

A comparison of water binding and mobility in contact lens hydrogels from NMR measurements of the water self-diffusion coefficient

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Abstract

Measurements of the water self-diffusion coefficient were made for a set of nine commercially available contact lens hydrogels, both at equilibrium water content (EWC) and as a function of reduced water content, using the pulsed field gradient NMR method. The data were shown to lie approximately on a universal curve, suggesting that water content (WC) itself was the predominant factor in determining the water diffusion coefficient. However, fitting of the data to a specific binding model suggested that subtle differences in the diffusional behaviour existed between the materials. These differences were measured in terms of the proportion of specifically bound water (p_{wb}). It was shown that the calculated proportions could be correlated with the EWC, and that they agreed reasonably well with the proportion of non-freezing water measured for similar materials using DSC. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Hydrogels are most commonly used today for the fabrication of soft, or disposable contact lenses, but are also used in other biomedical applications [1] such as for artificial implants, and as matrix materials for controlled drug release. In recent times there has been much interest in the interaction between the polymer and the water it binds, as this interaction is believed to determine some of the most important properties of the hydrogel.

A major disadvantage of hydrogel contact lenses is their tendency to dehydrate on the eye [2–6]. Although there have been many conflicting measurements of the extent of this dehydration, the majority of studies suggest that higher equilibrium water content (EWC) materials generally dehydrate to a greater extent on the eye [4,7,8]. This dehydration is thought to be related to the state of binding and average mobility of the water molecules in the hydrogel polymer. There is therefore interest in obtaining a better understanding of the hydration properties of contact lens hydrogels [9,10].

Proton nuclear magnetic resonance (NMR) has the potential to characterise this water binding and mobility in a directly quantifiable manner, and has been commonly used in studies of the water–polymer interaction [11–13].

In particular, the water self-diffusion coefficient (D), which can be measured using pulsed field gradient (PFG) NMR, is directly related to the potential for water to leave a hydrogel. Several NMR studies of diffusion in contact lens hydrogels have been performed in recent times [14,15].

The purpose of the current study is to use PFG NMR to measure the diffusional behaviour of water in a range of commercially available contact lens hydrogels of varying composition and EWC. It was anticipated that this would lead to a better understanding of those properties of the hydrogel that determine the rate of water diffusion, and how these properties might influence the potential of a particular hydrogel for on-eye dehydration.

2. Experimental

2.1. Sample protocol

A set of commercially available contact lens hydrogels was supplied by Benz Research and Development Corporation, Sarasota, FL, USA, Capricornia Contact Lens, Brisbane, Australia, and the Cornea and Contact Lens Research Unit, Sydney, Australia. The materials used are shown in Table 1 with their EWCs and compositions. The Benz and IGEL materials were supplied in the form of contact lens blanks or ‘buttons’, whereas actual contact lenses were used for the remaining samples.

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Table 1

The hydrogels used in this study. The Cibasoftware, SeeQuence2, Newvues and Acuvue hydrogels were supplied as actual contact lenses, whereas the Benz and IGEL materials were obtained in the form of contact lens blanks or 'buttons'

Hydrogel name	Composition	Nominal EWC at 20°C (%)	Measured EWC at 20°C (%)
Benz 38	HEMA	38	37.1 \pm 0.3
Benz G-5X	HEMA/GMA	58	58.4 \pm 0.3
Benz 55	HEMA/NVP	55	58.6 \pm 0.3
IGEL58	NVP/MMA	58	57.1 \pm 0.3
IGEL 67	NVP/MMA	67	67.1 \pm 0.3
Cibasoftware	HEMA	37.5	33.0 \pm 2.3
SeeQuence2	HEMA	38.6	33.8 \pm 2.1
Newvues	HEMA/NVP	55	52.7 \pm 2.0
Acuvue	HEMA/MA	58	55.9 \pm 2.1

All hydrogel samples were stored in sealed vials and equilibrated in phosphate buffered saline (PBS) at room temperature (approximately 22°C). The materials in button form were cut into smaller pieces to enable them to fit snugly into the 5 mm NMR tubes. Contact lens samples were rolled up before inserting in the tubes. PBS is a standard diluent used to hydrate commercial contact lenses and has constituents that mimic the pH and osmolality of the tears. Before measurement, each sample was removed from its vial, blotted thoroughly and quickly with lint free tissue and placed directly into the NMR tube. A Teflon vortex plug was used to restrict the air around the sample, and the tube was then sealed. It was then placed on a balance (accurate to \pm 0.05 mg) and weighed.

