} \\ &= \frac{dC_{W1}}{da_W} \frac{\partial a_W}{\partial t} + \sum_{i=1}^{N_R} \beta_{Wi} (\delta C_{WFi} - \delta C_{Wi}) \end{aligned} \quad (9)$$

[where use has been made of eq. (6)] with the boundary conditions

$$\begin{aligned} a_W(x = 0, t > 0) &= 1; \quad a_W(0 < x \leq \ell, t = 0) = a_{W0}; \\ \delta C_{Wi}(t = 0) &= 0 \end{aligned} \quad (10)$$

and by symmetry

$$\left(\frac{\partial a_W}{\partial x} \right)_{x=\ell} = 0 \quad (11)$$

Equations (8) and (9) were solved by an explicit finite difference method.^{4,5} With this method, from the known values of C_W , a_W , and δC_{Wi} at x and t , new values at x and $t + \Delta t$ can be computed. Thus, eq. (8) yields the increment in C_W (ΔC_W) at x , generated by the net influx of transported solvent molecules (governed by thermodynamic diffusion and solubility coefficients D_W and $S_W = C_W/a_W$, respectively)⁵ during the small time interval Δt . The occurrence of two terms on the right-hand side of eq. (9) reflects the fact that ΔC_W is made up of two parts, ΔC_{W1} and ΔC_{W2} . $\Delta C_{W2} = \sum_{i=1}^{N_R} \Delta \delta C_{Wi}$ represents the uptake without a change in the prevailing activity a_W as a result of the extra sorptive capacity generated during Δt by structural relaxation; ΔC_{W1} represents the uptake associated with a corresponding increase in activity Δa_W according to the instantaneous absorption isotherm (because the polymer at the new activity $a_W + \Delta a_W$ has not yet had time to relax appreciably). Note that all quantities

involved in the calculation of ΔC_{W2} are known. Hence, given ΔC_W from eq. (8), Δa_W follows, and the requisite new values $C_W + \Delta C_W$, $a_W + \Delta a_W$, and $\delta C_{Wi} + \Delta \delta C_{Wi}$ can all be evaluated.

Specialization of the model to the CA-water system

In the absence of a reasonably simple, rigorous, and generally applicable physically significant theory of water sorption by polymeric materials, $F_F(a_W)$ is expressed in refs. 4 and 5 as a polynomial because this is the formulation most commonly adopted for fitting all kinds of experimental data empirically. In our previous parametric studies,^{4,5} a quadratic polynomial sufficed to represent the salient characteristics of the most common type of polymer-solvent (including water) sorption isotherm (i.e., conformity to Henry's law, at sufficiently low a_W values, coupled with an increasing positive deviation with rising a_W).

For our present purposes, the addition of a high-power third term was found to be necessary to fit the high curvature of the CA-water absorption isotherm (presumably because of clustering of the sorbed water molecules) as a_W approaches 1. Thus, the following function has been used:

$$F_F(a_W) = K_{W1F} a_W + K_{W2F} a_W^2 + K_{WSF} a_W^s \quad (12)$$

where K_W 's and s are input constants, the values of which are deduced from the experimental absorption isotherm. Substitution from eq. (12) into eq. (2a) leads to

$$\begin{aligned} f_F(\delta a_W) &= F_F(a_W) - F_F(a_{W0}) = k_{W1F} \delta a_W \\ &\quad + k_{W2F} \delta a_W^2 + \dots + k_{WSF} \delta a_W^s \end{aligned} \quad (13)$$

where

$$\begin{aligned} k_{W1F} &= K_{W1F} + 2K_{W2F} a_{W0} + sK_{WSF} a_{W0}^{s-1} \\ k_{W2F} &= K_{W2F} + \frac{1}{2}s(s-1)K_{WSF} a_{W0}^{s-2} \end{aligned}$$

