

Sorption and Desorption Parameters of Water or Ethanol in Light-Cured Dental Dimethacrylate Resins

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ABSTRACT: Two cycles of sorption/desorption of water or ethanol by light-cured dental resins of bisphenol A glycol dimethacrylate (Bis-GMA), bisphenol A ethoxylated dimethacrylate (Bis-EMA) urethane dimethacrylate (UDMA) triethylene glycol dimethacrylate and decanediol dimethacrylate (D₃MA) were studied. The experimental curves $m_t = f(t)$ taken for the first water sorption by poly-Bis-GMA, poly-Bis-EMA and poly-UDMA showed a maximum. A maximum was also observed in the curve obtained for first sorption of ethanol by poly-Bis-GMA. In all other cases, the curves for sorption or desorption of water or ethanol showed Fickian behavior. The experimental data obtained for first sorption of water or ethanol were perfectly fitted to a new proposed equation, which predicts water or ethanol sorption with simultaneous extraction of unreacted the

monomer. This equation gave us the possibility for the determination of the diffusion coefficient of the extraction of the unreacted Bis-GMA during the water and ethanol sorption, as well as the diffusion coefficient of the extraction of the unreacted Bis-EMA and UDMA during the water sorption. The maximum water or ethanol absorbed at equilibrium and the diffusion coefficient are determined from the second sorption/desorption cycle during which the extraction of the monomer is negligible. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 463–475, 2008

Key words: water or ethanol sorption/desorption; diffusion coefficient; dental dimethacrylate resins; Bis-GMA; Bis-EMA; UDMA; TEGDMA; D₃MA

INTRODUCTION

Among a wide variety of applications, dimethacrylates are employed in preventive and restorative dentistry, which is concerned with the repair and treatment of the teeth, to give proper function and secondary good esthetics. Typically the commercially most widely used dental resins are prepared from polymerization of bisphenol A glycol dimethacrylate (Bis-GMA), bisphenol A ethoxylated dimethacrylate (Bis-EMA), urethane dimethacrylate (UDMA), triethylene glycol dimethacrylate (TEGDMA), and decanediol dimethacrylate (D₃MA) (Fig. 1). The first three viscous dimethacrylates are characterized as base monomers and the last two nonviscous are used as reactive diluents.^{1–3} Dental resins show a relatively high chemical and thermal stability. However, in oral environment they may absorb water and chemicals, such as those found in saliva or food (acids, bases, salts, alcohols, etc.) and may release components to their surrounding. The process of sorption and desorption of a liquid may produce deleterious

effects on the structure and function of the resin. These effects may include volumetric changes, such as swelling, physical changes, such as plasticization, softening and chemical changes, such as oxidation and hydrolysis.⁴ The properties of the resin may be permanently changed by these events; thus, the long-term survival of the resin, under oral conditions, is obviously of great importance. There is concern that the effects of liquid uptake and hydrolytic degradation may lead to a shortened service life of dental restorations. But an even greater concern is the possibility of biological effects elicited by the species evolved from dental resin restorations, thus requiring the effects of liquid uptake to be investigated and explained.⁴

Studies of the behavior of dental resins in a wet *in vitro* environment have been mainly conducted in distilled water^{5,6} and in oral/food simulating liquids, such as ethanol/water mixtures, which are among the best solvents for dental resins.^{7–10} The simplest and the most common technique for studying the sorption/desorption of a liquid in polymers is the method of the sorption/desorption kinetics. In this technique, a thin polymer sheet is placed in a bath of liquid at constant temperature, and the mass of the absorbed liquid M_t is measured as a function of time t to obtain the sorption curve $m_t = f(t)$. Then

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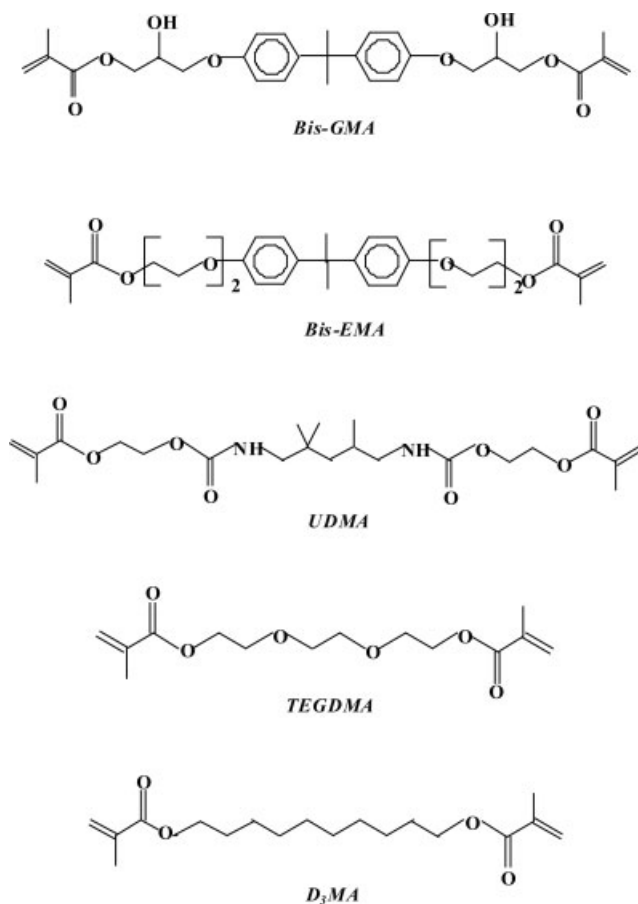


Figure 1 Chemical structure of the used dimethacrylate monomers.

the liquid is desorbed until a constant mass for the film is reached, and the desorption curve is recorded. These experimental curves help in the determination of the sorbed/desorbed liquid amount at equilibrium (M_{∞}), the percentage of the extracted mass of unreacted monomer (solubility), and the sorption/desorption diffusion coefficient, D , which expresses correspondingly the rate of the liquid sorption/desorption. The values of all these parameters depend on the chemical and physical structure of the resin and the chemical structure of the liquid. Important chemical characteristics include the hydrophilicity and the crosslinking density of the resin and the difference in the solubility parameter between the resin and the liquid. Important physical characteristics include the porosity of the resin.

This work is concerned with the study of the sorption/desorption kinetics of water or ethanol by the dental resins prepared by light curing ($\lambda = 470$ nm) of Bis-GMA, Bis-EMA, UDMA, TEGDMA, or D₃MA. The sorbed and desorbed liquid amount at equilibrium, the corresponding diffusion coefficients, and the solubility were determined by using an iterative method recently proposed by our research group.¹¹

EXPERIMENTAL SECTION

Materials

The dimethacrylate monomers used were Bis-GMA (Polysciences Europe GmbH, Lot no.493282), UDMA (Ivoclar-Vivadent, Lot No. B00338), TEGDMA (Aldrich Chemical, Lot No. 17529EA-503), D₃MA (Ivoclar-Vivadent, Batch-NR: F36539, Teile-NR: 300373), and Bis-EMA (Aldrich Chemical, Lot No. 03,514 HF). They were used as received without further purification. For light curing of the samples, 2 mol % of camphorquinone (CQ; Aldrich Chemical, Lot no. S12442-053) and 2 mol % of *N,N*-dimethylaminoethyl methacrylate (DMAEMA; Riedel-de Haën, Lot no. 20770) used as photosensitizer and reducing agent, respectively, were added to each sample. Because dimethacrylates, except TEGDMA and D₃MA, are viscous liquids, the CQ and DMAEMA were first dissolved in dichloromethane, and then a certain amount of this solution was added to the monomer, and the solvent was subsequently evaporated under vacuum.

