

Water Sorption Kinetics in Light-Cured Poly-HEMA and Poly(HEMA-co-TEGDMA); Determination of the Self-Diffusion Coefficient by New Iterative Methods

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Received 26 January 2007; accepted 27 April 2007

DOI 10.1002/app.26693

Published online 26 July 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The present investigation is concerned with the determination of self-diffusion coefficient (D) of water in methacrylate-based biomaterials following Fickian sorption by two new methods: the Iterative and the Graphical methods. The D value is traditionally determined by means of the initial slope of the corresponding sorption curve and the so-called Stefan's approximation. The proposed methods using equations without approximations and data resulting from the whole sorption range reach to accurate values of D , even when the sorption curve does not present an initial linear portion. In addition to D , the Graphical method allows the extrapolation of the mass of the sorbed water at equilibrium (M_∞), even when the equilibrium specimen's mass fluctuates around its limited value (m_∞). The test of the proposed procedures by means of ideal and Monte Carlo simulated data revealed that these methods are fairly applicable. The

obtained D values compared with those determined by means of the Stefan's method revealed that the proposed methods provide more accurate results. Finally, the proposed methods were successfully applied to the experimental determination of the diffusion coefficient of water (50°C) in the homopolymer of 2-hydroxyethyl methacrylate (HEMA) and in the copolymer of HEMA with triethylene glycol dimethacrylate (98/2 mol/mol). These polymers were prepared by light curing ($\lambda = 470$ nm) at room temperature in presence of camphorquinone and N,N -dimethylaminoethyl methacrylate as initiator. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2380–2390, 2007

Key words: Fickian diffusion coefficient; methacrylate polymers; poly-HEMA; poly(HEMA-co-TEGDMA); iterative method

INTRODUCTION

2-Hydroxyethyl methacrylate (HEMA) is a biocompatible monomethacrylate, which has found wide application in medicine. Copolymers of HEMA with *bis*-GMA are used in most contemporary dentine bonding systems.¹ Also, copolymers of HEMA with various dimethacrylates, most commonly with ethylene-glycol dimethacrylate, are used in preparation of soft contact lenses.² Contact lenses are constantly in contact with fluid, i.e., human tears (lachrymal fluid), which consists of 98.2% of water. Also, copolymers of HEMA with other mono-methacrylates have been identified as having potential for use in controlled release drug delivery systems. In these systems the drug is immersed in the core of the glassy polymer, and as the body fluids (water) migrate into the polymer plasticizing it, the trapped drug is allowed to diffuse through the swollen hydrogel matrix. Thus, the

rate of diffusion of water into the polymer controls the rate of release of drug.³ It is obvious that the water absorption characteristics of the HEMA copolymers are very important.

The simplest and the most common technique for studying the diffusion of water in polymers is the method of the sorption kinetics. In this technique, usually a thin polymer sheet of thickness L is placed in a bath of water and the mass of the sorbed water M_t is measured as a function of time t . The plots M_t/M_∞ versus $t^{1/2}$ (M_∞ being the sorbed mass of water at equilibrium) are referred as sorption curves. Usually, the initial portion of these curves is approximately linear. Then, the diffusion coefficient is traditionally determined by means of the initial slope of the corresponding sorption curve and the so-called Stefan's approximation⁴:

$$\frac{M_t}{M_\infty} = 4 \left(\frac{Dt}{\pi L^2} \right)^{1/2} \quad (1)$$

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However, this method is an approximate technique, which can reach to more or less approximate results. First, the Stephan's method requires experimental data of the initial stages of the sorption process. A calculus based on the method of propagation of errors showed that the errors on M_t/M_∞ values are more significant in the initial stages than those of the subsequent stages of the sorption curve. Second, eq. (1) is successfully applied to data where the parameter Dt/L^2 takes sufficiently small values.⁵ In such a case eq. (1) can be fitted to the initial portion of the sorption curve (usually up to $M_t/M_\infty = 0.5$). But, if this condition is fulfilled for small D values ($D < 10^{-12} \text{ m}^2 \text{ s}^{-1}$), it is questionable if it is still valid for higher values of D . A bibliographic research⁶⁻¹⁵ showed that the values of D of water for methacrylate-based polymers lie in the range from 10^{-13} to $10^{-10} \text{ m}^2 \text{ s}^{-1}$. Especially for poly-HEMA samples prepared by a range of different polymerization protocols the following values of $D \times 10^{11} (\text{m}^2 \text{ s}^{-1})$ at 37°C were found: (a) 2.00,¹³ (b) 1.55,¹⁶ (c) 2.1,¹⁷ (d) 1.72,³ (e) 1.96.¹⁸ Also, for poly-HEMA/TEGDMA copolymer (98/2 mol/mol) the reported values of $D \times 10^{11} (\text{m}^2 \text{ s}^{-1})$ at 38 and 50°C, being equal to 4.49 and 7.49, respectively,² can be considered as relatively high values.

For all these reasons, we thought to develop iterative methods, which can be applied in the whole range of possible values of D . The proposed methods using equations without approximations and data resulting from the whole sorption range reach to accurate values of D , even when the sorption curve does not present an initial linear portion.

It should be noted that the pulsed field gradient nuclear magnetic resonance (PFG-NMR) has been used recently for the determination of self-diffusion of water in a series of methacrylate-based biomaterials.¹⁹ This technique shows many advantages compared with the conventional gravimetric method for determining the characteristics of diffusion of solvents into polymer matrices,¹⁷ but it demands very expensive laboratory equipment.

THEORETICAL SECTION

Determination of the self-diffusion coefficient of water in thin polymer sheets

The solution of the one-dimensional Fick's second law for the sorption of a liquid in a thin plane sheet, in which diffusion through the edges may be neglected, is given by^{4,5}:

$$\frac{M_t}{M_\infty} = \frac{m_t - m_0}{m_\infty - m_0} = 1 - \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp\left(\frac{-(2i+1)^2 \pi^2 D t}{L^2}\right) \quad (2)$$

where M_t is the accumulate mass of the diffusing species at time t , M_∞ the mass sorbed at equilibrium (after infinite time), m_0 the mass of the dry specimen, m_t the mass of the specimen at time t , m_∞ the mass of the specimen at equilibrium, and L the thickness of the sheet.