For $3 \leq n \leq s$,

$$k_{WnF} = \frac{s!}{n!(s-n)!} K_{WSF} a_{W0}^{s-n}$$

According to what has already been said, the functions $f_i(\delta a_W)$ (representing the instantaneous absorption isotherm) and $f_i(\delta a_W)$ (denoting the sorption isotherm increments corresponding to partial and full relaxations) all have the form of eq. (13). As indicated in the previous section, two distinct relaxation processes are recognizable in the CA-water system; we use the designations $i = B$ and $i = C$ for the fast and

slow ones, respectively. The coefficients pertaining to $f_I(\delta a_W)$, $f_B(\delta a_W)$, and $f_C(\delta a_W)$ are symbolized by the replacement of the subscript F of those shown in eqs. (12) and (13) by I , B , and C , respectively; the relevant input parameters are given as fractions (α) of the corresponding ones for $F_F(a_W)$, namely, $\alpha_A = K_{WI}/K_{WF} = K_{W1I}/K_{W1F} = K_{W2I}/K_{W2F} = K_{WSI}/K_{WSF}$, $\alpha_B = K_{WB}/K_{WF}$, and $\alpha_C = K_{WC}/K_{WF}$. In conformity with eq. (4) and with eqs. (2a), (3), and (5) kept in mind, the values assigned to the defined α 's must fulfill the following condition:

$$\alpha_A + \alpha_B + \alpha_C = 1 \quad (14)$$

COMPUTER MODELING RESULTS AND DISCUSSION

As illustrated in Figure 1, an accurate fit of the absorption isotherm was obtained for the values of s and the K_{WF} coefficients given in the legend.

For the convenience of the computations, dimensionless parameters (denoted in bold type) were defined as follows:

$$\begin{aligned} x &= x/\ell; \quad t = D_W t/\ell^2; \quad C_W = C_W/C_W^0; \\ K_{WF} &= K_{WF}/C_W^0; \quad \delta C_W = \delta C_W/C_W^0; \quad \beta_W = \ell^2 \beta_W/D_W; \\ S_W &= S_W/C_W^0 = C_W/a_W \end{aligned} \quad (15)$$

β_W shows the magnitude of the relaxation rate constant on the diffusion timescale (represented by t). Thus, for both $\beta_W \rightarrow 0$ and $\beta_W \rightarrow \infty$, the absorption process follows Fickian kinetics corresponding to pure diffusion in the unrelaxed or fully relaxed polymer, respectively.

It should also be borne in mind that D_W here represents the thermodynamic diffusion coefficient, which affords a physically more rigorous measure of the mobility of diffusing molecules^{4,5,18} than the corresponding practical coefficient D_{WP} . In the absence of relaxation, these coefficients are related by a simple expression, which would be applicable here only to diffusion in the fully relaxed polymer:

$$D_{WP} = D_W \frac{d \ln a_W}{d \ln C_{WF}} \quad (16)$$

The second factor in eq. (16) follows from the sorption isotherm. Therefore, if D_{WP} is determined as a function of C_{WF} by one of the established methods available for this purpose,¹⁹ D_W is readily deducible. However, this step is rarely taken in practice. As a result, little is usually known about the behavior of D_W , which may differ substantially from that of D_{WP} , if the sorption isotherm exhibits marked curvature, as is the case here.

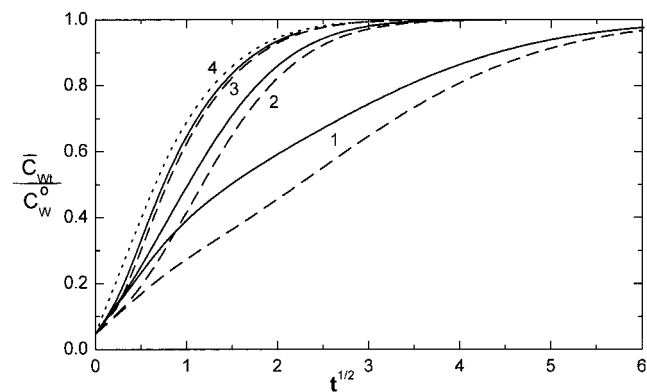


Figure 7 Dimensionless computed kinetic curves of \bar{C}_{Wt} in a polymeric film subject to a single relaxation process, characterized by $\alpha_A = (---) 0.30$ and $(—) 0.50$ and by $\beta_{WB} = (1) 0.1$, $(2) 1$, and $(3) 10$, in an absorption experiment covering the activity range of $a_W = a_{W0} = 0.1$ to $a_W = 1$. Fickian kinetics ($\beta_{WB} \rightarrow \infty$) are represented by line 4.

