Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 46 (2005) 12026–12031

polymer

www.elsevier.com/locate/polymer

States of water in partially swollen poly(vinyl alcohol) hydrogels

Wenbo Li[a], Feng Xue[a], Rongshi Cheng[a,b,*]

[a]College of Material Science and Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China
[b]College of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China

Received 31 March 2005; received in revised form 1 September 2005; accepted 6 September 2005

Abstract

A poly(vinyl alcohol) hydrogel was prepared by coupling poly(vinyl alcohol) with epichlorohydrin as cross-linking agent. Various amounts of water were added into the dry hydrogel to swell it and the quantity of water in various states in the partially swollen hydrogel were determined by DSC ice-melting technique. A parameter S denoted the degree of the saturation of swelling was introduced for describing the various stages of water absorption. The analytical results indicate that there exists two critical threshold degree of saturation. At the first threshold S^*, the freezable bound water starts to appear and at the second threshold S^{**}, the free water begins to appear. In the region of $S < S^*$, the adsorbed water exists only in the non-freezable form and increases linearly with S until reaching S^*. The sum of non-freezable and freezable bound water consists of the hydration layer around the chain segments of the network. The hydration number HN of the repeating unit of PVA hydrogel increases from zero to a limiting value about 2.5 as the degree of saturation varies from zero to one.

Keywords: DSC; States of water; Saturation of swelling

---

1. Introduction

The states of water absorbed in polymeric systems have been widely investigated using various techniques [1–16]. The behavior of water can be transformed in the presence of a polymer, depending on the degree of chemical or physical association between the water and polymer phases. It is generally accepted that the states of water in water containing hydrophilic polymer including hydrogel should be divided into three main categories, i.e. non-freezable bound, freezable bound and free water. The relative contents of these different water states could be differentiated and determined by DSC measurements. For a water-soluble hydrophilic polymer, the total amount of the sorbed or the added water may be extended from zero to infinity corresponding to its action just like a plasticizer to a solvent. However, the addition of water to a chemically cross-linked hydrogel is limited, no more water could be further sorbed as the swollen hydrogel reaching to a state of equilibrium swelling. How the state of water varies as adding water successively into a dry hydrogel is an interesting problem. The present work deals with a quantitative differential scanning calorimetric study on partially swollen chemically cross-linked poly(vinyl alcohol) hydrogels and the resulting data were expressed in terms of degree of saturation, i.e. a parameter describing the extent of added water reaching equilibrium swelling.

2. Experimental

2.1. Sample

A chemically cross-linked poly(vinyl alcohol) hydrogel sample was prepared in this laboratory via reaction of poly(vinyl alcohol) with epichlorohydrin. The equilibrium-swelling ratio Q_e of the dry gel defined by

$$Q_e = \frac{w_G + w_{eH}}{w_G} \tag{1}$$

is 2.84, where w_G is the weight of dry gel and w_{eH} is the weight of the absorbed water at equilibrium swelling. Follows Flory's formula, the average molar mass of the chain between two cross-linking points is calculated to be 712.

The partially swollen poly(vinyl alcohol) hydrogels were prepared by adding w_H grams of deionized water into w_G grams of dry gel. Hence by definition, the water content f_H

---

* Corresponding author. Address: College of Material Science and Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China. Tel.: +25 83597355; fax: +25 83317761.
E-mail address: rscheng@nju.edu.cn (R. Cheng).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.09.016

and swelling ratio Q of the partially swollen hydrogels are

$$f_H = \frac{w_H}{w_{SG}} = \frac{w_H}{w_G + w_H} \tag{2}$$

and

$$Q = \frac{w_{SG}}{w_G} = \frac{w_G + w_H}{w_G} \tag{3}$$

respectively, where w_{SG} is the total weight of the swollen gel. They are interrelated by

$$f_H = \frac{Q-1}{Q} \tag{4}$$

and

$$Q = \frac{1}{1-f_H} \tag{5}$$

The water contents of partially swollen samples were determined by thermogravimetric analysis (TGA) in continuous heating mode from 25 to 120 °C at a heating rate of 10 °C/min. A TA TGA-2050 thermal analyzer under nitrogen atmosphere was used. The weight losses for 15–25 mg of the swollen samples were recorded.

