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Hydrogels of β-cyclodextrin crosslinked by acylated poly(ethylene glycol): Synthesis and properties

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ABSTRACT

Networks of β-cyclodextrin have been prepared by reaction with acylated poly(ethylene glycol) with a molar mass of 600 g/mol. Samples with different β-cyclodextrin/poly(ethylene glycol) ratios: 1/4, 1/6, 1/8 and 1/10 have been prepared. Both components are bonded by ester groups, resulting in a network that can be degraded by hydrolysis in basic and acidic media. The maximum stability of the hydrogels is reached at pH 4. The hydrogel percentage water content depends on β-cyclodextrin content ranging from 82 to 98, and the swelling data obtained for these hydrogels fit well with a second order kinetics. The sorption behavior of these hydrogels has been tested by employing 1-naphthol as model molecule. The sorption capacity is close to other cyclodextrin networks previously reported and depends on the hydrogel composition and the concentration of 1-naphthol.

1. Introduction

Hydrogels are materials which can be synthesized with a large variety of properties and have practical applications in many fields such as: medicine, agriculture, pharmacy and in the food industry. Hydrogel properties depend on molecular structure and for this reason the synthesis of hydrogels with new molecular structures is an area of great academic and industrial interest.

A family of molecules with a great ability to form inclusion complexes with hydrophobic molecules or with the hydrophobic moieties of large molecules is Cyclodextrins. Cyclodextrins are a family of cyclic oligosaccharides consisting of six (α-CD), seven (β-CD) or eight (γ-CD) glucopyranose units, which are joined together by α (1−4)-linkage forming a torus-shaped ring structure. Cyclodextrins are obtained by degradation of starch. In these molecules, the primary and secondary hydroxyl groups of the glucopyranose units are located in the outer of the torus, and the cavity presents a relative hydrophobic character [1]. Consequently, they are able to build up host–guest complexes by inclusion of suitable hydrophobic molecules [2]. This capacity for forming inclusion complexes makes cyclodextrins useful in separation processes as chromatographic fillers[3,4] as drug release materials [5,6] and for contaminants removal [7]. However, cyclodextrins are water soluble and some applications require that they would be water insoluble. Because its capacity for forming complexes is not affected when attached to water insoluble polymeric chains there is great interest for synthesizing crosslinked cyclodextrins (hydrogels) using different chemicals, for example: epichlorohydrin [8–11], diisocyanates [12,13], dichlorides [12,13] and glutaric dialdehyde [14].

Recently our group reported the crosslinking of β-cyclodextrin (β-CD) with poly(ethylene glycol) (PEG) modified with isocyanate groups at both chain ends [15,16]. The modified PEG chains react with the hydroxyl groups of the cyclodextrin forming crosslinking points. Because the PEG is a hydrosoluble polymer, the network behaves as hydrogel. The swelling degree of the hydrogel can be regulated by varying the molar mass of the PEG.

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In this work we present a new synthetic route to crosslink β-CD with PEG. We have modified a commercial sample of poly(ethylene glycol) bis(carboxymethyl)ether (PEGBCOOH) into the acylated form bis(carboxymethyl) ether dichloride (PEGBCOCl). The PEG/β-CD crosslinking reaction is now performed via esterification, resulting in a more hydrophilic network than the previously reported, and susceptible of hydrolytic erosion.

The β-CD/PEGBCOCl hydrogel was synthesized using different β-CD/PEGBCOCl ratios. Their swelling behavior, hydrolysis resistance and capacity to adsorb 1-naphthol (model molecule) are reported.

2. Experimental part

β-cyclodextrin (β-CD) (99.5% of purity) was kindly supplied by Roquette Laisa España S.A., and was dried under vacuum at 373 K for 24 h and stored in a desiccator before use. Poly(ethylene glycol) bis(carboxymethyl) ether (PEGBCOOH) (Aldrich), with a nominal average molar mass of 600 g/mol, was used as received.

N,*N*-Dimethylformamide (DMF), dichloromethane and benzene (Panreac) HPLC grade were dried over 4A molecular sieves. Thionyl chloride (Aldrich) was used as received. Buffer solutions of pH 1–9 (Panreac) were used as received.