Preparation of specimens

Sorption and solubility 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. 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 CQ also absorbs ($\lambda_{\max} = 470$ nm, $\epsilon = 3.8 \times 10^4$ cm²/mol). Because of the large size of our specimen, this unit was used without the light guide at a distance of ~ 0.8 cm from the sample. The samples were irradiated for 200 s on each side. Then, the mold was dismantled and the resin was carefully removed by flexing the Teflon mold. Four specimen discs were prepared for each resin.

The volumes of all samples were calculated using their diameter and their thickness. The thickness of the samples was measured accurately at five points using a micrometer (0–25 mm, Moore and Wright, Sheffield, UK). Their diameter was measured using a No. 599 Vernier Caliper (0–17 cm, Rabone Chesterman).

Sorption and desorption measurements

All samples 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 ± 0.00001 g using a Mettler H54AR balance. This cycle was repeated until a constant mass was obtained. After this, the discs were immersed in water or ethanol at 37°C to simulate the physiological temperature condition. At fixed time intervals, they were removed, blotted dry to remove excess liquid, weighted, and returned to the liquid bath. The time intervals were more during the first days, and as the uptake slowed, the time was extended. The uptake of the liquid was recorded for 30 days. The samples were then transferred to a drying oven maintained at 37°C over silica gel and a process similar to that described earlier was repeated during desorption. After a time period of 30 days, the samples were placed back into the water or ethanol at 37°C , and a second sorption-desorption cycle was recorded using approximately the same time intervals.

THEORETICAL SECTION

Kinetics of Fickian sorption or desorption of a liquid in a resin disc

The rate of sorption of liquid by a resin following the Fick's diffusion law is given by the well-known equation:¹²

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

where M_t is the accumulate mass of the diffusing liquid at time t , M_∞ the mass of the sorbed liquid at equilibrium (after infinite time), m_o the mass of the dry disc, m_t the mass of the disc at time t , m_∞ the mass of the specimen at equilibrium, L the thickness of the disc, and D_s the diffusion coefficient of the liquid during the sorption process.

Analogous to the Fickian sorption, the Fickian desorption of a liquid can be expressed by the following equation:

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

Here D_d is the diffusion coefficient of the liquid during the desorption process, m_o the mass of the saturated with liquid disc, while m_∞ is the equilibrium mass of the disc at the end of the desorption.

Iterative method for the determination of the self-diffusion coefficients of a liquid during its Fickian sorption or desorption process in a resin disc

The diffusion coefficients of a liquid during its sorption or desorption process can be determined by means of an iterative method recently developed by our research group.¹¹ The basic principles of this method are described below:

In the case of the sorption of a liquid, eq. (1) can be rewritten as

$$m_t = m_\infty - \frac{8}{\pi^2} (m_\infty - m_o) \times \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp\left(\frac{-(2i+1)^2 \pi^2 D_s t}{L^2}\right) \quad (3)$$

This is an equation of the form

$$m_t = a - b \left(\frac{8}{\pi^2}\right) \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp(-2i+1)^2 ct = a - b \left(\frac{8}{\pi^2}\right) \left(\exp(-ct) + \frac{1}{9} \exp(-9ct) + \frac{1}{25} \exp(-25ct) + \dots\right) \quad (4)$$

where

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

In the case of desorption of a liquid, eq. (2) can be rewritten as

$$m_t = m_\infty + \frac{8}{\pi^2} (m_o - m_\infty) \times \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp\left(\frac{-(2i+1)^2 \pi^2 D_d t}{L^2}\right) \quad (6)$$

namely,

$$m_t = a + b \left(\frac{8}{\pi^2}\right) \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp(-2i+1)^2 ct = a + b \left(\frac{8}{\pi^2}\right) \left(\exp(-ct) + \frac{1}{9} \exp(-9ct) + \frac{1}{25} \exp(-25ct) + \dots\right) \quad (7)$$

where

$$\begin{aligned} a &= m_\infty \\ b &= m_o - m_\infty \\ c &= \frac{\pi^2 D_d}{L^2} \end{aligned} \quad (8)$$

The parameters a , b , and c of eqs. (4) and (7) can be determined by fitting the appropriate experimental plots $m_t = f(t)$ to eqs. (4) and (7). Then, m_∞ , m_o , and D can be calculated by means of eqs. (5) and (8). In this treatment, a nonlinear curve fitting technique, based on the so-called Levenberg–Marquardt algorithm,^{13,14} was used. Equations (4) and (7) 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 by eqs. (4) and (7), and it calculates the sum of the squared deviation between the original data and the calculated fit. The algorithm then varies the values of the parameters slightly and reevaluates the sum of the squared deviation until it finds the best fit.

The sums of the infinite series of eqs. (3) and (6) were approximated by a partial sum including l terms so that

$$\sum_{i=0}^l \frac{1}{(2i+1)^2} \exp\left(\frac{-(2i+1)^2 \pi^2 D t}{L^2}\right) - \sum_{i=0}^{l-1} \frac{1}{(2i+1)^2} \exp\left(\frac{-(2i+1)^2 \pi^2 D t}{L^2}\right) < 10^{-16}. \quad (9)$$

It should be noted that this iterative method was applied to simulated as well as to experimental values of sorption data with known values of the parameters a , b , and c . The obtained results were excellent.

With the values of m_∞ and m_o for the sorption and desorption process, the following important thermodynamic parameters concerning the equilibrium state can be calculated:

$$\begin{aligned} \text{WS\%} &= 100 \left(\frac{m_\infty(S) - m_o(S)}{m_o(S)} \right) \\ \text{WD\%} &= 100 \left(\frac{m_o(D) - m_\infty(D)}{m_\infty(D)} \right) \\ \text{SL\%} &= 100 \left(\frac{m_o(S) - m_\infty(D)}{m_\infty(D)} \right) \end{aligned} \quad (10)$$

where WS% is the percentage of the sorbed liquid during the sorption process, WD% is the percentage of the desorbed liquid during the desorption process, and SL% is the extracted amount of monomer known as “solubility” of the resin in the liquid under consideration.

Kinetics of Fickian sorption of a liquid by a resin disc and simultaneous Fickian desorption of unreacted monomer

In this case, the increase of the disc mass after sorption time t , due to the liquid sorption, can be calculated from the equation:

$$\begin{aligned} \text{mass gain} &= m_t^t - m_o \\ &= M_l^\infty \left(1 - \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp\left(\frac{-(2i+1)^2 \pi^2 D_l t}{L^2}\right) \right) \end{aligned} \quad (11)$$

where m_t^t would be the disc mass after t immersion time, if only the sorption of the considered liquid occurred, M_l^∞ is the absorbed liquid mass after a very long (infinity) immersion time, and D_l is the liquid diffusion coefficient.

