

This article was downloaded by:

On: 19 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

General Model of Transport of Water and Low-Molecular Weight Solute in Swelling Polymer

A. Ya. Polishchuk^a; G. E. Zaikov^a; J. H. Petropoulos^b

^a Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia ^b Demokritos National Research Centre for Physical Sciences, Athens, Greece

To cite this Article Polishchuk, A. Ya. , Zaikov, G. E. and Petropoulos, J. H.(1994) 'General Model of Transport of Water and Low-Molecular Weight Solute in Swelling Polymer', International Journal of Polymeric Materials, 25: 1, 1 – 12

To link to this Article: DOI: 10.1080/00914039408028572

URL: <http://dx.doi.org/10.1080/00914039408028572>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Intern. J. Polymeric Mater., 1994, Vol. 25, pp. 1–12
Reprints available directly from the publisher
Photocopying permitted by license only
© 1994 Gordon and Breach Science Publishers S.A.
Printed in Malaysia

General Model of Transport of Water and Low-Molecular Weight Solute in Swelling Polymer

A. YA. POLISHCHUK and G. E. ZAIKOV

*Institute of Chemical Physics, Russian Academy of Sciences, 4, Kosygin st.,
Moscow 117334, Russia*

and

J. H. PETROPOULOS

*Demokritos National Research Centre for Physical Sciences, 15130 Ag. Paraskevi,
Athens, P.O. Box 60228, Greece*

A mathematical model of the simultaneous transport of water and low molecular weight solute in a swelling polymer film has been generalized by consideration of the expansion of the film area and their effect on the parameters involved. The character of the kinetic curves for water uptake and solute desorption were examined as a function of (i) mobility of the low molecular weight compound, (ii) concentration and stress dependence of the diffusion coefficient of the solvent, and (iii) mechanical properties of the polymer (whose dependence on the concentration of water and solute has also been considered). The correlation of the expansion area of the water sorption curves was examined briefly, mostly as a check of the validity of the model.

KEY WORDS Transport, water, swelling polymers low molecular weight solute

Simultaneous transport of solvent (water) and low-molecular weight solute in swelling polymers has been considered in our previous papers^{1,2} in order to describe the process of drug release from hydrophilic polymeric matrices. The investigation reported in Reference 2 was based on the application of two models both of which were developed by Petropoulos.^{3–6} The first was the “differential swelling stress model,” describing the effect of differential swelling stresses on the diffusion coefficient of solvent as well as the effect of solvent and salt on the mechanical properties of the polymer, such as viscosity, elastic modulus, and the relaxation frequency. The second model dealt with the transport of the low-molecular weight compound itself taking into account the change of its activity as its concentration in the polymer varies. Being combined with each other and justified by experimental results these models assumed that:

- (i) the dependence of the diffusion coefficients of the solvent and the solute on the concentration of the solvent are in agreement with the theory of free volume,
- (ii) the swelling stress depends on the concentration of solvent and solute through corresponding dependences of elastic moduli and frequency of relaxation.

The main purpose of the aforementioned study² was to examine certain general features of the behaviour of polymer systems which are representative of those used for controlled release of drugs. For this reason some effects, of which the most essential are expansion of the film area, and variations of certain parameters during the transport process were not taken into account. We proceed to consider these effects here.

THE MODEL

The model presented here describes the transport of solvent by the diffusion equation of standard form

$$\partial C_w / \partial t = (\partial / \partial x)(D_w \partial C_w / \partial x) \quad 0 < x < 1 \quad (1)$$

where

$$D_w = D_{w0} \cdot \exp(k_{w1} C_w + k_{w2} f) \quad (2)$$

coupled with an equation describing the buildup and relaxation of the corresponding local differential swelling stresses along the plane of the film (i.e., at right angles to the direction of solvent penetration)

$$\begin{aligned} \partial f / \partial t = & (G_0 - G_\infty) \partial s / \partial t + \partial (s G_\infty) / \partial t \\ & + ((G_0 - G_\infty)^{-1} \partial (G_0 - G_\infty) / \partial t - \beta)(f - s G_\infty) \end{aligned} \quad (3)$$

The change in area caused by unconstrained solvent uptake is given by References 4 and 5.

$$A(C_w) = A(0) \cdot (1 + k_s C_w) \quad (4)$$

During the sorption of solvent its concentration (C_w) varies with x and a corresponding variation of A according to Equation (4) is expected. However, the actual area of a thin film is constrained to a uniform value \bar{A} , which is a function of time only. This leads to the creation of local strains

$$s = \bar{A}(t) / A(x, t) - 1 \quad (4a)$$

and corresponding local stresses f , which must add up to zero net overall stress. Hence, we have

$$\int_0^1 f(x, t) dx = 0 \quad (5)$$

We justified in Reference 2 that the plastisizing action of solvent and the opposite

action of the solute could be described by an exponential dependence of the instantaneous and long term elastic moduli on solvent and solute concentrations

$$G_0 = G_{00} \exp(-k_{g1}C_w + k_{g2}C_s)$$

$$G_\infty = G_{\infty 0} \exp(-k_{g1}C_w + k_{g2}C_s)$$

Also, we follow the findings of Reference 2 concerning the influence of solvent and solute on relaxation frequency. In particular, the experimental results quoted therein showed that both components cause a deviation of β in the same direction, and an exponential dependence is the best description of this effect

$$\beta = \beta_0 \exp(k_{d1}C_w + k_{d2}C_s)$$

In contrast with the previous study, we restricted the present investigation to conditions where the solute is completely soluble in the polymer. This condition is valid in many experimental systems^{1,7} and has been made in order to focus attention on the effect of varying the parameters which describe the behaviour of the diffusion coefficient of solute. Thus here we describe the transport of solute by equation

$$\partial C_s / \partial t = \partial / \partial x (D_s \cdot \partial C_s / \partial x) \quad 0 < x < 1 \quad (6)$$

where the diffusion coefficient of solute may be assumed to vary with the concentration of sorbed solvent as follows:

$$D_s = D_{s0} \exp(-k_{w3}/(C_w + k_{w4}))$$

as postulated by the free volume theory of Yasuda *et al.*⁸

CALCULATION PROCEDURE

For mathematical convenience dimensionless parameters were defined as follows:

$\bar{x} = x/l$	$\bar{k}_{w1} = k_{w1}C_{w0}$
$\bar{t} = D_{w0}t/l^2$	$\bar{k}_{w2} = k_{w2}G_{\infty 0}$
$\bar{C}_w = C_w/C_{w0}$	$\bar{k}_s = k_sC_{w0}$
$\bar{C}_s = C_s/C_{s0}$	$\bar{k}_{d1} = k_{d1}C_{w0}$
$\bar{D}_w = D_w/D_{w0}$	$\bar{k}_{d2} = k_{d2}C_{s0}$
$\bar{D}_s = D_s/D_{s0}$	$\bar{k}_{g1} = k_{g1}C_{w0}$
$\bar{f} = f/G_{\infty 0}$	$\bar{k}_{g2} = k_{g2}C_{s0}$
$\bar{G}_0 = G_0/G_{\infty 0}$	$\bar{k}_{w3} = k_{w3}C_{w0}$
$\bar{G}_\infty = G_\infty/G_{\infty 0}$	$\bar{k}_{w4} = k_{w4}C_{w0}$

$$M_{wt} = \int_0^1 C_w(x, t) dx \quad \begin{aligned} A(0) &= 1 \\ \bar{\beta} &= \beta_1^2/D_{w0} \\ \beta_0 &= \beta_0^2/D_{w0} \end{aligned}$$

$$M_{st} = 1 - \int_0^1 C_s(x, t) dx$$

The calculation procedure described in Reference 2 yields $\bar{C}_w(\bar{x}, \bar{t} + dt)$, $\bar{C}_s(\bar{x}, \bar{t} + dt)$ and $\bar{f}(\bar{x}, \bar{t} + dt)$ if all other terms referred to \bar{t} are known (dt is the step for t). The finite difference version of Equation (3) then gives

$$\bar{f}(\bar{x}, \bar{t} + dt) - s(\bar{x}, \bar{t} + dt)\bar{G}_x(x, t + dt) = F(\bar{x}, \bar{t}) \quad (7)$$

where

$$F(\bar{x}, \bar{t}) = \bar{f} - s\bar{G}_x + ((\bar{G}_0 - \bar{G}_x)\partial s/\partial \bar{t} + ((\bar{G}_0 - \bar{G}_x)^{-1}\partial(\bar{G}_0 - \bar{G}_x)/\partial \bar{t} - \bar{\beta})(\bar{f} - s\bar{G}_x)) \cdot dt$$

(all terms contained in the right hand side of this expression refer to time \bar{t} and are known).

Introducing Equations (4a), (5) and dimensionless expression

$$A(\bar{x}, \bar{t}) = (1 + k_s \cdot \bar{C}_w)$$

into (7) we get

$$\int_0^1 \bar{A}\bar{G}_x(\bar{t} + dt) \cdot d\bar{x}/(1 + k_s \cdot \bar{C}_w) = \int_0^1 \bar{G}_x(\bar{t} + dt) \cdot d\bar{x} - \int_0^1 F(\bar{x}, \bar{t}, t + dt) \cdot d\bar{x}$$

$$\bar{A} = \left(\int_0^1 \bar{G}_x(\bar{t} + dt) \cdot d\bar{x} - \int_0^1 F(\bar{x}, \bar{t}, t + dt) \cdot d\bar{x} \right) / \int_0^1 \bar{G}_x(\bar{t} + dt) \cdot d\bar{x}/(1 + k_s \cdot \bar{C}_w)$$

The whole calculation is started from the initial distributions of $\bar{C}_w(\bar{x}, 0)$, $\bar{C}_s(\bar{x}, 0)$ from which

$$\bar{f}(\bar{x}, 0) = (\bar{A}(0)/(1 + k_s \bar{C}_w(\bar{x}, 0)) - 1) \cdot \bar{G}_0(\bar{x}, 0)$$

and upon integration and application of Equation (5)

$$\bar{A}(0) = \int_0^1 \bar{G}_0(\bar{x}, 0) \cdot d\bar{x} / \int_0^1 \bar{G}_0(\bar{x}, 0) \cdot d\bar{x}/(1 + k_s \cdot \bar{C}_w(\bar{x}, 0))$$

whence $s(\bar{x}, 0)$, $\bar{f}(\bar{x}, 0)$, $\bar{D}_w(\bar{x}, 0)$ and $\bar{D}_s(\bar{x}, 0)$ follow.

Other calculations have been made in accordance with the procedure described in Reference 2.

RESULTS AND DISCUSSION

The results obtained may be divided by four groups which are characterized by different variations of the model parameters.

Variations of the parameters concerned with the value of \bar{D}_s and its dependence on the concentration of water

$$\bar{D}_s = \bar{D}_{s0} \exp(-\bar{k}_{w3}/(1 + \bar{k}_{w4}\bar{C}_w))$$

provides the opportunity for instructive comparison of the kinetics of water uptake and desorption of solutes of different mobility.

