

# Sorption of Binary Liquid Mixtures in Methacrylate-Based Biomaterials; Simultaneous Determination of the Diffusion Coefficients and the Uptake Fraction at Equilibrium of the Components of Ethanol-Water Mixtures by a New Iterative Method

Irini D. Sideridou,<sup>1</sup> Georgios E. Papanastasiou<sup>2</sup>

<sup>1</sup>Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-54124, Thessaloniki, Greece

<sup>2</sup>Laboratory of Physical Chemistry, Department of Chemistry, Aristotle University of Thessaloniki, GR-54124, Thessaloniki, Greece

Received 23 October 2006; accepted 9 April 2007

DOI 10.1002/app.26672

Published online 1 October 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** The present investigation is concerned with the development of a new iterative method permitting, for a Fickian sorption of a binary liquid mixture in thin polymer sheets, the simultaneous determination of the self-diffusion coefficients of the components of the mixture, and their uptake fractions at equilibrium. The approach is based on a new equation describing a parallel Fickian sorption of the components of the mixture into thin polymer sheets. The procedure was tested with ideal and Monte Carlo simulated data. The method, applied to ideal simulated data that corresponded to various values of  $D_1$ ,  $D_2$  and  $f$ , perfectly extracted the desired parameters. The application of the method to Monte Carlo simulated data

revealed that this method is fairly applicable even when the simulated data are considerably obscured by "noise". Finally, the proposed method was successfully applied to the experimental data concerning the sorption kinetics of ethanol-water mixture (75 vol % in EtOH) at 37°C in thin polymeric sheets of triethyleneglycol dimethacrylate (TEGDMA). © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1057–1066, 2008

**Key words:** iterative method; diffusion coefficient; ethanol-water mixture; biomaterials; poly(triethyleneglycol dimethacrylate)

## INTRODUCTION

This paper is part of a continuing research on the preparation, characterization, and the physical behavior of dimethacrylate-based polymers used as biomaterials.<sup>1–10</sup>

Monomethacrylates, such as methyl methacrylate (MMA), and dimethacrylates mainly the bisphenol-A-diglycidyl dimethacrylate (Bis-GMA) and triethyleneglycol dimethacrylate (TEGDMA) are widely used in dentistry and orthopedic surgery, because of their established biocompatibility.<sup>11,12</sup> Poly(methyl methacrylate) is used for the construction of denture bases, artificial teeth, and as bone cements; copolymers of dimethacrylates are used in pit and fissure sealants, crown, and bridge prostheses, dentine bonding agents, tooth restorative composites, and also as bone cements.<sup>1,7,8,11,12</sup> As these materials are required to give satisfactory long-term service in the oral cavity their water sorption char-

acteristics are important.<sup>3,4</sup> Absorbed water can release internal strains, facilitate the extraction of unreacted monomer with biological implications,<sup>6</sup> affect the bonding strength with tooth structure, and promote breakdown of the resin-filler bond resulting in decrease of mechanical properties.<sup>13</sup> Therefore, it is preferable that the amount of water absorbed by a polymeric dental material be small and that it gains (or loses) this water content as quickly as possible.

As it has been pointed out previously, water sorption affects the mechanical properties of polymers. In general, the sorption rate can be represented by the diffusion coefficient  $D$ . Once  $D$  is determined, it may be possible, using appropriate diffusion equations, to estimate the diffusion process of water. This process also expresses the evolution of the polymer properties. In certain cases, for example in forecasting the operating characteristics of a certain polymer in an aggressive medium, sorption properties of the polymer should be specified. Also, polymers with high diffusion coefficients should release water-soluble unreacted compounds more rapidly, because the transfer of water into the material allows the unreacted compounds to be dissolved and released.

Correspondence to: G. E. Papanastasiou (papanast@chem.auth.gr).

For all these reasons, the diffusion coefficient of water in a polymer can be considered as a very important parameter. Usually, this parameter is experimentally determined from data of sorption kinetics.

It is interesting to note that especially the ethanol-water mixture (75 vol % in ethanol) is recommended by the Food and Drug Administration (FDA) Guidelines of USA (1976, 1988) as a food simulator and may be considered clinically relevant; it has been the solvent of choice to simulate accelerated aging of dental polymeric materials.<sup>9,10,14-17</sup> In our recent work, concerning the study of the sorption kinetics of ethanol-water mixture (75 vol % in ethanol) in dimethacrylate-based dental resins, as well as in resin composites, the apparent diffusion coefficient of the mixture was determined.<sup>10</sup> However, the exact diffusion rate of such a mixture in a dental resin is characterized obviously by two diffusion coefficients  $D_1$  and  $D_2$  for water and ethanol, respectively. But, as far as we know, there is no method permitting the determination of  $D_1$  and  $D_2$  of the components of a mixture by using sorption data.

So, in an attempt to extend our researches to ethanol-water mixtures, we decided to develop a new iterative method allowing the simultaneous determination of  $D_1$  and  $D_2$  and also the uptake fractions at equilibrium of the components of the mixture ( $f$ ,  $1 - f$ ). The latter quantities are also important parameters. Indeed, since ethanol causes chemical degradation to resins, it is considered as a more aggressive solvent than water. So, it is interesting to know the percentage of the absorbed ethanol expressed by  $1 - f$ .

On the other hand, it was shown in the literature that the diffusion rate of methanol in poly(methyl methacrylate), in the presence of water in the polymeric matrix, depends on the water concentration.<sup>18</sup> This behavior was attributed to a plasticizing action of  $H_2O$ . However, the examination of an analogous effect in the case of the sorption of ethanol-water mixtures in methacrylate-based biomaterials requires of course the knowledge of  $D_1$  and  $D_2$  and  $f$  of the components of the mixture. This can be done by the proposed iterative method.

## THEORETICAL SECTION

### Model for Fickian sorption of mixtures of two miscible liquids in thin sheets of polymers

The one-dimensional Fick's second law describes the sorption kinetics of a liquid in a thin plane sheet:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where  $C$  is the concentration of the diffusing species,  $D$ , the diffusion coefficient and  $x$ , the direction of diffusion.

In the case where, during the diffusion process,  $D$  remains constant and the diffusion through the edges may be neglected, the integration of eq. (1) gives:<sup>19,20</sup>

$$\frac{M^t}{M^\infty} = 1 - \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp\left(\frac{-(2i+1)^2 \pi^2 D t}{L^2}\right) \quad (2)$$

where  $M^t$  is the accumulate mass of the diffusing species at time  $t$ ,  $M^\infty$ , the sorbed mass at equilibrium (after infinite time) and  $L$ , the thickness of sheet.

Let us consider now a thin sheet of a polymer placed in a mixture of two miscible liquids. Assuming that diffusion of the mixture proceeds by parallel Fickian process for each component we have:

$$M_1^t = M_1^\infty \times \left[ 1 - \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp\left(\frac{-(2i+1)^2 \pi^2 D_1 t}{L^2}\right) \right] \quad (3)$$

where  $M_1^t$  is the accumulate mass at time  $t$ ,  $M_1^\infty$  is the sorbed mass at equilibrium (after infinite time), and  $D_1$  is the self-diffusion coefficient of the diffusing liquid 1.