Also the mass loss of the disc, due to the extraction of the unreacted monomer after time t from the beginning of the sorption process, would be

$$\begin{aligned} \text{mass loss} &= m_o - m_m^t \\ &= M_m^\infty \left(1 - \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp\left(\frac{-(2i+1)^2 \pi^2 D_m t}{L^2}\right) \right) \end{aligned} \quad (12)$$

where m_m^t would be the disc mass if only the extraction of the monomer took place, M_m^∞ is the mass of the extracted monomer after a very long (infinity) extraction time, and D_m is the diffusion coefficient of the monomer.

Then the disc mass at time t will be

$$\begin{aligned} m_t &= m_o + \text{mass gain} - \text{mass loss} \\ &= a + d \left\{ 1 - \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp(-(2i+1)^2 b t) \right\} \\ &\quad - f \left\{ 1 - \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp(-(2i+1)^2 c t) \right\} \end{aligned} \quad (13)$$

where

$$\begin{aligned} a &= m_o \\ b &= \frac{\pi^2 D_l}{L^2} \\ c &= \frac{\pi^2 D_m}{L^2} \\ d &= M_l^\infty \\ f &= M_m^\infty \end{aligned} \quad (14)$$

The percentage increase of the disc mass at equilibrium (after infinity time), which is due to the liquid sorption, can be calculated from the following equation:

$$\text{Liquid\%} = 100 \left(\frac{M_l^\infty}{m_o} \right) \quad (15)$$

While the percentage of the monomer, extracted after infinity time, can be calculated from the following equation:

$$\text{Extr.\%} = 100 \left(\frac{M_m^\infty}{m_o} \right) \quad (16)$$

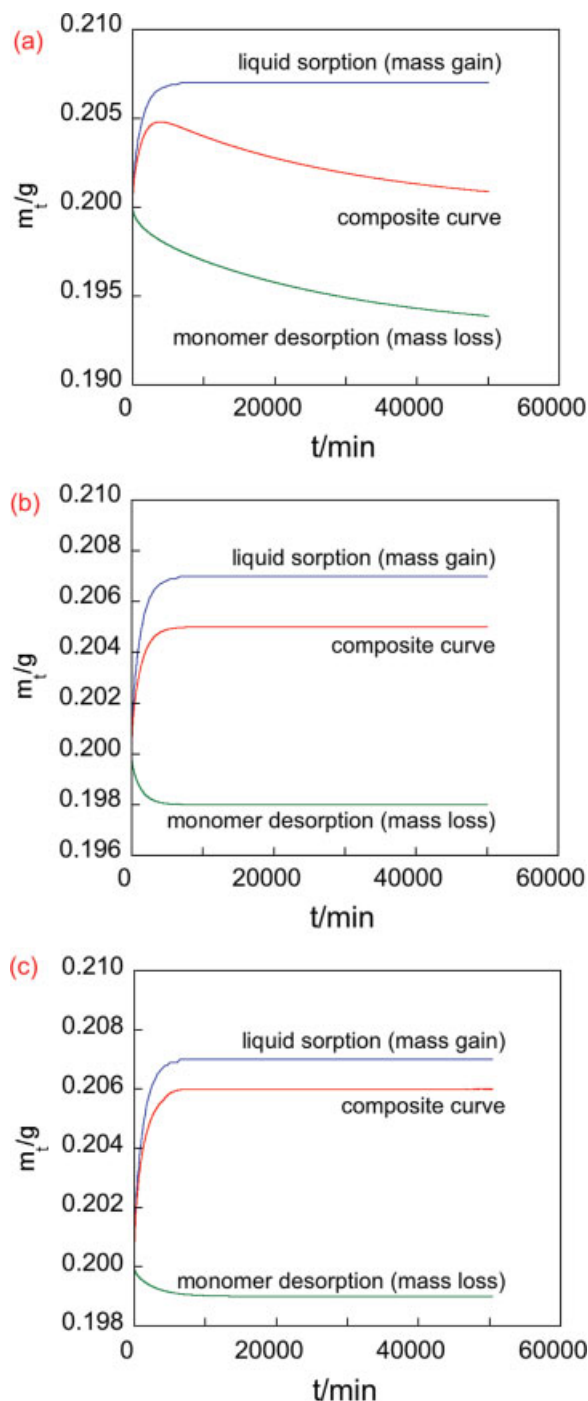


Figure 2 Graphical representation of eq. (13) produced with $m_o = 0.2$ g and $L = 0.1$ cm. (a) $D_l = 1.2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $D_m = 5.5 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, $M_l^\infty = 7.0 \times 10^{-3} \text{ g}$ (3.5%), $M_m^\infty = 7.2 \times 10^{-3} \text{ g}$ (3.6%); (b) $D_l = 1.2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $D_m = 1.2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $M_l^\infty = 7.0 \times 10^{-3} \text{ g}$ (3.5%), $M_m^\infty = 2.0 \times 10^{-3} \text{ g}$ (1.0%); (c) $D_l = 1.2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $D_m = 5.5 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, $M_l^\infty = 7.0 \times 10^{-3} \text{ g}$ (3.5%), $M_m^\infty = 1.0 \times 10^{-3} \text{ g}$ (0.5%) [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Graphical representation of eq. (13)

The shape of the curve representing eq. (13) for several characteristic values of the parameters $L, m_o, D_l, D_m,$

M_l^∞, M_m^∞ is shown in Figure 2. In Figure 2 the curve of the sorption of the considered liquid $m_t^l = f(t)$, as well as the desorption curve, $m_t^d = f(t)$, of the monomer are shown. These curves were the result of eqs. (11) and (12), respectively. It was found that when $D_l \gg D_m$, the curve $m_t = f(t)$ shows a maximum [Fig. 2(a)]. On the contrary, when $D_l \cong D_m$ and $M_w^\infty > M_m^\infty$, the curve shows "Fickian behavior" [Fig. 2(b)]. Finally, when $D_l > D_m$ and $M_l^\infty \gg M_m^\infty$, the curve also shows "Fickian behavior" [Fig. 2(c)].

In all liquid-resin systems with sorption behavior shown in Figure 2(a–c), the maximum increase of the disc mass is less than the absorbed amount of liquid at equilibrium. The former quantity can be considered as an apparent magnitude of the absorbed liquid:

$$\text{WS\%} = 100 \left(\frac{m_t^{\max} - m_o}{m_o} \right) \quad (17)$$

in which m_t^{\max} is the disc mass at the maximum of the sorption curve. This quantity is given by the equation:

$$m_t^{\max} = m_p + m_l + fr \times m_{\text{mon}} \quad (18)$$

where m_p is the resin mass, m_l the absorbed liquid mass, m_{mon} the mass of the monomer contained initially in the disc and fr a numerical coefficient taking values between 0 and 1. The quantity $fr \times m_{\text{mon}}$ expresses the fraction of the extractable monomer contained in the disc at the maximum of the curve [Fig. 2(a)]. Also the initial disc mass is

$$m_o = m_p + m_{\text{mon}} \quad (19)$$

and

$$\begin{aligned} \text{WS} &= m_t^{\max} - m_o \\ &= m_l + fr \times m_{\text{mon}} - m_{\text{mon}} \\ &= m_l - (1 - fr)m_{\text{mon}} \end{aligned} \quad (20)$$

Obviously, the quantity $(1 - fr)m_{\text{mon}}$ expresses the mass of the monomer extracted after a time interval equal to t_{\max} , and it is less than the solubility SL , which expresses the total amount of monomer extracted after infinite time.