The preparation of the PEGBCOCl was carried out according to the method previously employed by Lin et al. [17] and Chacon et al. [18] (see Fig. 1). A solution of PEGBCOOH (10 g) in dichloromethane (40 mL) was treated at room temperature with an excess of thionyl chloride (7.5 mL) under constant stirring for 24 h. Then, the dichloromethane and the excess of thionyl chloride were removed under vacuum, at 40 °C. In order to remove traces of thionyl chloride left, several milliliters of benzene were added to the PEGBCOCl, and the solution evaporated under vacuum. This procedure was repeated twice. The PEGBCOCl was dissolved in DMF (25% w/w). A solution of β-CD in DMF (16.5% w/w) was also prepared. Hydrogels were synthesized by injecting the required amounts of the PEGBCOCl and β-CD solutions in the reactor. The mixture is maintained under vigorous stirring for 10 min at room temperature, and then is transferred to moulds composed by two pieces of sylanized glass separated by a Teflon disc, and stored at 50 °C for 48 h. After reaction, the hydrogels were purified by immersing in DMF for 48 h and then in methanol for 72 h; the solvents were replaced every 24 h. Finally, the hydrogels were dry at room temperature (22 °C) for 48 h and then dried in a vacuum oven at 50 °C to constant mass. Hydrogels with β-CD /PEGBCOCl molar ratios 1/4, 1/6, 1/8 and 1/10 were prepared.

Infrared spectra of the dry hydrogel and pure components were recorded with a ReactIR™ 1000 Reaction Analysis System (ASI Applied Systems, Mettler-Toledo Corp.) equipped with a light conduit and DiComp (diamond composite) insertion probe, used as a multiple reflection ATR (attenuated total reflection) element. Spectra were taken with resolutions of 4 cm^{-1} and were averaged over 128 scans.

The composition of the hydrogels was determined from analysis by SEC of their hydrolysis degradation products in 0.1 N sodium hydroxide. To carry out the hydrolysis approximately 14 mg of the gel were introduced into a 10 mL volumetric flask and an aqueous NaOH 0.1 N solution is added to fill the flask to the mark. The mixture was maintained at room temperature for 24 h to complete the hydrolysis. Then the mixture was injected in the chromatograph. The SEC experiments were carried out in a chromatograph composed of a Knauer HPLC64 pump, a Knauer differential refractometer, a Rheodyne injector loop of 100 μL and one TSKgel Alpha-3000 column, using water as eluent at a flow of 0.7 mL/min. To determine β-CD and PEGBCOOH elution times, pure compounds were treated in a similar way that the hydrogels and injected in the chromatograph.

Swelling kinetics was determined by submerging hydrogels disks (7 mm diameter, 1 mm thickness) in water, at 25 °C. Samples were taken at different times, water was removed from the sample surface by lightly blotting with filter paper and weighed. Experiments were repeated twice.

1-Naphthol sorption capacity of the hydrogels was determined as follows: finely divided dry gel weighting approximately 28 mg were mixed with 8 mL of an aqueous solution of 1-naphthol, of known concentration in a capped amber vial. The mixture is stirred for 48 h maintaining the temperature at 30 °C by using a thermostated bath. The amount of remaining 1-naphthol in the aqueous phase was determined by filtering the solution (Millipore Millex-HV 0.45 μm) and then analysed by UV spectroscopy (GBC Instruments Cintra 303) using the peak at 321 nm. Sorption experiments were carried out using three different 1-naphthol concentrations: 2.1×10^{-4}, 5.2×10^{-4} and 10.4×10^{-4} mol/L, and repeated twice.