Similarly, for the sorption of the liquid 2 we have:

$$M_2^t = M_2^\infty \times \left[ 1 - \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp\left(\frac{-(2i+1)^2 \pi^2 D_2 t}{L^2}\right) \right] \quad (4)$$

where  $M_2^t$  and  $M_2^\infty$  are the accumulate masses at time  $t$  and equilibrium respectively, while  $D_2$  represents the self-diffusion coefficient of the diffusing liquid 2.

At time  $t$  the sorbed mass of the mixture,  $M_{\text{mixt}}^t$ , is equal to:

$$M_{\text{mixt}}^t = M_1^t + M_2^t = M_1^\infty \times \left[ 1 - \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp\left(\frac{-(2i+1)^2 \pi^2 D_1 t}{L^2}\right) \right] + M_2^\infty \times \left[ 1 - \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp\left(\frac{-(2i+1)^2 \pi^2 D_2 t}{L^2}\right) \right] \quad (5)$$

Dividing eq. (5) by  $M_1^\infty + M_2^\infty$  one obtains:

$$y_t = \frac{M_{\text{mixt}}^t}{M_{\text{mixt}}^\infty} = f \left[ 1 - \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp\left(\frac{-(2i+1)^2 \pi^2 D_1 t}{L^2}\right) \right] + (1-f) \left[ 1 - \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp\left(\frac{-(2i+1)^2 \pi^2 D_2 t}{L^2}\right) \right] \quad (6)$$

$$M_{\text{mixt}}^{\infty} = M_1^{\infty} + M_2^{\infty} \quad (7)$$

$$f = \frac{M_1^{\infty}}{M_1^{\infty} + M_2^{\infty}} \quad (8)$$

$$1-f = \frac{M_2^{\infty}}{M_1^{\infty} + M_2^{\infty}} \quad (9)$$

It is evident from eqs. (8) and (9) that  $f$  and  $(1-f)$  denote the uptake fraction at equilibrium of the liquids 1 and 2, respectively.

The first term of eq. (6) is related to the diffusion of liquid 1 in the polymer sheet, while the second term expresses the contribution of liquid 2 to the whole sorption process of the mixture. An example of the graphical representation of eq. (6) is given in Figure 1.

It results from eq. (6) that  $y_t$  (the normalized uptake of the mixture at time  $t$ , which is a quantity experimentally determinable) depends on the values of  $D_1$ ,  $D_2$ , and  $f$ .

The determination of the values of  $D_1$ ,  $D_2$ , and  $f$ , for a Fickian sorption process, could be obtained by fitting eq. (6) to experimental data. This fitting can be done by the proposed iterative method.

#### Iterative method for the determination of $D_1$ , $D_2$ and $f$ of a Fickian sorption of a binary liquid mixture in a polymer

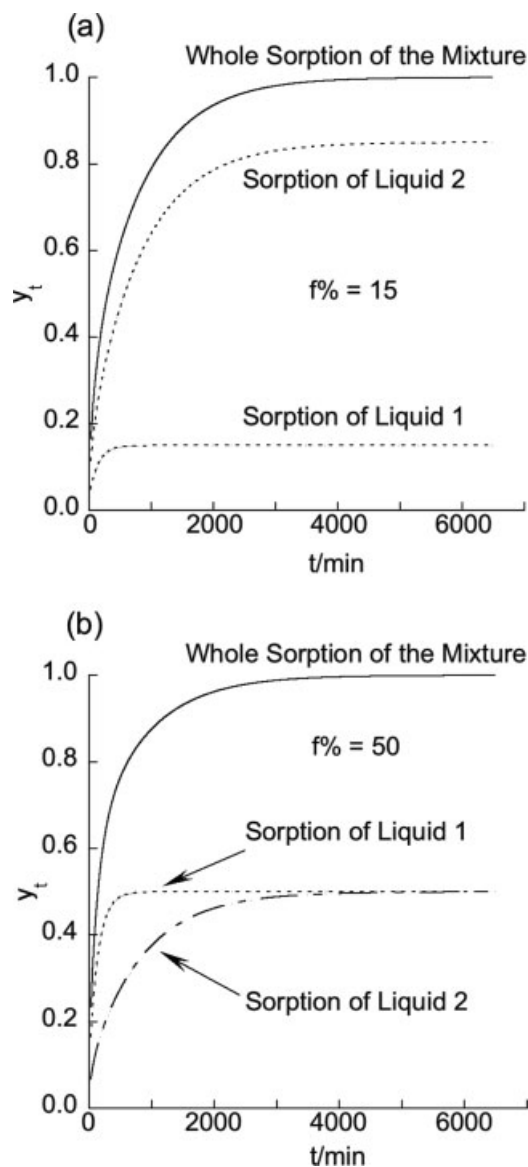
This method is based on the main principles of previously proposed procedures that were used for the determination of the thermodynamic dissociation constant of weak acids,<sup>21-23</sup> as well as for the determination of the rate constants of various chemical and electrochemical reactions.<sup>24-29</sup>

Let us consider an experimental plot  $y_t^{\text{exp}} = M_{\text{mixt}}^t / M_{\text{mixt}}^{\infty} = f(t)$  of a Fickian sorption containing  $N$  experimental points. To fit eq. (6) to this plot, we assume first that the value of  $f$  is known. In a second step, we consider that the values of  $D_1$  and  $D_2$ , *a priori* possible, are defined by a set  $S$  containing infinity elements (points). In each element of  $S$  corresponds a pair of values of  $D_1$  and  $D_2$ .

Now, using the known value of  $f$  and an element of  $S$ , chosen arbitrarily, it is possible to trace the theoretical curve  $y_t^{\text{calc}} = f(t)$ ,  $y_t^{\text{calc}}$  being the calculated values of  $M_{\text{mixt}}^t / M_{\text{mixt}}^{\infty}$  by means of eq. (6). Also, it is possible to calculate, by means of the experimental  $y_t^{\text{exp}}$  and  $t$  data, the sum of squared residuals  $SSR$ :

$$SSR = \sum_{i=1}^N (y_i^{\text{exp}} - y_i^{\text{calc}})^2 \quad (10)$$

where  $y_i^{\text{exp}}$  and  $y_i^{\text{calc}}$  are the experimental and calculated values of  $M_{\text{mixt}}^t / M_{\text{mixt}}^{\infty}$  of the  $i$ th experimental point, respectively.



**Figure 1** Graphical representation of eq. (6) produced with  $D_1 = 1.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ,  $D_2 = 2 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ . (a)  $f = 0.15$  and (b)  $f = 0.50$ .

In an ideal case, where the experimental data are free from any errors,  $SSR$  will tend to zero to the extent where the chosen values of  $D_1$  and  $D_2$  also approach the exact values of the diffusion coefficients. Hence, the minimum value of  $SSR$  that could be obtained, by means of the available experimental data, evidently corresponds to the best approximation to the exact values of  $D_1$  and  $D_2$ .