The tube containing the sample was equilibrated in the NMR probe for at least 15 min at 20°C prior to commencing the measurements. After the NMR measurements were complete, the sample was removed, re-weighed and the water loss (if any) calculated. In all cases this water loss was less than 5%. The hydrogel was then dried at least overnight (for larger samples the period was several days) at 80°C in a drying oven, then weighed and the water content calculated.

2.2. Preparation of hydrogels at different water contents

These experiments were performed using the same protocols as described above, except that between measurements, the same sample was partially dried using a drying oven, then equilibrated at this reduced hydration and weighed, the process being repeated several times until the WC reached 10–15% of EWC. Appropriate equilibration times were estimated based on calculations of the diffusive path length according to:

$$\langle r^2 \rangle = 6Dt \quad (1)$$

The calculations were performed using a diffusion coefficient based on prior measurements of D for similar materials and by setting the diffusive path length (r) equal to the

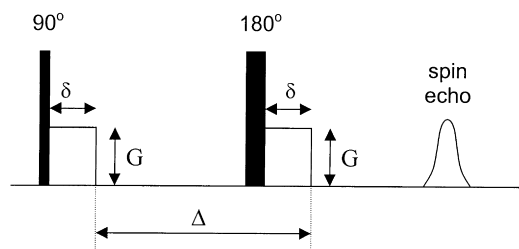


Fig. 1. The Stejskal–Tanner pulsed field gradient spin-echo pulse sequence.

sample thickness. Imperfect equilibration was checked for all samples by making two measurements of D that were at least 15 min apart and checking the reproducibility.

Since the drying process would presumably result in higher PBS concentrations (in the hydrogel) than at EWC, it was important to consider the effect on diffusion coefficient of these higher concentrations. Straightforward calculations showed that the molar concentration of NaCl in the gel increased in all cases to no more than 450 mM (about triple the concentration of NaCl in normal PBS (140 mM NaCl)). To represent the approximate range of increased concentration of NaCl in the gels, a second buffer was made up that contained four times (560 mM NaCl) the molar concentration of NaCl in normal PBS, and D was measured for this solution. The D value for the 560 mM NaCl PBS solution showed a -4.1% variation from that for normal PBS. This result implies that the reduction in D due to the increased buffer concentration would be approximately 4% in the worst case, but less than this in most samples. The error in the measured D value for the gels was typically 5% and this error is therefore expected to dominate, except for the lowest WC gels.

2.3. NMR measurements

Experiments were carried out using a Bruker MSL200 NMR spectrometer operating at 200 MHz for protons, with variable temperature control (accurate to \pm 1°C). Diffusion was measured using an actively shielded gradient set with maximum gradient \sim 100 G/cm in all three orthogonal directions. The shape and rise/ring down of the gradient pulses were optimised by using a small amount of gradient pulse pre-emphasis.

The self-diffusion coefficient (D) was measured using the standard Stejskal–Tanner [16] PFG spin-echo technique, which is shown in Fig. 1. The sequence incorporates identical gradient pulses before and after the 180° pulse in a 90–180° spin-echo sequence. The gradient amplitude (G) was stepped over a 16 point acquisition. The sequence measures the attenuation of signal due to diffusion of proton magnetisation within the sample, resulting in incomplete refocussing of the spin-echo by the 180° pulse. The attenuation is related to D via the Stejskal–Tanner equation

$$\ln \left(\frac{S(G)}{S(0)} \right) = -\gamma^2 D \delta^2 G^2 \left(\Delta - \frac{\delta}{3} \right) \quad (2)$$

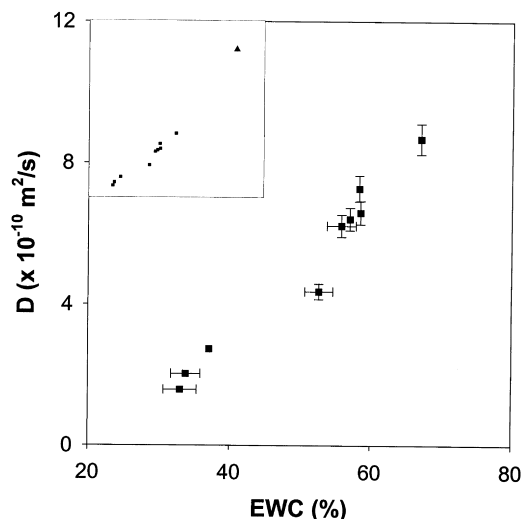


Fig. 2. D (SE) vs EWC for hydrogels at 20°C. The inset is all data (plotted on a larger scale) with the measured D value for PBS at 20°C included for comparison.

where $S(G)$, $S(0)$ are the measured signal amplitudes in the presence and absence of the gradient pulses; γ , the gyro-magnetic ratio of the proton; δ , the duration of the gradient pulses and Δ , their separation (see Fig. 1); G , the (stepped) gradient amplitude and D , the self-diffusion coefficient. For

measurements of D in the hydrogel samples, the maximum gradient amplitude G_{\max} and Δ were kept fixed, with δ adjusted to achieve a baseline for the highest gradient amplitude. However, when diffusion coefficients were measured over a very large range of temperatures or water contents, it was sometimes necessary to alter G_{\max} and/or Δ to ensure a baseline was achieved (or alternatively, that it was not achieved too quickly).