Stephan showed by empirical way⁵ that, for very small values of the parameter Dt/L^2 , eq. (2) can be successfully replaced by eq. (1). However the Stephan's method based on the empirical eq. (1) provides more or less approximate values of D . Exact values of D , for a Fickian sorption process, could be obtained by fitting eq. (2) to experimental data. This fitting can be done by the proposed methods.

Iterative method for the determination of the self-diffusion coefficient of a Fickian sorption of a liquid in a thin polymer sheet

Let us consider an experimental plot $y^{\text{exp}} = M_t/M_\infty = f(t)$ of a Fickian sorption containing N experimental points. To fit eq. (2) to this plot we assume first that the values of D lie in an interval (a, b) . Choosing arbitrarily from this interval a value for D , it is possible to trace the theoretical curve $y^{\text{calc}} = f(t)$, y^{calc} being the calculated values of M_t/M_∞ by means of eq. (2), and calculate, by means of the experimental M_t/M_∞ and t data, the sum of squared residuals SSR:

$$\text{SSR} = \sum_{i=1}^N (y_i^{\text{exp}} - y_i^{\text{calc}})^2 \quad (3)$$

where y_i^{exp} and y_i^{calc} are the experimental and calculated values of M_t/M_∞ of the i th experimental point respectively.

In an ideal case, where the experimental data are free from any errors, SSR will tend to zero to the extent where the chosen value of D also approaches the exact value of the diffusion coefficient. 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 value of the diffusion coefficient. Therefore, by seeking within the interval (a, b) the D values, it is possible to trace n curves $y^{\text{calc}} = f(t)$, n being the number of D values taken for these calculation. For each of these curves, the calculation of SSR permits to trace the curve $\text{SSR} = f(D)$. This curve is expected to present a pronounced minimum at a value of D equal to D_{min} , which can be considered as the best approximation to the exact value of the sought diffusion coefficient.

It is noted that Ghi et al. proposed an analogous procedure,¹⁷ which was concerned with the diffusion of water into an infinite cylinder of radius α , where

transfer occurs only in the radial direction. The method of Ghi et al. however was based on an equation completely different than that used in the present investigation. Consequently, it was not *a priori* evident that the use of eq. (2) would also converge to the desired value of D .

The proposed iterative approach is a general and simple method, which does not require the use of specialized numerical techniques. This method is based on the analysis of the plot relating M^t/M^∞ with t . The determination of M^t/M^∞ values from the experimental m_t data requires of course the knowledge of the values of m_o and m_∞ . In many cases, however, because of the experimental errors, the specimen's mass at equilibrium fluctuates around m_∞ . This problem can be approached by the following graphical method, which allows the simultaneous determination of m_∞ , m_o , and D .

Graphical method for the determination of the self-diffusion coefficient of a Fickian sorption of a liquid in a thin polymer sheet

Equation (2) can be rewritten as:

$$m_t = a - b \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp[-(2i+1)^2 c t] \quad (4)$$

where

$$\left. \begin{aligned} a &= m_\infty \\ b &= m_\infty - m_o = M_\infty \\ c &= \frac{\pi^2 D}{L^2} \end{aligned} \right\} \quad (5)$$

The parameters a , b , and c can be determined by fitting the experimental plot $m_t = f(t)$ to eq. (4). Then, m_∞ , m_o , and D can be calculated by means of eq. (5). In this treatment, a nonlinear curve fitting technique, based on the so-called Levenberg-Marquardt algorithm,^{20,21} was used. Equations (2) and (4) were programmed with KaleidaGraph (Synergy Software, version 4.03). The algorithm starts with the initial guesses for the unknown parameters (a , b , and c) that are supplied with eq. (4) and it calculates the sum of the squared deviation between the original data and the calculated fit. The algorithm then varies the parameter value slightly and re-evaluates the sum of the squared deviation until it finds the best fit.

To establish the reliability of the proposed procedures, it must first be shown that they actually work by comparison with a system where the answer is already known. In this respect, it was considered necessary to test the proposed methods first with simulated data corresponding to various values of

the diffusion coefficient and second to experimental data resulting from the sorption of water in a thin polymer sheet.

Application of the methods using simulated data

Simulated $y (= M_t/M_\infty)$ and m_t values as a function of t were derived by means of eqs. (2) and (4). These calculations were realized by means of appropriate programs written in C++ programming language. In all these calculations L was taken equal to 0.1 cm, while the values of m_o and m_∞ were taken equal to 0.145 and 0.230 g, respectively. The sums of the infinite series of eqs. (2) and (4) were approximated by a partial sum including l terms so that:

$$\sum_{i=0}^l \frac{1}{(2i+1)^2} \exp\left(\frac{-(2i+1)^2 \pi^2 Dt}{L^2}\right) - \sum_{i=0}^{l-1} \frac{1}{(2i+1)^2} \exp\left(\frac{-(2i+1)^2 \pi^2 Dt}{L^2}\right) < 10^{-16} \quad (6)$$

First the sorption of a liquid in a thin polymer sheet, with a relatively high value of $D = 7.49 \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$, was considered. This is the highest value of D , which was found in literature for methacrylate-based biomaterials and it refers to poly-(HEMA-co-TEGDMA).² However, as it was pointed out previously, Stephan's approximation is valid for small values of D . So, we chose this value for D to examine if the Stephan's method is valid even for such high values. 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 methods to extract the value $D = 7.49 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$.

In a first attempt the iterative method was applied to the simulated (ideal) M_t/M_∞ data reported in Table I. The variation of SSR with D is presented graphically in Figure 1. The curve $\text{SSR} = f(D)$ presents a pronounced minimum at $D = (7.49 \pm 0.01) \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, which exactly coincides with the theoretical value of D . At the minimum of this curve the corresponding value of SSR is equal to 1.953×10^{-12} . This minimum value of SSR expresses the goodness of the fit of the simulated data to eq. (3). The uncertainty in the extracted value of the diffusion coefficient was taken equal to the step of the variation of D values in Figure 1.