Since the equilibrium-swelling ratio Q_e is a constant for a given network, it is convenient to define a parameter S named as degree of saturation to express the amount of sorbed water as

$$S = \frac{w_H}{w_{eH}} = \frac{Q-1}{Q_e - 1} \tag{6}$$

Then the total weight of sorbed water per unit weight of dry gel will be

$$\frac{w_H}{w_G} = Qf_H = Q-1 \tag{7}$$

A plot of w_H/w_G versus S will be a straight line starting from the origin (0,0) and ending at $(1, Q_e - 1)$. The aim of the present work is to investigate how the various states of water absorbed by the hydrogel distribute in the region below the straight line from point (0,0) to point $(1, Q_e - 1)$ by DSC ice-melting measurements.

2.2. Differential scanning calorimetry

A TA MDSC-2910 instrument was used to measure the ice-melting behavior of the partially swollen poly(vinyl alcohol) hydrogels. 5–10 mg of swollen hydrogel with known degree of swelling Q and water content f_H were weighed and sealed in DSC aluminium pans. The empty pans were pretreated in boiling water for 1 h. and dried before use. The sealed samples were placed in the TA instrument and cooled to -40 °C to freeze the swollen hydrogel and then heated from -40 to 40 °C at a heating rate of 2 °C/min, to avoid the time lag of response caused by a faster heating rate. Temperatures and enthalpies of melting of the samples were calibrated using pure water as the standard; their standard deviations were found to be within ± 0.5 °C and ±5%, respectively.

3. Results and discussion

3.1. Freezable and non-freezable water

The obtained DSC ice-melting diagrams of partially swollen poly(vinyl alcohol) hydrogels are shown in Fig. 1. They vary considerably with the water content of the swollen gel, from no ice-melting signal at low f_H through multi-peak signal at intermediate f_H and finally to a single peak at high f_H. These signals correspond to the ice melting of freezable water in the partially swollen hydrogels. The total weight of water presented in a swollen hydrogel w_H must be the sum of two main parts, namely the weight of freezable water w_{fH} and that of non-freezable water w_{nfH} accompanied with w_G gram of dry gel

$$w_H = w_{fH} + w_{nfH} \tag{8}$$

The amount of freezable water could be evaluated from the DSC endothermic ice-melting profile of the frozen gel. The enthalpy of melting obtained by integration and normalization ΔH_m is in unit of J/g of swollen gel. The latent heat of water $\Delta H = 333.5$ is in unit of J/g of pure water. Neglecting the small differences in the melting enthalpies of ice of different crystal structures, the ratio of $\Delta H_m/\Delta H$ represents gram of freezable water per gram of swollen gel, i.e.

$$\frac{w_{fH}}{w_{SG}} = \frac{\Delta H_m}{\Delta H} \tag{9}$$

From the inter correlations mentioned above, it is easy to write the ratios of the weight of freezable and non-freezable

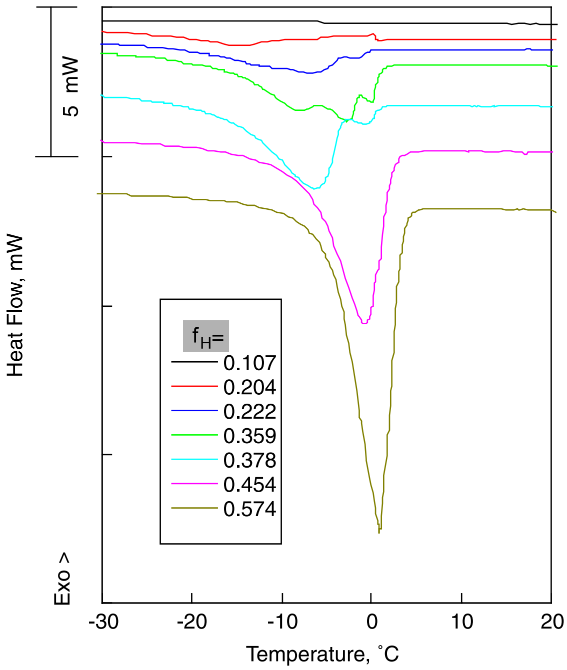

Fig. 1. The DSC ice-melting diagrams of partially swollen poly(vinyl alcohol) hydrogels.