Consequently,

$$(1 - fr)m_{\text{mon}} = \lambda SL < SL \quad (21)$$

where λ is a numerical coefficient satisfying the condition $0 \leq \lambda \leq 1$.

$\lambda \rightarrow 1$ when $fr \rightarrow 0$, while $\lambda \rightarrow 0$ when $fr \rightarrow 1$.

Combination of eqs. (20) and (21) gives

$$\text{WS} = m_l - \lambda SL. \quad (22)$$

By dividing eq. (22) with m_o we have

$$\frac{\text{WS}}{m_o} = \frac{m_l}{m_o} - \lambda \frac{SL}{m_o}$$

or

$$\text{WS\%} = \text{Liquid\%} - \lambda \text{SL\%}.$$

Assuming that the total absorbed liquid is desorbed during the desorption process, namely, $\text{Liquid\%} = \text{WD\%}$, it results in

$$\text{WS\%} = \text{WD\%} - \lambda \text{SL\%}. \quad (23)$$

Now we can define a parameter R from the equation

$$R = \frac{\text{WS\%} + \text{SL\%}}{\text{WD\%}} = \frac{\text{WD\%} + (1 - \lambda)\text{SL\%}}{\text{WD\%}}. \quad (24)$$

Since $\lambda \leq 1$ and $\text{SL} \geq 0$, we have $(1 - \lambda)\text{SL\%} \geq 0$ and $R \geq 1$.

The parameter R is unity only when $\lambda = 1$ and $fr = 0$. The last condition shows that at $t = t_{\text{max}}$, the mass of the extractable monomer contained in the disc ($fr \times m_{\text{mon}}$) is zero, which means that it was completely extracted. So, the sorption curve must not pass through a maximum value but must simply show a plateau [Fig. 2(b,c)]; t_{max} expresses now the minimum time where the mass of the disc attains a limited value. In such cases, the following relationship must be valid:

$$\text{WS\%} = \text{WD\%} - \text{SL\%}. \quad (25)$$

In addition, at the plateau of the curves $m_t = f(t)$, which do not present maxima, by means of an analogous calculus, eq. (25) is again produced. Consequently, for systems where the shape of the sorption curve shows Fickian behavior, it is expected that $R = 1$.

RESULTS AND DISCUSSION

Water sorption and desorption

The experimental curves $m_t = f(t)$ obtained for the first sorption of water by poly-BisGMA, poly-Bis-EMA, and poly-UDMA showed a maximum followed by a decrease in the water uptake (Fig. 3). Such a maximum in the sorption curve has been also observed in several liquid-polymer systems, and it was suggested to be due to the relaxation phenomena of polymer chains.¹⁵⁻¹⁷ The solvent can be absorbed into the sample before the polymer chains have a chance to completely relax, and the structural rearrangements, which the sample experiences as the chains eventually reorient themselves, lead to rejection of some of the solvent from the sample. This partial exclusion of the penetrant will be more pronounced in instances when the diffusion rate is faster than the rate of chain relaxation, since most of the solvent absorption is into an unrelaxed network.¹⁵ This behavior however does not occur in our case, because our experimental curves $m_t = f(t)$

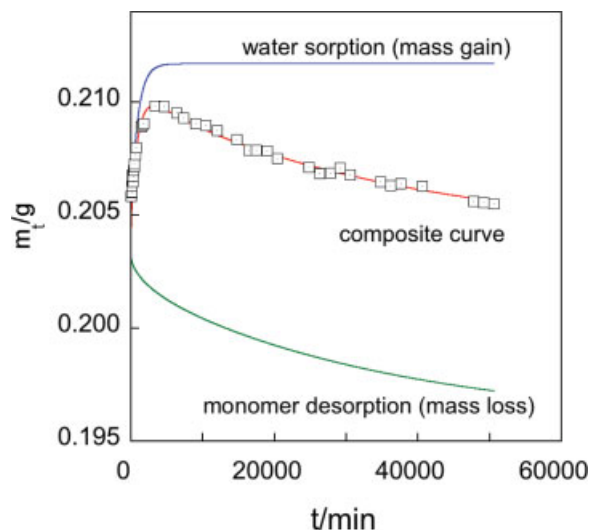


Figure 3 Variation of m_t with t in the case of the first sorption of water by poly-Bis-GMA at 37°C. $L = 0.101$ cm. (\square), Experimental data; (—), graphical representation of eq. (13). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

obtained for the second water sorption process do not show a maximum, but a Fickian behavior; Fickian sorption occurs when the rate of diffusion is significantly slower than the rate of relaxation of the polymer chains.¹⁷ Nevertheless, for the above mentioned resins it was found that their experimental curves $m_t = f(t)$ obtained for the first water sorption are perfectly fitted to eq. (13); this equation predicts the presence of a maximum due to the extraction of unreacted monomer simultaneously with the water sorption. It is well known that the light-cured dental resins contain some quantity of the unreacted monomer, which can be extracted by water.^{5,18} As an example, the fitting of eq. (13) to the experimental data for poly-Bis-GMA is shown in Figure 3. In the same figure the theoretical curves of the water sorption and the monomer extraction, which were traced by means of eqs. (11) and (12) respectively are also shown. In this treatment, the iterative method described previously was again used. From this fitting, the values of a , b , c , d , and f were calculated, while by means of eqs. (14)–(16), the parameters Water% (percentage amount of absorbed water), Extr.% (percentage amount of the extracted monomer), D_w (diffusion coefficient of the water), and D_m (diffusion coefficient of the monomer) were determined (Table I). It is observed that $D_w \gg D_m$ confirming the presence of the maximum in the sorption curve, according to the theoretical predictions reported previously.

Despite the fact that the experimental curves $m_t = f(t)$ for the materials poly-BisGMA, poly-Bis-EMA, and poly-UDMA showed maxima; however, the initial part (up to maximum) of these curves presented

TABLE I
Thermodynamic and Kinetic Parameters for First Water Sorption^a

Resin	Water% ^b	Extr.% ^b	WS ₁ % ^b	$D_w \times 10^{8b}$ (cm ² s ⁻¹)	$D_m 10^{8b} \times$ (cm ² s ⁻¹)	$D_{s1} 10^{8c} \times$ (cm ² s ⁻¹)
Bis-GMA	3.48 ± 0.18	3.46 ± 0.07	2.35 ± 0.16	1.18 ± 0.13	5.44 ± 0.70	1.40 ± 0.23
Bis-EMA	1.76 ± 0.01	2.49 ± 0.04	1.25 ± 0.04	2.19 ± 0.16	4.64 ± 0.10	3.13 ± 0.51
UDMA	3.08 ± 0.18	2.25 ± 0.20	2.39 ± 0.15	1.04 ± 0.11	6.67 ± 0.65	1.10 ± 0.13
TEGDMA	–	–	5.60 ± 0.17	–	–	1.72 ± 0.12
D ₃ MA	–	–	0.45 ± 0.13	–	–	4.30 ± 0.19

^a Mean values ± standard deviation of four replicates.