In a second step, for reasons of comparison, the Stephan's method was applied. It was found that the initial portion of the plot M_t/M_∞ versus $t^{1/2}$ (sorption curve), at least up to $t = 25$ min, slightly differs from a perfect straight line ($R^2 = 1$), the determined value of R^2 being equal to 0.9998. The slope of this

TABLE I
Ideal and Monte Carlo (M-C) Simulated Data of the Water Sorption in a Thin Polymer Sheet ($D = 7.49 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, $L = 0.1 \text{ cm}$, $m_o = 0.14500 \text{ g}$, $m_\infty = 0.23000 \text{ g}$)

t (min)	M_t/M_∞		m_t		t (min)	M_t/M_∞		m_t	
	Ideal ^a	M-C ^b	Ideal ^c	M-C ^d		Ideal ^a	M-C ^b	Ideal ^c	M-C ^d
5	0.33829	0.33200	0.17375	0.17495	55	0.92931	0.90199	0.22399	0.22654
10	0.47814	0.45133	0.18564	0.18736	60	0.94337	0.94190	0.22519	0.22350
15	0.58305	0.59488	0.19456	0.19639	65	0.95464	0.95254	0.22614	0.22560
20	0.66613	0.66161	0.20162	0.20317	70	0.96366	0.93850	0.22691	0.22615
25	0.73256	0.71911	0.20727	0.20468	75	0.97089	0.93727	0.22753	0.22702
30	0.78576	0.82398	0.21179	0.21307	80	0.97668	0.99365	0.22802	0.22745
35	0.82837	0.81149	0.21541	0.21589	85	0.98132	0.97504	0.22841	0.22908
40	0.86251	0.85326	0.21831	0.21906	90	0.98503	0.99911	0.22873	0.22998
45	0.88985	0.91617	0.22064	0.22194	95	0.98801	1.00195	0.22898	0.22953
50	0.91176	0.90993	0.22250	0.22236	100	0.99039	0.99560	0.22918	0.22891

^a Values that exactly fit to eq. (2).

^b Mean values of six normally distributed deviates generated from the ideal data with $s/M_\infty = 0.02$.

^c Values that exactly fit to eq. (4).

^d Mean values of six normally distributed deviates generated from the ideal data with coefficient of variation = 0.01.

line was found equal to 0.1489 ± 0.0009 . Comparison of this value with eq. (1) leads to $D = (4.35 \pm 0.05) \times 10^{-5} \text{ cm}^2 \text{ min}^{-1}$ or $D = (7.26 \pm 0.09) \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. So, despite the fact that we used ideal simulated data (data without any errors), Stephan's method is unable to extract the exact value of D . The deviation between theoretical and extracted value of D is equal to 3.1%. Also, the above results prove that the initial portion of the sorption curve can be expressed by the empirical eq. (1) only in a first approximation. On the contrary, the iterative method applied to the same initial portion of the sorption curve, namely up to $t = 25 \text{ min}$, perfectly extracts the value $D = 7.49 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$.

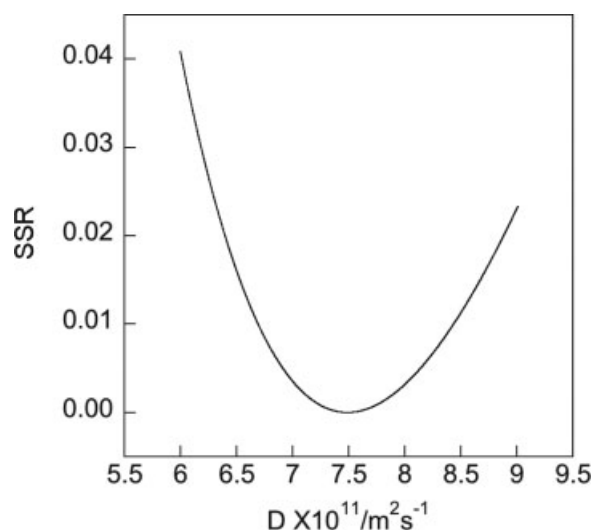


Figure 1 Variation of the Sum of Squared Residuals (SSR) with D in the case of simulated sorption data produced with $L = 0.1 \text{ cm}$ and $D = 7.49 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$.

Finally, the graphical method was applied to the simulated (ideal) m_t data reported in Table I. The fit of the simulated plot $m_t = f(t)$ to eq. (4) was excellent; the square of the correlation coefficient R^2 was equal to unity. The values of a , b , and c (with their standard deviations provided by the applying algorithm) were found, respectively, equal to $0.229999 \pm 1.3 \times 10^{-6} \text{ g}$, $0.085007 \pm 3.9 \times 10^{-6} \text{ g}$, and $0.044359 \pm 4.3 \times 10^{-6} \text{ min}^{-1}$. By combining these values with eq. (6), one obtains:

$$m_o = 0.145 \pm 5.2 \times 10^{-6} \text{ g}$$

$$m_\infty = 0.230 \pm 1.3 \times 10^{-6} \text{ g}$$

$$D = (7.49 \pm 0.0007) \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$$

The standard deviations of the above values were calculated by applying a simple calculus of propagation of error.²² It results from the above values that the proposed graphical method, applied to ideal simulated data, perfectly extracts the sought parameters D , m_o , and m_∞ .

However, it has more experimental interest the question of how well the proposed iterative techniques are able to cope with data containing experimental errors. To investigate this, a Monte Carlo (M-C) technique²³ was used, which was detailed previously²⁴ and need not 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^{calc}, t_i) of the theoretical curve $y^{\text{calc}} = M_t/M_\infty = f(t)$, a number N_1 of normally distributed random variables $y_{i,j}$ with mean y_i^{calc} and standard deviation S_i were produced. At the experimental level, this implies that, at each value of t , the fractional water uptake M_t/M_∞ was