Table 1
The ice-melting enthalpies and melting temperatures of partially swollen PVA hydrogels

f_H	Q	S	ΔH_m J/g swollen gel	w_{nfH}/w_G	w_{fH}/w_G	T_{MI} (°C)	T_{mM} (°C)	T_{mH} (°C)
0.107	1.12	0.065	0.0	0.120	0.000	–	–	–
0.204	1.26	0.139	12.0	0.212	0.045	−14.68	−7.09	0.71
0.222	1.29	0.155	28.4	0.177	0.109	−10.70	−7.04	−1.79
0.359	1.56	0.304	77.0	0.202	0.358	−7.96	−2.72	−0.02
0.378	1.61	0.330	89.6	0.179	0.430	–	−6.30	−0.64
0.454	1.83	0.452	125.9	0.144	0.687	–	−0.77	–
0.574	2.35	0.732	178.2	0.101	1.248	–	0.85	–

water to the weight of dry gel as:

$$\frac{w_{fH}}{w_G} = Q\frac{\Delta H_m}{\Delta H} \tag{10}$$

$$\frac{w_{nfH}}{w_G} = Q\left(f_H - \frac{\Delta H_m}{\Delta H}\right) \tag{11}$$

respectively. The average number of bound water molecules to a monomer-repeating unit can be expressed as

$$n = \frac{44}{18}\left[Q\left(f_H - \frac{\Delta H_m}{\Delta H}\right)\right] \tag{12}$$

The overall ice-melting enthalpies obtained by integration and the evaluated weight ratios w_{fH}/w_G, w_{nfH}/w_G of various hydrogels are listed in Table 1. The peak melting temperatures are also listed in the table; the subscript L, M and H refer to the three multiple peaks at lower, medium and higher temperatures, respectively.

The ratios of weight of non-freezable and freezable water to that of dry hydrogel as a function of degree of saturation S is shown in Fig. 2. The weight ratio of the freezable water to dry gel increases almost linearly with the degree of saturation S beyond a critical threshold value S^*. Linear regression fit to the data gives $S^*=0.113$ and the limiting value of w_{fH}/w_G at equilibrium swelling i.e., at $S=1$ equals to 1.782. Meanwhile, the ratio w_{nfH}/w_G increases linearly from zero at $S=0$ with S up to a plateau value of at S^* and then keeps constant up to $S=0.35$. Starting from this point, it decreases gradually with degree of saturation. The plateau value of $w_{nfH}/w_G=0.20$ corresponds to the number of bound water molecules to a monomer equals to 0.5 in this region. That is to say, two monomers will bond to a water molecule in average. This bound water molecule may join two hydroxyl groups that belong to two neighboring network chains or two adjacent hydroxyl groups in the same chain through hydrogen bonding as shown schematically in Fig. 3(A) and (B), where x is the average degree of polymerization of the chain between two cross-linking points. The ratio of non-freezable bound water to freezable water w_{nfH}/w_{fH} drops rapidly with increasing S when $S>S^*$ as shown in Fig. 4. The origin of the non-freezable bound water is a topic with much discussion in recent literature [17–22]. The present results suggest that the non-freezable bound water is the water molecule has two hydrogen bounds directly fixed to polymer network chain. The diminution of w_{nfH}/w_G as more water was introduced into the dry gel indicates that these two end fixed hydrated water gradually change to one end fixed as shown in Fig. 3(C) and merges with the freezable hydrated water. The free hydrogen atom of the one end fixed hydrated water (Fig. 3(C)) may be joined with another free water molecule forming a structure like Fig. 3(D).

