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The thermal behaviour of water in hydrogels

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Abstract

The melting enthalpy and the absorption enthalpy of water in polymethacrylic acid and copolymers of methacrylic acid and hydroxyethylmethacrylate have been determined. The melting enthalpy of water in hydrogels increased by increasing the equilibration time at −15°C, but was always smaller than that of pure water. The absorption enthalpy of water was negative and decreased by increasing the initial water content of the hydrogels. However, the observed lack in melting enthalpy of water was not fully compensated by the negative change in absorption enthalpy. This led to the conclusion that a part of the water does not freeze during the cooling–heating process.

The glass transition temperatures were determined as a function of the water content. Upon hydration, the glass transition temperature decreased in temperature. The amount of water necessary to decrease the glass transition temperature to 0°C was approximately equal to the amount of non-freezable water in the hydrogels.

These observations lead to the conclusion that the amount of non-freezable water cannot be explained by different types of water, but is based either on a restriction of the diffusion of water in hydrogels or on a restriction of a further growth of ice crystals after transformation of the hydrogel from rubbery state (high flexibility of the polymer network) to glassy state (low flexibility of the polymer network).

Keywords: DTA; Glass transition; Heat of absorption; Heat of melting; Hydrogel; Water

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1. Introduction

The physical properties of hydrogels have been studied in order to create a better understanding between the physical and chemical properties of this particular group of polymers on the one hand and the pharmaceutical properties on the other. The physical properties that have been studied are, for example, the swelling behaviour [1–4], glass transition temperatures [5–8], polymer–water interactions [9,10], and the interfacial properties [11]. The pharmaceutical characteristics include the release of drugs [12–15] from the polymers and the bioadhesive properties [16–19]. To describe the diffusion of solute through hydrogels several theories have been developed. Some of these theories have been based on the distribution of water in free, intermediate and bulk water [14].

The methods that were used to determine the amount of free, bulk and intermediate water include dilatometry [20–23], NMR relaxation [23], conductivity measurements, absorption on measurements and thermal analysis [20,21,23,24]. Using the latter technique the amount of bound water was based on the lack of melting enthalpy of water in hydrogels [20,21]. The amount of bound water was estimated from the difference between the measured enthalpy of melting and the enthalpy of melting calculated combining the amount of absorbed water in the hydrogels and the enthalpy of melting of pure water. In this interpretation the lack of the melting enthalpy of water was ascribed to a thermodynamic difference between regions of water in hydrogels. Another interpretation for the lack in melting enthalpy was given by Pouchly et al. [24]. The formation of ice crystals in hydrogels is hindered by kinetic factors. More recently Roorda et al. [7] related the incomplete freezing of water to a change in glass transition temperature of the polymer during the freezing process: the growth of ice crystals in the gel during freezing is accompanied by a decrease in water content in the hydrogel and therefore results in an increase in the glass transition temperature. If the glass transition temperature reaches the freezing point of water the diffusion of water through the hydrogel is decreased by several orders of magnitude, which hinders further formation of ice crystals. All studies were carried out with polyhydroxyethylenemethacrylate (p-HEMA).

In this study the melting enthalpy of water, the absorption enthalpy of water and glass transition temperatures of polymethacrylic acid (p-MAA) and copolymers of methacrylic acid (MAA) and HEMA were measured in order to find out if the mechanism proposed by Roorda et al. [7] can be considered as a more general one.

2. Experimental

2.1. Sample preparation

The monomers were purified as follows: hydrochinon, which serves as an inhibitor, was removed from the monomers by elution over an Amberlite A26 column. Traces of methacrylic acid (MAA) were removed, if necessary, by elution over a basic Al_2O_3 column.

The polymers were synthesized by radical polymerization. The following compositions were used: HEMA:MAA = 1:3 m/m (monomer molar ratio), referred to as 75% MAA; HEMA:MAA = 3:1 m/m, referred to as 25% MAA; and pure MAA. To remove the residual monomers the polymers were washed intensively with water, after which the gels were dried under vacuum at 110°C. A part of the dried gels was swollen in acetone, grained and dried again. The dried hydrogels were equilibrated over saturated salt solutions. Fully hydrated hydrogels were obtained by equilibration in distilled water.

2.2. *Measurements*

The absorption enthalpy of water in the hydrogel was measured by immersing the partly swollen and grained hydrogels in water. The experiments were carried out in a laboratory-made isoperibolic calorimeter, a description of which is given elsewhere [25].