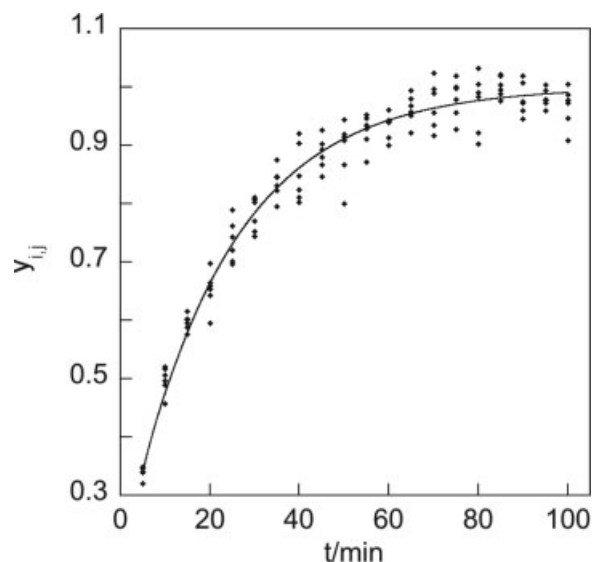


Figure 2 Monte Carlo data of M_t/M_∞ produced with $L = 0.1$ cm, $D = 7.49 \times 10^{-11}$ m² s⁻¹, and $s/M_\infty = 0.02$. (—) Graphical representation of eq. (2).

measured N_1 times (with a precision equal to S_i). A calculus based on the method of propagation of errors²² showed that:

$$S_i = \sqrt{2 \left[1 + (y_i^{\text{calc}})^2 \right]} \frac{s}{M_\infty} \quad (7)$$

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 in a thin polymer sheet ($L = 0.1$ cm) with $D = 7.49 \times 10^{-11}$ m² s⁻¹ was again treated. In this treatment the value of s/M_∞ was taken equal to 0.02. At the experimental level, this value means that, for M_∞ equal to 0.085 g, the weight of the specimens was determined

with a very significant error s (0.0017 g), namely 170 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 normally distributed random variables $y_{i,j}$ are presented graphically in Figure 2. The mean values $\bar{y}_{i,j}$ are summarized in Table I. Evidently, these values would coincide with the corresponding y_i^{calc} values only in the case where the number N_1 of the produced random variables $y_{i,j}$ tended to infinity.

The M-C data of m_t , which are also reported in Table I, were produced as previously, assuming however that the value of the coefficient of variation (s/m_t) was equal to 0.01. It results from the values of Table I that these M-C data were produced with values of standard deviation, s , greater than 0.0017 g. At the experimental level, this means that the weight of the specimens was determined with a very significant error $s > 0.0017$ g, namely with an error, which was at least 170 times greater than the accuracy of a balance of five decimal places.

The obtained results, for these M-C data, by means of the various methods are summarized in Table II.

The results of Table II show that the proposed iterative methods (iterative and graphical) are able to extract the diffusion coefficient with small error, even when the water uptake was determined with a very significant error (170 times greater than the accuracy of a balance of five decimal places). These results are in very close agreement with their true magnitudes. Also, the extracted quantities m_o and m_∞ by means of the proposed graphical method are in very close agreement with their true magnitudes. On the contrary, the application of the Stephan's method in the linear portion of the sorption curve (up to 25 min) of the above M-C data led, as previously, to the value $D = (7.08 \pm 0.19) \times 10^{-11}$ m² s⁻¹, which is within 5.5% of its true magnitude.

TABLE II
Comparison of the Determined Values of the Magnitudes D , m_o , m_∞ by Means of the Various Methods (Iterative, Graphical, and Stephan's) and the Simulated Data of Table I

Parameters	Theoretical values	Method		
		Iterative	Graphical	Stephan's
Ideal data				
$D \times 10^{11}$ (m ² s ⁻¹)	7.49	7.49 ± 0.01	7.49 ± 0.001	7.26 ± 0.09
SSR	—	1.95×10^{-12}	—	—
m_o (g)	0.145	—	$0.145 \pm 5.0 \times 10^{-6}$	—
m_∞ (g)	0.230	—	$0.230 \pm 1.0 \times 10^{-6}$	—
R^2	—	—	1.0000	0.9998
Monte Carlo data				
$D \times 10^{11}$ (m ² s ⁻¹)	7.49	7.41 ± 0.01	7.47 ± 0.37	7.08 ± 0.19
SSR	—	6.8×10^{-3}	—	—
m_o (g)	0.145	—	0.1475 ± 0.0025	—
m_∞ (g)	0.230	—	0.2300 ± 0.0006	—
R^2	—	—	0.9941	0.9993

Finally, the proposed methods were also tested to various simulated data produced with values of D in the range (10^{-13} to 10^{-10}) $\text{m}^2 \text{s}^{-1}$. The results were excellent.

It is worth noting that, for sufficiently small values of the diffusion coefficient ($D < 10^{-12}$ $\text{m}^2 \text{s}^{-1}$), the Stefan's method was fairly applicable.

The very positive tests concerning the applicability of the proposed methods using simulated data encouraged us to test these methods on experimental data concerning the diffusion of water at 50°C in poly-HEMA as well as in the copolymer of HEMA/TEGDMA (98/2 mol/mol) prepared in our laboratory. At this temperature, the above copolymer presents the highest value of D (7.49×10^{-11} $\text{m}^2 \text{s}^{-1}$) found in literature for methacrylate-based biomaterials.² For such values the previous study showed that the accuracy of the traditionally used Stefan's method is questionable.

EXPERIMENTAL

Materials

The monomers used were HEMA (Batch no. 0.1128MU; Aldrich Chemical) and TEGDMA (Lot no. 17529EA-503; Aldrich Chemical, Germany); they were used as received without further purification. To make the monomers capable for light curing, 2 mol % of camphorquinone (CQ) (Lot no. S12442-053; Aldrich Chemical), used as photosensitizer, and 2 mol % of *N,N*-dimethylaminoethyl methacrylate (DMAEMA) (Lot no. 20770; Riedel-de Haën), used as reducing agent, were added to each sample.