In the presence of relaxation processes giving rise to deviations from Fickian absorption kinetics, no comparable explicit methods of determining D_{WP} or D_W are available. Accordingly, we follow here an implicit model-dependent approach, by which the model previously described is used to reproduce the observed non-Fickian kinetics as closely as possible on the basis of as few, not independently known, model parameters as possible. In this respect, our previous practice^{4,5} of treating D_W and β_W as constants in each computation is justified here. In any case, assigning a constant mean effective value to a D_W dependent on the concentration (within reasonable limits) is a good approximation as far as the simulation of overall absorption kinetics is concerned (regardless of the fact that the corresponding concentration profiles may differ markedly).^{4,19} However, no material effect of relaxation on D_W (except indirectly via the effect on C_W) is expected.¹⁸ The minimum number of model parameters required to characterize relaxation processes B and C are the relaxation frequencies β_{WB} and β_{WC} and the corresponding initial state parameters α_A and α_B [which are sufficient to determine α_C as well via eq. (14)].

The information required to arrive at realistic *a priori* estimates of these parameters was extracted from the observed non-Fickian kinetic features, which are most clearly discernible in the experimental kinetic curves for $a_{W0} = 0.1$. Thus, a parametric study of the S shape of the kinetic curve (see examples in Fig. 7; cf. ref. 5) pointed to α_A values well below $\alpha_A = 0.5$ and to β_{WB} values in the region of $\beta_{WB} \approx 1$ –10. However, as illustrated in Figure 8, good estimates of α_C (and hence of α_B , once α_A is given) and β_{WC} were readily obtainable from the vertical position of the slowly rising upper part of the experimental kinetic curve and the ensuing kinetics (controlled by relaxation C), respectively.

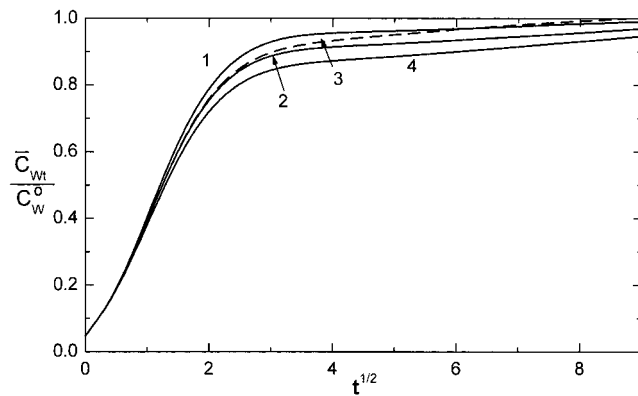


Figure 8 Dimensionless computed kinetic curves of \bar{C}_{wt} in a polymeric medium subject to relaxation processes B and C , characterized by $\alpha_A = 0.30$, $\beta_{WB} = 1$, $\beta_{WC} = (-) 0.01$ and $(- -) 0.03$, and $\alpha_B = (1) 0.65$, $(2,3) 0.60$, and $(4) 0.55$, in an absorption experiment covering the activity range of $a_w = a_{w0} = 0.1$ to $a_w = 1$.

On this basis, a further adjustment of the aforementioned input parameter values required the computation of only a limited number of dimensionless simulated kinetic curves for direct comparison with the relevant experimental data (because the variability of the results illustrated in Figure 2 appears to be largely due to the variability of film properties, notably C_{w0}^0 , rather than to errors of measurement, experimental curves were fitted individually and films of the same C_{w0}^0 value were chosen for a comparison of the results for different a_{w0} values). The comparison was effected by the replotting of the normalized experimental data for $a_{w0} = 0.1$ on the dimensionless timescale $D_{WA}t/\ell^2$, where D_{WA} denotes the experimental value of D_W yielding the best obtainable superposition of the data on a given computed kinetic curve. An example of the results obtained from this kind of kinetic analysis is shown in Figure 9. The corresponding D_{WA} values are given in the first row of Table I. These values, as well as those from another example (given in the fourth row of Table I), illustrate the significant effect that relaxation B can have on the resulting D_{WA} value. In particular, one can see that, if a non-Fickian system subject to a relaxation process governed by $\beta_{WB} = 1$ is (incorrectly) treated as Fickian, D_W would (in either example) be underestimated by a factor of approximately 3.