For this set of calculations $\bar{k}_{w3}/\bar{k}_{w4}$ was set equal to 13.8 with $\bar{D}_s(\bar{C}_w = 0)/\bar{D}_{s0} = 10^{-6}$, $\bar{D}_w(\bar{C}_w = 1, \bar{f} = 0) = e$, which correspond to reasonable ratios between

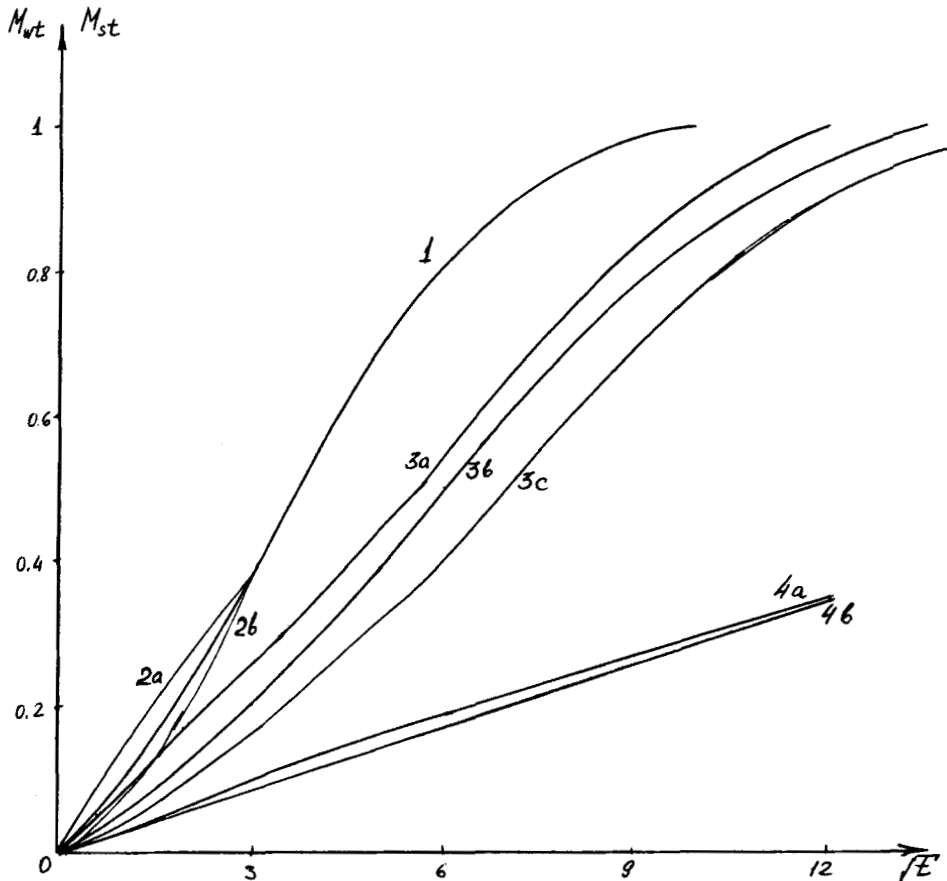


FIGURE 1 Computed kinetic curves of water uptake (1) and solute desorption (2-4). Variations of $\bar{D}_s \cdot \bar{D}_w(1,0) = e$. 2a— $\bar{D}_{s0} = 1000$, $\bar{D}_s(1) = 10$; 2b— $\bar{D}_{s0} = 100$, $\bar{D}_s(1) = 7$; 3a— $\bar{D}_{s0} = 1000$, $\bar{D}_s(1) = 1$; 3b— $\bar{D}_{s0} = 100$, $\bar{D}_s(1) = 1$; 3c— $\bar{D}_{s0} = 10$, $\bar{D}_s(1) = 0.7$; 4a— $\bar{D}_{s0} = 100$, $\bar{D}_s(1) = 0.1$; 4b— $\bar{D}_{s0} = 10$, $\bar{D}_s(1) = 0.1$.