Photopolymerization kinetics

The photopolymerization of HEMA and HEMA/TEGDMA mixture (98/2 mol/mol) was followed first by FTIR spectroscopy using a Perkin-Elmer Spectrum One, to find the optimum irradiation time for obtaining the highest possible degree of polymerization. A small drop of each sample (HEMA or mixture HEMA/TEGDMA 98/2 mol/mol) was placed between two translucent polyethylene strips, which were pressed between two NaCl crystals. The sample was irradiated for successive short periods of time. The FTIR spectrum (resolution 4 cm^{-1} , 32 scans) was recorded at zero time and immediately after each period of exposure to visible-light. For each spectrum the height of aliphatic C=C peak absorption at 1637 cm^{-1} and the carbonyl C=O peak absorption at 1714 cm^{-1} was calculated by the use of a baseline

method. The percent monomer conversion of the cured specimen is then calculated as:

$$\begin{aligned} \% \text{Conversion} \\ = 100 \times \left[1 - \frac{(A_{\text{C}=\text{C}}/A_{\text{C}=\text{O}})_{\text{polymer}}}{(A_{\text{C}=\text{C}}/A_{\text{C}=\text{O}})_{\text{monomer}}} \right] \quad (8) \end{aligned}$$

By this way the optimum irradiation time was found to be 200 s for both samples and the final degree of conversion was about 89% for poly-HEMA and 85% for poly(HEMA-co-TEGDMA). This result shows the presence of unreacted monomer HEMA in poly-HEMA and HEMA and probably TEGDMA in poly(HEMA-co-TEGDMA).

Preparation of specimens

Sorption tests were determined according to the method described in ADA Specification no. 27 (or ISO 4049) for 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). 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, where it also absorbs CQ ($\lambda_{\text{max}} = 470 \text{ nm}$, $\epsilon = 3.8 \times 10^4 \text{ cm}^2/\text{mol}$). Due to the large size of our specimen, this unit was used without the light guide, at a distance from the sample $\sim 0.8 \text{ cm}$. The discs were irradiated on each side for 200 s. It must be noticed here that the conversion degree of discs is not the same with that determined earlier in the study of photopolymerization kinetics for thin films of polymers; in the case of discs the conversion degree may probably be lower. After the preparation of the discs, 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

The specimens were placed in a desiccator and transferred in a preconditioning oven at 50°C . After 24 h, they were removed, stored in the desiccator for 1 h, and weighted to an accuracy of $\pm 0.00001 \text{ g}$ using a Mettler H54AR balance. This cycle was repeated until a constant mass (m_i) was obtained.

Following, the discs were immersed in water 50°C. At fixed time intervals they were removed, blotted dry to remove excess liquid, weighted, and returned to the water. The uptake of the liquid was recorded for 12 h. During the first sorption the solvent also leached the unreacted monomer out. The samples were then transferred to a drying oven maintained at 50°C and a similar process to that earlier repeated during desorption. After a time period of 12 h, the samples were placed back into water at 50°C and a second sorption–desorption cycle was recorded using approximately the same time intervals. For each sorption–desorption cycle, the water sorption, expressed as weight %, was calculated as the difference between the dry mass of the disk before water sorption and after each immersion time, until reaching a plateau (i.e., maximum water sorption). Solubility, expressing the weight% of the monomer which did not react and can be extracted by water, was calculated as the difference in dry mass before immersion and after drying the disk that had reached its maximum water sorption.

DETERMINATION OF THE DIFFUSION COEFFICIENT D OF WATER IN POLY-HEMA AS WELL AS IN POLY(HEMA-*co*-TEGDMA)

First, the curves $m_t = f(t)$ of the first sorption process were examined. It was found that these curves presented a maximum value of m_t . Such a maximum was not appeared in the corresponding curves of the second sorption process. As an example, the curves $m_t = f(t)$ of the first and second sorption of water in poly-HEMA are compared in Figure 3. This behavior, also reported in literature,²⁵ was attributed to the existence of sufficient amount of unreacted monomer into the disk during the first sorption process. For further experimental evidence of this assumption, we examined in a first attempt the weight% of the extracted by the water unreacted monomer (solubility) during the two sorption–desorption cycles.

The first sorption–desorption cycle showed that the samples of poly-HEMA and poly(HEMA-*co*-TEGDMA) prepared by light-curing ($\lambda = 470$ nm) at room temperature have a solubility of 6.37 ± 0.24 and 6.24 ± 0.37 wt % correspondingly. During the second sorption–desorption cycle the solubility values were not significantly greater than zero. This result reveals that the water leached out unreacted monomer during mainly the first sorption process. So, the maximum shown in the first sorption may be due to the simultaneous extraction of unreacted monomer with the water sorption. During the second sorption process, where the water does not extract any quantity of unreacted monomer, the curves $m_t = f(t)$ must not present a maximum.

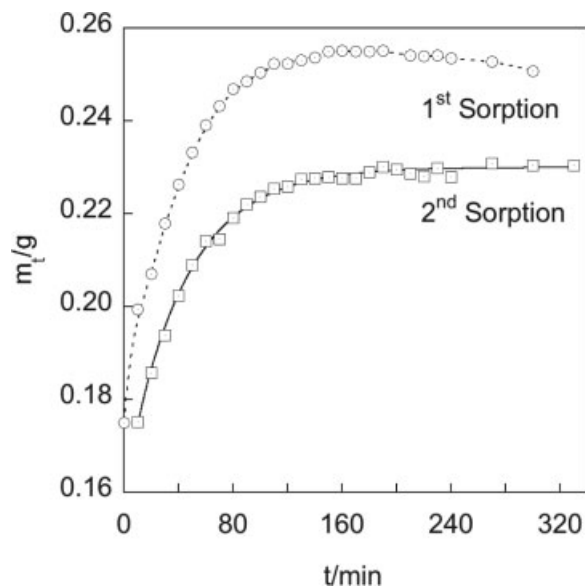


Figure 3 Variation of the m_t with t in the case of the water sorption in poly-HEMA at 50°C. (\square) Experimental data of the second sorption of water. (—) Graphical representation of eq. (4) produced with $L = 0.0775$ cm, $m_0 = 0.14452$, $m_\infty = 0.230002$, and $D = 2.35 \times 10^{-11}$ m² s⁻¹.

Indeed, as it is shown in the example of Figure 3, the curve $m_t = f(t)$ of the second sorption process does not present any maximum value. Taking into account these results we decided to analyze the experimental data of the second sorption process.

Experimental data of the second sorption process of water at 50°C in poly-HEMA and in the copolymer of HEMA with TEGDMA (98/2 mol/mol) are reported in Table III.