Initially D was measured for the hydrogels shown in Table 1 at 20°C, all at their respective EWC's. Following this, measurements of D were performed for each material equilibrated at reduced WC. The lowest hydration corresponding to approximately 10–15% of EWC represented the limit of measurable D using our hardware. In all cases, this equation was well fitted to the individual data sets. Fits were performed with two free parameters ($S(0)$ and D) using a Levenberg–Marquardt non-linear least squares regression.

3. Results

Fig. 2 is a plot of the measured D against EWC, at 20°C. The error bars on the EWC axis reflect the uncertainty in measuring the hydrogel wet and dry masses using an analytical balance accurate to ~ 0.5 mg. These errors are largest

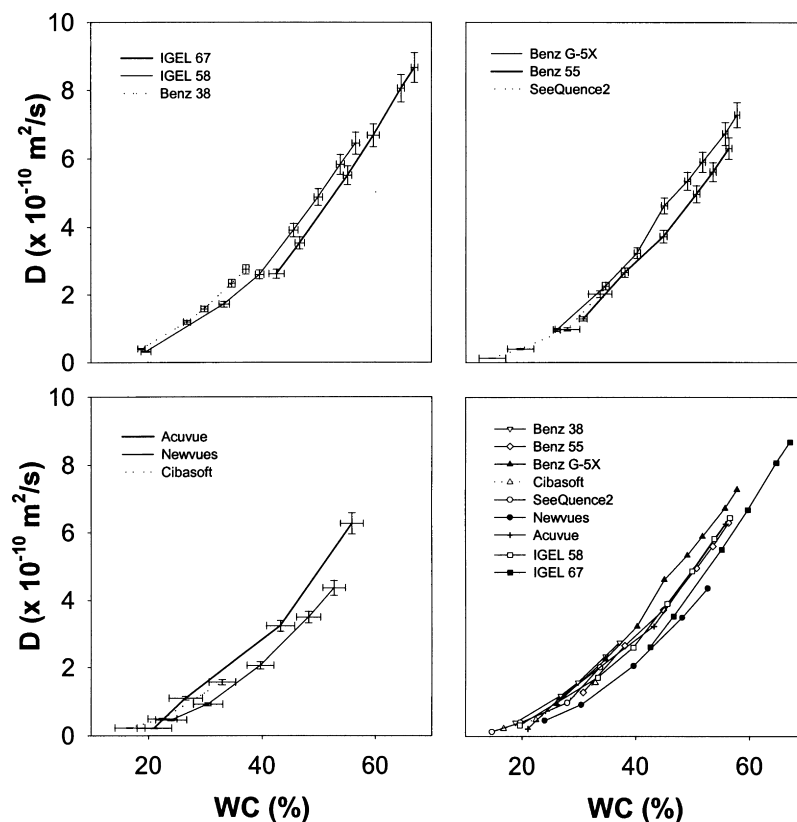


Fig. 3. D vs WC at 20°C for hydrogels equilibrated at varying WC. The last plot includes all data on the same graph. The samples studied in contact lens form, (Cibasoft, SeeQuence2, Newvues and Acuvue), show the largest WC errors and hence the largest uncertainties in the fit parameters (see Table 2).

for the samples of smallest absolute mass (i.e. those in contact lens form). The calculation of the error in the D values was based on preliminary reproducibility measurements which showed that the dominant source of error stemmed from systematic variations between different samples of the same type, with the reproducibility being typically about 5%. The error bars in D shown in Fig. 2 and later figures are representative of this systematic inter-sample reproducibility.

As Fig. 2 shows, D increases with increasing EWC. The inset is the same data on a larger scale, with the measured diffusion coefficient for PBS at 20°C added. As can be seen, the gel data extrapolate to approximately this value. The behaviour shows that D seems to be predominantly dependent on EWC (i.e. the relative amounts of water and dry polymer mass). As the number of water molecules per unit mass of polymer increases, the ability of these water molecules to diffuse increases (approximately linearly in this WC range) toward that of free water (100% EWC). The specific polymer composition does not seem to significantly influence the rate of water self-diffusion, since hydrogels of similar EWC but different polymer composition exhibit similar D values. This suggests that all these hydrogels are (to a first approximation) similar in terms of how the polymer network constrains the diffusion of water—only the relative water content is important.