Downloaded At: 12:26 19 January 2011

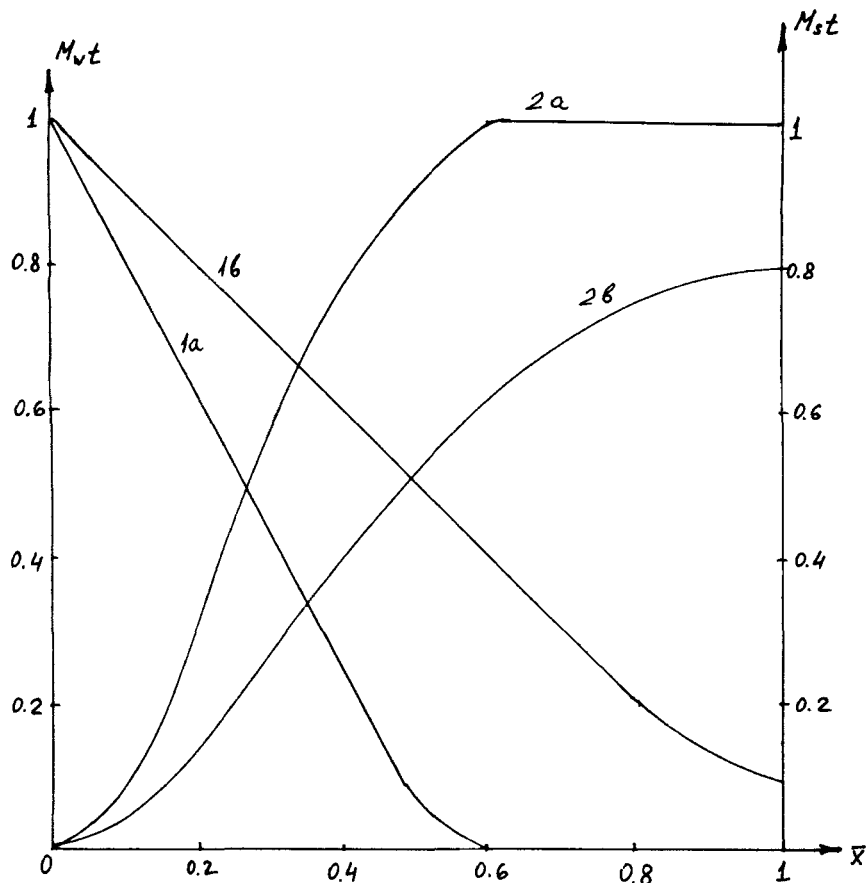


FIGURE 1b Distribution of solvent (1) and solute (2) at $\bar{t} = 8(a)$, $12(b)$ in case of $2a$.

diffusion coefficients of solute in dry polymer and in solution (keeping other parameters set equal to 1, except for $\bar{k}_s = 0.1$).

The variations affected involved changes of \bar{D}_{s0} in the range of 10 to 1000, and of \bar{k}_{w3} in the range 3.45 to 13.8, which permitted investigation of the behaviour of the system for $0.1 \leq \bar{D}_s(\bar{C}_w = 1) \leq 10$, and for $0.001 \leq \bar{D}_s(\bar{C}_w = 1))/\bar{D}_{s0} \leq 0.07$ (Figure 1).

The influence of all the parameter variations indicated above have a negligible influence on water uptake, and the kinetic curve of water sorption is slightly S-shaped (Figure 1, curve 1). For high values of $\bar{D}_s(\bar{C}_w = 1) = 10$ (of order of 10) the expected result for solute desorption to follow water uptake has been obtained. Moderate values of $\bar{D}_s(\bar{C}_w = 1)$ (of order of 1) lead to non-Fickian release kinetics, the rate of which increases with \bar{k}_{w3} . Desorption of low-molecular weight solute with small values of $\bar{D}_s(\bar{C}_w = 1)$ (of order of 0.1) becomes Fickian again due to the fact that water uptake is completed at an early stage. The influence of \bar{k}_{w3} on the rate of desorption is negligible for this case (Figure 1, curves 3a, 3b). The profiles of \bar{C}_w (Figure 1b, solid lines) are diffuse and seem quite linear, while profiles of \bar{C}_s are quite steep.

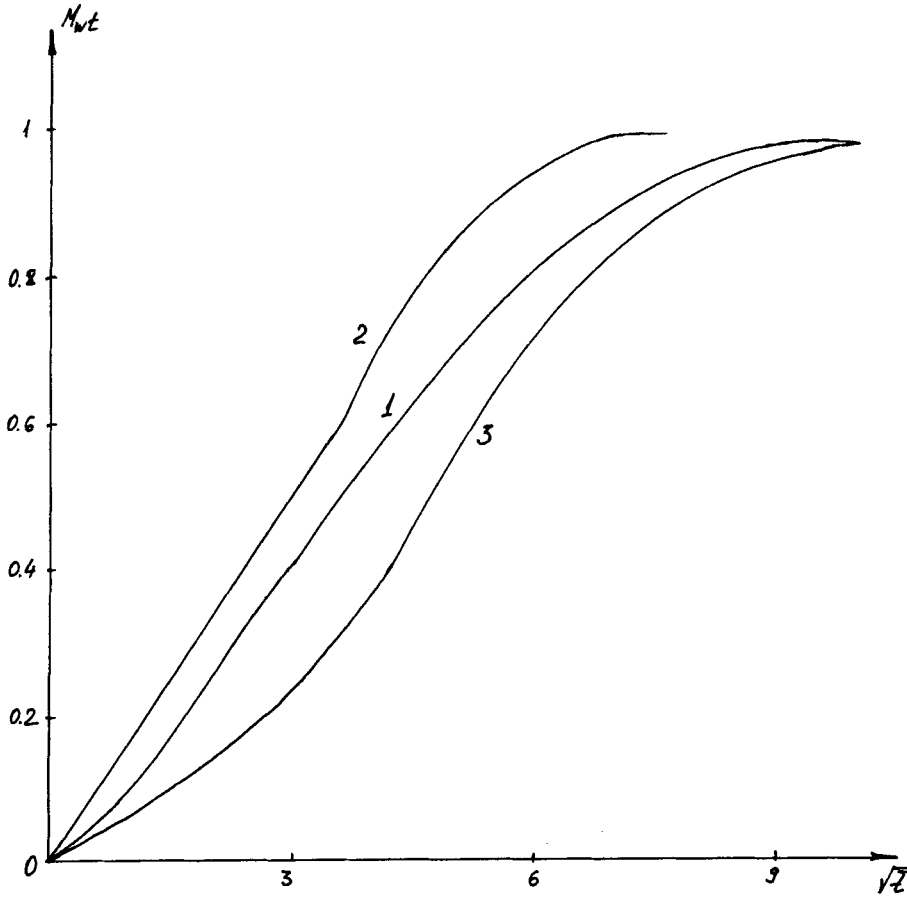


FIGURE 2 Computed kinetic curves of water uptake. Variations of \bar{D}_w , $\bar{D}_{s0} = 1000$, $\bar{D}_s(1) = 10$. 1— $\bar{D}_w(1, \text{const})/\bar{D}_w(0, \text{const}) = e$, $\bar{D}_w(\text{const}, f_{\text{max}})/\bar{D}_w(\text{const}, 0) = \exp(f_{\text{max}})$. 2— $\bar{D}_w(1, \text{const})/\bar{D}_w(0, \text{const}) = 20000$, $\bar{D}_w(\text{const}, f_{\text{max}})/\bar{D}_w(\text{const}, 0) = \exp(f_{\text{max}})$. 3— $\bar{D}_w(1, \text{const})/\bar{D}_w(0, \text{const}) = e$, $\bar{D}_w(\text{const}, f_{\text{max}})/\bar{D}_w(\text{const}, 0) = \exp(20 \cdot f_{\text{max}})$.