The thickness of the used specimens was, respectively, equal to 0.0775 and 0.0944 cm, while their diameters were 1.460 and 1.425 cm.

It should be noted that the diverse responses of polymers to the sorption of a penetrant are generally classified into three categories²⁶: Case I or Fickian diffusion, in which the driving force is the concentration gradient and occurs when the rate of the penetrant diffusion, R_{dif} , is much slower than the relaxation rate, R_{relax} , of the polymer chains ($R_{\text{dif}} \ll R_{\text{relax}}$).^{3,27} For Fickian diffusion the conformational changes in the polymer structure appear to take place instantaneously.²⁸ 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.³ The Case III or anomalous diffusion occurs in the transition region between Cases I and II, when the rates of penetrant diffusion and polymer relaxation are comparable.

First, by means of the data of Table III, the sorption kinetics of water in poly-HEMA was studied. The water sorption properties of poly-HEMA and its

TABLE III
Experimental Data of the Water Sorption in Poly-HEMA ($L = 0.0775 \pm 0.0008$ cm) and in the Poly(HEMA-co-TEGDMA) (98/2 mol/mol) ($L = 0.0944 \pm 0.0013$ cm), $T = 50^\circ\text{C}$

t (min)	Poly-HEMA		Poly(HEMA-co-TEGDMA)	
	m_t (g)	M_t/M_∞	m_t (g)	M_t/M_∞
0	0.14509	0.00000	0.15195	0.00000
10	0.17515	0.35825	0.17946	0.32210
20	0.18582	0.48304	0.19042	0.44991
30	0.19382	0.57661	0.19747	0.53213
40	0.20235	0.67637	0.20235	0.58904
50	0.20893	0.75333	0.20975	0.67534
60	0.21413	0.81415	0.21463	0.73224
70	0.21464	0.82012	0.21889	0.78192
80	0.21909	0.87216	0.22302	0.83009
90	0.22199	0.90608	0.22602	0.86507
100	0.22371	0.92620	0.22833	0.89201
110	0.22550	0.94713	0.22756	0.88303
120	0.22590	0.95181	0.23028	0.91475
130	0.22746	0.97006	0.23206	0.93551
140	0.22763	0.97205	0.23294	0.94577
150	0.22802	0.97661	0.23410	0.95930
160	0.22769	0.97275	0.23437	0.96245
170	0.22769	0.97275	0.23508	0.97073
180	0.22898	0.98784	0.23567	0.97761
190	0.23015	1.00152	0.23640	0.98612
200	0.22962	0.99532	0.23630	0.98496
210	0.22868	0.98433	0.23595	0.98087
220	0.22810	0.97754	0.23660	0.98845
230	0.22990	0.99860	0.23684	0.99125
240	0.22802	0.97661	0.23600	0.98146
270	0.23094	1.01076	0.23675	0.99020
300	0.23046	1.00515	0.23605	0.98204
330	0.23045	1.00503	0.23688	0.99172

copolymers have been extensively investigated and reviewed.²⁹ Poly-HEMA has been found^{13,16–18} to follow Fickian diffusion (Case I), with a diffusion coefficient, ranged at 37°C between 1.55×10^{-11} and $2.00 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$.

The results presented in Table III show that at the equilibrium the specimen's mass fluctuates around the limited value m_∞ . However, in the iterative method, to calculate the values of M^t/M^∞ , it is necessary to know the accurate value of m_∞ . For this reason, we applied first the graphical method, which allows the simultaneous determination of m_∞ , m_0 , and D .

The obtained results by means of the various methods are summarized in Table IV. The value of R^2 ($= 0.9962$) and Figure 3 show that the fit of the experimental plot $m_t = f(t)$ to eq. (4) is excellent. This fact provides further experimental evidence that the water sorption in poly-HEMA proceeds via a Fickian process.

In the iterative method, the obtained values of m_∞ and m_0 were used to calculate the values of

TABLE IV
Values of the Parameters D , m_0 , and m_∞ Determined by Means of the Various Methods (Iterative, Graphical, and Stephan's) and the Experimental Data Reported in Table III

Parameters	Method		
	Iterative	Graphical	Stephan's
Water sorption in poly-HEMA			
$D \times 10^{11}$ ($\text{m}^2 \text{ s}^{-1}$)	2.35 ± 0.01	2.35 ± 0.05	2.23 ± 0.03
SSR	2.92×10^{-3}	–	–
m_0 (g)	–	0.1445 ± 0.0018	–
m_∞ (g)	–	0.23002 ± 0.00029	–
R^2	–	0.9962	0.9997
Water sorption in poly(HEMA-co-TEGDMA)			
$D \times 10^{11}$ ($\text{m}^2 \text{ s}^{-1}$)	2.83 ± 0.01	2.83 ± 0.08	2.61 ± 0.05
SSR	2.58×10^{-3}	–	–
m_0 (g)	–	0.1518 ± 0.0015	–
m_∞ (g)	–	0.23759 ± 0.00033	–
R^2	–	0.9971	0.9994

M^t/M^∞ . The obtained values are reported in Table III along with the corresponding experimental m_t values.

The variation of SSR with D is presented graphically in Figure 4. The curve $\text{SSR} = f(D)$ presents a pronounced minimum at $D = (2.35 \pm 0.01) \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$, which exactly coincides with the value of D extracted previously by the graphical method. The uncertainty in the extracted value of the diffusion coefficient was taken equal to the step of the variation of D values in Figure 4.

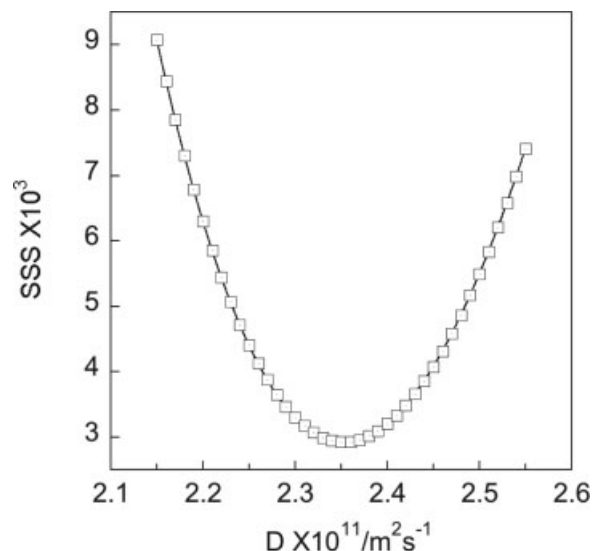


Figure 4 Variation of the Sum of Squared Residuals (SSR) with D in the case of the sorption of water in poly-HEMA at 50°C .

