Solute retention and the states of water in polyethylene glycol and poly(vinyl alcohol) gels

Takayuki Baba [a], Ryosaku Sakamoto [a], Masami Shibukawa [b,*], Koichi Oguma [a]

[a] *Department of Materials Technology, Faculty of Engineering, Chiba University, 1-33 Yayoi-cho, Inage, Chiba 263-8522, Japan*
[b] *Department of Applied Molecular Chemistry, College of Industrial Technology, Nihon University, 1-2-1 Izumi-cho, Narashino 275-8575, Japan*

Abstract

The states of water sorbed in a cross-linked polyethylene glycol (PEG) gel, TSKgel Ether-250, and cross-linked poly(vinyl alcohol) (PVA) gels of different pore sizes, TSKgel Toyopearl HW-40S, 50S, 55S and 75S, were investigated by means of differential scanning calorimetry (DSC). It was found that there were three types of water in these hydrogels, non-freezing water, freezable bound water and free water. The amount of water that functions as the stationary phase in the column packed with the each gel was also estimated by a liquid chromatographic method. The estimated amount of the stationary phase water is in good agreement with the sum of the amount of non-freezing water and that of freezable bound water for HW-40S, 50S and 55S, while it agrees with the amount of only non-freezing water for HW-75S and Ether-250. This means that the stationary phase water consists of non-freezing water and freezable bound water for HW-40S, 50S and 55S, while only non-freezing water functions as the stationary phase in HW-75S and Ether-250 gels. This result can be attributed to the difference in the structure of the gels; the PVA gels containing PVA at relatively high concentrations, HW-40S, 50S and 55S, have a homogeneous gel phase, whereas HW-75S and Ether-250 have a heterogeneous gel phase consisting hydrated polymer domains and macropores with relatively hydrophobic surface. The freezable bound water in Toyopearl HW-40S, 50S and 55S can be regarded as a component of a homogeneous PVA solution phase, while that in HW-75S and Ether-250 may be water isolated in small pores of the hydrophobic domains. The results obtained by the investigation on the retention selectivity of these hydrogels in aqueous solutions supported our postulated view on the structures of the hydrogels.
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1. Introduction

Water-swollen hydrophilic polymer gels are one of the widely used materials for separation and/or purification as various separation membranes, column packings for liquid chromatography, etc. These materials contain a substantial amount of water in their polymer networks and show their characteristic physicochemical properties depending not only on the water content but also on the states of water. There have so far been reported many investigations on the role of water in the separations performed with these hydrogels. Particularly, the gas permselectivity of water-swollen membranes has been extensively investigated in order to

clarify the dependence of the permeability on the states of water in the membranes [1–7]. Much research on the water-swollen hydrogels by means of differential scanning calorimetry (DSC) [4–22,31], NMR [20,21–23], and other techniques [24–30] has demonstrated that the state of water sorbed in these hydrogels is different from that of ordinary bulk water. Higuchi et al. [4,5] found that there were free water and hydration water in poly(vinyl alcohol-co-itaconic acid) and gel cellophane membranes, and that the diffusion and solubility of various gases in hydration water were different from those in free water. Hirata et al. [7] investigated the dissolved oxygen permeability through different cation forms of Nafion membranes and concluded that the oxygen permeability was governed by the fraction of hydration water in the membrane and the mobility of the hydration water.

Distribution of solute compounds from aqueous solutions into water incorporated in polymer membranes has also been

* Corresponding author. Tel.: +81-47-474-2554;
fax: +81-47-474-2579.
E-mail address: m5sibuka@cit.nihon-u.ac.jp (M. Shibukawa).

discussed using two to four-state models for water in hydrogels [13,31–36]. In most of the studies that have so far been carried out, the quantitative information on water in the different states is obtained by means of DSC and the distribution coefficient of a solute compound for the individual water phase in the hydrogels is estimated indirectly by batch methods assuming that the solute concentration in the water which shows the thermal transition behaviour different from that of the bulk water is not equal to the concentration in the bulk water.