However, among the infinity of elements of  $S$ , there is of course one corresponding to the true values of  $D_1$  and  $D_2$ . In an attempt to determine the values of the diffusion coefficients corresponding to this element, we assume that we have an initial estimation of  $D_2$  equal to  ${}^{\circ}D_2$ . Starting from this value and seeking the  $D_1$  value within an interval of

*a priori* possible values of this parameter, it is possible to trace  $n_1$  curves  $y_i^{\text{calc}} = f(t)$ ,  $n_1$  being the number of  $D_1$  values taken for these calculations. For each of these curves, the calculation of the sum of squared residuals ( ${}^1SSR_1$ ) permits to trace the curve  ${}^1SSR_1 = f(D_1)$ . This curve is expected to present a pronounced minimum ( ${}^1SSR_1^{\text{min}}$ ) at a value of  $D_1$  equal to  ${}^1D_1^{\text{min}}$ , which can be considered as the first approximation to the exact  $D_1$  value.

In a second step, using the value  ${}^1D_1^{\text{min}}$  as an initial estimation of  $D_1$  and seeking the  $D_2$  value within an interval of *a priori* possible values of this parameter, it is possible to trace  $n_2$  curves  $y_i^{\text{calc}} = f(t)$ ,  $n_2$  being the number of  $D_2$  values taken for these calculations. For each of these curves the calculation of  ${}^1SSR_2$  (the sum of squared residuals) permits to trace the curve  ${}^1SSR_2 = f(D_2)$ . This curve is expected to present a pronounced minimum ( ${}^1SSR_2^{\text{min}}$ ) at a value of  $D_2$  equal to  ${}^1D_2^{\text{min}}$ , which can be considered as the first approximation to the exact  $D_2$  value. These operations, namely the determination of  ${}^1D_1^{\text{min}}$ ,  ${}^1D_2^{\text{min}}$ ,  ${}^1SSR_1^{\text{min}}$ , and  ${}^1SSR_2^{\text{min}}$  consist the 1st cycle of approximations.

In the 2nd cycle, using the value  ${}^1D_2^{\text{min}}$  as an estimation of  $D_2$ , one obtains the values  ${}^2D_1^{\text{min}}$ ,  ${}^2D_2^{\text{min}}$ ,  ${}^2SSR_1^{\text{min}}$ , and  ${}^2SSR_2^{\text{min}}$ .

These operations can be repeated in  $n$  cycles of approximations to obtain the values  ${}^nD_1^{\text{min}}$ ,  ${}^nD_2^{\text{min}}$ ,  ${}^nSSR_1^{\text{min}}$ , and  ${}^nSSR_2^{\text{min}}$ . If the sequences  $\{{}^nD_1^{\text{min}}\}$  and  $\{{}^nD_2^{\text{min}}\}$  converge to limiting values we have:

$$\lim({}^nD_1^{\text{min}}) = \lim_f D_1^{\text{min}} \quad \text{and} \quad \lim({}^nD_2^{\text{min}}) = \lim_f D_2^{\text{min}} \quad (11)$$

At the true value of  $f$ , the above limiting values express the best approximation to the exact value of  $D_1$  and  $D_2$ . It is noted that as  $n$  increases,  ${}^nD_1^{\text{min}}$  and  ${}^nD_2^{\text{min}}$  are expected to be better and better estimations of the desired diffusion coefficients. One stops the iteration when  ${}^nD_1^{\text{min}}$  and  ${}^nD_2^{\text{min}}$  remain constant between two successive cycles. In that moment we have:

$${}^nSSR_1^{\text{min}} = {}^nSSR_2^{\text{min}} = \lim_f SSR^{\text{min}} \quad (12)$$

and therefore

$${}^nR = \frac{{}^nSSR_2^{\text{min}}}{{}^nSSR_1^{\text{min}}} = 1 \quad (13)$$

However, in the case where  $f$  is not *a priori* known, we can repeat all the above calculations using  $n_3$  values of  $f$ , *a priori* possible, evenly spaced in an interval ( $f_1, f_{\text{stop}}$ ) so that

$$n_3 = \frac{f_{\text{stop}} - f_1}{\delta f} \quad (14)$$

where  $\delta f$  is the difference between two successive values of  $f$  taken for these calculations (increment step).

At each value of  $f$ , the quantities  $\lim_f D_1^{\text{min}}$ ,  $\lim_f D_2^{\text{min}}$ , and  $\lim_f SSR^{\text{min}}$  are registered. The plot of  $\lim_f SSR^{\text{min}}$  as a function of  $f$  is expected to present a pronounced minimum at a value of  $f$  equal to  $f_{\text{min}}$ , which can be considered as the best approximation to the exact value of  $f$ . Also, the corresponding  $\lim_{f_{\text{min}}} D_1^{\text{min}}$  and  $\lim_{f_{\text{min}}} D_2^{\text{min}}$  values are the best approximations to the exact values of the sought diffusion coefficients  $D_1$  and  $D_2$ .

Thanks to simplicity, in the next paragraphs of this paper, the quantities  $\lim_f D_1^{\text{min}}$ ,  $\lim_f D_2^{\text{min}}$ , and  $\lim_f SSR^{\text{min}}$  will be abbreviated to  $\lim D_1$ ,  $\lim D_2$ , and  $\lim SSR$ .

It is worth noting that the proposed iterative method reached identical results even when, instead of the sum of squared residuals  $SSR$ , the Chi-Square function (eq. (15))<sup>30</sup> was minimized.

$$\chi^2 = \sum_{i=1}^N \frac{(y_i^{\text{exp}} - y_i^{\text{calc}})^2}{y_i^{\text{calc}}} \quad (15)$$

However, we observed in all cases of this paper that when the parameter  $SSR$  instead of  $\chi^2$  was minimized, the overall procedure was faster.

Finally, it should be noted that the test of the reliability of the proposed procedure requires of course reliable experimental data with known values of  $D_1$ ,  $D_2$ , and  $f$ . But the absence in the literature of such data forced us to test and apply this method to simulated data corresponding to various values of diffusion coefficients.

### Application of the iterative method using simulated data

Simulated  $y_i^{\text{calc}}$  ( $= M_{\text{mixt}}^t / M_{\text{mixt}}^\infty$ ) values as a function of  $t$  were derived by means of eq. (6). Calculations throughout in this paper were realized by means of appropriate programs written in C++ programming language. In all these calculations  $L$  was taken equal to 0.1 cm. The sums of the infinite series of eq. (6) were approximated by partial sums including  $l$  terms so that:

$$\sum_{i=0}^l \frac{1}{(2i+1)^2} \exp\left(\frac{-(2i+1)^2 \pi^2 D_j t}{L^2}\right) - \sum_{i=0}^{l-1} \frac{1}{(2i+1)^2} \exp\left(\frac{-(2i+1)^2 \pi^2 D_j t}{L^2}\right) < 10^{-16} \quad (16)$$

where  $D_j$  ( $j = 1$  or  $2$ ) is the diffusion coefficient of liquid 1 or 2.