Figure 10 provides an illustration of the results of a check on the aforementioned parameter values, in the sense that the absorption kinetics observed for higher a_{w0} values may also be reproduced reasonably successfully on the basis of the same model parameter values. The main point to note here (see Table I) is that the resulting D_{WA} values decrease substantially as a_{w0} (and hence C_{w0}^0) is raised; this indicates that D_W has a negative concentration dependence [this being true for D_{WP} also because, for the type of sorption isotherm

under consideration here, the second factor in eq. (16) also turns out to be a decreasing function of concentration]. A similar tendency to decrease with rising a_{w0} is expected for β_{WB} and β_{WC} (on the basis of studies of the relaxation induced in CA by other sorbates, which reveal a clear tendency of β_W to vary inversely with the size of the increment in the concentration or activity covered by the absorption experiment).^{17,20} Accordingly, it was considered appropriate to use the same values of β_{WB} and β_{WC} for all a_{w0} values in the aforementioned computations (a choice that is certainly not contradicted by the results obtained).

On the basis of the overall goodness of fit obtained in this manner, we concluded that the correct value of β_{WB} lies close to 1; hence, the correct values (D_{WA}^0) of D_W should lie close to those given in the sixth column of Table I. Considerably better discrimination should be achievable in the case of glassy polymer films less prone to variability of properties than CA.

Another point worth noting in Table I is that although the absolute D_{WA} values depend materially on the value of β_{WB} used (as discussed previously), their dependence on a_{w0} is much the same, and this remains true for $\beta_{WB} \rightarrow \infty$; this indicates that, even if relaxation is completely ignored, a reasonably good picture of the concentration dependence of D_W may still emerge. However, as also shown in Table I, the degree of concentration dependence may vary significantly from one film specimen to another. The results that we have obtained so far suggest a link between a stronger declining tendency of D_W with a higher value of C_{w0}^0 ,

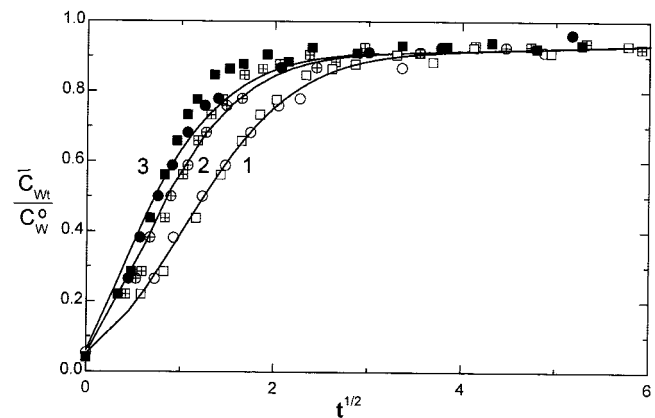


Figure 9 Comparison of experimental \bar{C}_{wt} (normalized) data for two CA films (identified by circles or squares), characterized by $C_{w0}^0 = 0.17$ g/g for $a_{w0} = 0.10$, with pertinent dimensionless simulated curves computed for a range of β_{WB} values. The main parameter values of the latter were $\alpha_A = 0.30$, $\alpha_B = 0.60$ ($\alpha_C = 0.10$), $\beta_{WC} = 0.01$, and $\beta_{WB} = (1) 1$, $(2) 10$, and $(3) \infty$. The experimental data (represented correspondingly by open, crossed, or filled points) have been plotted on a dimensionless timescale, $D_{WA}t/\ell^2$, where D_{WA} is each time chosen for the best superposition on the relevant simulated curve. The resulting D_{WA} values are given in the first row of Table I.