However, the water that shows the DSC behaviour different from that of the bulk water does not necessarily have a different affinity to solutes from that of the bulk water. In the previous studies [37–39], we have demonstrated that the amount of water in the gels which exhibits the affinity to solutes different from that of bulk water and functions as the stationary phase in liquid chromatography can be determined by a liquid chromatographic method we presented [40]. This method makes it possible to compare the amount of water that exhibits a characteristic behaviour in DSC measurements with that of water that shows a different affinity to solutes in the hydrogels. DSC classifies water in the gels according to the melting or freezing point and gives the amount of water in the each state based on measurement of the enthalpy of the phase transition. The states of water are usually identified as follows [41]: free water, which shows similar temperature and enthalpy of melting/crystallization to those of bulk water; freezable bound water or intermediate water, which exhibits a melting/crystallization temperature shifted with respect to that of bulk water; and non-freezing water, which shows no detectable phase transition over the range of temperatures normally associated with bulk water.

We investigated the thermal phase transition behaviour of water in cross-linked dextran (DEX), poly(vinyl alcohol) (PVA), and polyacrylamide (PAA) gels used as liquid chromatography column packings by DSC and showed that there are non-freezing water and freezable bound water in these hydrogels as well as free water [38]. The amount of the stationary phase water estimated by the liquid chromatographic method was in good agreement with the sum of the amount of freezable bound water and that of non-freezing water in these gels. On the other hand, for water incorporated in hydrophobic polystyrene–divinylbenzene copolymer (PS-DVB) gels, not only freezable bound water but also non-freezing water did not work as the stationary phase and were similar to the bulk water with respect to the affinity to the solute compounds [39]. These results indicate that the affinity of water to solute compounds or the solute solubility in water in the polymer gels cannot be expected from the DSC behaviour of the water.

In this study, we have extended our investigation to cover other types of gel column packings, and have obtained an interesting result on the roll of freezable bound water and non-freezing water in the separation process, which differs from the results obtained not only for the PS-DVB gels but also for the hydrophilic polymer gels which we previously

studied. In the present paper we describe the results of the studies on the states of water incorporated in a polyethylene glycol (PEG) gel and several PVA gel packings with different pore volumes. Based on the results obtained, the states of water in the hydrogels are discussed in relation to the separation selectivity of the gels in aqueous solutions.

2. Experiment

2.1. Materials

Water was purified with a Milli-Q system (Nihon Millipore, Tokyo, Japan) and used throughout the experiments. All chemicals were of reagent-grade and obtained from commercial sources. Methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, benzyl alcohol, phenethyl alcohol, acetone, 2-butanone, 3-methyl-2-butanone, 3,3-dimethyl-2-butanone, acetonitrile, phenylacetonitrile, nitromethane, nitroethane and nitropropane were obtained from Kanto Chemicals (Tokyo, Japan). A cross-linked PEG gel, TSKgel Ether-250 and cross-linked PVA gels, TSKgel Toyopearl HW-40S, HW-50S, HW-55S and HW-75S (Tosoh, Tokyo, Japan) were used in this study. Blue Dextran 2000 (Mw = 2×10^6) from Pharmacia Fine Chemicals (Uppsala, Sweden) was used as a reference material for evaluation of the interstitial volume or interparticulate volume in the column packed with the each gel packing material.

2.2. Chromatographic conditions

Chromatographic measurements were performed on an HPLC system consisting of a Hitachi (Tokyo, Japan) L-6200 pump, an L-4000 UV-detector and an Erma Optical Works (Tokyo, Japan) ERC-7510 refractometric detector. Water or aqueous solutions of sodium chloride and sodium perchlorate with ionic strength of 0.1 M were used as eluent and degassed through an Erma Optical Works (Tokyo, Japan) ERC-3325 degasser. The columns were thermostated at 308 K using a GL Sciences (Tokyo, Japan) Model 556 LC column oven. A pre-packed Toyopearl HW-75S column (300 mm × 8.0 mm i.d.) was obtained from Tosoh (Tokyo, Japan). The other gel packings were packed into stainless steel columns as described previously [38]. Sizes of the columns used were 150 mm × 4.6 mm i.d. for Ether-250 and 100 mm × 8 mm i.d. for HW-40S, 50S and 55S, respectively.