It should be noted that  $l$  increases as the parameter  $D_j t / L^2$  decreases. Thus, summation requires 1334 terms when  $D_j t / L^2$  is equal to  $3 \times 10^{-7}$ , while seven terms are sufficient to fulfill the condition<sup>(16)</sup> for a value of  $D_j t / L^2$  equal to  $3.6 \times 10^{-2}$ .

**TABLE I**  
**Ideal and Monte Carlo (M-C) Simulated Data of the Sorption of a Mixture in a Thin Polymer Disc**  
 ( $L = 1.0 \text{ mm}$ ,  $D_1 = 1.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ,  $D_2 = 2.00 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  and  $f = 0.15$ )

$t/\text{min}$	$y_t = M_{\text{mixt}}^t/M_{\text{mixt}}^\infty$		$t/\text{min}$	$y_t = M_{\text{mixt}}^t/M_{\text{mixt}}^\infty$	
	Ideal <sup>a</sup>	M-C <sup>b</sup>		Ideal <sup>a</sup>	M-C <sup>b</sup>
30	0.1648	0.1613	750	0.7160	0.7133
60	0.2331	0.2300	780	0.7260	0.7244
90	0.2852	0.2839	810	0.7356	0.7373
120	0.3284	0.3293	840	0.7449	0.7369
150	0.3655	0.3577	870	0.7539	0.7565
180	0.3981	0.4006	900	0.7625	0.7561
210	0.4272	0.4247	930	0.7708	0.7632
240	0.4534	0.4533	960	0.7788	0.7812
270	0.4774	0.4786	1020	0.7941	0.7995
300	0.4995	0.4984	1620	0.8989	0.8956
330	0.5200	0.5144	2220	0.9503	0.9552
360	0.5391	0.5356	2820	0.9756	0.9667
390	0.5571	0.5586	3420	0.9880	0.9870
420	0.5740	0.5670	4020	0.9941	0.9956
450	0.5901	0.5884	4620	0.9971	0.9979
480	0.6053	0.6024	5220	0.9986	0.9912
510	0.6198	0.6168	5820	0.9993	0.9940
540	0.6337	0.6292	6420	0.9997	1.0007
570	0.6469	0.6412	7020	0.9998	0.9992
600	0.6596	0.6571	7620	0.9999 <sub>2</sub>	1.0026
630	0.6718	0.6705	8220	0.9999 <sub>6</sub>	0.9981
660	0.6835	0.6868	8820	0.9999 <sub>8</sub>	0.9943
690	0.6947	0.6930	9420	0.9999 <sub>9</sub>	0.9960
720	0.7056	0.6965			

<sup>a</sup> Values that exact fit eq. (6).

<sup>b</sup> Mean values of six normally distributed deviates generated from the ideal data with  $s/M_{\text{mixt}}^\infty = 0.005$ .

First the sorption of a liquid mixture in a thin polymer sheet with  $D_1 = 1.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ,  $D_2 = 2.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ , and  $f = 0.15$  was considered. The results obtained are reported in Table I. It is now examined whether it is possible using these data and by means of the proposed iterative method to extract the above values of  $D_1$ ,  $D_2$ , and  $f$ . To investigate this, we applied the proposed procedure assuming that  $f$  lies in the interval of values (0.1, 0.2).

Starting from  $f = 0.1$ , we assumed first that  ${}^0D_2 = 1.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ .

At  $f = 0.1$ , after four cycles of approximations, the proposed method converges to the following limited values:

$$\begin{aligned} \lim D_1 &= 1.879 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}, \lim D_2 \\ &= 2.134 \times 10^{-12} \text{ m}^2 \text{ s}^{-1} \text{ and } \lim \text{SSR} = 4.262 \times 10^{-4} \end{aligned}$$

Identical limited values are obtained if one starts from any very different initial estimation of  $D_2$ , for example equal to  ${}^0D_2 = 1.0 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ .

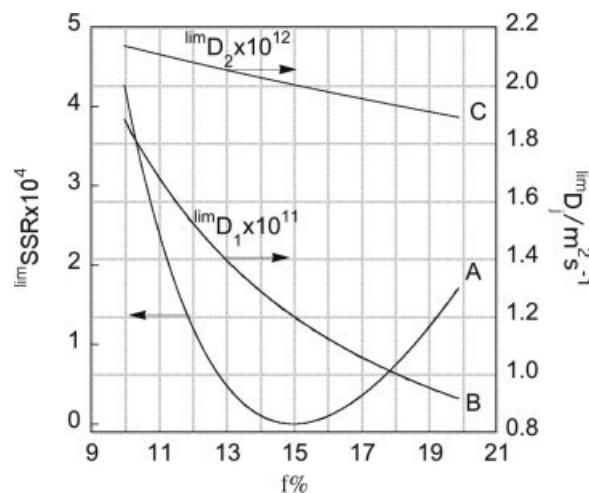
It should be noted that, in all cycles of approximations, the graphs  ${}^n\text{SSR}_j = f(D_j)$  ( $j = 1$  or  $2$ ) presented a pronounced minimum allowing the determination of  ${}^nD_1^{\text{min}}$ ,  ${}^nD_2^{\text{min}}$ ,  ${}^n\text{SSR}_1^{\text{min}}$ , and  ${}^n\text{SSR}_2^{\text{min}}$ .

All the above calculations realized at  $f = 0.1$  were repeated using 100 values of  $f\%$  ( $= 100f$ ), evenly spaced in the interval (10%, 20%). At each value of  $f\%$ , the quantities  $\lim D_1$ ,  $\lim D_2$ , and  $\lim \text{SSR}$  were registered. The variation of these quantities with  $f\%$  is presented graphically in Figure 2. It can be seen that the plot of  $\lim \text{SSR}$  against  $f\%$  presents a pronounced minimum at  $f\% = 15$  exactly. The corresponding values to these minimum values of  $\lim D_1$  and  $\lim D_2$  were equal to  $1.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  and  $2.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  (see Fig. 2).

The above results show that the proposed iterative method, applied to ideal simulated data, perfectly extracts the sought parameters  $D_1$ ,  $D_2$ , and  $f$ .

The iterative method was also tested to various simulated data produced with values of  $D_j$  ( $j = 1$  or  $2$ ) that lay in the range  $(10^{-11} - 10^{-13}) \text{ m}^2 \text{ s}^{-1}$ . The results were excellent when the ratio  $D_1/D_2$  was greater than 3. For smaller values of this ratio, the proposed iterative method converges to the desired values of the sought parameters only when the trial estimations of  $f$  are taken from a very narrow interval of values, where the true value of  $f$  is included.