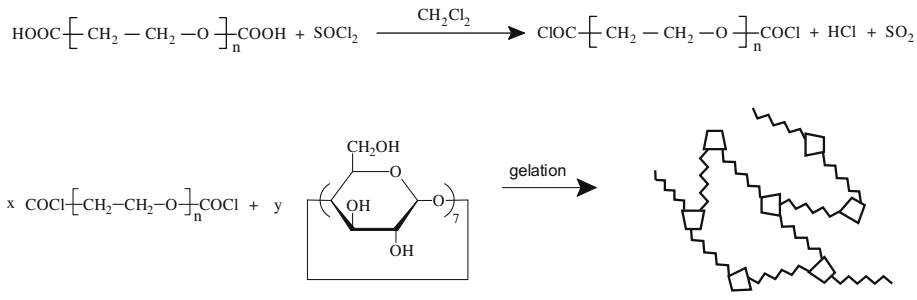

Fig. 1. Modification of PEGBCOOH to PEGBCOCl with thionyl chloride and reaction among PEGBCOCl and β-CD, together with an idealized outline of the structure of the gel.

3. Results and discussion

3.1. Synthesis and characterization

Poly(ethylene glycol) (PEG) can be prepared with a variety of end chain groups and some modified PEGs, as PEG-BCCOOH, are commercially available. In PEGBCOOH, the terminal carboxyl groups can be easily transformed into acyl chloride ones by reaction with thionyl chloride [17,18]. The resulting acylated poly(ethylene glycol) (PEGBCOCl) is then capable to react with hydroxyl containing molecules by esterification. The reaction with molecules, as β-CD, containing more than two hydroxyl groups can conduce to network formation. Fig. 1 shows this strategy for the synthesis of PEG/β-CD networks, where β-CD is used as a crosslinker.

To study *in situ* the gel formation mechanism (crosslinking), the reaction was followed by IR using an ATR insertion probe. The procedure to obtain the hydrogel was similar to that described before, but now the reaction was carried out in a round-bottom three-neck flask reactor under magnetic stirring, and a FTIR probe was inserted in the flask through the central neck, while the side ones were blocked using a septa. The reactor was placed in an oil bath at 30 °C and purged with dry nitrogen (background). A solution of PEGBCOCl in DMF (25% w/w) was injected into the flask and, later on, a solution of β-CD in DMF (16.5% w/w). The reaction, corresponding to a 1/6 β-CD/PEGBCOCl molar ratio, was followed for 48 min, when gel point is obtained. IR spectra were taken every 3 min.

Fig. 2 shows an amplification of the IR spectra in the region 1720–1840 cm^{-1} (carbonyl bands). The peak at 1806 cm^{-1} due to the stretching vibrations of the carbonyl groups of the acyl chloride decreases with reaction time, while the peak due to the carbonyl group of the ester (1752 cm^{-1}) increases indicating the formation of ester groups. By considering the above discussions the hydrogel structure proposed in Fig. 1 is confirmed.

Fig. 3 shows the infrared spectra of two of the gels with different β-CD/PEGBCOCl ratios (after being purified) and

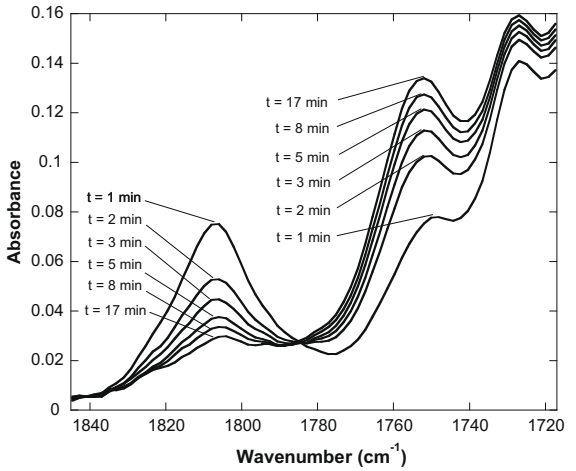

Fig. 2. Time dependence of the infrared spectra for the reaction of PEGBCOCl with β-CD in DMF at 30 °C.