2.3. DSC measurements

Samples of TSKgel Ether-250 and Toyopearl HW-40S, 50S, 55S and 75S for DSC measurement were taken from the columns packed with these packing materials and 1–8 mg sample was placed in an aluminium sample vessel. The water content of the sample was adjusted by allowing water to vaporize from the sample in a desiccator containing silica gel at room temperature or in an oven at 363 K. The

sample vessel was then sealed hermetically. Any water leakage was not observed for weighing performed before and after DSC measurements. A Seiko Instruments Inc. (Chiba, Japan) DSC-120 differential scanning calorimeter equipped with a cooling device was used to measure the phase transition of water sorbed in the polymer gel. DSC curves were obtained by cooling at the scanning rate of 1 or 2 K/min from 298 to 223 K and then heating at the same rate as that for the cooling process to 298 K after maintaining 223 K for 10 min. The temperatures of crystallization and melting of water sorbed in the polymer gels were calibrated using the melting peaks of pure water and HPLC-grade acetonitrile. After DSC measurements, the sample vessel was punctured with tweezers and placed in an oven overnight at 363 K to dry samples. Total water content of each sample, w_t (g/g dry gel), was calculated as follows:

$$w_t = \frac{W_w}{W_g} \tag{1}$$

where W_w and W_g denote the weight of water in the gel and that of dry polymer gel, respectively.

3. Results and discussion

3.1. Estimation of the amounts of stationary phase water in PEG and PVA gels

The stationary phase volume, V_s, can be estimated by the following equation:

$$V_s = V_t - V_m \tag{2}$$

where V_t and V_m are the total liquid phase volume and the mobile phase volume in the column, respectively. We determined V_t value of the each column according to the following equation:

$$V_t = \frac{W_t(c) - W_g(c)}{\rho} \tag{3}$$

where ρ is the density of water at 308 K, and $W_t(c)$ and $W_g(c)$ denote the total weight of the contents in the column and that of the dry polymer gel, respectively. On the other hand, the V_m values were calculated by the following equation [40]:

$$V_m = \frac{V_A^{YX} V_B^{WZ} - V_A^{WZ} V_B^{YX}}{V_A^{YX} + V_B^{WZ} - V_A^{WZ} - V_B^{YX})} \tag{4}$$

where V_A^{YX} is the retention volume of analyte ion, A, when eluted with the solution of the electrolyte, YX. We used inorganic anions, IO_3^-, NO_3^-, I^- and SCN^- as probe analyte ions and NaCl and $NaClO_4$ as mobile phase electrolytes. The interstitial or interparticulate volume, V_{int}, was assumed to be equal to the retention volume of Blue Dextran 2000.

The V_t, V_m, V_s and V_{int} values obtained for the each column are listed in Table 1. As is evident from Table 1, the

Table 1
V_t, V_m, V_s and V_{int} values (ml) for the columns packed with TSKgel Toyopearl HW-40S, 50S, 55 S, 75S and TSKgel Ether-250

Polymer gel	V_t	V_m	V_s	V_{int}
Toyopearl				
HW-40S[a]	3.79	2.01 ± 0.11	1.78 ± 0.11	1.35
HW-50S[a]	4.20	2.90 ± 0.09	1.30 ± 0.09	1.43
HW-55S[a]	4.41	3.42 ± 0.06	0.99 ± 0.06	1.44
HW-75S	12.5	11.62 ± 0.05	0.79 ± 0.05	5.58
Ether-250	1.88	1.43 ± 0.02	0.45 ± 0.02	0.61

[a] Data from Ref. [38].

order of these values is $V_t > V_m > V_{int}$ for all the hydrogel columns studied, indicating that a fraction of water in the gel ($V_m - V_{int}$) functions as the mobile phase, while the other fraction ($V_t - V_m = V_s$) does as the stationary phase.