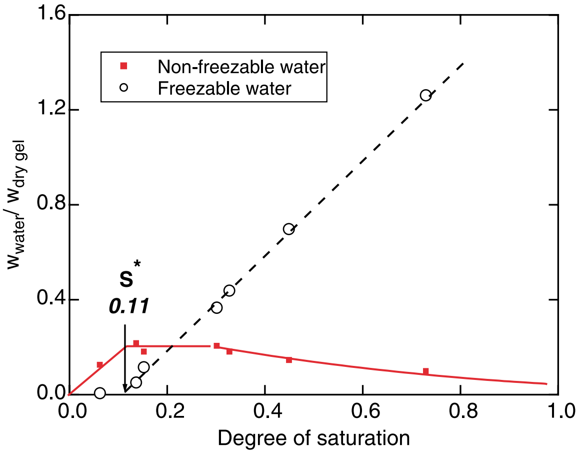

Fig. 2. Plot of w_{water}/w_{drygel} against degree of saturation.

3.2. Subdivision of freezable water

The DSC ice-melting heating curves of the swollen PVA gel with various degree of saturation possess multiple endothermic peaks as shown in Fig. 1 and with various peak melting temperatures ranging from −14 to 0.8 °C as listed in Table 1. This behavior evidently suggests the freezable water should subdivide into several kinds with different ice structure. In light of earlier classification [23], the freezable water consists two

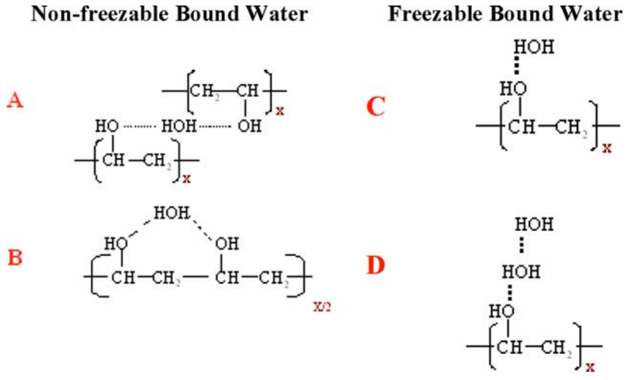

Fig. 3. Schematic structures of hydration water in PVA hydrogel.

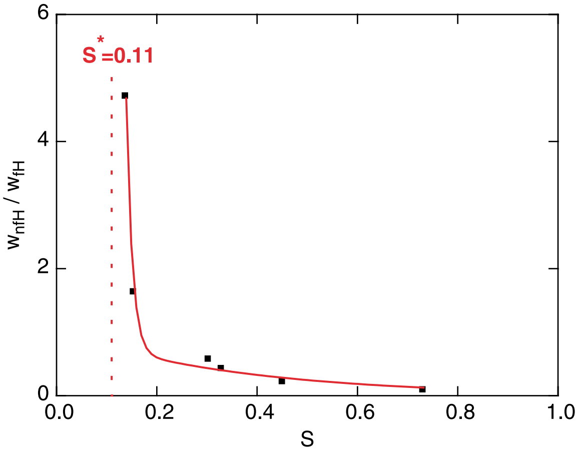

Fig. 4. Variation of the ratio w_{nfH}/w_{fH} with degree of saturation.

parts, namely freezable bound water and free water, according to their increasing melting points. The free water has the same melting point as that of pure bulk water. The present results of DSC measurements showed that in the middle range of saturation, the appearance of three peaks has no doubt. It is clearer to show this feature in the enlarged heat flow—temperature DSC curves represented in Fig. 5.