To help to determine whether the data of Fig. 2 could indeed be approximated by a universal curve, or whether there were genuine outlying points on the plot which might be correlated with composition, each sample was hydrated to several different WCs as described in the experimental section. Fig. 3 shows these results plotted as D against WC.

As Fig. 3 shows, the behaviour of D is broadly similar to that shown in Fig. 2, although the plots clearly become non-linear at hydrations below about 40%. While the results are again consistent with all the data lying on or close to a universal curve, supporting the idea that D depends predominantly on the proportion of water in the gel, there is some suggestion of systematic differences between materials in these plots.

3.1. The specific binding model

The presence of the polymer will modify the diffusional behaviour of water in a PBS hydrated hydrogel, relative to that in ‘bulk’ PBS. At the simplest level the diffusion of a particular water molecule in a hydrogel can be viewed as being decreased relative to that in bulk PBS due to two factors. Firstly water molecules may be periodically bound to the polymer at one or more sets of specific binding sites. By specifically bound, we mean that at any instant in time, a certain proportion of the hydrogel water molecules are effectively immobilised such that they cannot diffuse. Presumably this occurs due to hydrogen bonding of these water molecules to polar groups on the polymer (e.g. hydroxyl, carboxyl and amide groups). Secondly, when the water molecules are not specifically bound, they will diffuse with

Table 2
Results of exponential decay fits for each gel

Gel name	EWC (%)	D_0 ($\times 10^{-10}$ m ² /s)	k
Benz 38	38	10.8 \wedge 0.8	0.82 \wedge 0.04
Benz G-5X	58	15.0 \wedge 0.5	1.00 \wedge 0.03
Benz 55	55	14.2 \wedge 0.8	1.07 \wedge 0.06
IGEL 58	58	15.5 \wedge 0.6	1.15 \wedge 0.04
IGEL 67	67	17.3 \wedge 0.2	1.42 \wedge 0.02
Cibasoft	37.5	7.4 \wedge 1.5	0.76 \wedge 0.09
SeeQuence 2	38.6	12.2 \wedge 4.6	0.93 \wedge 0.18
Newvues	55	11.9 \wedge 0.7	1.13 \wedge 0.05
Acuvue	58	14.3 \wedge 2.1	1.07 \wedge 0.15

an apparent water diffusion coefficient, D_w , that will generally be less than the diffusion coefficient of PBS due to the presence of the polymer chains which will hinder the translational motion of the hydrogel water molecules.

If the molecule spends an average time bound to the polymer, t_b and an average time moving between polymer sites, t_f then:

$$t_f = \frac{t_b(1 - p_{wb})}{p_{wb}} \quad (3)$$

where p_{wb} is the fraction of water molecules specifically bound to the polymer at any instant in time. From Eq. (1), it can be seen that the time t_f is proportional to the mean square displacement:

$$\langle r^2 \rangle = 6D_w t_f = 6D_w \frac{t_b(1 - p_{wb})}{p_{wb}} \quad (4)$$

Since the molecule does not diffuse during time t_b , $\langle r^2 \rangle$ is also its mean square displacement during an effective time ($t_b + t_f$) so that the apparent diffusion coefficient, D_{app} is given by:

$$D_{app} = \frac{\langle r^2 \rangle}{6(t_b + t_f)} \quad (5)$$

From Eqs. (4) and (5) it follows that:

$$D_{app} = D_w(1 - p_{wb}) \quad (6)$$

Using the definition of WC it can be shown that $p_{wb} = A \times (100 - WC)/WC$, where $A = m_{wb}/m_p$, m_{wb} is the mass of specifically bound water and m_p is the mass of the dry polymer. Therefore, on a plot of the measured D_{app} against $(100 - WC)/WC$, the slope will equal $-(m_{wb}/m_p) \times D_w$ and the intercept will equal D_w . If m_{wb} is assumed to remain constant as the gel is dehydrated until the state where $m_{wb} = m_w$ (total mass of water), the relationship should be linear. Fig. 4 shows the data of Fig. 3 plotted in this way (on the same scale) for each gel.