3.2. Thermal phase transition behaviour of water sorbed in the PEG and PVA gels

Fig. 1 shows typical DSC heating curves of water sorbed in TSKgel Ether-250 and Toyopearl HW-40S and 75S. Two peaks were observed for the samples of Ether-250 and HW-75S, while one peak was observed for the HW-40S sample. The HW-50S and 55S samples showed similar
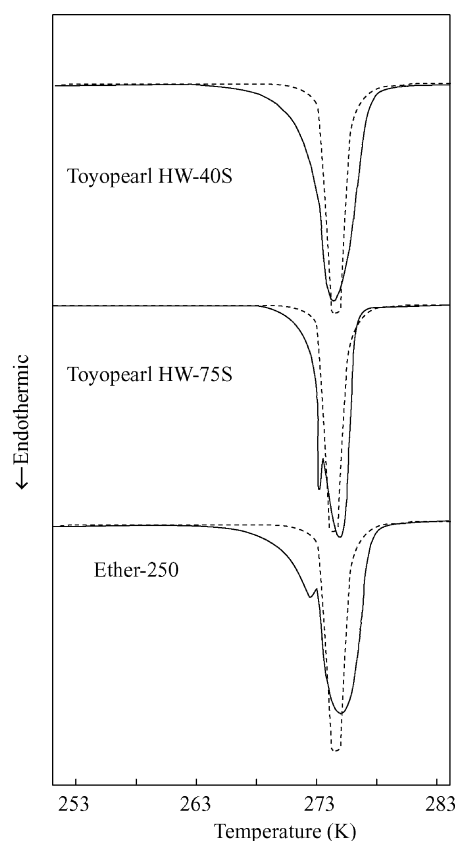

Fig. 1. DSC heating curves of water sorbed in TSKgel Toyopearl HW-40S, HW-75S and TSKgel Ether-250. Broken lines denote the DSC curves for pure water.

DSC curves to that of HW-40S. In the cooling curves only one sharp peak was observed for all the samples. We used the heating curves to investigate the states of water because little information was obtained from the cooling curves.

As can be seen from Fig. 1, melting of water sorbed in all the samples starts at a temperature lower than that of pure water; the DSC heating curve of pure water is shown by the broken line. The water melting at 273 K is free water and that melting below 273 K is regarded as freezable bound or intermediate water. Contrary to HW-40S, 50S, 55S and other hydrophilic polymer gels that we have so far investigated [38], a distinct peak of freezable bound water was observed for TSKgel Ether-250 and Toyopearl HW-75S. We recently reported that two clear peaks corresponding to free water and freezable bound water were also observed for water incorporated in a hydrophobic PS-DVB gel sample. However, the repeatability of the area of these two peaks was poor; the area of the peak for freezable bound water decreased, while that for free water increased with consecutive measurements for an identical sample. In other words, the freezable bound water incorporated in the pores of the PS-DVB gel came out of the pores in the crystallization or melting process and was converted to the free water. On the other hand, the reproducible results were obtained for peak areas of the freezable bound water and the free water in the Ether-250 and HW-75S samples. This result indicates that water incorporated in PS-DVB gels does not strongly interact with polymer matrices so that the gel cannot keep its shape during the phase transition of water, whereas the hydrated structures of PEG and PVA gels are relatively stable.

In order to clarify the states of water that functions as the stationary phase, we calculated the amounts of the individual water fractions. The amount of free water, w_f, and that of freezable bound water, w_{fb}, expressed in g/g dry gel, were estimated from DSC heating curves as follows:

$$w_f = \frac{Q(\geq 273\,\mathrm{K})}{\Delta H W_g} \tag{5}$$

$$w_{fb} = \frac{Q(< 273\,\mathrm{K})}{\Delta H W_g} \tag{6}$$

where $Q(<273\,\mathrm{K})$ and $Q(\geq 273\,\mathrm{K})$ are the heats absorbed in the heating process, which are calculated from areas of the peaks below and above 273 K in the DSC heating curve, respectively and ΔH is the heat of fusion of water calculated at various temperatures [13]. The amount of non-freezing water, w_n, was calculated by subtracting w_f and w_{fb} from total water content of water, w_t, as follows:

$$w_n = w_t - w_f - w_{fb} \tag{7}$$

Figs. 2 and 3 show dependencies of the w_f, w_{fb} and w_n values on w_t for the samples of Toyopearl HW-40S and TSKgel Ether-250, respectively. The w_f value decreases as w_t decreases, while both w_{fb} and w_n are constant until the free water vanishes. In the region in which $w_f = 0$, w_{fb} linearly decreases with decrease in w_t, while w_n is still constant until
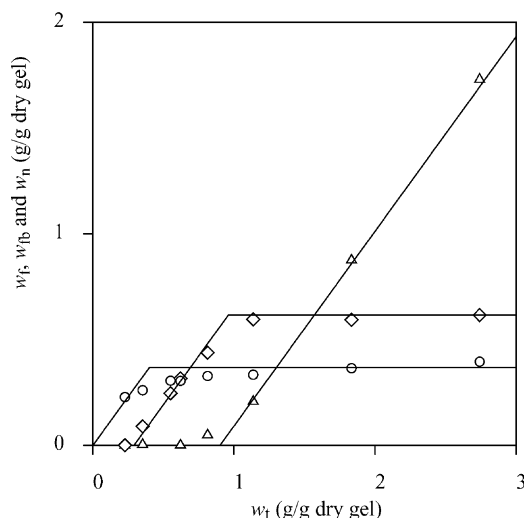

Fig. 2. Dependence of w_f, w_{fb} and w_n on total water content for Toyopearl HW-40S. *Symbols*: ($\triangle$) w_f; ($\diamond$) w_{fb}; ($\bigcirc$) w_n.

the freezable bound water disappears. Toyopearl HW-50S, 55S and 75S exhibited a similar DSC behaviour. This result also reveals that the hydrated structure of the PEG and PVA gels are different from that of the PS-DVB gels.

The amount of the stationary phase water, w_x, was estimated and compared with w_{fb} and w_n. The w_x value can be calculated as:

$$w_x = \frac{\rho V_s}{W_g(c)} \tag{8}$$

where ρ is the density of water at 308 K. On the other hand, the water regain, S_r, is calculated by:

$$S_r = \frac{W_t(c) - W_g(c) - \rho V_{int}}{W_g(c)} \tag{9}$$

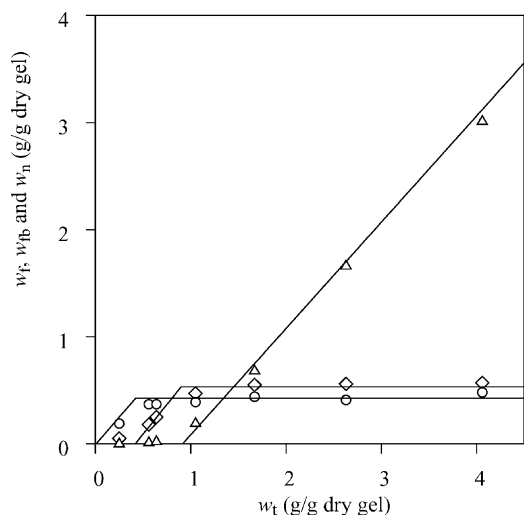The w_x and S_r values for TSKgel Ether-250 and Toyopearl HW series samples are listed in Table 2 together with the

Fig. 3. Dependence of w_f, w_{fb} and w_n on total water content for TSKgel Ether-250. *Symbols*: ($\triangle$) w_f; ($\diamond$) w_{fb}; ($\bigcirc$) w_n.