Besides the heat flow signal, TA DSC instrument measures and records the temperature of the sample pan simultaneously and regards it as the system temperature. The derivative of the system temperature T with respect to time t, i.e. the experimental recorded dT/dt of the sample deviates from the programmed heating or cooling rate as the phase transition of the sample takes place. For a simple transition on heating, the dT/dt generally deviate to a lower value and immediately raises forming a pair of negative and positive peaks. The positive peak usually locates at the end of transition. Therefore, the variation of dT/dt with temperature provides an additional information and criterion on judging the occurrence of thermometric phase changes. The dT/dt curves of various swollen hydrogels are also drawn in Fig. 5 in addition to the heat flow curves. The occurrence of three peaks both in the heat flow and dT/dt curves could be identified. The location of the positive dT/dt peaks and its maximum values are listed in Table 2. According to the order of raising temperature, we assign peak I and II are bound water with different ice structure and peak III is the free water. The bound water I and II are both resulted from the hydrogen bonding of water with the chain segments, we may denote it as hydration water.

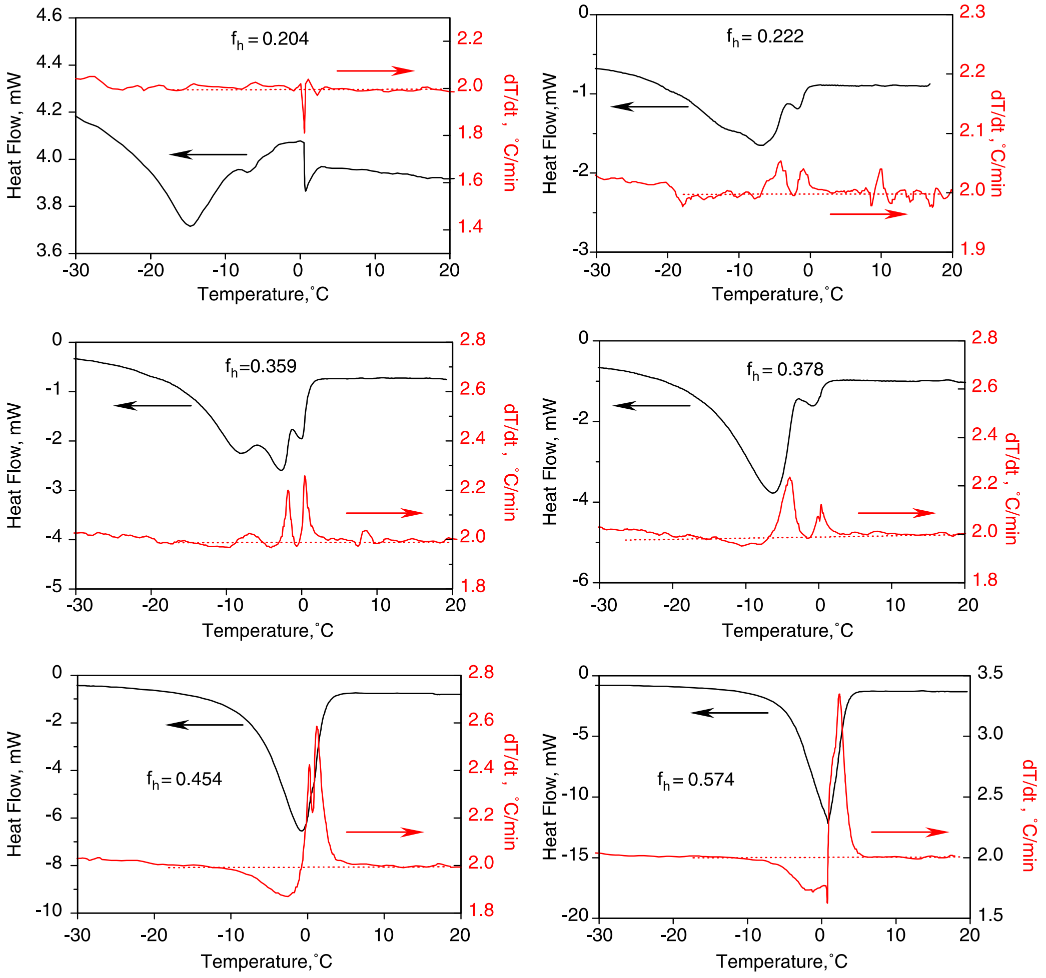

Fig. 5. The enlarged heat flow DSC curves and variation of dT/dt with temperature for various swollen PVA hydrogels.