^b Values of sorbed water (Water%) extracted monomer (Extr.%) diffusion coefficient of water (D_w) diffusion coefficient of monomer (D_m); these parameters were calculated by fitting the experimental data of first water sorption to eq. (13).

^c Apparent values for sorbed water (WS₁) and diffusion coefficient (D_{s1}) calculated by fitting the initial part of the experimental curve $m_t = f(t)$ to eq. (4); for TEGDMA and D₃MA, WS₁ and D_{s1} were obtained by fitting the whole sorption curve to eq. (4).

apparent Fickian behavior. So, by fitting the initial parts of these curves to eq. (4), the values of WS₁% and D_{s1} were obtained. These values are also reported in Table I. As mentioned previously, the quantity WS₁% expresses the apparent percentage of the absorbed water, and it is always less than Water% [Table I, Fig. 2(a)]. The second quantity (D_{s1}) is also an apparent magnitude related to the water diffusion coefficient during its sorption process, as well as to the diffusion coefficient of the monomer extraction. It was found that D_{s1} was lower than the true value D_w (Table I).

The experimental curves $m_t = f(t)$ obtained for poly-TEGDMA and poly-D₃MA showed Fickian behavior. However, the analysis of eq. (13), reported previously, showed that even when the shape of the sorption curves is similar to that of a Fickian sorption [Fig. 2(b,c)], the relative composite curve could deviate from the real water sorption curve. So, for these materials, the fitting of the experimental curves $m_t = f(t)$ to eq. (4) probably gives apparent values of the parameters WS₁% and D_{s1} (Table I).

For all the studied resins, the experimental curves $m_t = f(t)$ concerning the water desorption followed Fickian behavior. These curves were perfectly fitted to eq. (7). The calculated percentage of the water desorbed during the first desorption process (WD₁%), the percentage of the extracted monomer during the first sorption process (solubility) (SL₁%), and the desorption diffusion coefficient of water (D_{D1}) are reported in Table II. A comparison of the values of Tables I and II leads to the relation Water% ≈ WD₁%, that is, the theoretically predicted amount of absorbed water (Water%) is equal to the experimentally determined desorbed amount of H₂O (WD₁%). This finding confirms the validity of eq. (13) and proves that all the absorbed water during the first sorption is desorbed during the first desorption process. So, the quantity WD₁% also expresses the actual amount of sorbed water. Also, the comparison of the values of Tables I and II reaches the relation Extr.% ≈ SL₁%. This result indicates that the theoret-

ically predicted amount of the extracted monomer (Extr.%), by means of eq. (13), is equal to the experimentally determined solubility (SL₁%). This result also confirms the validity of eq. (13).

Finally, in Table II, the experimental values of the parameter R_1 [defined by eq. (24)] are reported. For poly-Bis-GMA, poly-Bis-EMA, and poly-UDMA, $R_1 > 1$ confirming that, for these resins, the experimental sorption curve has the form of the composite curve shown in Figure 2(a). For poly-TEGDMA and poly-D₃MA, $R_1 = 1$ confirming that for these resins, the experimental sorption curve is analogous to the composite curve shown in Figure 2(c); the condition $M_w^z \gg M_m^z$ is satisfied because WS₁% ≫ SL₁%.

The experimental curves $m_t = f(t)$ obtained for the second water sorption showed Fickian behavior. The parameter R_1 takes for all resins values about equal to unity due to the decreased amount of the extracted monomer. In Table III are presented the thermodynamic and kinetic parameters obtained for the second water sorption and desorption. The solubility of resins in water during the second sorption (SL₂%) is much lower than that found during the first sorption (SL₁%). The very low values of SL₂% indicate that water extracts monomer mainly during the first sorption.

The correlation results of the thermodynamic parameters WS₁%, WS₂%, WD₁%, and WD₂% are

TABLE II
Water Desorption (WD₁%) Solubility (SL₁%) and Desorption Diffusion Coefficient (D_{D1}) for the First Water Desorption^a

Resin	WD ₁ %	SL ₁ %	$D_{D1} \times 10^8$ (cm ² s ⁻¹)	R_1 ^b
Bis-GMA	3.48 ± 0.12	3.32 ± 0.05	0.45 ± 0.04	1.6
Bis-EMA	1.87 ± 0.06	2.48 ± 0.16	1.95 ± 0.18	2.0
UDMA	3.17 ± 0.03	2.35 ± 0.25	0.46 ± 0.03	1.5
TEGDMA	6.20 ± 0.14	0.59 ± 0.12	2.44 ± 0.19	1.0
D ₃ MA	0.52 ± 0.13	0.05 ± 0.09	7.67 ± 3.46	1.0

^a Mean values ± standard deviation of four replicates.

^b $R_1 = (WS_1\% + SL_1\%)/WD_1\%$.

TABLE III
Thermodynamic and Kinetic Parameters for Second Water Sorption and Desorption^a

Resin	WS ₂ %	$D_{S2} \times 10^{8b}$ (cm ² s ⁻¹)	WD ₂ %	$D_{D2} \times 10^{8c}$ (cm ² s ⁻¹)	SL ₂ %
Bis-GMA	3.07 ± 0.07	0.58 ± 0.02	3.45 ± 0.05	0.49 ± 0.01	0.58 ± 0.03
Bis-EMA	1.55 ± 0.06	1.91 ± 0.13	1.81 ± 0.04	2.15 ± 0.13	0.44 ± 0.06
UDMA	4.59 ± 1.61	1.76 ± 0.25	3.14 ± 0.03	0.54 ± 0.05	1.24 ± 0.23
TEGDMA	6.28 ± 0.07	2.29 ± 0.04	8.26 ± 0.55	2.73 ± 0.61	-0.15 ± 0.07
D ₃ MA	0.48 ± 0.03	8.92 ± 2.30	0.50 ± 0.13	13.80 ± 5.15	0.04 ± 0.07

^a Mean values ± standard deviation of four replicates.

^b Second sorption diffusion coefficient.

^c Second desorption diffusion coefficient.

reported in Table IV. However, to test the statistical significance of the obtained values of the correlation coefficient R , we assumed firstly that the population correlation coefficient ρ is equal to zero (null hypothesis H_0). This test has been made by means of the Fisher's transformation method. The results of the Table IV show that in all cases and at the significance level of 95%, the hypothesis H_0 is rejected. Consequently, these results also reveal the existence of a strong positive correlation between the above mentioned thermodynamic parameters. Especially, the parameters WD₁% and WD₂% show a perfect linear dependence.

$$WD_2\% = 0.992 WD_1\%$$

or

$$WD_1\% \approx WD_2\%$$

namely, the desorbed masses of water, during the first and second desorption cycle, are equal.