What is immediately apparent is that the data are non-linear. On the assumption that m_{wb} is constant (until $m_{wb} = m_w$), the specific binding model predicts that D_{app} should go to zero when $p_{wb} = 1$ or $m_w = m_{wb}$. Assuming a linear relationship, the WC for which $p_{wb} = 1$ will correspond to the intercept with the $x = (100 - WC)/WC$ axis. However,

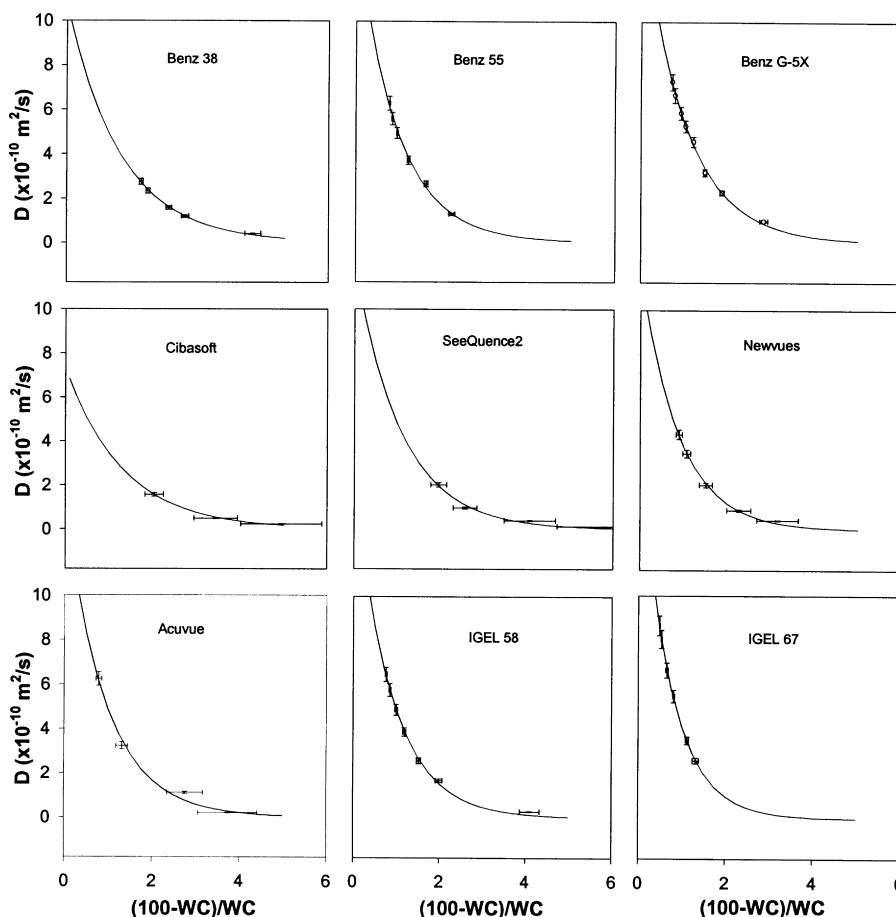


Fig. 4. D_{app} vs $(100 - WC)/WC$ at 20°C for each of the hydrogels studied, including fits to an exponential decay (see Eq. (7)).

as can be seen D_{app} does not approach zero linearly, instead having an asymptotic approach. The decreasing slope from left to right on the x -axis suggests that $A = m_{wb}/m_p$ (or simply m_{wb}) decreases as water content decreases. It was found empirically that the overall behaviour of the data was well described by an exponential decay

$$D_{app} = D_0 e^{-kx} \quad (7)$$

In this case, D_0 will describe the effective diffusion coefficient of the 'free' (unbound) water in the gel, and therefore is similar to D_w . The coefficient in the exponent describes the rate at which the slope (and hence m_{wb}/m_p) decreases as the factor $(100 - WC)/WC$ increases (i.e. WC decreases). Eq. (7) was fitted to the data of each gel using a Levenberg–Marquardt non-linear regression. The results are shown in Table 2 and the fitted curves are shown on the plots of Fig. 4.

As can be seen in Table 2, there are trends of increasing D_0 , and increasing k value with increasing EWC.¹ These

¹ For this data analysis, the EWC was taken to be the nominal EWC (which may differ slightly from the measured EWC primarily due to blotting inconsistencies). Since the measurements were made as a function of water content itself, the data was correlated with the nominal EWC, rather than any measured EWC.

trends are shown graphically in Fig. 5, together with linear regression lines in each case. The behaviour of D_0 with EWC suggests (linear regression analysis of variance (LRANOVA) $p = 0.0021$) that the effective gel 'free' water diffusion rate is higher for a higher WC gel. The results for k suggest (LRANOVA $p = 0.009$) that the rate of decrease of the slope of the D_{app} vs $(100 - WC)/WC$ plot is higher for a higher EWC gel. This implies that the effective mass of specifically 'bound' water (m_{wb}) with respect to mass of polymer (m_p) (in the specific binding model) decreases with increasing $x = (100 - WC)/WC$ (i.e. decreasing WC) at a greater rate for a higher EWC gel.