The enthalpy of melting of water in the hydrogels was measured with differential thermal analysis (DTA) using a Mettler TA 3000 instrument. The DTA scans were performed as follows. The samples (approximately 3 mg) were cooled down at a rate of 1°C min^{-1} to −100°C to initiate crystallization. Then the samples were heated to −15°C. At this temperature the samples were equilibrated during several time periods, after which the melting enthalpies were measured by heating the samples to 20°C using a heating rate of 1°C min^{-1}.

The glass transition temperatures were measured using a heating rate of 10°C min^{-1} from at least 40°C below to at least 30°C above the expected glass transition temperature. To avoid water loss at elevated temperatures (above 100°C), high pressure DTA pans were developed in our laboratory. In view of the small changes in heat capacity upon passing the glass transition temperature, samples of approximately 30 mg were used. After the measurements the samples were checked for water loss.

3. Results and discussion

3.1. *Melting enthalpies*

In Fig. 1 the melting enthalpies of water in the polymer network are plotted as a function of the equilibration period at −15°C. The melting enthalpies were calculated from the melting enthalpies measured per gram hydrogel and the amount of water present in the hydrogels. The values are presented in Table 1. The curves in Fig. 1 clearly indicate the importance of the kinetics in performing DTA experiments: at least 12 h of equilibration were necessary to obtain a maximum value for the enthalpy of melting, but even then the enthalpy of melting was substantially lower than the melting enthalpy of pure water, being 334 J per g water.

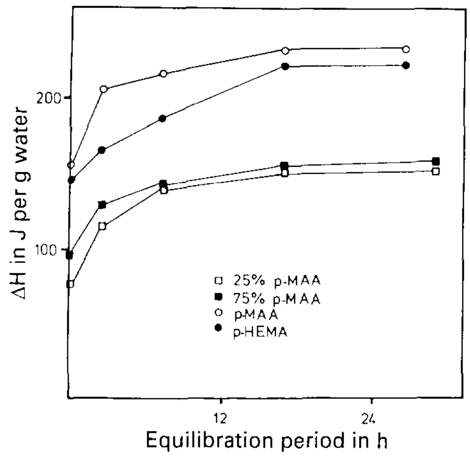

Fig. 1. Melting enthalpy of water as function of the equilibration period at −15°C; data for p-HEMA has been taken from Ref. [7].

Table 1
Enthalpy of melting (ΔH_m expressed in J per g water) after equilibration at −15°C during 24 h together with the amount of water present in the polymer after equilibration in water (expressed in g water per g dry polymer) and the maximum interaction enthalpy (ΔH_{abs} expressed in J per g water), measured by submerging grained dry polymer in water

	p-HEMA	25% p-MAA	75% p-MAA	p-MAA
ΔH_m	224	152	162	234
Amount of water	0.70	0.49	0.70	1.5
ΔH_{abs}	−37	−73	−119	−71
ΔH_{tot}	261	225	281	305

3.2. Absorption enthalpies

The absorption enthalpies are given in Fig. 2 and Table 1. The absorption enthalpies are all negative. A larger initial water content resulted in a strong decrease in the absorption enthalpy, but if the initial water content exceeded a certain value only a very small heat exchange could be measured, varying between 0.5 and 1.5 J per g dry polymer, that did not change upon further increase in water content. This small absorption enthalpy measured at higher initial water content might be due to a reorientation of the polymer chains at the interface of the polymer during the wetting process.

In p-HEMA only absorption of the first water molecule per monomer unit resulted in a decrease of about 25 J per g water in the absorption enthalpy (5 molecules of water per monomer unit can be absorbed in p-HEMA), while in p-MAA the absorption of 1.9 water molecules in the dry polymer (maximum

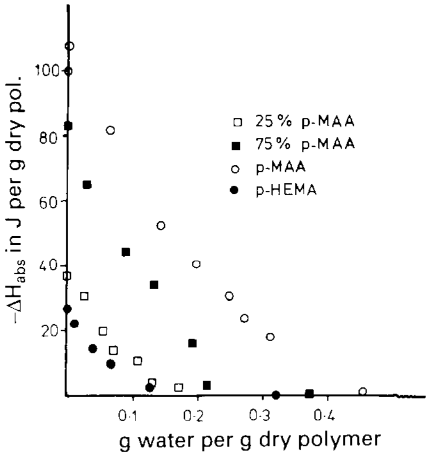

Fig. 2. Absorption enthalpy as a function of the initial water content in the hydrogels.