The correlation of the kinetic parameters D_{S1} , D_{S2} , D_{D1} , and D_{D2} (Table V) showed that there is a strong positive correlation between these parameters, as those previously, by means of the tests on the significance of the obtained values of R . The null hypothesis H_0 (assuming that the population coefficient $\rho = 0$) is again rejected; especially for the parameters

D_{D1} , D_{D2} , and D_{S2} , D_{D2} , the following linear relationships were found:

$$D_{D2}/\text{cm}^2\text{s}^{-1} = -5.86 \times 10^{-9} + 1.667 (D_{D1}/\text{cm}^2\text{s}^{-1}),$$

$$D_{D2}/\text{cm}^2\text{s}^{-1} = -4.62 \times 10^{-9} + 1.290 (D_{S2}/\text{cm}^2\text{s}^{-1}).$$

The observed strong positive correlation between the kinetic parameters could be explained by assuming that the diffusion kinetics of the water in the studied materials is governed by similar mechanisms independently of the resin structure.

Finally, no correlation was established between the thermodynamic and kinetic parameters. This result indicates that the sorbed or desorbed amount of water does not depend on the rate of sorption or desorption process.

Ethanol sorption and desorption

Among the experimental curves $m_t = f(t)$ obtained for the ethanol sorption, only the curve obtained for the first sorption of EtOH in poly-Bis-GMA showed a maximum (Fig. 4). The curves presented in Figure 4 show the very good fitting of eq. (13) to the experimental data. From this fitting, the following quantities were calculated:

TABLE IV
Statistical Data of the Correlation (Fisher's z-Transformation) of the Parameters WS₁%, WS₂%, WD₁%, and WD₂% Determined from Sorption/Desorption of Water by Dental Resins

	R	Count	Z-value	P-value	Confidence limits	
					95% lower	95% upper
WS ₁ %, WS ₂ %	0.996	5	4.462	<0.0001	0.943	1.000
WS ₁ %, WD ₁ %	0.986	5	3.480	0.0005	0.791	0.999
WS ₁ %, WD ₂ %	0.986	5	3.482	0.0005	0.792	0.999
WS ₂ %, WD ₁ %	0.995	5	4.187	<0.0001	0.918	1.000
WS ₂ %, WD ₂ %	0.995	5	4.184	<0.0001	0.917	1.000
WD ₁ %, WD ₂ %	1.000	5	7.990	<0.0001	1.000	1.000

Hypothesized population correlation coefficient $\rho = 0$.

TABLE V
Statistical Data of the Correlation (Fisher's z-Transformation) of the Diffusion Coefficients D_{S1} , D_{S2} , D_{D1} , and D_{D2} Determined from Sorption/Desorption of Water by Dental Resins

	R	Count	Z-value	P-value	Confidence limits	
					95% lower	95% upper
D_{S1}, D_{D1}	0.919	5	2.236	0.0254	0.192	0.995
D_{S1}, D_{S2}	0.891	5	2.020	0.0433	0.043	0.993
D_{S1}, D_{D2}	0.902	5	2.094	0.0363	0.094	0.994
D_{D1}, D_{S2}	0.984	5	3.408	0.0007	0.771	0.999
D_{D1}, D_{D2}	0.996	5	4.374	<0.0001	0.936	1.000
D_{S2}, D_{D2}	0.994	5	4.102	<0.0001	0.908	1.000

Hypothesized population correlation coefficient $\rho = 0$.

$$D_{\text{EtOH}} = (5.4 \pm 0.4) \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$$

$$D_m = (1.10 \pm 0.09) \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$$

$$\text{EtOH}\% = 13.65 \pm 0.9$$

$$\text{Extr.}\% = 10.4 \pm 0.8$$

where D_{EtOH} is the diffusion coefficient of ethanol, D_m , the diffusion coefficient of monomer during its extraction by ethanol, EtOH%, the percentage amount of the absorbed ethanol, and Extr.%, the percentage monomer amount that was extracted after a very long (infinity) immersion time in ethanol.

The parameters $WS_1\%$, $WD_1\%$, D_{S1} , D_{D1} , and $SL_1\%$ calculated for the first ethanol sorption/desorption are presented in Table VI. For poly-Bis-GMA, as in the case of water sorption, it was found that

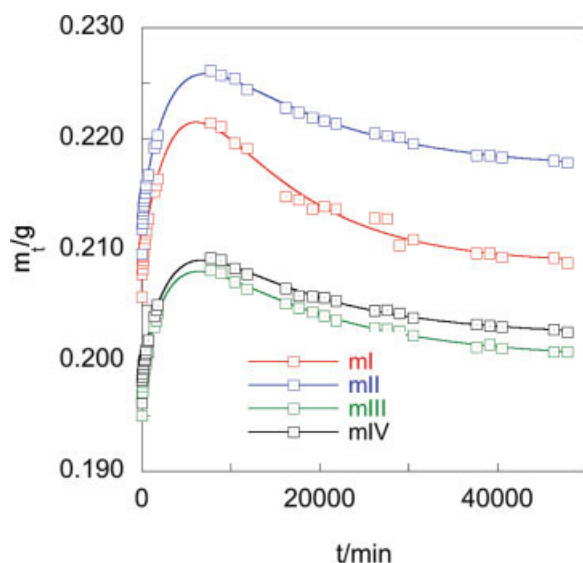


Figure 4 Variation of m_t with t of four independent experiments during the first sorption of ethanol in poly-Bis-GMA at 37°C. $L(\text{I}) = 0.1013$ cm, $L(\text{II}) = 0.1018$ cm, $L(\text{III}) = 0.0977$ cm, and $L(\text{IV}) = 0.0976$ cm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$\text{EtOH}\% \approx \text{WD}_1\% \quad \text{and}$$

$$\text{Extr.}\% \approx \text{SL}_1\%.$$

It is worth noting that poly-Bis-GMA showed the highest value of solubility.

The values obtained for $WS_2\%$, $WD_2\%$, D_{S2} , D_{D2} , and $SL_2\%$ during the second ethanol sorption/desorption are shown in Table VII.

From the comparison of the values of the solubility in water and ethanol (Fig. 5), the following conclusions are drawn:

1. For poly-Bis-GMA and poly-D₃MA, the following relations are valid:

$$(\text{SL}_1\%)_{\text{EtOH}} \approx (\text{SL}_1\%)_{\text{H}_2\text{O}}$$

and

$$(\text{SL}_1\%)_{\text{EtOH}} > (\text{SL}_1\% + \text{SL}_2\%)_{\text{H}_2\text{O}}$$

This means that in these resins a significant amount of monomer remains in the resins, even after the second water sorption.

2. For poly-Bis-EMA and poly-UDMA, it is

$$(\text{SL}_1\%)_{\text{EtOH}} \approx (\text{SL}_1\%)_{\text{H}_2\text{O}}.$$

3. Poly-TEGDMA showed a negative value for $SL_1\%$. Also small negative values were observed for $SL_2\%$ in all resins. The negative values could be attributed to the inclusion of ethanol into the resins.