The specific binding model parameters can be calculated at any WC for each gel by calculating the tangential slope and y-intercept (D_w) at that WC from the fitted exponential decays. These parameters were initially calculated at the nominal EWC, for each hydrogel. The calculated values for the 'free' water diffusion coefficient, D_w and the mass of bound water relative to dry polymer mass, A ($= \text{slope}/D_w = m_{wb}/m_p$), are shown in Table 3. From the A values, the number of bound water molecules per total water molecules (p_{wb}) can be calculated using p_{wb} (at EWC) $= A \times (100 - \text{EWC})/\text{EWC}$. These bound water proportions are also shown in Table 3.

Table 3
Specific binding model fitted parameters for each gel, at EWC at 20°C

Gel name	D_w (at EWC) ($\times 10^{-10}$ m ² /s)	A (at EWC) ($= m_{wb}/m_p$)	p_{wb} (at EWC) (%)
Benz 38	6.7 \pm 1.1	0.350 \pm 0.120	57 \pm 20
Benz G-5X	12.5 \pm 1.4	0.580 \pm 0.088	42 \pm 6
Benz 55	11.1 \pm 0.8	0.570 \pm 0.160	47 \pm 13
IGEL 58	12.4 \pm 1.1	0.626 \pm 0.112	45 \pm 8
IGEL 67	14.7 \pm 3.7	0.834 \pm 0.050	41 \pm 2
Cibasoft	4.7 \pm 1.0	0.336 \pm 0.293	56 \pm 49
SeeQuence 2	6.9 \pm 0.4	0.375 \pm 0.607	60 \pm 96
Newvues	9.1 \pm 1.9	0.588 \pm 0.160	48 \pm 13
Acuvue	11.5 \pm 5.3	0.612 \pm 0.436	44 \pm 32

As Table 3 shows, the calculated values for D_w increase with increasing EWC as was the case for D_0 from the exponential fits. The calculated A values ($= m_{wb}/m_p$) also increase with increasing EWC. This behaviour is shown in the plot of Fig. 6, which also shows a linear regression (LRANOVA $p < 0.0001$) performed on this data. The errors shown were calculated by propagation of the intrinsic errors in D_0 and k (see Table 2). The results suggest that, as

expected, the higher EWC hydrogels bind more water per unit mass of polymer than the lower EWC gels. This is due to the greater hydrophilicity of the higher EWC polymers.

In contrast, the results for the *proportion of water molecules* that are bound (p_{wb}) (see Table 3) indicate that this proportion is higher for the lower EWC gels. This trend is shown in Fig. 7. Despite the relatively large errors in p_{wb} exhibited by the samples in actual contact lens form, a linear regression performed on the data resulted in LRANOVA $p < 0.0001$, which implies a greater than 99.99% chance of a genuine correlation existing. The specific binding model suggests that in a 38% EWC HEMA gel hydrated to its EWC at 20°C, more than half ($p_{wb} = 57$ –60%) of the water is specifically ‘bound’ to the polymer. It also suggests that, while for a higher EWC gel the ratio of bound water mass to polymer mass ($A = m_{wb}/m_p$) is increased (see Fig. 6), the proportion of the water that is ‘bound’ to the polymer (p_{wb}) is reduced. In all cases, greater than 40% of the water was calculated to be specifically ‘bound’.

Following from the behaviour of p_{wb} shown by Fig. 7, for the hydrogels at their EWC, the behaviour of p_{wb} can also be calculated as a function of WC for each material. This

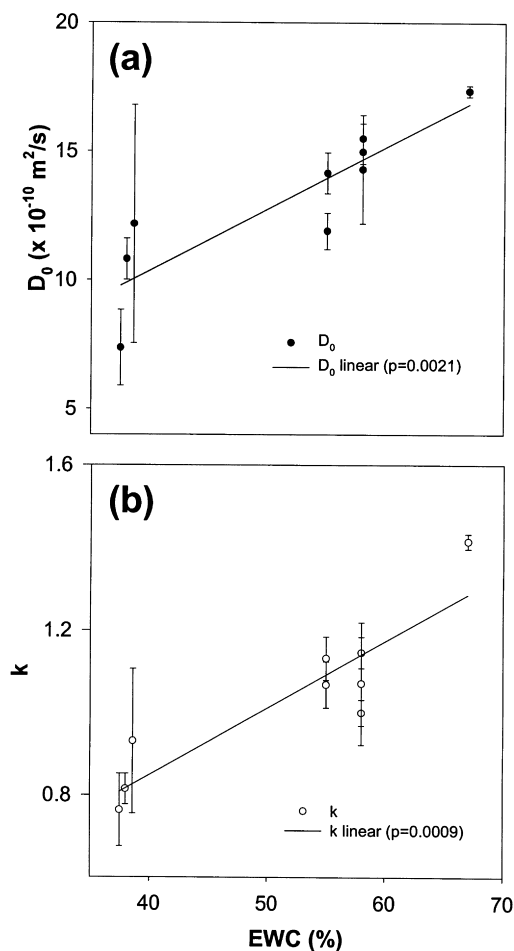


Fig. 5. (a) D_0 vs EWC and (b) k vs EWC, based on exponential decay fits to the data of Fig. 4 and the specific binding model. The error bars represent standard errors calculated by the non-linear regressions based on Eq. (7) (see Table 2). The solid lines are linear regressions performed on the data.