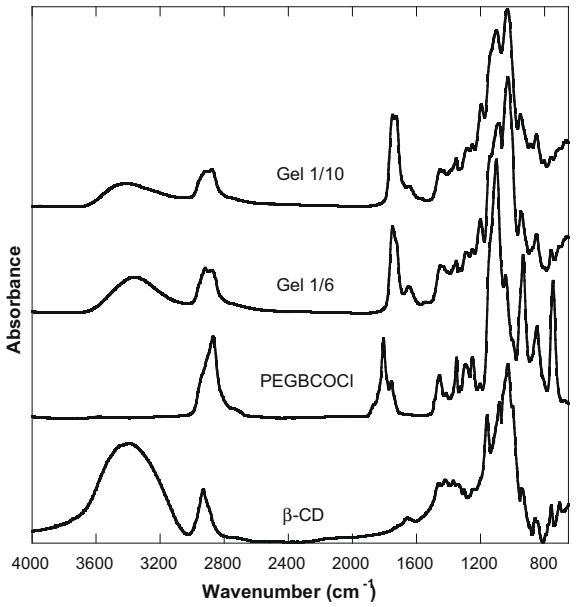

Fig. 3. ATR infrared spectra of PEGBCOCl, β-CD, and gels with a β-CD/PEG molar ratio of 1/6 and 1/10.

the spectra of the pure reagents: β-CD and PEGBCOCl. In the spectra of the hydrogels it can be observed a band at 1750 cm^{-1}, due to the ester group, and also the presence of bands that corresponds to PEG (1099 cm^{-1}) and β-CD (1028 cm^{-1}). The relative contribution of these bands is in agreement with the different β-CD/PEG molar ratios employed in the feed for these gels. Also, the band due to the hydroxyl groups (3200–3600 cm^{-1}) decreases as the β-CD/PEG molar ratios does in the feed, but also because as the amount of PEGBCOCl increases, more hydroxyl groups react with the acyl chloride to form ester groups. In consequence, the infrared spectra of the purified gels confirm the structure proposed in Fig. 1.

The compositions of the prepared gels were determined by analyzing their degradation products after the complete hydrolysis of the networks. Under alkaline hydrolysis conditions, the networks must be completely converted into PEGBCOOH and β-CD, that are stable to basic hydrolysis [19,20]; and both components can be separated and quantified by SEC.

Fig. 4 shows that one of the hydrolysis products has the same elution time that the PEGBCOOH, confirming the hydrolysis reaction. The β-CD peak does not interfere with the PEGBCOOH peak since it elutes at very large times in our columns. To determine the PEGBCOOH content in the product of the hydrolysis, a calibration was carried out using different PEGBCOOH concentrations and measuring its area under the peak. The hydrogel compositions, expressed as weight percent of β-CD, are shown in Table 1, where it can be observed that the experimental hydrogel composition was similar to the composition charged in the reactor.

3.2. Gel stability to hydrolysis

It is well known that ester groups hydrolyze in basic and acidic media [21]. When this occurs the degree of

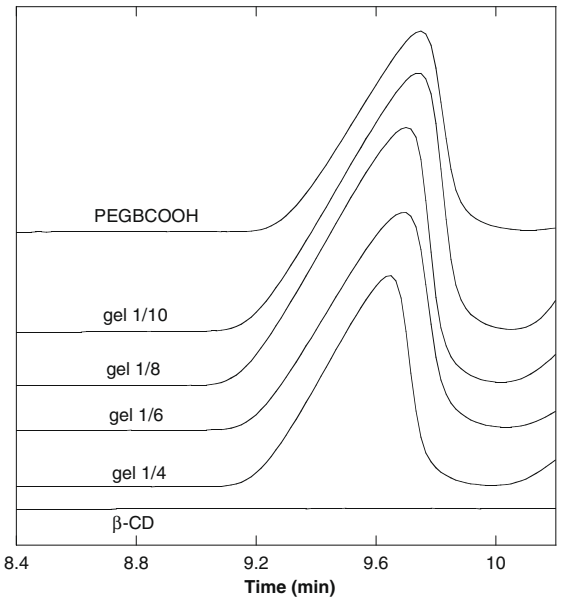

Fig. 4. Chromatograms of β-CD, PEGCOOH and hydrolyzed hydrogels.

Table 1
Experimental and theoretical hydrogel compositions.