TABLE I
Examples of Experimental Estimates of D_W for Various a_{W0} Values Derived on the Basis of Various Values of β_{WB} as Explained in the Text and in the Legends of Figures 9 and 10

Film sample	C_W^0 (g/g)	a_{W0}	$D_{WA} \times 10^7$ (cm ² /s)			$D_{WA}/D_{WA} (a_{W0} = 0.1)$		
			$\beta_{WB} = \infty$	$\beta_{WB} = 10$	$\beta_{WB} = 1$	$\beta_{WB} = \infty$	$\beta_{WB} = 10$	$\beta_{WB} = 1$
A1	0.17	0.10	1.8	2.6	4.8	1	1	1
A2		0.70	0.60	0.81	1.4	0.30	0.31	0.29
A3		0.85	0.36	0.50	0.78	0.20	0.19	0.16
B1	0.15	0.10	1.4	1.9	3.5	1	1	1
B2		0.70	0.85	1.14	2.0	0.61	0.60	0.57

and this would be consistent with the physical interpretation of the decline of D_W in terms of the clustering of the imbibed water molecules (cf. the Introduction section) on the assumption that a higher C_W^0 value entails a higher degree of clustering.

CONCLUSIONS

We have reported here an experimental study of non-Fickian absorption of liquid water by CA films conditioned to different a_{W0} values (and corresponding sorbate C_{W0} values). The observed absorption kinetics exhibited two distinct non-Fickian features resulting from short- and long-term viscous structural relaxations (labeled B and C, respectively) of the swelling polymer matrix, each leading to an increased absorption capacity of the matrix for the penetrant.

On the basis of a model of non-Fickian absorption in a swellable polymeric matrix subject to multiple structural relaxations also presented here, the behavior of the CA-water system could be characterized by the

following minimum set of parameters: the effective thermodynamic diffusion coefficient, D_W ; the absorption isotherm for the fully relaxed polymer, $C_{WF}(a_W)$ (measured directly); the initial state parameters, α_A and α_B (which characterize the sorption capacity of unrelaxed and partly relaxed polymer, respectively, with respect to C_{WF}); and the relaxation frequencies, β_{WB} and β_{WC} (which determine the rates of relaxations B and C, respectively).

Information about the latter four parameters was extracted from the non-Fickian features of the experimental curves for $a_{W0} = 0.1$ (at which such features were most prominent). In particular, α_C and β_{WC} were estimated directly from the long-time tail of the kinetic curve, which was rate-controlled by relaxation C.

The approach adopted from this point on (which could serve as a good example of a general method of kinetic analysis of non-Fickian absorption data) was to use initial estimates of α_A and β_{WB} (derived from the shape of the dimensionless C_{Wt} -versus- \sqrt{t} curve on the basis of a brief preliminary parametric study) to obtain dimensionless computed curves for $a_{W0} = 0.1$, which were compared with the relevant experimental data replotted on a dimensionless $D_{WA}t/\ell^2$ scale, where D_{WA} is the experimental value of D_W required to optimize the superposition of the corresponding experimental and computed kinetic curves. Then, α_A and especially β_{WB} (the variable of primary importance here⁵) were varied, and this procedure was repeated as necessary to achieve satisfactory coincidence of the experimental and computed curves and thus to obtain the final estimate (D_{WA}^0) of D_W .

The usefulness of our modeling approach to non-Fickian water absorption by CA was demonstrated by the fact that the experimental kinetic curves pertaining to different a_{W0} values (or concentration) were also successfully reproduced by the same set of optimum input parameter values, and it was further supported by the results of a final and more exacting test involving the accurate predictive simulation of water uptake coupled with the parallel release of an osmotically active solute, as described in part II of this series.