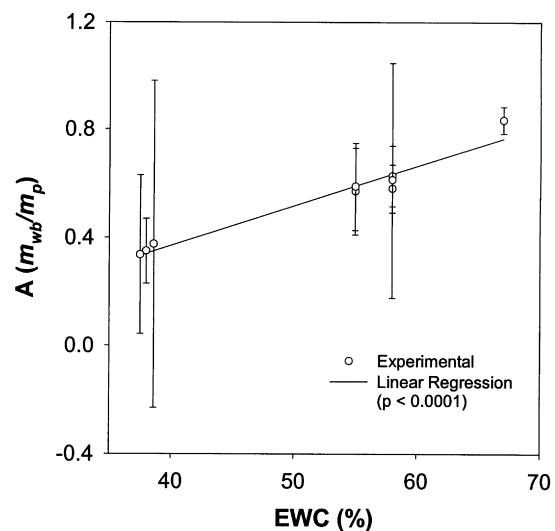


Fig. 6. $A (= m_{wb}/m_p)$ vs EWC for gels at EWC and 20°C, calculated from the parameters D_0 and k extracted from the fits of Fig. 4. The solid line is a linear regression performed on the data.

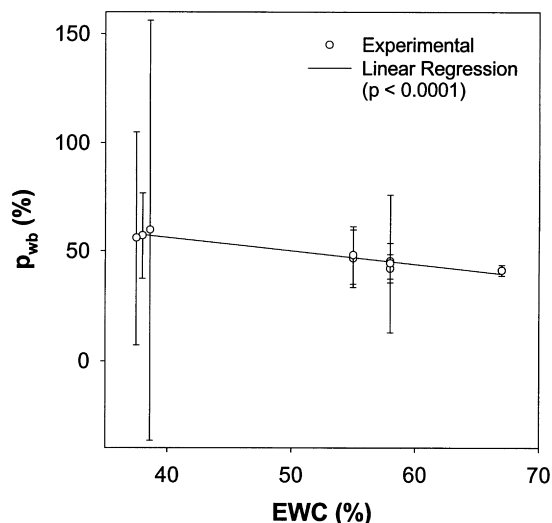


Fig. 7. Proportion of bound water (p_{wb}) at 20°C vs EWC from the specific binding model, for gels at or near EWC.

behaviour was calculated for each material based on the tangent to the exponential decays (see Fig. 4) at each WC, and is shown in Fig. 8. As the curves show, p_{wb} clearly increases as WC decreases. This is consistent with the intuitive notion that the most mobile (least strongly ‘bound’) water is lost first as a material dehydrates, leaving a higher proportion of more strongly ‘bound’ water. From the approximate slopes of the curves of Fig. 8 the rate of increase of p_{wb} (with decreasing WC) can be seen to be generally higher for the lower EWC gels, although it is not in general linear.

It can also be seen from Fig. 8 that, at a particular water content (e.g. 38%), p_{wb} is generally higher for a higher EWC material. Once again, this is thought to stem from the increased hydrophilicity of the higher EWC materials, leading to an increased proportion of specifically bound water when hydrated to the same WC as a lower EWC hydrogel.

3.2. Comparison of the specific binding results with differential scanning calorimetry (DSC)

One of the most commonly used techniques to study the

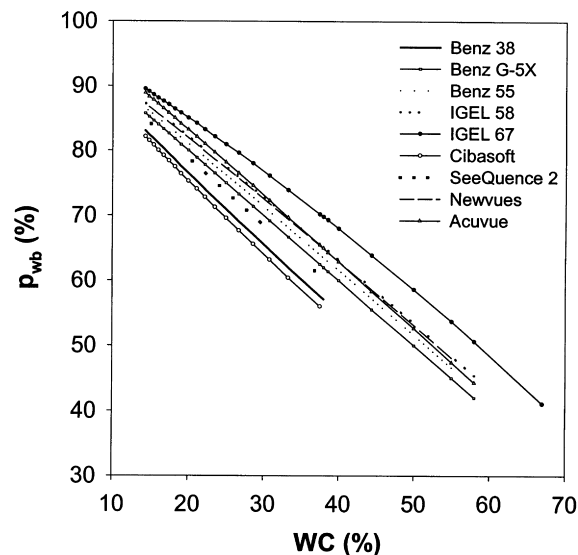


Fig. 8. Proportion of bound water (p_{wb}) vs WC, for each gel at 20°C.