Sample	% β-CD (exp.)	% β-CD (theor.)
Gel 1/4	28.2	32.1
Gel 1/6	25.9	24.0
Gel 1/8	20.5	19.1
Gel 1/10	16.5	15.9

crosslinking of the hydrogel decreases modifying its swelling behavior and eventually the hydrogel will dissolve. The Flory–Rhener theory [22], indicates that the swelling capacity increases as the crosslinking decreases. To determine stability, hydrogels were submerged in tampon solutions from pH 1 to 9 and maintained at 25 °C using a thermostated bath until complete visual disappearance. According to the data presented in Table 2 for two hydrogels with different β-CD/PEGBCOCl ratios, it can be concluded that the stability of the hydrogels is very low in basic media and also at pH 1. The highest stability of hydrogels is attained at pH 4. The dissolution is much faster at basic pH, in agreement with a most effective basic than acid catalyst for ester hydrolysis [21]. Table 2 shows that for all pH's complete dissolution occurs earlier when using a higher β-CD/PEGBCOCl ratio (1/6). This behavior can be explained taking into account the structure proposed for the gel (Fig. 1), an increase in the β-CD/PEGBCOCl ratio implies a small number of PEG chains bounded for cyclodextrin ring. As cyclodextrin ring acts like crosslinker, less ester linkages need to be broken at the β-CD/PEGBCOCl higher ratio, thus the time for complete hydrogel hydrolysis will be lower.

Table 2
Time (in hours) for complete hydrogel dissolution, at 25 °C.

Hydrogel ratio	pH								
	1	2	3	4	5	6	7	8	9
1/6	20	120	600	1248	912	336	48	12	6
1/10	24	552	1440	>1824	>1824	768	144	20	12

For some applications, materials which can be hydrolyzed at desired rates are needed. In pharmaceutical applications, compounds with controlled erosion rates are currently used to release drugs [23]. The rapid erosion of these hydrogels in basic media may be a consequence of the ability of cyclodextrins to act as catalyst for hydrolysis, particularly in basic media. It has been reported that cyclodextrins can act as catalyst for ester hydrolysis of compounds which form inclusion complexes [24–26].

3.3. Hydrogel swelling

Because the hydrogels have the best stability toward hydrolysis at pH 4, water swelling experiments were carried out at this pH (adjusted by using HCl 0.1 M) and at 25 °C. The degree of swelling was determined by using Eq. (1), where W% is the hydrogel percentage water content:

$$W\% = 100 \times \frac{(\text{wet weight} - \text{dry weight})}{\text{wet weight}} \quad (1)$$

In Table 3, *W%* values are shown for all the prepared hydrogels at 298 K, after 24 h, when the swelling equilibrium is attained. Higher equilibrium swelling values are obtained at the higher β-CD content (excepting the 1/10 ratio). This can be explained taking into account that a reduction in the β-CD content of the hydrogels conduces to a more compact structure in the network, with more PEG chains bonded by cyclodextrin ring, reducing the swelling capacity of the hydrogel.

The presented results can be compared with the previously reported by Cesteros et al. [15] for cyclodextrin networks prepared from PEG (M_n = 600 g/mol) end-capped with isocyanate groups, by using hexamethylene isocyanate as reactant. In these hydrogels, for similar PEG/β-CD ratios, notably lower equilibrium swelling values (61–65%) were obtained. These results point out the relevance of the hydrophobicity of the PEG chain ends on the swelling capacity of this kind of hydrogels.

The swelling kinetics of the hydrogels were also measured at pH 4 from samples cut into discs with similar dimensions. Fig. 5 shows the swelling kinetics for hydrogels prepared with different β-CD/PEGBCOCl ratios.

The swelling data obtained for these hydrogels fit well with a second order kinetics, also proposed for the previously studied networks [16]:

$$\frac{dW}{dt} = K(W_\infty - W)^2 \quad (2)$$

Table 3
W% of the hydrogels, at 298 K and pH 4, for different compositions.