Statistic comparison of parameters $WS_1\%$, $WS_2\%$, $WD_1\%$ and $WD_2\%$ for ethanol sorption/desorption (Table VIII) showed linear dependence between $WD_1\% - WD_2\%$ and $WS_2\% - WS_1\%$:

$$\text{WD}_2\% = 0.984 \times \text{WD}_1\% \quad (R^2 = 0.997)$$

$$\text{WD}_2\% = 0.986 \times \text{WS}_2\% \quad (R^2 = 0.991).$$

TABLE VI
Absorbed ($WS_1\%$) and Desorbed Ethanol ($WD_1\%$) Sorption Diffusion Coefficient (D_{S1}) and Desorption Diffusion Coefficient (D_{D1}) and Solubility (SL_1) for First Ethanol Sorption and Desorption Process^a

Resin	$WS_1\%$	$D_{S1} \times 10^8$ (cm ² s ⁻¹)	$WD_1\%$	$D_{D1} \times 10^8$ (cm ² s ⁻¹)	$SL_1\%$
Bis-GMA	5.76 ± 0.33	1.28 ± 0.43	14.09 ± 1.11	3.76 ± 0.64	10.94 ± 0.34
Bis-EMA	4.19 ± 0.31	0.304 ± 0.07	6.82 ± 0.29	0.21 ± 0.02	2.18 ± 0.18
UDMA	9.24 ± 0.34	0.62 ± 0.08	12.28 ± 0.26	3.33 ± 0.46	2.83 ± 0.36
TEGDMA	9.32 ± 0.37	0.18 ± 0.01	8.18 ± 0.71	1.28 ± 0.26	-0.98 ± 0.17
D ₃ MA	5.32 ± 0.15	1.24 ± 0.05	7.43 ± 0.21	0.89 ± 0.18	2.24 ± 0.22

^a Mean values ± standard deviation of four replicates.

TABLE VII
Thermodynamic and Kinetic Parameters for the Second Ethanol Sorption and Desorption^a

Resin	$WS_2\%$	$D_{S2} \times 10^8$ (cm ² s ⁻¹)	$WD_2\%$	$D_{D2} \times 10^8$ (cm ² s ⁻¹)	$SL_2\%$
Bis-GMA	14.19 ± 0.36	0.55 ± 0.01	14.33 ± 0.15	4.18 ± 0.37	0.12 ± 0.39
Bis-EMA	7.22 ± 0.15	0.17 ± 0.02	6.53 ± 0.17	0.19 ± 0.01	-0.37 ± 0.04
UDMA	12.01 ± 0.22	0.80 ± 0.06	11.65 ± 0.36	3.00 ± 0.25	-0.32 ± 0.07
TEGDMA	8.29 ± 0.33	0.31 ± 0.03	8.26 ± 0.55	2.73 ± 0.61	-0.15 ± 0.07
D ₃ MA	7.62 ± 0.07	1.20 ± 0.22	7.53 ± 0.07	1.28 ± 0.29	-0.02 ± 0.22

^a Mean values ± standard deviation of four replicates.

That is, the amount of ethanol absorbed during the second sorption is equal to that desorbed during the first and second desorption:

$$WD_1\% \approx WD_2\% \approx WS_2\%$$

Contrary to the behavior observed in the case of the water sorption, statistic correlation of the parameters D_{S1} , D_{S2} , D_{D1} , and D_{D2} , (Table IX) revealed significant correlation between D_{D1} and D_{D2} only. In all other cases and at the significance level of 95%, the null hypothesis H_0 (assuming that the population coefficient $\rho = 0$) is significantly valid. However, the comparison of the values of D_{S2} and D_{S1} for poly-TEGDMA, poly-UDMA, and poly-D₃MA showed that there is a relatively good linear correlation ($R = 0.989$) (Fig. 6). These resins are characterized by an aliphatic flexible chain between the methacrylate moieties, contrary to poly-Bis-GMA and poly-Bis-EMA, which contain aromatic rigid rings (Fig. 1).

In Figure 7, the values of the parameter D_{S2} , concerning the sorption of water and ethanol are comparatively reported. It is worth noting that the parameter D_{S2} expresses better the corresponding diffusion rate than the coefficient D_{S1} ; the very small values of $SL_2\%$ in comparison with the $SL_1\%$ values prove that the unreacted monomer is mainly extracted during the first sorption process. So, we can consider that the values of D_{S2} are practically free of any influence of the unreacted monomer. In poly-Bis-GMA it was found that

$$(D_{S2})_{H_2O} \approx (D_{S2})_{EtOH},$$

while in all other resins

$$(D_{S2})_{H_2O} > (D_{S2})_{EtOH}.$$

Poly-D₃MA showed the highest value for D_{S2} for both water and ethanol sorption.

The diffusion coefficient depends on several factors, such as the amount of unreacted monomer, the porosity, the crosslink density, the presence of polar/hydrophilic groups, etc. It was found that the

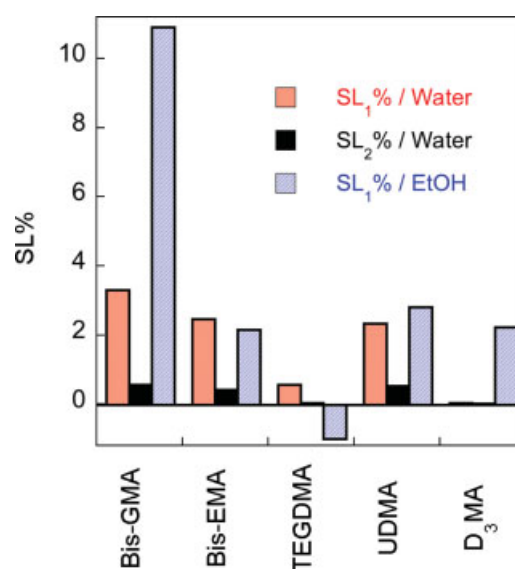


Figure 5 Values of solubility (SL%) of the studied resins in water and ethanol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE VIII
Statistical Data of the Correlation (Fisher's z-Transformation) of the Quantities WS₁%, WS₂%, WD₁%, and WD₂% Determined from Sorption/Desorption of Ethanol for the Studied Dental Resins

	R	Count	Z-value	P-value	Confidence limits	
					95% lower	95% upper
WS ₁ %, WS ₂ %	0.263	5	0.381	0.7031	-0.806	0.930
WS ₁ %, WD ₁ %	0.230	5	0.332	0.7400	-0.818	0.925
WS ₁ %, WD ₂ %	0.273	5	0.396	0.6921	-0.803	0.931
WS ₂ %, WD ₁ %	0.999	5	5.464	<0.0001	0.986	1.000
WS ₂ %, WD ₂ %	0.999	5	5.483	<0.0001	0.986	1.000
WD ₁ %, WD ₂ %	0.997	5	4.675	<0.0001	0.958	1.000

Hypothesized population correlation coefficient $\rho = 0$.

presence of polar/hydrophilic sites in the polymer structure may provide trapping sites that cause water to stop and interact, which severely hinder diffusion.^{19,20} Also in dental adhesive resins with no trapping sites, the transport of water proceeds relatively unhindered and consequently the diffusion coefficient is enhanced.²¹ So, the relatively high value of diffusion coefficient D_{S2} found for water diffusion in poly-D₃MA (Fig. 7) could be attributed to the higher hydrophobicity of this resin than the other resins (Fig. 1).