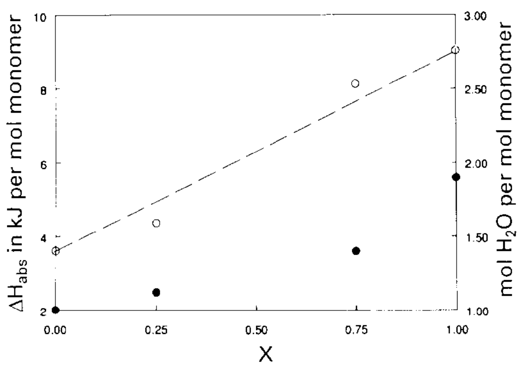

Fig. 3. Absorption enthalpy of water in initial dry polymers expressed in kJ per mol monomer (●) together with the amount of water that results in a decrease in absorption enthalpy expressed in mol H_2O per mol monomer (○), both as function of the mole fraction (x) MAA in the polymer.

amount of water is 7 molecules per monomer unit) resulted in a decrease of about 105 J per g water in absorption enthalpy.

In Fig. 3 the absorption enthalpy of water in the dry polymer (ΔH_{abs}), expressed in kJ per mol monomer, is plotted against the composition of the (co)polymer together with the amount of water that resulted in a change in the absorption enthalpy (expressed in mol water per mol monomer). No linear relationship was found between the absorption enthalpy and the composition of the copolymer, which strongly indicates that the absorption of water by the polymer does not obey an ideal mixing behaviour.

3.3. Glass transition temperatures

The glass transition occurred in a temperature range that occasionally even exceeded 30°C. In this study the temperature at which the polymer has been transformed from the rubber to the glass state has been taken as the glass transition temperature (T_g). Therefore the rubber to glass transition already starts 20–30°C below the temperatures given in Fig. 4. From this figure it is clear that an increase in water content decreases T_g, which could be expected since water is an excellent plasticizer. The water contents at which T_g approaches that of the freezing temperature of water, are presented in Table 2.

3.4. Combination of the thermodynamic parameters

Although the melting enthalpy of water increases by increasing the equilibrium period at −15°C, the maximum enthalpy of melting is far below the melting

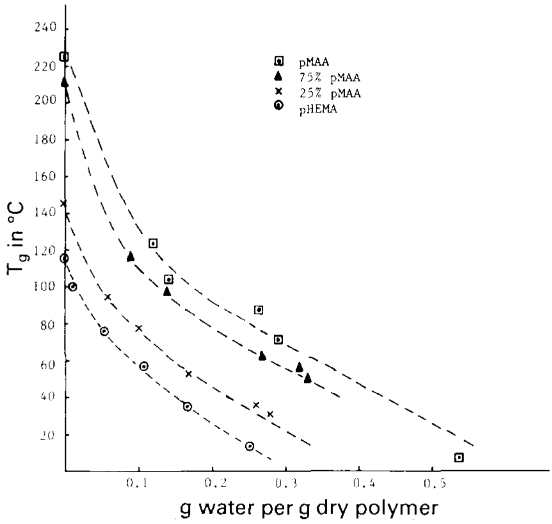

Fig. 4. Glass transition temperature as function of water content.

Table 2
Fraction of non-freezable water (nfw) and freezable water (fw) compared with the fraction water that changes the absorption enthalpy (absw) and the fraction of water that is needed to lower the glass transition temperature to just above 0°C

Polymer	fw	nfw	absw	glw
p-MAA	0.70	0.30	0.28	0.36
25% p-MAA	0.48	0.52	0.32	0.68
75% p-MAA	0.45	0.55	0.36	0.61
p-HEMA	0.67	0.33	0.20	0.38

enthalpy of pure water (334 J per g water; see Table 1). One possible explanation for the lack in melting enthalpy can be found in a large exothermal absorption enthalpy. Indeed, a large exothermal absorption enthalpy has been found upon absorption of water in hydrogels, but correcting the melting enthalpies for the absorption enthalpies ($\Delta H_{tot} = \Delta H_m - \Delta H_{abs}$) resulted in values for the enthalpy (ΔH_{tot}) involved in the melting process that are still significantly below the melting enthalpy of pure water (see Table 1). In calculating ΔH_{tot} the interaction of ice with the polymer network was assumed to be negligible. This is a reasonable assumption, because ice is expected to crystallize in a separate phase. From the significant difference between ΔH_{tot} and the melting enthalpy of ice one can conclude that a part of the water does not freeze during a cooling–heating cycle, not even after equilibration for 24 h at $-15°C$.