Gel	1/4	1/6	1/8	1/10
W% (g water/g xerogel)	98.0	89.6	82.0	84.7

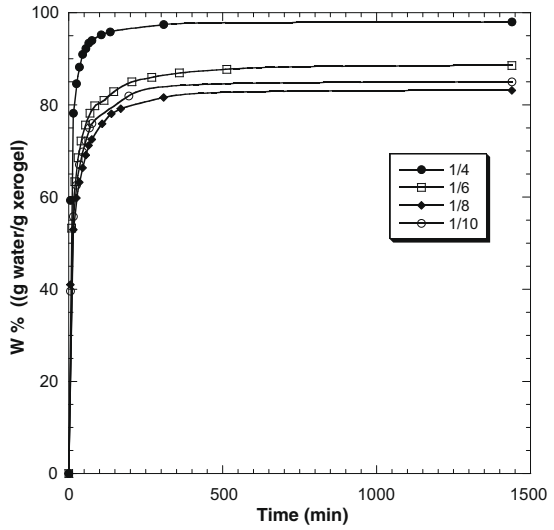

Fig. 5. Variation of the water content (W%) with time, at 298 K, for the different hydrogels.

where W is the weight fraction of water in the hydrogel at a given time, W_∞ is the weight fraction of water at the swelling equilibrium condition and K is the overall transfer coefficient.

The integrated form of the Eq. (2) is given by

$$\frac{t}{W} = A + Bt \tag{3}$$

where $A = 1/KW_\infty^2$ and $B = 1/W_\infty$.

In Fig. 6 it can be observed that by plotting t/W against time a straight line is obtained, from which K can be evaluated from the intercept value (A). The K and W_∞ values obtained using the least-squares method are shown in Table 4. An excellent correlation is found between the values of W_∞ calculated according to Eq. (3) and the experimental ones (Table 3). On the other hand, K values reported for cyclodextrin hydrogels crosslinked with a PEG modified hexamethylene isocyanate at its chain ends [16], are smaller (between 7 and 9×10^4 min^{-1}) than the values obtained here. This can be explained because they have more hydrophobic groups.

Table 4
W_∞ and K values for the hydrogels as a function of β-CD/PEGBCOCl ratio.

Hydrogel ratio	W_∞ (g water/ g xerogel)	$K \times 10^4$ (g water/ g xerogel)$^{-1}$ min^{-1}
1/4	0.98	32.3
1/6	0.90	12.6
1/8	0.83	14.2
1/10	0.85	13.7

3.4. Sorption capacity of the hydrogels for 1-naphthol

Taking into account the ability of cyclodextrins to form inclusion complexes with different molecules, we studied the sorption capacity of our hydrogels against α-naphthol. This molecule and its isomer 2-naphthol have been used as inclusion models in networks containing β-CD [28–30] due to its high formation complex constants with β-CD [27]. To measure the sorption capacity (q) of 1-naphthol by the hydrogels synthesized here, three concentrations of 1-naphthol in water were used (2.1×10^{-4}, 5.2×10^{-4} and 10.4×10^{-4} mol/L) in batch experiments.

In Fig. 7 is presented the sorption capacity of these hydrogels for different starting concentrations of 1-naphthol.

It has not been possible to obtain reliable results for gels of composition 1/4 due to their high capacity of swelling, their mechanical properties are very poor, so that after the magnetic agitation in the experimental protocol the filtration of their solution is not possible.

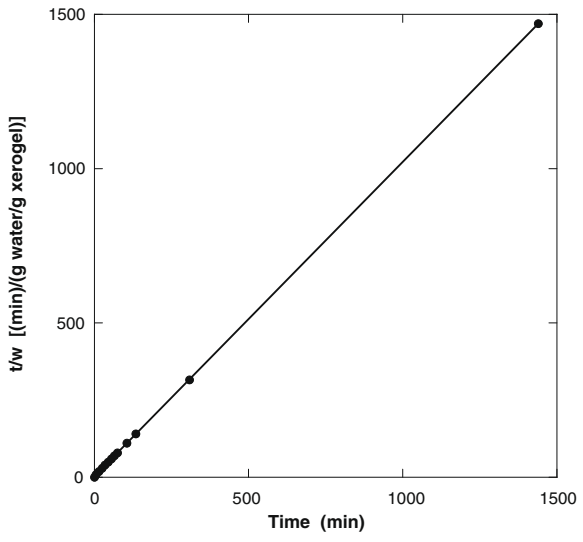

Fig. 6. Second order kinetic for the hydrogel of 1/4 molar composition.