Finally, no correlation was established between the thermodynamic and kinetic parameters determined for ethanol sorption and desorption. This result indicates that the sorbed or desorbed amount of ethanol does not depend on the rate of sorption or desorption, as it was observed in the case of water sorption/desorption. The mechanism through which water diffuses into polymeric materials can be summarized as either a simple process of infiltration into the free space or specific molecular interaction of available hydrogen bond at hydrophilic sites. However, the governing factor depends on the polymer structure.²² The former mechanism is controlled by the free space available, such as commonly occurring microvoids and other morphological defects; an

increase in the free space should result in an increase in both the water absorbed and diffusion coefficient. The diffusion of water by molecular interaction is, on the other hand, controlled by the available hydrogen bond at hydrophilic sites. In our experiments, resins with low water- and ethanol-uptake showed a high diffusion coefficient (e.g., poly-D₃MA) and resins with high water- and ethanol-uptake showed a relatively low diffusion coefficient (e.g., poly-TEGDMA). This finding supports the molecular interaction theory for the diffusion of water and ethanol in dental dimethacrylate resins.

CONCLUSIONS

The experimental curves $m_t = f(t)$ obtained for the first water sorption by poly-BisGMA, poly-Bis-EMA, and poly-UDMA presented a maximum. This behavior was attributed to the synergistic effect of the water sorption and the simultaneous desorption of the unreacted monomer. A new equation describing this effect was produced [eq. (13)]. The fitting of this equation to the experimental data allowed us to determine the diffusion coefficient of the water, the water% uptake at equilibrium, as well as the

TABLE IX
Statistical Data of the Correlation (Fisher's z-Transformation) of the Diffusion Coefficients D_{S1} , D_{S2} , D_{D1} , and D_{D2} Determined from Sorption/Desorption of Ethanol by Dental Resins

	R	Count	Z-value	P-value	Confidence limits	
					95% lower	95% upper
D_{S1} , D_{D1}	0.543	5	0.861	0.3893	-0.651	0.964
D_{S1} , D_{S2}	0.575	5	0.926	0.3547	-0.624	0.967
D_{S1} , D_{D2}	0.534	5	0.843	0.3990	-0.658	0.963
D_{D1} , D_{S2}	0.190	5	0.272	0.7853	-0.832	0.918
D_{D1} , D_{D2}	0.955	5	2.673	0.0075	0.465	0.997
D_{S2} , D_{D2}	0.119	5	0.169	0.8654	-0.853	0.906

Hypothesized population correlation coefficient $\rho = 0$.

extracted mass of the unreacted monomer (solubility).

Also, in all cases it was shown that the determined parameters WS_1 and D_{S1} are apparent magnitudes. The first quantity expresses the apparent percentage of the absorbed water or ethanol, while the second quantity is related to the water diffusion coefficient, during its sorption process, as well as to the diffusion coefficient of the monomer extraction. The actual value of water sorbed is expressed by parameter $WD_1 = WD_2$ (water desorbed during first and second desorption). Based on this parameter, the studied resins follow the order: TEGDMA > Bis-GMA > UDMA > Bis-EMA > D₃MA. Unreacted monomer is mainly extracted by water during the first sorption ($SL_1\% \gg SL_2\%$). Comparison of the values of $SL_1\%$ obtained for various resins in water show the following order: Bis-GMA > Bis-EMA \approx UDMA \gg TEGDMA > D₃MA.

Taking into account that ethanol extracts also unreacted monomer, we can assume that the determined values WS_1 and D_{S1} are apparent values. The amount of ethanol sorbed by resins is expressed by the parameters $WS_2 = WD_2 = WD_1$. Based on this parameter, the resins follow the order: Bis-GMA > UDMA > TEGDMA > D₃MA > Bis-EMA. This order is completely different from the order found in the case of water, indicating that the sorbed water or ethanol depends both on the resin and the solvent structure.

The solubility of resins in ethanol follows the order Bis-GMA \gg UDMA > D₃MA > Bis-EMA > TEGDMA.

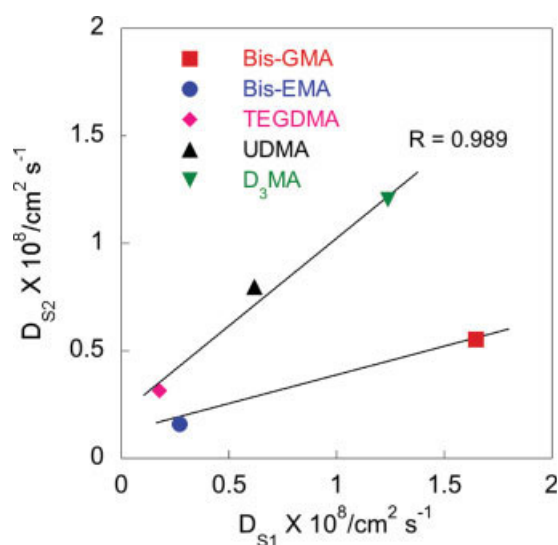


Figure 6 Dependence of the diffusion coefficient D_{S2} on the D_{S1} for the ethanol desorption from resins. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

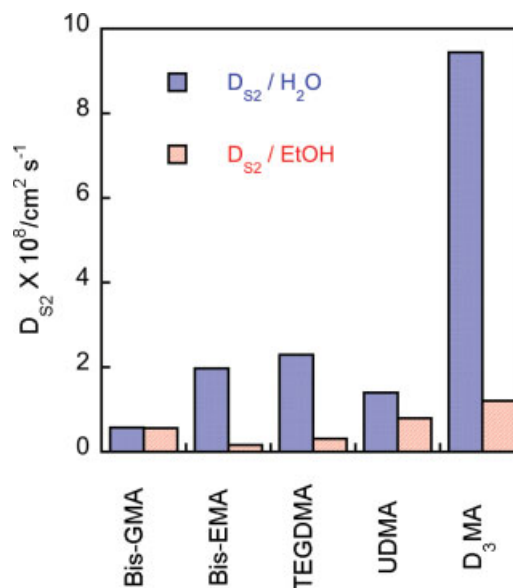


Figure 7 Values of parameters D_{S2} obtained for the sorption of water and ethanol by the resins. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Also it was found that for poly-Bis-GMA and poly-D₃MA, the solubility $SL_1\%$ in ethanol is much higher than the sum of solubility ($SL_1\% + SL_2\%$) in water, which indicates that water does not extract all the amount of unreacted monomer even during the second sorption. In poly-Bis-EMA and poly-UDMA, $SL_1\%$ in ethanol is almost equal to SL_1 in water.

As far as the diffusion coefficient is concerned, it was found to be independent of the amount of water or ethanol sorbed. Poly-D₃MA showed low water- or ethanol-uptake but the highest diffusion coefficient for both water and ethanol sorption, indicating that this process is governed by the formation of hydrogen bonds at polar sites.

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