Table 2
w_{fb}, w_n, w_x and S_r values (g/g dry gel) for TSKgel Toyopearl HW-40S, 50S, 55S, HW-75S and TSKgel Ether-250

Polymer gel	w_{fb}	w_n	w_x	S_r
Toyopearl				
HW-40S[a]	0.61 ± 0.01	0.40 ± 0.02	1.02 ± 0.06	1.40
HW-50S[a]	0.61 ± 0.02	0.40 ± 0.03	1.06 ± 0.07	2.28
HW-55S[a]	0.56 ± 0.01	0.37 ± 0.00	0.96 ± 0.06	2.93
HW-75S	0.07 ± 0.02	0.31 ± 0.10	0.30 ± 0.05	2.59
Ether-250	0.59 ± 0.05	0.44 ± 0.05	0.49 ± 0.02	1.38

[a] Data from Ref. [38].

w_{fb} and w_n values. It is noteworthy that the w_x value for TSKgel Ether-250 and Toyopearl HW-75S is approximately equal to the w_n value. This means that only non-freezing water functions as the stationary phase in TSKgel Ether-250 and Toyopearl HW-75S gels. On the other hand, the results obtained for the other PVA gels, Toyopearl HW-40S, 50S and 55S, as well as for DEX and PAA gels indicate that both freezable bound water and non-freezing water function as the stationary phase in these gels [38].

This interesting result seems to originate from the difference in structures of these polymer gels. Toyopearl HW gels are packing materials usually used for aqueous size-exclusion chromatography. Among the Toyopearl HW gels used in this study, HW-75S has the largest exclusion limit as shown in Table 3. Therefore, the pore size of HW-75S is considered to be much larger than those of the other Toyopearl HW gels. The S_r value for HW-75S is smaller than that for HW-55S. This is probably because the molecular weight of Blue Dextran 2000 is smaller than the exclusion limit of HW-75S and this marker compound partially penetrates into the pores of the gel. The pore size of Toyopearl HW gels is presumably controlled by changing degree of cross-linkage using a suitable cross-linking agent. On the other hand, it has been reported that PVA in aqueous solution forms intermolecular and/or intramolecular hydrogen bonds with hydroxyl groups on the polymer chains [42–44]. Takigawa et al. [44] investigated the swelling and mechanical properties of PVA gels obtained by swelling precursors in various solvents and showed that the structure of the PVA gels varies with the solvent; PVA gels have a

Table 3
Some physical properties of Toyopearl HW-40S, 50S, 55 S, 75S and TSKgel Ether-250 gel beads[a]

Polymer gel beads	Particle size (μm)	Exclusion limits (MW)	Pore diameter (nm)
Toyopearl			
HW-40S	10–40	2.10×10^3–3.90×10^3	
HW-50S	20–40	1.26×10^4–2.34×10^4	
HW-55S	20–40	1.05×10^5–1.95×10^5	
HW-75S	20–40	5.00×10^6–11.5×10^6	
TSKgel Ether-250	5		25

[a] Manufacturer's data.

uniform structure with flexible PVA chains in water, while those swollen in methanol, ethanol and formamide have a two-phase structure, which is composed of PVA-rich and solvent-rich phases. The PVA chains in the PVA-rich phase are tightly associated with one another by hydrogen bonding. They reported that this two-phase structure was fixed by annealing of the gels at 398 K after evaporation of the solvent. Therefore it can be assumed that the PVA hydrogel prepared by swelling the annealed gel in water has microcrystalline domains formed by hydrogen bonding and macropores containing water phase. Toyopearl HW-40S, 50S and 55S containing PVA may have a homogeneous gel phase, whereas HW-75S may have a heterogeneous structure consisting microcrystalline PVA-rich domains and water phase located in macropores compartmentalized by the microcrystalline domains. The non-freezing water is considered to be associated with hydroxyl groups of the polymer chains for all the PVA gels. On the other hand, the freezable bound water in Toyopearl HW-40S, 50S and 55S can be regarded as a component of a homogeneous PVA solution phase, while that in HW-75S may be water isolated in small pores similarly to the water incorporated in PS-DVB gels. The freezable bound water in Toyopearl HW-40S, 50S and 55S may not be distinguished from the non-freezing water in the solution state.