The second group of variations involve parameters concerned with the dependence of the diffusion coefficient of water

$$\bar{D}_w = \exp(\bar{k}_{w1}\bar{C}_w + \bar{k}_{w2}\bar{f})$$

The difference between a weak *versus* a strong dependence of \bar{D}_w on the concentration of water (\bar{C}_w) and stress (\bar{f}) is illustrated in Figures 2 and 3 (curve 1 and curves 2 and 3 respectively). The effect of varying the value of β_0 in the case of a strong dependence of \bar{D}_w on \bar{C}_w and \bar{f} is illustrated in Figure 3 (curves 2 and 3).

The acceleration of water sorption coupled with minor changes of the shape of the kinetic curve is the main result of the strong dependence of \bar{D}_w on \bar{C}_w (Figures 2 and 3, curve 2). An increase of \bar{k}_{w2} (Figure 2, curve 3) decelerated water uptake due to the strong dependence of \bar{D}_w on \bar{f} , and the kinetic curve assumed more of

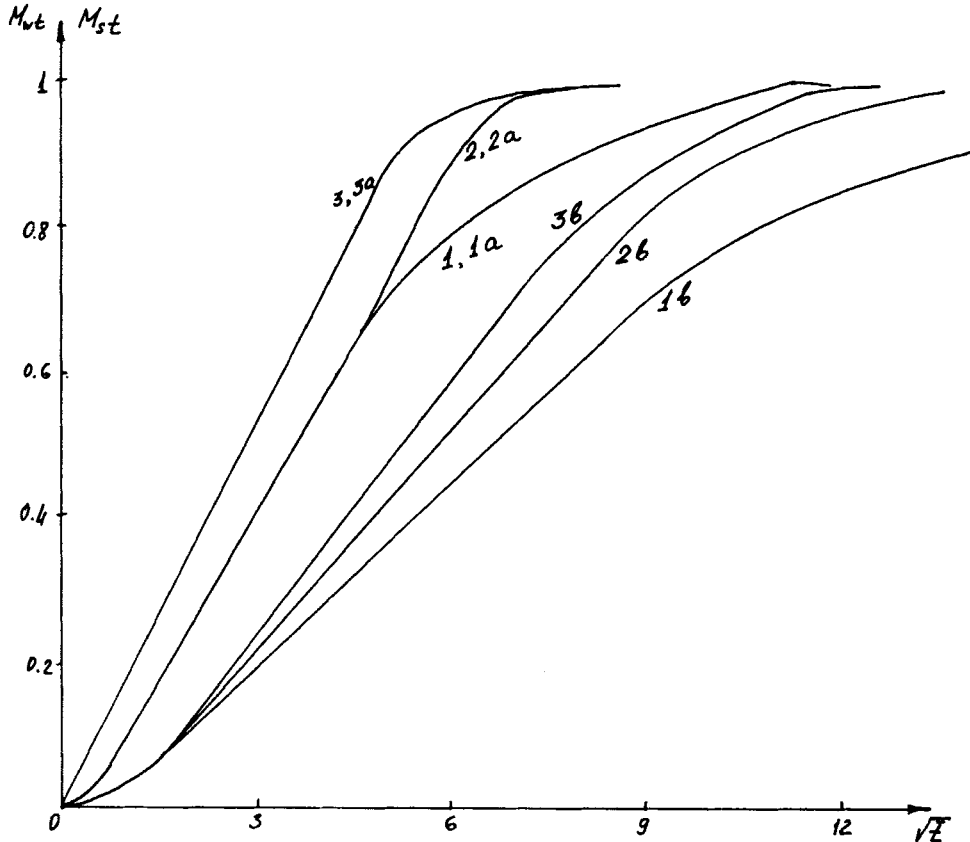


FIGURE 3 Computed kinetic curves of water uptake (1-3) and solute desorption (labelled by letters). Variations of \bar{D}_w , $\bar{D}_s(1)$. 1— $\bar{D}_w(1, \text{const})/\bar{D}_w(0, \text{const}) = e$, $\bar{D}_w(\text{const}, f_{\text{max}})/\bar{D}_w(\text{const}, 0) = \exp(f_{\text{max}})$. $\beta_0 = 1$; 2— $\bar{D}_w(1, \text{const})/\bar{D}_w(0, \text{const}) = 20000$, $\bar{D}_w(\text{const}, f_{\text{max}})/\bar{D}_w(\text{const}, 0) = \exp(10 \cdot f_{\text{max}})$. $\beta_0 = 1$; 3— $\bar{D}_w(1, \text{const})/\bar{D}_w(0, \text{const}) = e$, $\bar{D}_w(\text{const}, f_{\text{max}})/\bar{D}_w(\text{const}, 0) = \exp(10 \cdot f_{\text{max}})$. $\beta_0 = 100$; a— $\bar{D}_s(1) = 10$, $b = \bar{D}_s(1) = 1$.

an S-shape. The latter is in contrast with previous model computations,² in which expansion of the area was not taken into account. In the aforesaid computations Fickian sorption curves and diffuse profiles of water in the film were obtained for similar cases.