Table 2
The location of dT/dt peaks and its maximum values

f_H	S	Peak temperature (°C)			(dT/dt)max (°C/min)		
		Peak 1	Peak 2	Peak 3	Peak 1	Peak 2	Peak 3
0.107	0.065	–	–	–	–	–	–
0.204	0.139	−13.60	−5.57	1.09	2.01	2.02	2.04
0.222	0.155	−4.05	−0.94	9.88	2.05	2.04	2.04
0.359	0.304	−6.98	−1.81	0.47	2.03	2.20	2.26
0.378	0.33	−3.93	−0.05	0.37	2.22	2.07	2.12
0.454	0.452	–	−0.29	1.23	–	−2.42	2.58
0.574	0.732	–	−0.31	2.37	–	−1.77	3.35

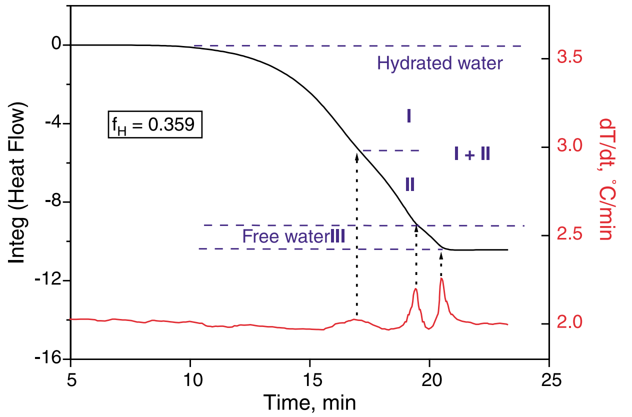

Fig. 6. Subdivision of multi ice-melting peak area based on the variation of dT/dt.

Since the positive dT/dt peak locates at the end of an endothermic transition, we are able to subdivide the integral heat flow curve into three regions using the peak temperature as boundaries into bound water I, bound water II and free water III. An example for $f_H=0.359$ is drawn in Fig. 6. The enthalpy of each species could directly read from the digitalized integral curve. The melting enthalpies of different states of water thus obtained were listed in Table 3.

Based on the data in Table 3, if regards $\Delta H_{m1,2}$ and ΔH_{m3} referred to the melting enthalpy of freezable hydrated water and free water, respectively, a plot of enthalpy versus degree of saturation (Fig. 7) shows that the freezable hydrated water increases gradually starting from S^* while the free water begins to appear at a second critical threshold $S^{**}=0.32$. Now, we are able to construct a distribution diagram of the various states of water appeared in the partially swollen PVA hydrogel as Fig. 8.

Table 3
Subdivision of the enthalpies of the freezable water

f_H	S	ΔH_{m1} J/g swollen gel	ΔH_{m2} J/g swollen gel	$\Delta H_{m1,2}$ J/g swollen gel	ΔH_{m3} J/g swollen gel
0.107	0.065	–	–	–	–
0.204	0.139	7.1	4.0	11.1	0.9
0.222	0.155	25.7	2.4	28.1	0.4
0.359	0.304	37.2	29.7	67.0	10.1
0.378	0.33	81.2	7.4	88.6	1.0
0.454	0.452	–	–	109.9	16.0
0.574	0.732	–	–	118.4	59.8

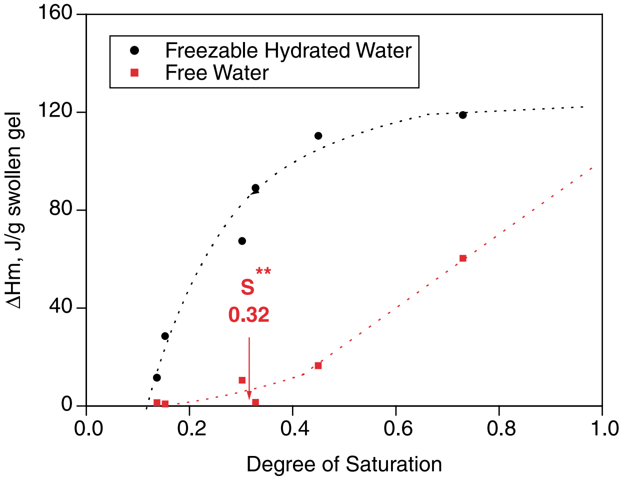

Fig. 7. The variation of the melting enthalpies of freezable and free water with degree of saturation.