The structure of Ether-250 can also be considered to be similar to that of HW-75S. It has been known that PEG in water forms a structure which is stabilized by water bridges [45–47]. Graham et al. [45] studied the association of water with cross-linked PEG gels and showed that the ether oxygen atom takes one to three molecules of water to form hydrates. Based on the results obtained they constructed a postulated plausible structure for a water-swollen PEG gel, which contains a helix repeating every seven ethylene oxide units; it comprises an exterior shell of the $-CH_2CH_2-$ units of the PEG with the ether groups turned inwards to a hydrated shell of 3 mol of water per ether group. The non-freezing water in the Ether-250 gel beads may correspond to the hydrated water although the number of water molecules associated with one ether group in the Ether-250 gel is calculated from its w_n value to be 1.1 assuming that the content of cross-linking agent is negligible. The structure that Graham et al. presented indicates the possibility that PEG in water presents a relatively hydrophobic surface to the bulk water. We have demonstrated that the water in pores of the hydrophobic PS-DVB gels has similar properties to those of the bulk water with respect to the interaction with solute compounds and does not function as the stationary phase [39]. It is thus presumed that the freezable bound water in Ether-250 is water incorporated in the hydrophobic domains in the gels and the depression of the melting point of the water is attributed to isolation of water phase in the small pores as described in the previous study on the states of water in PS-DVB gels [39]. Contrary to PS-DVB gels, however, the structures of the water-swollen Ether-250 and HW-75S gels are so stable due to the hydration of the

hydrophilic groups that the freezable bound water does not come out of the pores during the crystallization or melting process.

3.3. Solute retention selectivity of PEG and PVA gels

We investigated the retention behaviour of some non-ionic organic compounds on the columns packed with the PEG and PVA gels in order to clarify the relationship between the state of water in the gel phase and the solute retention selectivity. We used the distribution coefficient, K_D, calculated by the following equation as the retention parameter:

$$K_D = \frac{V_R - V_m}{V_s} \tag{10}$$

where V_R stands for the retention volume. Although the stationary phase in some hydrogels can be regarded as a mixture or solution of the polymer chain and water as described above, we adopted the volume of water which functions as the stationary phase as the V_s value for calculating K_D because it is difficult to evaluate the fraction of the polymer which works as components of the stationary phase.

Fig. 4 shows $\log K_D$ of the solute compounds obtained for Toyopearl HW-50S, 55S and 75S columns plotted against $\log K_D$ values obtained for Toyopearl HW-40S column. The slopes of the plots for HW-50S, 55S and 75S are 1.03, 1.11 and 1.61, respectively. This indicates that a PVA gel that has smaller w_x exhibits higher retention selectivity among Toyopearl HW series samples. As described above, the sta-
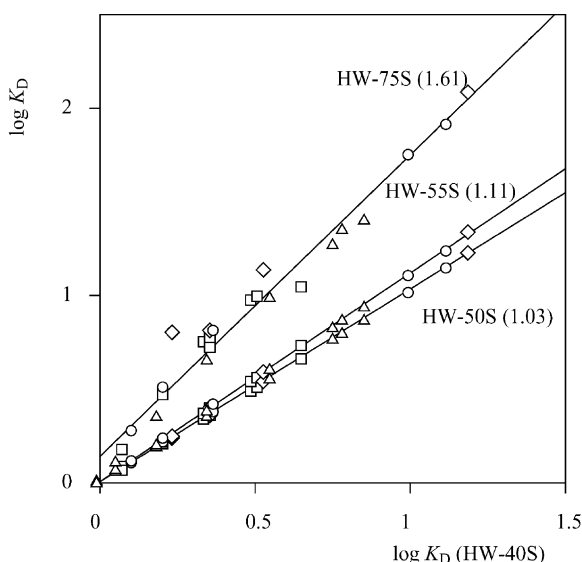