However, of more experimental interest is the question of how well the proposed iterative technique is able to cope with data containing random extraneous contributions, such as annoying experimental "noise". To investigate this, a Monte Carlo technique<sup>31</sup> was used, which was detailed previously<sup>27</sup> and there is no need to be repeated here. The main idea of this procedure is based on the fact that often random experimental errors closely follow a Gaussian (or normal) statistical distribution. Thus, at each point  $(y_i^{\text{calc}}, t_i)$  of the theoretical curve  $y_i^{\text{calc}} = M_{\text{mixt}}^t/M_{\text{mixt}}^\infty = f(t)$ , a number  $N_1$  of normally distributed random variables  $y_{i,j}$  ( $j = 1$  to  $N_1$ ) with mean  $y_i^{\text{calc}}$  and standard deviation  $S_i$  were produced.



**Figure 2** Variation of  $\lim \text{SSR}$  and  $\lim D_j$  ( $j = 1$  or  $2$ ) with  $f\%$  obtained by means of the ideal simulated data of Table I.

At the experimental level, this implies that at each value of  $t$ , the fractional water uptake  $M_{\text{mixt}}^t/M_{\text{mixt}}^\infty$  was measured  $N_1$  times (with a precision equal to  $S_i$ ). A calculus based on the method of propagation of errors<sup>32</sup> showed that:

$$S_i = \sqrt{2 [1 + (y_i^{\text{calc}})^2]} \frac{s}{M_{\text{mixt}}^\infty} \quad (17)$$

where  $s$  is the error (standard deviation) of the determination of the specimen weight.

Using this technique, as an example, the sorption of a liquid mixture in a thin polymer sheet ( $L = 0.1$  cm) with  $D_1 = 1.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ,  $D_2 = 2.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ , and  $f = 0.15$  was again treated. In this treatment the value of  $s/M_{\text{mixt}}^\infty$  was taken equal to 0.005. At the experimental level, this value means that for  $M_{\text{mixt}}^\infty$  equal to 0.02 g, the weight of the specimens was determined with a very significant error  $s$  (0.0001 g), namely 10 times greater than the accuracy of a balance of five decimal places. At each time  $t_i$ , six values  $y_{i,j}$  were created and the results were averaged. The mean values  $\bar{y}_{i,j}$  are summarized in Table I. Evidently these values would coincide with the corresponding  $y_i^{\text{calc}}$  values only in the case where the number  $N_1$  of the produced random variables  $y_{i,j}$  tended to infinity.

For these Monte Carlo Data and by means of 100 values of  $f\%$ , evenly spaced in the interval (10%, 20%), the quantities  $\lim D_1$ ,  $\lim D_2$ , and  $\lim SSR$  were calculated. As previously, it was found that the plot of  $\lim SSR$  against  $f\%$  presented a pronounced minimum at  $f\% = 14.6 \pm 0.01$ . The corresponding values of  $\lim D_1$  and  $\lim D_2$  were equal to  $(1.210 \pm 0.001) 10^{-11} \text{ m}^2 \text{ s}^{-1}$  and  $(1.992 \pm 0.001) 10^{-12} \text{ m}^2 \text{ s}^{-1}$ . The uncertainties of the above values were taken equal to the variation step of  $f\%$ ,  $D_1$  and  $D_2$  in the plots  $\lim SSR$  versus  $f\%$  and  ${}^n SSR_j$  versus  $D_j$  ( $j = 1$  or  $2$ ). It is worth noting that the above results were independent of the initial estimation  ${}^o D_2$  used in these calculations. For example, using as  ${}^o D_2$ , the values  $1.0 \times 10^{-13}$  or  $1.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  the proposed procedure reached identical results.

The values of  $D_1$ ,  $D_2$  and  $f$ , equal to  $1.21 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ,  $1.992 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  and 0.146, respectively, obtained by means of the iterative method, are in good agreement with their true magnitudes ( $1.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ,  $2.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  and 0.15). Thus, the proposed iterative method is able to extract the sought parameters with small error, even when the uptake of the mixture was determined with significant error (10 times greater than the accuracy of a balance of five decimal places).

The very positive tests concerning the applicability of the iterative method using simulated data encouraged us to apply this method on experimental data concerning the diffusion of an EtOH–H<sub>2</sub>O mixture

(75 vol % in EtOH) at 37°C in thin discs of poly-TEGDMA.

## EXPERIMENTAL

### Materials

The monomer used was TEGDMA (Aldrich Chemicals, Lot No. 17529EA-503); it was used as received without further purification. To make the samples capable for light curing, 2 mol % of camphorquinone (CQ) (Aldrich Chemicals, Lot no. S12442-053) used as photosensitizer, and 2 mol % of *N,N*-dimethylaminoethyl methacrylate (DMAEMA) (Riedel-de Haën, Lot no. 20,770), used as reducing agent, were added to each sample. Bi-distilled water was used throughout. Absolute ethanol (Carlo Erba) was used without further purification.

### Preparation of specimens

Sorption tests were determined according to the method described in ADA specification no. 27 (ISO 4049) based filling materials. Specimen discs were prepared by filling a Teflon mold (15 mm in diameter and 1 mm in thickness) with the unpolymerized material, taking care to minimize entrapped air. The upper and lower surface of the mold was overlaid with glass slides covered with a polyester Mylar film. The completed assembly was held together with spring clips and irradiated using a XL 3000 dental photocuring unit (3M Company, St. Paul, MN, USA). This source consisted of a 75 W tungsten halogen lamp, which emits radiation between 420 and 500 nm and has the maximum peak at 470 nm, and also absorbs CQ ( $\lambda_{\text{max}} = 470$  nm,  $\epsilon = 3.8 \times 10^4 \text{ cm}^2/\text{mol}$ ). Due to the large size of our specimen, this unit was used without the light guide, at a distance from the sample approximately 0.8 cm. Two specimen discs were prepared, which were irradiated on each side for 200 s. Then, the mold was dismantled and the discs were carefully removed by flexing the Teflon mold. The thickness of the samples was measured accurately at five points using a micrometer (0–25 mm, Moore and Wright, Sheffield, UK).

### Sorption of water, ethanol, or ethanol–water mixture (75 vol % in EtOH)

The specimens were placed in a desiccator and transferred in a preconditioning oven at 37°C. After 24 h they were removed, stored in the desiccator for 1 h, and weighted to an accuracy of  $\pm 0.00001$  g using a Mettler H54AR balance. This cycle was repeated until a constant mass ( $m_i$ ) was obtained. Then, the discs of TEGDMA homopolymer were immersed in the studied solvent (water, ethanol, or mixture of 75 vol % ethanol–water) at 37°C. At fixed

time intervals they were removed, blotted dry to remove excess liquid, weighted, and returned to the studied solvent. The time intervals were more during the first days and as the uptake slowed more extended. The uptake of the liquid was recorded until a constant mass of the specimen was obtained. During the sorption, the solvent also leached the unreacted monomer out. The samples were then transferred to a drying oven maintained at 37°C and a process similar to that described above was repeated during desorption. Then, the samples were placed back into the studied solvent at 37°C and a second sorption process was recorded using approximately the same time intervals.