Because the influence of \bar{C}_w and \bar{f} are in opposite directions their effects tend to cancel at low M_{wt} values, as shown by curves 1 and 2 in Figure 3. These curves show, however, that there is a substantial deviation between the cases of a strong dependency of \bar{D}_w on \bar{C}_w and \bar{f} at high M_{wt} values. Acceleration of water sorption is the consequence of the increase of $\beta_0 \rightarrow 100$ (Figure 3, curve 3), and the shape of the curve becomes Fickian (at the same time the profile of water in the film remains sharp because of the strong dependence of \bar{D}_w on \bar{C}_w).

As shown by curves 1a-3a in Figure 3, for high $\bar{D}_s(\bar{C}_w = 1)$ values, both the kinetics and the rate of solute release are governed by the corresponding features of water uptake. In contrast to this (curves 1b-3b in Figure 3), for moderate $\bar{D}_s(\bar{C}_w = 1)$ values, only the rate of solute release is affected by changes in the rate of

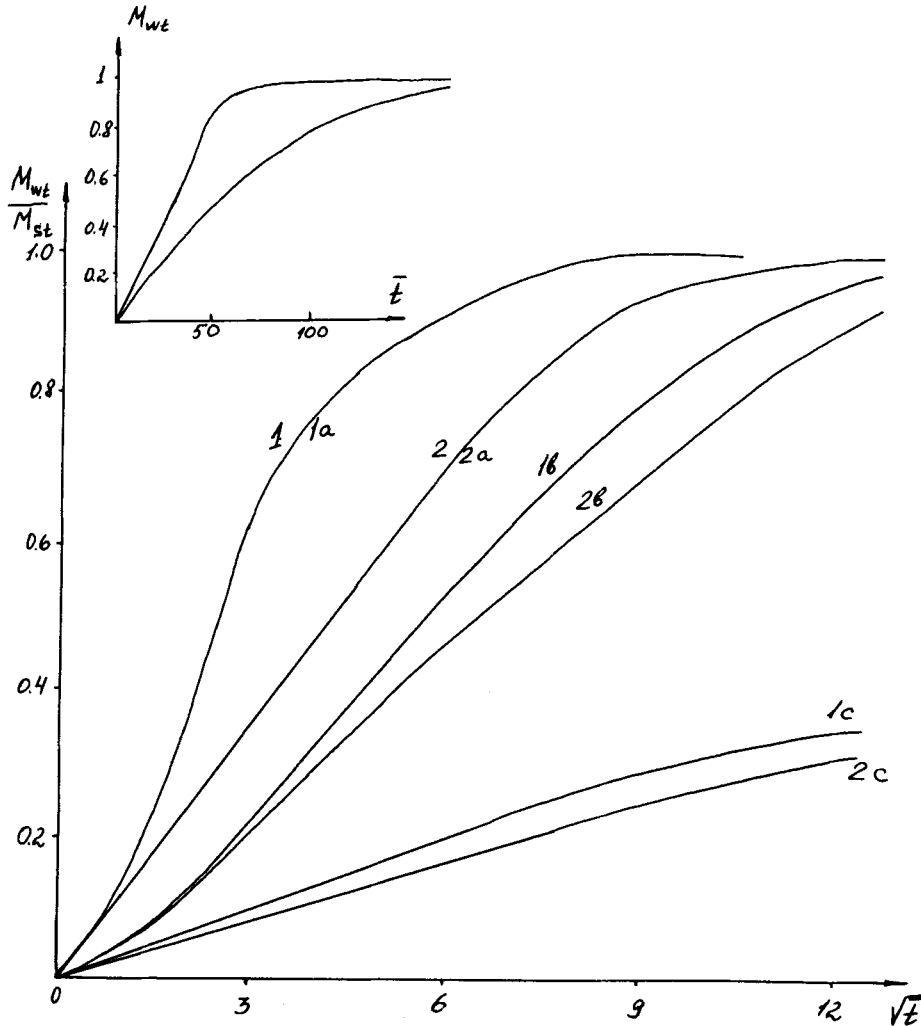


FIGURE 4 Computed kinetic curves of water uptake (1, 2) and solute desorption (labelled by letters). Variations of elastic moduli and $\bar{D}_s \cdot \bar{D}_w(1, 0) = e$. 1— $G_i(0, 1)/G_i(1, 0) = 10^5$; 2— $G_i(C_w = 0, C_s = 1)/G_i(C_w = 1, C_s = 0) = 20$; a— $\bar{D}_s(1) = 10$, b— $\bar{D}_s(1) = 1$, c— $\bar{D}_s(1) = 0.1$.

water uptake (whatever the underlying causes may be), the kinetics of release remain essentially unchanged.

Variations of mechanical properties have been considered in the form of the strong dependence of elastic moduli on the concentration of solvent and of solute.

A 5-orders decrease of elastic moduli (Figure 4, curve 1), which was used to represent the strong dependence on the concentration of water, causes almost case-II diffusion of water until $M_{wt} = 0.6$, while non-linear uptake was observed at higher values of M_{wt} . A strong dependence of elastic moduli on solute concentration (Figure 4, curve 2) is characterized by Fickian water uptake.