3.3. Hydration number

Evidently, the non-freezable bound water and the freezable hydrated water both are hydration water via hydrogen bonding of water molecule with segmental hydroxyl group. However, they are in different states. As mentioned above, the non-freezable bound water is those water molecule whose two hydrogen atoms are firmly fixed to the segmental hydroxyl by hydrogen bonding as shown in Fig. 3(A) and (B). The mobility of such water molecule is completely retarded and could not freeze to ice upon cooling. On the other hand, the mobility of the one end fixed hydrated water (Fig. 3(C) and (D)) is partially retained and could freeze upon cooling forming freezable hydrated water I and II.

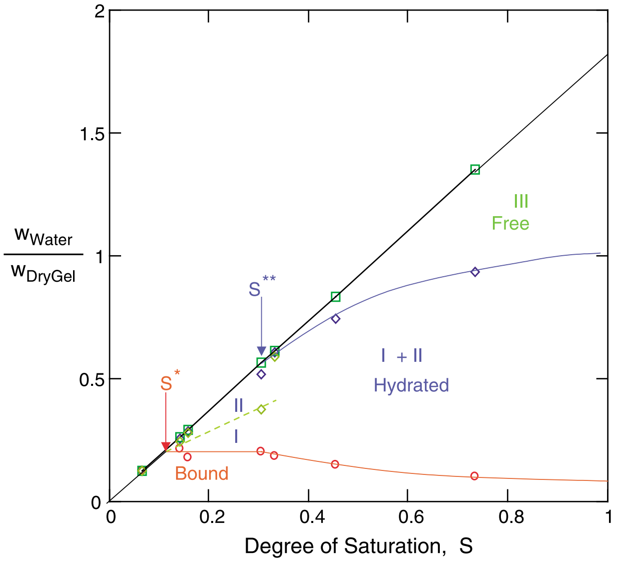

Fig. 8. The distribution diagram of various water states in partially swollen PVA hydrogel.

Table 4
The overall hydration number of partially swollen PVA hydrogel

S	$W_{\mathrm{hydration}}/W_{\mathrm{G}}$	HN
0.065	0.120	0.29
0.139	0.254	0.62
0.155	0.285	0.70
0.304	0.514	1.26
0.330	0.604	1.48
0.452	0.743	1.82
0.732	0.930	2.27

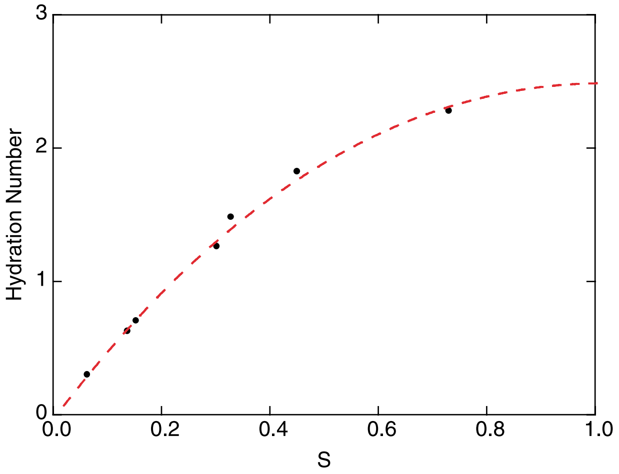

Fig. 9. The variation of hydration number of PVA hydrogel with the degree of saturation of swelling.