Fig. 4. Values of $\log K_D$ for Toyopearl HW-50S, 55S and 75S plotted against $\log K_D$ for Toyopearl HW-40S. Values in parenthesis give the slopes of the plots. *Symbols*: (△) methanol, ethanol, 1-propanol, 1-butanol, 1-hexanol, benzyl alcohol and phenyl alcohol; (□) acetone, 2-butanone, 3-methyl-2-butanone, 3,3-dimethyl-2-butanone, 2-penta-none, 4-methyl-2-petanone, 3-pentanone and 2,4-dimethyl-3-pentanone; (○) acetonitrile, butylnitrile, benzonitrile and phenylacetonitrile; (◇) nitromethane, nitroethane, nitropropane and nitrobenzene. Data for Toyopearl HW-40S, 50S and 55S are from Ref. [38].
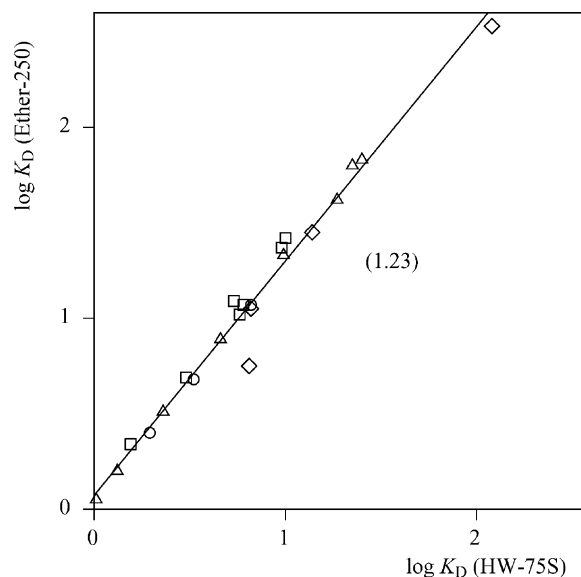

Fig. 5. Values of $\log K_D$ for TSKgel Ether-250 plotted against $\log K_D$ for Toyopearl HW-75S. See Fig. 4 for other details.

tionary phase of HW-40S, 50S and 55S can be regarded as a mixture or solution of the PVA polymer and water. The larger the concentration of the polymer in the stationary phase, the difference in property between the stationary phase and the bulk water phase must be greater. The dependence of the solute retention selectivity of the PVA gels on w_x is consistent with this postulated structure.

It should be noted that the $\log K_D$ versus $\log K_D$ plots for HW-75S are much more scattered compared to the plots for HW-50S and 55S. This may result from the difference in structure of the gel phase between HW-75S and the other PVA gels. It is very interesting that the plots of $\log K_D$ values obtained on TSKgel Ether-250 against the values on HW-75S shown in Fig. 5 give a straight line despite the difference of polymer materials. The linearity and correlation of the plots is even better than those for HW-75S versus HW-40S. This suggests that Ether-250 and HW-75S have similar gel phase structures, which may consist relatively hydrophobic domains constructed by the exterior shell of $-CH_2CH_2-$ (PEG) or $-CH_2CH-$ (PVA) units and hydrated water domains.

4. Conclusions

The results obtained in the present study reveal that the water-swollen hydrogels exhibit separation selectivity depending on the structures of the hydrogels and the states of water in the gels. It has been found by the DSC measurements that there are three different states of water in PEG and PVA hydrogels, non-freezing water, freezable bound water and bulk water. However, the evaluation of the amount of stationary phase water by the liquid chromatographic method has elucidated that the water that shows the

thermal transition behaviour different from that of the bulk water does not necessarily have a different affinity to solutes from that of the bulk water. Both of non-freezing water and freezable bound water in densely cross-linked gels, HW-40S, 50S and 55S, work as the stationary phase, while only non-freezing water functions as the stationary phase in HW-75S and Ether-250 gels. This can be interpreted in terms of the structures of the gels and the interaction of water molecules with the polymer matrices. Toyopearl HW-40S, 50S and 55S may have a uniform gel phase, whereas HW-75S and Ether-250 have a heterogeneous structure consisting of hydrated polymer-rich domains formed by hydrogen bonding and pores with relatively hydrophobic surface. The freezable bound water in the former gels can be regarded as a component of a homogeneous polymer solution phase, while that in the latter gels may be water isolated in small pores of the hydrophobic domains. The depression of the melting point of the freezable bound water in HW-75S and Ether-250 gels can be ascribed to isolation of water clusters in the small pores. The column packed with HW-75S showed the similar retention selectivity to that of the Ether-250 column for organic compounds having various functional groups compared to that of the other PVA columns. This result also fits our postulated view on the structures of the PEG and PVA gels.

Acknowledgements

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