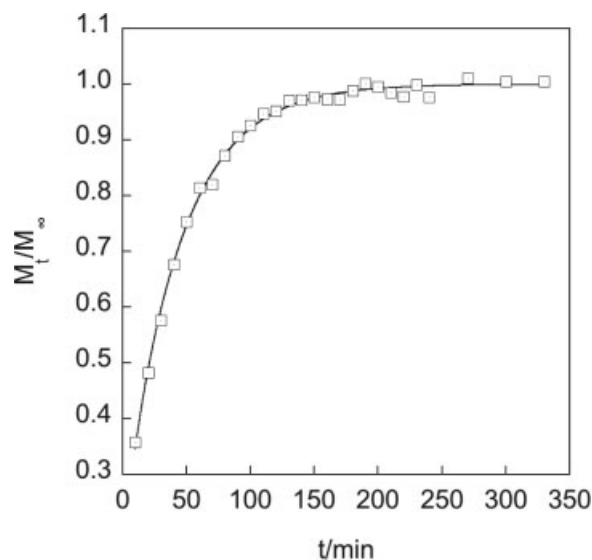


Figure 5 Variation of the M_t/M_∞ with t in the case of the water sorption in poly-HEMA at 50°C. (\square) Experimental data. (—) Graphical representation of eq. (2) produced with $L = 0.0775$ cm and $D = 2.35 \times 10^{-11}$ m² s⁻¹.

The value of 2.35×10^{-11} m² s⁻¹, determined for the self-diffusion coefficient of water 50°C in poly-HEMA, is in accepted agreement with the values reported in literature,^{3,13,16–18} which ranged between 1.55×10^{-11} and 2.00×10^{-11} m² s⁻¹, taking into consideration that the literature values were measured at a lower temperature (37°C). On the other hand, the water uptake at equilibrium ($S\%$) calculated from eq. (9) was found equal to 59.2%. This value is in close agreement with the value of 59.27% reported in literature²⁵ concerning the sorption of water in poly-HEMA at 37°C.

$$S\% = \left(\frac{m_\infty - m_0}{m_0} \right) \times 100 \quad (9)$$

In the attempt to test the exactness of the iterative method, calculated values of M^t/M^∞ , by means of eq. (2) and the determined value of D , are compared with the corresponding experimental data in Figure 5. The agreement is excellent confirming that the sorption of the water in poly-HEMA proceeds via a Fickian process.

The iterative method was also applied to various segments of the curve $M^t/M^\infty = f(t)$. The obtained values of D remained practically constant. This behavior proves that the diffusion of water in poly-HEMA is not a concentration-dependent process. Thus, the implicit assumption in the proposed approaches that during the diffusion process the coefficient D remains constant seems to be valid.

For comparison reasons, the Stephan's method was applied. It was found that the initial portion of

the experimental sorption curve $M_t/M_\infty = f(t^{1/2})$, at least up to $t = 60$ min, was an excellent straight line ($R^2 = 0.9997$). The obtained value of D was equal to $(2.23 \pm 0.03) \times 10^{-11}$ m² s⁻¹. This value diverges from the value of D , which was obtained previously by means of the graphical or the iterative method, about 5.1%. This divergence is attributed to the approximate character of eq. (1).

On the contrary, the iterative method applied to the same initial segment of the sorption curve, namely up to $t = 60$ min, provides the value $D = 2.36 \times 10^{-11}$ m² s⁻¹. This value slightly differs from the value (2.35×10^{-11} m² s⁻¹) obtained from the application of the iterative or the graphical method in the entire sorption range.

In a second attempt, the sorption kinetics of water in the copolymer of HEMA with TEGDMA (98/2 mol/mol) was studied. The obtained results by means of the various methods are summarized in Table IV. As previously, it was found that the fit of the experimental plot $m_t = f(t)$ of the second sorption to eq. (4) was excellent (Fig. 6); the square of the correlation coefficient R^2 was equal to 0.9971.

In the iterative method, it was found that the variation of SSR with D (Fig. 6) presented a pronounced minimum at $D = (2.83 \pm 0.01) \times 10^{-11}$ m² s⁻¹, which exactly coincides with the value of D extracted by the graphical method.

In Figure 7, calculated values of M^t/M^∞ , by means of eq. (2) and the determined value of D , are compared with the corresponding experimental data. The agreement is excellent confirming that the water

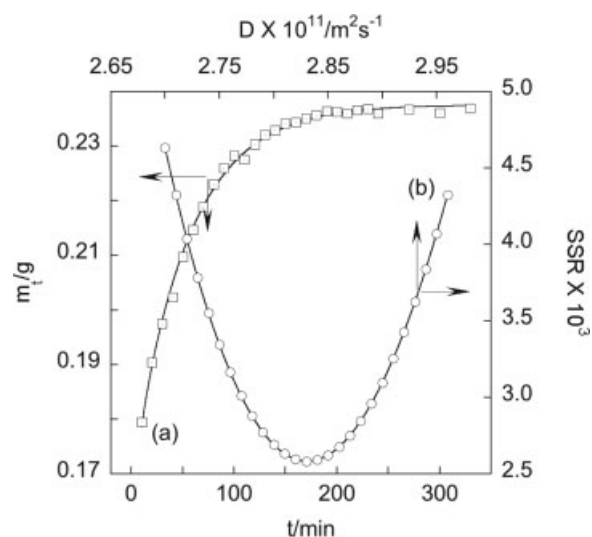


Figure 6 Sorption of water in poly(HEMA-co-TEGDMA) at 50°C. (a) Variation of m_t with t . (\square) Experimental data. (—) Graphical representation of eq. (4) produced with $L = 0.0944$ cm, $m_0 = 0.15184$, $m_\infty = 0.23759$, and $D = 2.83 \times 10^{-11}$ m² s⁻¹. (b) Variation of the Sum of Squared Residuals (SSR) with D .