In order to calculate the amount of non-freezable water, one of course has to take into account the absorption enthalpy of water. However, in this study only the initial absorbed water resulted in a heat exchange between polymer and surrounding water. Therefore, due to this asymmetry of ΔH_{abs} with respect to water absorption, in a first approach, the ΔH_m of water was taken equal to that of pure water (334 J g^{-1}). In fact by doing this, three assumptions were made: (a) the water crystallizes in a separate phase and does not interact with the polymer network; (b) by withdrawing water from the polymer by the freezing process at sub-zero temperatures, the absorption enthalpy and therefore the interaction enthalpy between polymer and water still exhibit the same composition dependence as at room temperature (see Fig. 2); (c) the absorption enthalpy is not dependent on temperature.

In calculating the fraction of freezing water (fw) with the above mentioned assumptions it appeared that the fraction of water that changed the absorption enthalpy (x_{abs}) was smaller than the fraction of water that did not freeze upon cooling (nfw) and that there was no evidence for any correlation between the values for the two fractions (see Table 2). The next question that arose was whether it is possible that x_{abs} represents a different type of water and that a part of the water molecules stick to certain absorption sites in the polymer network to cause the exothermal ΔH_{abs}. This question can only be answered for p-HEMA. The water mobility in p-HEMA has been studied extensively. In one study the dynamic behaviour of water molecules in p-HEMA gels was studied using ^{17}O nuclear magnetic relaxation at various hydration levels in p-HEMA [26]. In these studies it was found that all the water was attributed to the NMR signal and no evidence could be found for the existence of two relaxation processes. From these findings it was concluded that on the timescale of the relaxation process no different types of water are present in p-HEMA. Similar results were obtained by measuring the self-diffusion coefficient of water in p-HEMA by pulse field gradient NMR. Only one water self-diffusion coefficient was found, which reduced in value at lower water contents. From the existence of one type of water even on the timescale of the NMR relaxation process one may conclude that the water molecules do not stick to certain sites resulting in thermodynamically different types of water, but that the absorption enthalpy is equally distributed over all the water molecules present in p-HEMA.

An explanation must still be found for the lack in enthalpy of the non-freezable water in hydrogels. In Table 2 the water fraction (x_{gl}) necessary to reduce the glass transition temperature to 0°C is presented. Comparing these values with the non-freezing part of the water one may draw the conclusion that a relation exists between these values. If the fraction of non-freezing water is low (p-MAA = 0.30) then the fraction of water that reduces the glass transition temperature to 0°C is also low. In all four hydrogels the water necessary to reduce the glass transition to 0°C exceeds the non-freezable water. This is probably due to the fact that in these studies the highest possible temperature of the glass transition was taken as the glass transition temperature. The glass transition starts 20–30°C below the temperatures plotted in Fig. 4. It seems that the freezing process terminates as soon as the rubber state of the polymer changes into its glass state. This can be explained by (a) a reduction of the water self-diffusion coefficient that inhibits the formation of ice crystals, or (b) the low flexibility of the polymer chains that inhibits the formation of ice crystals. The results of this study lead to the conclusion that the mechanism behind the non-freezable part of the water found by Roorda et al. [7] should be regarded as a more general mechanism, instead of one specific for p-HEMA. That this mechanism is a general one has also been confirmed by experiments carried out by Pouchly et al. [10]. They measured the interaction enthalpy and the melting enthalpy of water in poly(2-(2-hydroxy)ethoxyethylmethacrylate). The glass transition temperature of the dry polymer is 11°C [27], which is close to 0°C. The melting enthalpy and the interaction enthalpy were both measured at a water content of 1.185 g water per g polymer. Combining the enthalpy of melting with the absorption enthalpy, the total enthalpy change involved in the melting of water appeared to be 326 J per g water, which is close to the value of pure water, thus indicating that almost all the water in the polymer can be frozen before the glass transition sets in.

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