#### Determination of the self-diffusion coefficient of H<sub>2</sub>O and EtOH as well as their uptake fraction at equilibrium by means of the sorption of EtOH-H<sub>2</sub>O mixture in poly-TEGDMA

Mean values of  $M^t/M^\infty$  as a function of the time  $t$  of two independent experiments are reported in Table II. The data of this table concern the diffusion of EtOH-H<sub>2</sub>O mixture (75 vol % in EtOH) in poly (TEGDMA) discs during the second sorption process. The thickness of the used specimens was, respectively, equal to 0.0974 cm and 0.0955 cm, while their diameters were 1.380 cm and 1.345 cm.

On the basis of these experimental results we examined whether it is possible by means of the proposed approach to extract the experimental values of  $D_1$ ,  $D_2$ , and  $f$ . Nevertheless, this method is valid when it is applied on systems where the sorption is Fickian, as well as: (a) there are no interactions between the two penetrants during the sorption process and (b) the system is not concentration-dependent, which means that the diffusion coefficients  $D_1$  and  $D_2$  remain constant.

TABLE II  
Experimental Data of the Sorption of EtOH-H<sub>2</sub>O Mixture (75 vol % in Ethanol) in Polymer Sheets Prepared from TEGDMA

$t/\text{min}$	$y_t = M^t/M^\infty$	$t/\text{min}$	$y_t = M^t/M^\infty$
30	0.1380	720	0.5424
60	0.1866	780	0.5663
90	0.2266	1440	0.7157
120	0.2584	1620	0.7427
150	0.2899	1800	0.7687
180	0.2998	3060	0.9245
210	0.3162	4665	0.9712
240	0.3395	7320	0.9857
300	0.3736	8820	0.9893
360	0.4033	10200	0.9902
420	0.4347	11700	0.9913
480	0.4622	13200	0.9931
600	0.5050	17520	0.9951

$T = 37^\circ\text{C}$ ,  $L = 0.0965$  cm,  $M_{\text{mixt}}^\infty = 0.01953$  g.

However, it is legitimate to consider that the above conditions are fulfilled when the water and ethanol uptake at equilibrium are relatively low. Obviously, experimental estimations of these quantities are the absolute solubility values of EtOH and H<sub>2</sub>O when poly(TEGDMA) sheets are placed in pure ethanol and water. For this reason, we determined experimentally the water and ethanol uptake at equilibrium in poly(TEGDMA) at 37°C. In each experiment, the corresponding solvent uptake at equilibrium, expressed as a percentage of the mass of the dry,  $m_{\text{dry}}$ , TEGDMA specimen was calculated according to the following equation:

$$s\% = \left( \frac{m_\infty - m_{\text{dry}}}{m_{\text{dry}}} \right) 100 = \left( \frac{M^\infty}{m_{\text{dry}}} \right) 100 \quad (18)$$

where  $m_\infty$  is the mass of the polymer specimen at equilibrium.

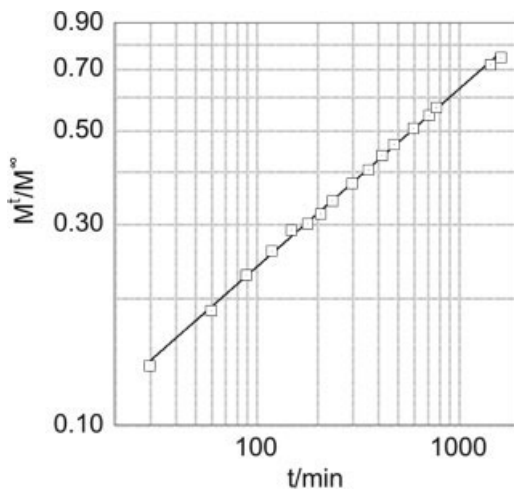
It was found that the mean values of  $s\%$  for H<sub>2</sub>O and EtOH were respectively, equal to  $6.30 \pm 0.07$  and  $8.3 \pm 0.3$ . These values can be considered as sufficiently low in comparison with the corresponding values of other methacrylate-based polymers reported in literature. Indeed, the value of  $s\%$  of H<sub>2</sub>O in poly(2-hydroxyethyl methacrylate), at 37°C, was found equal to 59.27%.<sup>33</sup>

The diverse responses of polymers to the sorption of a penetrant are generally classified in three categories<sup>34</sup>: Case I or Fickian diffusion. In this case the driving force is the concentration gradient and occurs when the rate of the penetrant diffusion,  $R_{\text{dif}}$ , is much slower than the relaxation rate,  $R_{\text{relax}}$ , of the polymer chains ( $R_{\text{dif}} \ll R_{\text{relax}}$ ).<sup>35,36</sup> For Fickian diffusion the conformational changes in the polymer structure appear to take place instantaneously.<sup>37</sup> In Case II diffusion the relaxation rate is slow in comparison with the rate of penetrant, so the relaxation (or mobility) of the polymer chains is the controlling force for diffusion.<sup>35</sup> The Case III or anomalous diffusion occurs in the transition region between Case I and II, when the rates of penetrant diffusion and polymer relaxation are comparable.

It was argued in the literature that the various types of diffusion can be distinguished by the shape of the plots  $M^t/M^\infty = f(t)$ .<sup>38</sup> Indeed, it was found in many systems<sup>33,39-41</sup> that the initial portion of these plots can be fitted to the following empirical equation:

$$\frac{M^t}{M^\infty} = kt^n \quad (19)$$

where  $k$  is a constant that depends on the structural characteristic of the polymer network, while the exponent  $n$  is characteristic of the mode of the penetrant transport.<sup>33</sup> This equation may be applied to thin films where diffusion through edges is insig-



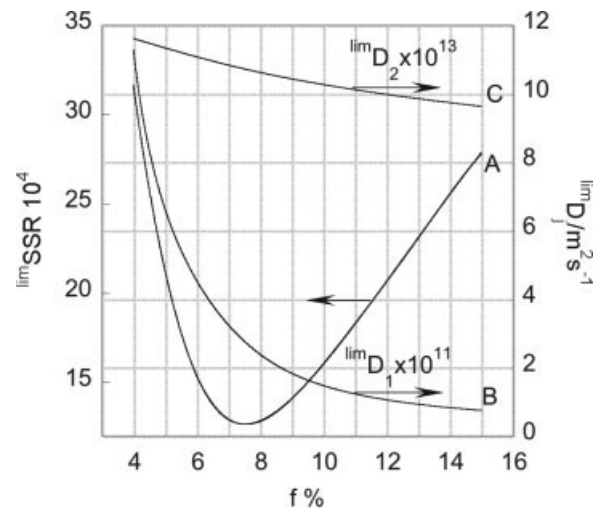
**Figure 3** Variation of  $\log(M^t/M^\infty)$  with  $\log t$  of the experimental data of Table II ( $M^t/M^\infty \leq 0.7427$ ).

nificant and the values of  $n$  should indicate the dominant mechanism of the penetrant uptake process. The mechanism is Fickian (Case I) for values of  $n$  equal or less than 0.5.<sup>33,40</sup> A value of  $n = 1.0$  indicates Case II diffusion, while if  $n$  is between 0.5 and 1.0, the diffusion is termed as anomalous diffusion (Case III diffusion). For  $n > 1.0$ , the transport mechanism is known as Super Case II transport.<sup>38</sup>

It results from Figure 3 that the experimental data reported in Table II can be perfectly fitted, by least squares, to eq. (19) for values up to  $M^t/M^\infty \approx 0.75$  ( $R^2 = 0.9987$ ). The obtained values of  $k$  and  $n$  were equal to 0.0336 and 0.422, respectively. The value  $n = 0.422$  suggests that the sorption of EtOH–H<sub>2</sub>O mixture (75 vol % in EtOH) in poly(TEGDMA) discs during the second sorption process follows Fickian mechanism, further evidencing the adequacy of the selected experimental system.