The following conclusions, on points of general practical importance or relating to the diffusion be-

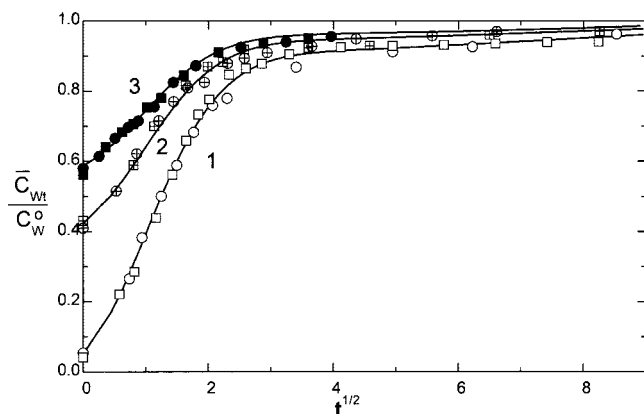


Figure 10 Comparison of duplicate experimental data from films with similar C_W^0 values, plotted in a dimensionless form as in Figure 9 and extending over a range of a_{W0} values, with pertinent simulated curves (computed as in Fig. 9 for $\beta_{WB} = 1$): $a_{W0} =$ (1) 0.1 (open points; identical to line 1 and corresponding points in Fig. 9), (2) 0.70 (crossed points), and (3) 0.85 (filled points). The resulting D_{WA} values (for this and other values of β_{WB}) are given in the first three rows of Table I.

havior of water in CA films, are also noteworthy. First, the deduced D_{WA} values decrease systematically with increasing a_{W0} (or C_{W0}), and this indicates that D_W tends to decrease with an increasing concentration of imbibed water; the extent of this concentration dependence is variable but seems to be linked to the C_W^0 value of the film used. Second, D_{WA} , at a given value of a_{W0} , depends materially on the assumed value of β_{WB} , but its concentration dependence does not; this suggests that, in practice, neglecting the effect of relaxation can lead to substantially erroneous estimates of the absolute magnitude of D_W but can still yield a realistic picture of its concentration dependence.

This work was performed in the framework of the "Excellence in the Research Institutes" program.

References

1. Papadokostaki, K. G.; Petropoulos, J. H.; Amarantos, S. G. *J Appl Polym Sci* 1998, 67, 277.
2. Papadokostaki, K. G.; Petropoulos, J. H.; Amarantos, S. G. *J Appl Polym Sci* 1998, 69, 1275.
3. Papadokostaki, K. G.; Herouvim, M. E. *J Appl Polym Sci* 2002, 84, 2028.
4. Petropoulos, J. H.; Papadokostaki, K. G.; Amarantos, S. G. *J Polym Sci Part B: Polym Phys* 1992, 30, 717.
5. Papadokostaki, K. G.; Polishchuk, A. Y.; Petrou, J. K. *J Polym Sci Part B: Polym Phys* 2002, 40, 1171.
6. Lee, P. I. *Polymer* 1984, 25, 973.
7. Brazel, C. S.; Peppas, N. A. *Eur J Pharm Biopharm* 2000, 49, 47.
8. Charalambopoulou, G. C.; Kikkinides, E. S.; Papadokostaki, K. G.; Stubos, A. K.; Papaioannou, A. T. *J Controlled Release* 2001, 70, 309.
9. Long, F. A.; Thomson, L. J. *J Polym Sci* 1955, 15, 413.
10. Wellons, J. D.; Williams, J. L.; Stannett, V. J. *J Polym Sci Part A-1: Polym Chem* 1967, 5, 1341.
11. Hopfenberg, H. B.; Kimura, F.; Rigney, P. T.; Stannett, V. J. *J Polym Sci Part C: Polym Symp* 1969, 28, 243.
12. Pegoraro, M. *Makromol Chem Suppl* 1981, 5, 179.
13. Roussis, P. P. *Polymer* 1981, 22, 768.
14. Roussis, P. P. *Polymer* 1981, 22, 1057.
15. Perrin, L.; Nguyen, Q. T.; Sacco, D.; Lochon, P. *Polym Int* 1997, 42, 9.
16. Toprak, C.; Agar, J. N.; Falk, M. *J Chem Soc Faraday Trans* 1979, 75, 803.
17. Sanopoulou, M.; Petropoulos, J. H. *Macromolecules* 2001, 34, 1400.
18. Petropoulos, J. H. *J Polym Sci Polym Phys Ed* 1984, 22, 1885.
19. Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Clarendon: Oxford, 1975; Chapter 10.
20. Sanopoulou, M.; Petropoulos, J. H. *Polymer* 1997, 38, 5761.