Therefore, the weight of hydration water in partially swollen hydrogel consists of two parts and may be written as

$$w_{\mathrm{hydration}} = w_{\mathrm{nfH}} + w_{\mathrm{hyd}} \tag{13}$$

where w_{nfH} is the weight of non-freezable bound water and w_{hyd} is the weight of freezable hydrated water including form I and II per w_{G} gram of dry hydrogel. Then the overall hydration number of partially swollen PVA hydrogel will be

$$\mathrm{HN} = \frac{44}{18}\frac{w_{\mathrm{hydration}}}{w_{\mathrm{G}}} \tag{14}$$

The calculated results are listed in Table 4 and a plot of the hydration number versus degree of saturation of swelling is shown in Fig. 9.

Notably the hydration number thus obtained is an average value of the whole system. It starts from zero at $S=0$ and increases gradually to a limiting value of 2.5 at $S=1$ as shown in Fig. 9.

4. Conclusions

1. The concept of the degree of saturation of swelling of a hydrogel S was introduced for describing the various stages of water absorption.
2. There exist two critical threshold degree of saturation. At the first threshold S^*, the freezable bound water starts to appear and at the second threshold S^{**}, the free water begins to appear.
3. In the region of $S<S^*$, the adsorbed water exists only in the non-freezable form and increases linearly with S until reaching S^*. Then the amount of non-freezable water per gram of dry gel remains constant until reaching S^{**}. Afterwards it vanishes gradually with increasing S.
4. The non-freezable water is a sort of hydration water fixed to the chain segments with two hydrogen bonds for each water molecule.
5. From the obtained results, a distribution diagram for various states of water in partially swollen PVA hydrogel was constructed.
6. The hydration number NH of the repeating unit of PVA hydrogel increases from zero to a limiting value about 2.5 as the degree of saturation varies from zero to one.

References

[1] Bastow TD, Hodge RM, Hill AJ. J Membr Sci 1997;131:207.
[2] McBrierty VJ, Martin SJ, Karasz FE. J Mol Liq 1999;80:179.
[3] Hirata Y, Miura Y, Tanaka S, Nakagawa T. J Membr Sci 2000;176:21.
[4] Capitani D, Mensitieri G, Porro F, Proietti N, Segre AL. Polymer 2003;44:6589.
[5] McBrierty VJ, Quinn FX, Keely C. Macromolecules 1992;25:4281.
[6] Ahmad M, Huglin M. Polym Int 1994;33:273.
[7] Shibukawa M, Aoyagi K, Sakamoto R, Oguma K. J Chromatogr A 1999;832:17.
[8] Qu X, Wirsen A, Albertsson AC. Polymer 2000;41:4589.
[9] Baba T, Sakamoto R, Shibukawa M, Oguma K. J Chromatogr A 2004;1040:45.
[10] Guan Y, Shao L, Yao K. J Appl Polym Sci 1996;61:393.
[11] Muta H, Ishida K, Tamaki E, Satoh M. Polymer 2002;43:103.
[12] Scherer JR, Bailey GF, Kint SF. J Phys Chem 1985;89:312.
[13] Malladi DP, Scherer JR, Kint SF, Bailey GF. J Membr Sci 1984;19:209.
[14] Hatakeyema T, Yamauchi A, Hatakeyema H. Eur Polym J 1984;20:61.
[15] Higuchi A, Iijima T. Polymer 1985;26:1207.
[16] Zhang W-Z, Satoh M, Komiyama J. J Membr Sci 1989;42:303.
[17] Murase N, Gonda K, Watanabe T. J Phys Chem 1986;90:5420.
[18] Liu WG, Yao KD. Polymer 2001;42:3943.
[19] Cha WI, Hyon SH, Ikada Y. Makromol Chem 1993;194:2433.
[20] Roorda WJ. J Biomater Sci, Polym Ed 1994;5:383.
[21] MuÈller-Plathe F. Macromolecules 1998;31:6721.
[22] Patil RD, Mark JE, Apostolov A, Vassileva E, Fakirov S. Eur Polym J 2000;36:1055.
[23] Pedley DG, Tighe BJ. Br Polym J 1979;11:130.