The above results encouraged us to apply the proposed iterative method to the data of Table II. Using these experimental data and by means of 1100 values of  $f^0$ , evenly spaced in the interval (4%, 15%), the quantities  $\lim D_1$ ,  $\lim D_2$ , and  $\lim SSR$  were calculated. The variation of these quantities with  $f^0$  is presented graphically in Figure 4. It results from Figure 4 that the variation of  $\lim SSR$  with  $f$  presents a pronounced minimum. The corresponding values to these minimum values of  $f^0$ ,  $\lim D_1$  and  $\lim D_2$  were equal to  $(7.52 \pm 0.01)$ ,  $(2.750 \pm 0.001) 10^{-11} \text{ m}^2 \text{ s}^{-1}$  and  $(10.715 \pm 0.001) 10^{-13} \text{ m}^2 \text{ s}^{-1}$ , respectively. The uncertainties of these values were taken equal to the variation step of  $f^0$ ,  $D_1$ , and  $D_2$  in the plots  $\lim SSR$  versus  $f^0$  and  ${}^n SSR_j$  versus  $D_j$  ( $j = 1$  or  $2$ ).

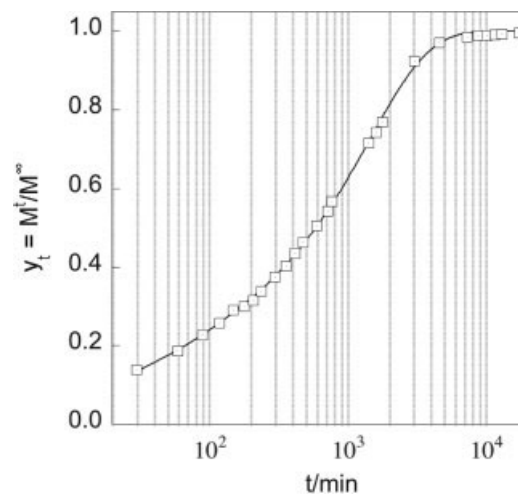
As previously, the obtained results were also independent of the initial estimation  ${}^0 D_2$  used in these calculations. For example, using as  ${}^0 D_2$  the values  $1.0 \times 10^{-13}$  or  $1.0 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$  the proposed procedure reached identical results.



**Figure 4** Variation of  $\lim SSR$  and  $\lim D_j$  ( $j = 1$  or  $2$ ) with  $f$  obtained by means of the experimental data of Table II.

In the attempt to test the exactness of these values, by means of eq. (6) the plot of  $M^t/M^\infty$  against  $t$  was traced and compared with the corresponding experimental data (Fig. 5). The agreement is excellent. This agreement provides further experimental evidence that the sorption of the studied mixture in polymers discs of TEGDMA proceeds via a parallel Fickian process without any interactions between the two penetrants. Also, the implicit assumption that the diffusion coefficients  $D_1$  and  $D_2$  are constant seems to be valid.

It is worth noting that Grinsted et al.<sup>18</sup> studied the diffusion of methanol in poly(methyl methacrylate) (PMMA) as a function of water concentration by NMR imaging. They found that the diffusion rate of methanol increased with increasing water concentra-



**Figure 5** Variation of  $M^t/M^\infty$  with  $\log t$ . ( $\square$ ) Experimental data of Table II, (—) Graphical representation of eq. (6) produced with  $D_1 = 2.75 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ,  $D_2 = 1.072 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ , and  $f = 0.0752$ .



tion. In addition, the diffusion of methanol changed from Case II to Fickian (Case I) when the water content was increased. This change in methanol diffusion behavior was explained by the presence of water that acted as plasticizer. It should be noted that water, being a good plasticizer, penetrates into the polymer matrix establishing attractive forces with the polymer chain segments. These attractive forces reduce the cohesive forces between the polymer chains and increase the segmental mobility.<sup>39</sup> Accepting an analogous behavior for the experimental system studied here, we can consider that the sorption of ethanol–water mixture in TEGDMA indeed follows a Fickian mechanism. These results reveal also the adequacy of the selected experimental system in the test of the proposed iterative method.

On the other hand, Volkov et al.<sup>42</sup> studied at microscopic level the self-diffusion of water–ethanol mixtures in polyacrylic acid (PAA) membranes by PFG (pulsed-field gradient)-NMR spectroscopy. They proved that there are two types of channels where the transfer of the molecules takes place: an ionogenic hydrophilic channel which is selective for water and a hydrophobic channel for the diffusion of ethanol molecules. Accepting an analogous behavior for the sorption of ethanol–water mixtures in TEGDMA we can consider that: (a) there is not possibility of any interaction between the diffusing molecules of ethanol and water and (b) the only particles which penetrate into the polymeric matrix are the ethanol and water molecules excluding the penetration of any associate, which is probably formed between the molecules of ethanol and water; thus, for the present system, the additive rule expressed by eq. (7) seems to be valid.

It was argued in literature that the diffusion coefficients of alcohols in PMMA matrix decrease with increasing molecular size of the penetrants.<sup>43</sup> Also, it was found in the literature that the diffusion coefficient of ethanol in sulfonated polyethylene, measured by the pulsed-gradient spin-echo NMR method, is much smaller than that of water.<sup>44</sup> This conclusion is in agreement with our preliminary experiments concerning the diffusion rate of pure water and ethanol in poly(TEGDMA). Indeed, from the linear initial portion of the sorption curves ( $M^t/M^\infty$  vs.  $t^{1/2}$ ), using the so-called Stephan's approximation,<sup>4</sup> our preliminary results showed that the diffusion coefficient of water is about 8.5 times greater than that of the pure ethanol. Taking into account these preliminary results as well as the literature data, we attribute to water the obtained values of  $D_1$  and  $f\%$ , respectively, equal to  $2.75 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$  and 7.52%, while the values  $D_2$  and  $(1-f)\%$ , respectively, equal to  $10.72 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$  and 92.48%, are attributed to ethanol. Further investigations concerning the elucidation of the sorption mechanism of water and etha-

nol in methacrylate-based biomaterials are in progress in the Laboratory of Organic Chemical Technology of Aristotle University of Thessaloniki.

## CONCLUSIONS

The present investigation is concerned with the development of a new iterative method permitting, for a Fickian sorption of a liquid mixture of two liquids in thin polymer sheets, the simultaneous determination of the self-diffusion coefficients, and the uptake fraction at equilibrium of the components of the mixture. The proposed approach is based on a new equation describing a parallel Fickian sorption of the components of the mixture into thin polymer sheets.