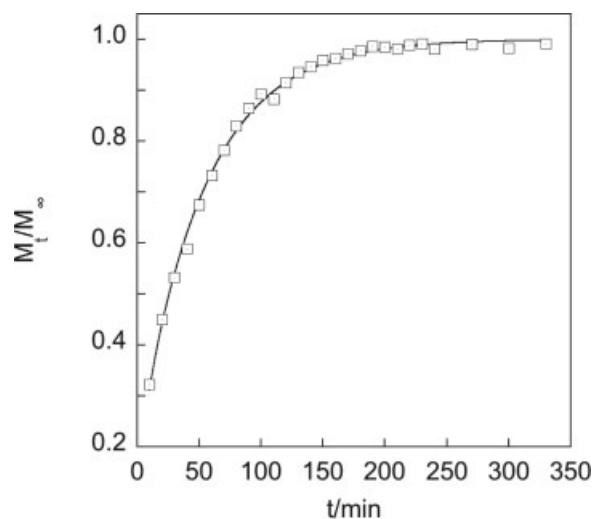


Figure 7 Variation of the M_t/M_∞ with t in the case of the water sorption in poly(HEMA-*co*-TEGDMA) at 50°C. (□) Experimental data. (—) Graphical representation of eq. (2) produced with $L = 0.0944$ cm and $D = 2.83 \times 10^{-11}$ m² s⁻¹.

sorption in poly(HEMA-*co*-TEGDMA) proceeds also via a Fickian process.

As previously, the iterative method was applied to various segments of the curve $M_t/M_\infty = f(t)$. No significant variations in the values of D were observed. This behavior proves that the diffusion of water in poly(HEMA-*co*-TEGDMA) is a process independent of the water concentration.

The application of the Stephan's method showed that the plot $M_t/M_\infty = f(t^{1/2})$ was an excellent straight line at least up to $t = 80$ min ($R^2 = 0.9994$). The obtained value of D was equal to $(2.61 \pm 0.05) \times 10^{-11}$ m² s⁻¹. This value diverges from the value of D , which was obtained previously by means of the graphical or the iterative method, about 7.8%. This divergence is attributed to the approximate character of eq. (1).

It is noted that the diffusion of water in poly(HEMA-*co*-TEGDMA) with 2 mol % of TEGDMA was studied by Peniche et al.² The copolymer was prepared by thermally initiated free radical polymerization (60°C for 24 h) using 2,2'-azobisisobutyronitrile (1 wt %) as initiator. The obtained value of D (7.49×10^{-11} m² s⁻¹) was different from that obtained in the present study. This deviation in the value of D could be attributed mainly in the different polymerization protocol.

The obtained results in the present investigation show that the presence (in small content) of added crosslinker (TEGDMA) causes a small increase in the values of D over that for poly-HEMA. On the contrary, the water uptake at equilibrium ($S\%$), equal to 56.5%, is smaller in poly(HEMA-*co*-TEGDMA) than in poly-HEMA.

It is known that both intrinsic hole volume and polarity of a polymer affect the water uptake and diffusion coefficient. However, it was found that the polar interactions between polymer and water and not the geometrical characteristics of the polymer structure provide the rate-limiting step of water sorption.^{30,31} The polar/hydrophilic sites provide trapping sites that cause water to stop and interact, which severely hinder diffusion and decrease the diffusion coefficient. In poly-HEMA the attachment of the water molecules takes place by hydrogen bonding to the polar/hydrophilic —OH groups. By the introduction of TEGDMA monomer units in poly(HEMA-*co*-TEGDMA) some of the hydroxyl groups were removed and some less polar/hydrophilic —OCH₂CH₂— groups were introduced. This seems to cause a decrease to equilibrium water uptake and increase of the diffusion coefficient.

Finally, it should be noted that the present procedure was designed to be applied to the sorption of water in homopolymers and copolymers of HEMA, where the diffusion coefficient of water presents relatively high values. However, there is no reason why the proposed analysis could not be applied to the Fickian sorption of water in any polymer matrix.

CONCLUSIONS

The proposed approaches present many advantages compared with the traditionally used Stephan's method, which is based on the so-called Stefan's approximation. First, they use equations without approximations, which are valid throughout the sorption range. Second, on the contrary to the conventional Stephan's method, which requires experimental data of the initial stages of the sorption process (where the experimental errors are more significant than those of the subsequent stages), the proposed procedures are able to determine the accurate value of D by means of data resulting from the whole sorption range. Thus, the proposed methods reach to accurate values of D , even when the sorption curve does not present an initial linear portion. In addition to D , the Graphical method allows the extrapolation of the mass of the sorbed water at equilibrium (M_∞), even when the equilibrium specimen's mass, because of the experimental errors, fluctuates around m_∞ .

The reliability of the proposed procedures was tested with ideal (free from any experimental errors) and Monte Carlo simulated data. It was found that the proposed methods, applied to ideal simulated data that correspond to various values of D , perfectly extract the sought diffusion coefficient. On the other hand, the application of the methods to Monte Carlo simulated data revealed that these methods

are fairly applicable even when the simulated sorption data are considerably obscured by errors.

The results of the proposed approaches were compared with D values, which were obtained by means of the traditionally used Stephan's method. This comparison revealed that the proposed methods provide more accurate results than the Stephan's method especially for relatively high D values.

Finally, the proposed methods were successfully applied to the experimental determination of the diffusion coefficient of water (50°C) in poly-HEMA and in the copolymer of HEMA with TEGDMA (98/2 mol/mol). These polymers were prepared by light curing ($\lambda = 470$ nm) at room temperature in presence of CQ and DMAEMA as initiator. The obtained values of D for poly-HEMA and poly(HEMA-co-TEGDMA) were equal to 2.35×10^{-7} and 2.83×10^{-7} cm² s⁻¹, respectively, and the water uptake 59.2 and 56.5 wt % correspondingly.

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