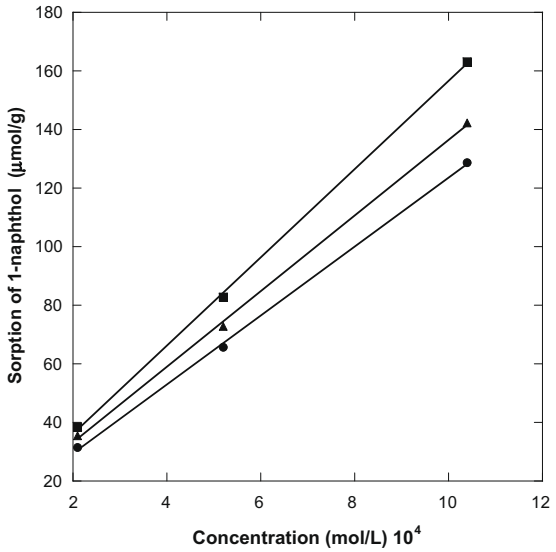

Fig. 7. Hydrogel sorption capacity as a function of 1-naphthol concentration, at 30 °C. β-CD/PEGBCOCl ratio: 1/6 (●); 1/8 (■) and 1/10 (▲).

Fig. 7 shows that by increasing the 1-naphthol concentration more of this compound is adsorbed (higher q) and that the sorption capacity increases linearly. Similar behavior has been reported when adsorbing 1- and 2-naphthol by other hydrogels containing β-CD [28,30]. Fig. 7 also shows that the sorption capacity of 1-naphthol does not follow a pattern when using hydrogels with different β-CD content. This has been attributed to the fact that not only the cyclodextrin cavities act as sorption elements for naphthol molecules, but also the cavities generated by the chemical structure of the network and its interactions with the 1- or 2-naphthol (physical sorption, hydrogen bonding, hydrophobic interactions), play an important role in the sorption process.

When comparing these hydrogels with the previously reported hydrogels obtained from β-CD and PEG (M_n = 600 g/mol) end-capped with isocyanate groups [31], similar sorption capacity was found when using aqueous solutions of 1-naphthol with concentrations of 5.2 and 10.4×10^{-4} mol/L. The presence of the urethane or ester groups does not seem to have an important role in the sorption capacity of the network.

Our data can also be compared with those reported by García-Zubiri et al. [30] for cyclodextrin networks prepared by reacting succinyl chloride,1,6-hexamethylene diisocyanate, toluene-2,4-diisocyanate or epichlorohydrin with β-CD; when using a concentration of 1-naphthol of 5.2×10^{-4} mol/L, a sorption capacity (q) of 91–140 μmol/g was obtained. These values are higher than the values obtained here. However, these hydrogels contained a larger amount of β-CD (between 43% and 74%) than the hydrogels prepared here (16.5–26%).

Crini et al. [28] reported a sorption capacity of 105 μmol/g of β-naphthol when using hydrogels prepared by crosslinking β-CD with epichlorohydrin, and a starting concentration of β-naphthol of 5×10^{-4} mol/L. The β-CD content of their hydrogels was 20%, which is similar to our hydrogel with a 1/8 ratio (20.5%). The lower sorption capacity of our hydrogels (82.8 μmol/g) can be explained because the β-naphthol forms more stable inclusion complexes with β-CD than the 1-naphthol [27].

4. Conclusions

A new method to prepare hydrogels containing β-CD and PEG has been developed. This kind of hydrogels can be easily degraded via hydrolysis in acid or basic media, and the degradation rate can be controlled by the β-CD/PEG ratio in the hydrogels. The hydrogels prepared here have a good sorption capacity comparable to other β-CD containing networks. For all these reasons and since the PEG and β-CD are biocompatible, the reported hydrogels can have potential applications in biomedical devices.

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