The reliability of the proposed procedure was tested with ideal (free from any extraneous "noise") and Monte Carlo simulated data.

It was found that the proposed iterative method, applied to ideal simulated data that correspond to various values of  $D_1$ ,  $D_2$ , and  $f$ , perfectly extracts the desired parameters. On the other hand, the application of the iterative method to Monte Carlo simulated data revealed that this method is fairly applicable even when the simulated sorption data are considerably obscured by "noise".

Finally, the proposed iterative method was successfully applied to the experimental data concerning the sorption kinetics of EtOH–H<sub>2</sub>O mixture (75 vol % in ethanol) in thin polyTEGDMA discs. The obtained values are equal to  $D_{\text{water}} = 2.75 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ,  $D_{\text{EtOH}} = 10.72 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ , and  $f\% = 7.52$ .

Despite the fact that the proposed iterative method requires laborious calculations, it can be easily applied thanks to the opportunities offered today by high-speed personal computers. Thus, using a common computer the extraction of the desired parameters ( $D_1$ ,  $D_2$ ,  $f$ ) from a sorption curve requires only a few minutes.

Finally, it should be noted that the present procedure was designed to be applied to the sorption of ethanol–water mixtures in methacrylate-based biomaterials. However, there is no reason why the proposed analysis could not be applied to the Fickian sorption of any binary mixtures in any polymer matrix.

## References

1. Sideridou, I.; Tserki, V.; Papanastasiou, G. *Biomaterials* 2002, 23, 1819.
2. Achilias, D. S.; Sideridou, I. *J Macromol Sci A Pure Appl Chem* 2002, 39, 1435.
3. Sideridou, I.; Tserki, V.; Papanastasiou, G. *Biomaterials* 2003, 24, 655.
4. Sideridou, I.; Achilias, D. S.; Spyroudi, C.; Karabela, M. *Biomaterials* 2004, 25, 367.

5. Sideridou, I.; Achilias, D. S.; Kyricou, E. *Biomaterials* 2004, 25, 3087.
6. Sideridou, I. D.; Achilias, D. S. *J Biomed Mater Res B* 2005, 74, 617.
7. Achilias, D. S.; Sideridou, I. D. *Macromolecules* 2004, 37, 4254.
8. Sideridou, I. D.; Achilias, D. S.; Karava, O. *Macromolecules* 2006, 39, 2072.
9. Sideridou, I. D.; Karabela, M. M.; Bikiaris, D. N. *Dent Mater*, to appear.
10. Sideridou, I. D.; Achilias, D. S.; Karabela, M. M. *J Biomed Mater Res Part B: Appl Biomater* 2007, 81B, 207.
11. Craig, R. G. *Restorative Dental Materials*; Mosby: St Louis, MO, 1997.
12. Linden, L. A. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRS Press: New York, 1996; p 1839.
13. Ferracane, J. L. *Dent Mater* 2005, 22, 211.
14. Wu, W.; McKinney, J. E. *J Dent Res* 1982, 61, 1180.
15. McKinney, J. E.; Wu, W. *J Dent Res* 1985, 64, 1326.
16. Lee, S.-Y.; Greener, E. H.; Mueller, H. J.; Chiu, C.-H. *J Dent Res* 1994, 22, 352.
17. Lee, S.-Y.; Greener, E. H.; Mueller, H. J. *J Dent Res* 1995, 23, 27.
18. Grinsted, R. A.; Clark, L.; Koenig, J. L. *Macromolecules* 1992, 25, 1235.
19. Kovacs, A. *J Chim Phys* 1948, 45, 258.
20. Crang, J. *The Mathematics of Diffusion*; Clarendon Press: Oxford, 1975.
21. Papanastasiou, G.; Ziogas, I.; Kokkinidis, G. *Anal Chim Acta* 1993, 277, 119.
22. Papanastasiou, G.; Ziogas, I. *Talanta* 1995, 42, 827.
23. Papanastasiou, G.; Kokkinidis, G. *Collect Czech Chem Commun* 2003, 68, 1345.
24. Cayzergues, P.; Georgoulis, C.; Papanastasiou, G. *J Chim Phys* 1977, 74, 1112.
25. Cayzergues, P.; Georgoulis, C.; Papanastasiou, G. *C. R. Acad Sci Paris Ser C* 1977, 285, 163.
26. Papanastasiou, G.; Papoutsis, A.; Tsirtou, M.; Ziogas, I. *J Solution Chem* 1996, 25, 203.
27. Papanastasiou, G.; Kokkinidis, G.; Papadopoulos, N. *J Electroanal Chem* 1991, 305, 19.
28. Kokkinidis, G.; Papanastasiou, G.; Hasiotis, C.; Papadopoulos, N. *J Electroanal Chem* 1991, 309, 263.
29. Papanastasiou, G.; Kokkinidis, G.; Papadopoulos, N. *J Electroanal Chem* 1993, 352, 153.
30. Chung, C. A. *Simulation Modeling Handbook. A Practical Approach*; CRC Press: London, 2004.
31. Dahlquist, G.; Björck, A. *Numerical Methods*; Prentice-Hall: Englewood Cliffs, NJ, 1969.
32. Young, H. D. *Statistical Treatment of Experimental Data*; McGraw-Hill: New York, 1962.
33. Franson, N. M.; Peppas, N. A. *J Appl Polym Sci* 1983, 28, 1299.
34. Alfrey, T.; Gurnee, E. F.; Lloyd, W. G. *J Polym Sci C* 1966, 12, 249.
35. Hill, D. J. T.; Moss, N. G.; Pomery, P. J.; Whittaker, A. K. *Polymer* 2000, 41, 1287.
36. Massaro, L.; Zhu, X. X. *Prog Polym Sci* 1999, 24, 731.
37. Vrentas, J. S.; Vrentas, C. M. *J Polym Sci Part B: Polym Phys* 1992, 30, 1005.
38. Frisch, H. L. *Polym Eng Sci* 1980, 20, 2.
39. Thimmegowda, M. C.; Sathyanarayana, P. M.; Shariff, G.; Ashalatha, M. B.; Ramani, R.; Ranganathaiah, C. *J Biomater Sci Polym Ed* 2002, 13, 1295.
40. Veličković S. J.; Kalagasidis Krušić, M. T.; Pjanović, R. V.; Bošković-Vragolović, N. M.; Griffiths, P. C.; Popović, I. G. *Polymer* 2005, 46, 7982.
41. Gulsen, D.; Chauhan, A. *J Membr Sci* 2006, 269, 35.
42. Volkov, V. I.; Korotchkova, S. A.; Ohya, H.; Guo, Q. *J Membr Sci* 1995, 100, 273.
43. Sfirakis, A.; Rogers, C. E. *Polym Eng Sci* 1981, 21, 542.
44. Freger, V.; Korin, E.; Wisniak, E.; Korngold, E.; Ise, M.; Kreuer, K. D. *J Membr Sci* 1999, 160, 213.