The results relating to the kinetics of solute release (Figure 4, curves labelled by letters) confirm previous conclusions that the value of \bar{D}_s gives rise to three

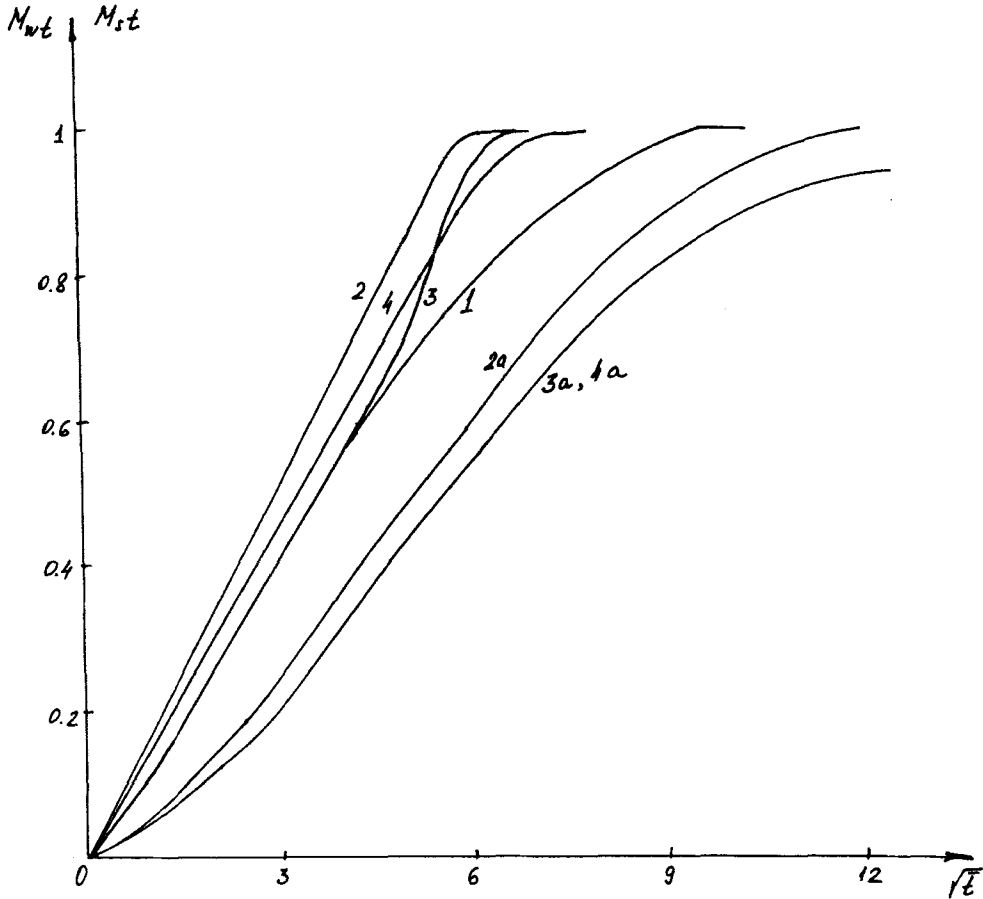


FIGURE 5 Computed kinetic curves of water uptake (1-4) and solute desorption (labelled by a). Variations of frequency of stress relaxation. $\bar{D}_s(1) = 1$, $\bar{D}_s(1, 0) = e$. 1— $\beta_0 = 1$, $\beta(C_w = 0, C_s = \text{const})/\beta(C_w = 1, C_s = \text{const}) = \exp(-1)$, $\beta(C_w = \text{const}, C_s = 1)/\beta(C_w = 1, C_s = \text{const}) = e$; 2— $\beta_0 = 100$, $\beta(C_w = 0, C_s = \text{const})/\beta(C_w = 1, C_s = \text{const}) = \exp(-1)$, $\beta(C_w = \text{const}, C_s = 1)/\beta(C_w = 1, C_s = \text{const}) = e$; 3— $\beta_0 = 1$, $\beta(C_w = 0, C_s = \text{const})/\beta(C_w = 1, C_s = \text{const}) = 0.01$, $\beta(C_w = \text{const}, C_s = 1)/\beta(C_w = 1, C_s = \text{const}) = e$; 4— $\beta_0 = 1$, $\beta(C_w = 0, C_s = \text{const})/\beta(C_w = 1, C_s = \text{const}) = \exp(-1)$, $\beta(C_w = \text{const}, C_s = 1)/\beta(C_w = 1, C_s = \text{const}) = 100$.

possibilities of release kinetics which are: (i) desorption closely corresponding to water uptake ($\bar{D}_s \gg 1$) (1a, 2a); (ii) non-Fickian desorption the rate of which tends to increase as sorption of water accelerates ($\bar{D}_s \cong 1$) (1b, 2b); (iii) Fickian desorption following complete water uptake at $\bar{D}_s \ll 1$ (1c, 2c).

A study of the variation of the parameters appearing in the expression for the relaxation frequency

$$\bar{\beta} = \bar{\beta}_0 \exp(\bar{k}_{a1}\bar{C}_w + \bar{k}_{a2}\bar{C}_s)$$

is represented in Figure 5.