behaviour of water in hydrogels has been differential scanning calorimetry (DSC). Generally from a DSC experiment, information about the states of water in a hydrogel and their respective proportions are obtained by measuring heat changes during phase transitions such as freezing or thawing. Typically these states have been termed ‘non-freezing’, ‘immobilised’ or ‘bound water’, and ‘free’ or ‘non-bound’ water. In a DSC experiment, the ‘non-freezing’ water is commonly thought to be water closely associated with (bound or immobilised by) the polymer, or represents a metastable supercooled state which is inhibited from attaining a true equilibrium state during cooling (freezing) by motional barriers [17].

A comparison of the calculated specific binding (p_{wb}) values obtained in this study was made with the proportions of ‘non-freezing’ water measured by Mirejovsky and co-workers [9] for similar hydrogels. This comparison is shown in Table 4, and as can be seen, the p_{wb} values show reasonable agreement with the DSC results. The trends of increasing amount of ‘non-freezing’ water with decreasing EWC agree with the trends shown for the specifically ‘bound’ water. However, for the higher water content

Table 4

Comparison of ‘bound’ water proportions measured at 20°C using the specific binding model (see Table 3) and ‘non-freezing’ water proportions measured using DSC by Mirejovsky [9] for similar contact lens materials

Current study using specific binding model				Study by Mirejovsky using DSC			
Material	EWC (%)	Composition	% bound water	Material	EWC (%)	Composition	% non-freez'g water
Benz 38, Cibasoft and SeeQuence 2	37.5–38.6	HEMA	56–60	Hydron Zero 6	35	HEMA	72
Newvues	55	HEMA/NVP/MA	48	Softcon EW	52	HEMA/NVP/MA	44
Acuvue	58	HEMA/MA	44	Acuvue	53	HEMA/MA	28
IGEL 67	67	NVP/MMA	41	Vistamarc	53	HEMA/MA	33
				Hydron Z-67	64	NVP/MMA	35
				Sof-form 67	63	NVP/MMA	37

materials the proportions of specifically ‘bound’ water are higher than those measured by DSC. This could be because the EWCs measured by Mirejovsky et al. were in all cases lower than the nominal EWCs, an effect they attributed to the PBS they used. Despite this, the results generally support the idea that the slope of the specific binding plot (Fig. 4) at EWC provides an estimate of the proportion of effectively ‘bound’ water that is similar to the proportion of ‘non-freezing’ water measured using DSC.

4. Conclusions

The specific binding model suggests that the diffusional behaviour of water in these hydrogels can be modelled by assuming the existence of a proportion of specifically ‘bound’ water that (at any instant in time) is effectively immobilised, but which is in rapid exchange with the remaining ‘free’ water. The non-linear behaviour of the plots of Fig. 4 suggests that the absolute mass of specifically ‘bound’ water decreases, although the *proportion* of water specifically bound was shown to increase as a gel dehydrates. The parameters measured using this description were shown to vary approximately linearly with the EWC as did the calculated proportion of specifically ‘bound’ water (p_{wb}) at the EWC, for each material. It was also shown that for two hydrogels at the same WC, p_{wb} is generally higher for a material with a higher EWC. This is thought to be due to the increased hydrophilicity of the higher EWC polymers. The rate of increase of p_{wb} as the gels dehydrated was found to be generally lower for a higher EWC material. It should also be mentioned that while a decrease in bound water content with overall WC would be predicted by a simple equilibrium between bound and free water described by an equilibrium constant, our results are not consistent with such a simple model which would predict a constant ratio between bound and free water components.

Our results suggest that, while the hydrogel water diffusion coefficients depend largely on overall water content, subtle differences with polymer composition may exist. These differences can be quantified in terms of the proportion of specifically bound water and were shown to approximately correlate with the equilibrium water content. This is

thought to be due to the higher hydrophilicity of a higher EWC material.

Increased water mobility is generally associated with a higher potential for the water to leave the hydrogel. Therefore, the general dominance of the WC in determining the diffusion coefficient in these hydrogels concurs with the conventional wisdom regarding on-eye dehydration [4,7,8], that higher EWC materials generally dehydrate to a greater extent on the eye. Similar studies may be used in the future to identify materials which show anomalous diffusive behaviour and which therefore have an improved potential to maintain their EWC on the eye.

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