Curve 1 corresponds to a moderate value of $\bar{\beta}_0$ and a weak dependence of $\bar{\beta}$ on

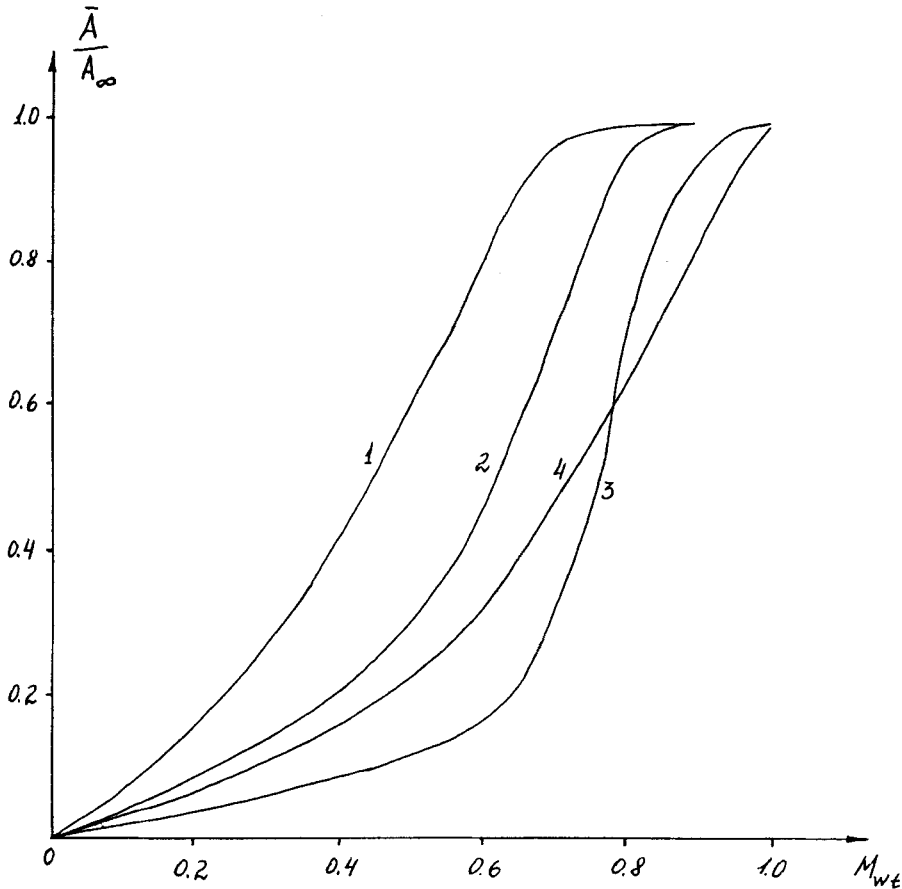


FIGURE 6 Computed correlation of area expansion with corresponding curves of water uptake. Lines labelled: 1—as in Figure 1 (curve 1). 2—as in Figure 2 (curve 2). 3—as in Figure 4 (curve 1). 4—as in Figure 5 (curve 4).

the concentration of water and solute and it looks Fickian. Because of solute desorption, a deceleration of water uptake was observed for the case of a strong dependence of stress relaxation on the concentration of solute (Figure 5, curve 4) in comparison with the case for the same initial value of $\bar{\beta}$ corresponding to unfilled dry polymer (Figure 5, curve 2). The strong dependence of β on the concentration of solvent (Figure 5, curve 3) causes a further deceleration of water uptake at lower values of $M_{wt} \leq 0.6$. At higher values of M_{wt} deviation of the kinetic curve of water sorption above the Fickian one was observed, and this leads to a higher velocity of water uptake in comparison with the case for the strong dependence on content of solute.

Examples of area expansion in relation to M_{wt} are given in Figure 6. The conclusions drawn in References 2 and 4 remain valid here. The best confirmation of these correlations is the influence of the presence of solute the kinetics of area expansion. In particular, the weak dependencies of \bar{G}_i or $\bar{\beta}$ on \bar{C}_w or \bar{C}_s in correlation

to \bar{A} vs M_{wr} are quite linear; while this correlation becomes markedly concave, if the dependence of \bar{D}_w or $\bar{\beta}$ or \bar{G}_i on \bar{C}_w is strong. Because the dependence of area expansion is essential for many reasons, further consideration is required to describe possible changes of the curves.

THE NOMENCLATURE

C_w	= solvent (water) concentration in polymer;
C_s	= solute concentration in polymer;
D_w	= (Fickian) diffusion coefficient of water in polymer;
D_{wo}	= diffusion coefficient of water in dry and unstressed polymer;
D_s	= (Fickian) diffusion coefficient of solute in polymer;
D_{so}	= diffusion coefficient of solute in pure water;
l	= thickness of polymer film;
f	= mechanical stress;
s	= swelling strain;
G_0, G_x	= initial and final elastic moduli;
β	= frequency of stress relaxation.

References

1. A. Ya. Polishchuk, L. A. Zimina, R. Yu. Kosenko, A. L. Iordanskii and G. E. Zaikov, *Polymer Degrad. and Stab.*, **31**, 247 (1991).
2. A. Ya. Polishchuk, G. E. Zaikov and J. H. Petropoulos, *Int. J. Polym. Mat.*, **19**, 1 (1992).
3. J. H. Petropoulos and P. P. Roussis. In: *Permeability of Plastic Films and Coatings*. Ed. by H. B. Hopfenberg, New York, p. 219 (1974).
4. J. H. Petropoulos and P. P. Roussis, *J. Membr. Sci.*, **3**, 343 (1978).
5. J. H. Petropoulos, *J. Membr. Sci.*, **18**, 37 (1983).
6. J. H. Petropoulos, S. G. Amarantos and K. G. Papadokostaki, *Proc. of 12th International Symposium on Controlled Release of Bioactive Materials*, Geneva, p. 1 (1985).
7. N. N. Madyuskin, A. L. Iordanskii and G. E. Zaikov, *Proceedings of the 7th All-Union Symposium on Synthetic Medical Polymers*, Minsk, p. 63 (1985), (Russian).
8. H. Yasuda, C. E. Lamaze and A. Peterlin, *J. Polym. Sci. A2*, **9**, p. 1117 (1971).