States of water in cationically charged poly(vinyl alcohol) membranes

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Differential scanning calorimetry (d.s.c.) and pulsed ^1H nuclear magnetic resonance (n.m.r.) measurements were carried out on cationically charged poly(vinyl alcohol) (PVA) membranes to obtain information about the states of water in polymer matrices. From the d.s.c. data, water present in the polymer matrices is classified as (i) freezable and (ii) non-freezable, whereas n.m.r. measurements indicate its classification into (i) free and (ii) bound water. The amounts of free and bound water depend on the mobility of polymer chains and distinguish between freezable and non-freezable. The correlation time obtained from spin–lattice relaxation indicates that the mobility of water in poly[vinyl alcohol-*co*-(*N*-(3-trimethylammoniopropyl)-acrylamide chloride)] (PVA-N) membranes ($H = 0.358$) is approximately 10^4 times shorter than in bulk water.

(Keywords: cationically charged poly(vinyl alcohol) membranes; differential scanning calorimetry; nuclear magnetic resonance; states of water; mobility of water; freezable water; non-freezable water)

INTRODUCTION

The states of water in polymer systems, including hydrogels and aqueous polymer solutions, have been investigated by many workers, using n.m.r.[1–9], d.s.c.[10–17],i.r.[18–20], Raman[21,22], d.t.a.[23] and other techniques[24,25]. Water in polymer systems is known to be affected by specific interaction with polymer chains. Accordingly, the effect varies with the polymer structure, that is with the degree of polymerization, with the conformation and with functional groups. Water that does not freeze as a result of the interaction with polymer has been called (variously) bound, non-freezing, non-freezable or unfrozen water.

Chemical shifts, relaxation times (spin–lattice relaxation (T_1) and spin–spin relaxation (T_2)) and self-diffusion coefficients (D_{self}) are obtained[2] from n.m.r. measurements, whereas d.s.c. gives the transition temperature, specific heat, and transition enthalpy. I.r. investigations give the shift in the absorption wavenumber of a specific bond in the water molecule. Using this information, various states of water have been proposed. It appears now that water in polymer matrices can be divided in two parts: one, called bound water (from n.m.r. measurements), is affected strongly by interaction with the polymer, i.e. bound (non-freezable) water (from d.s.c. measurements); whereas the remainder is called free water (n.m.r.), i.e. freezable water (d.s.c.).

D.s.c. investigations

Burghoff and Pusch[13] studied the water in cellulose acetate membranes by means of d.s.c. and observed the greater partial heat capacity of sorbed water in the membranes than that in bulk water or dry membranes. The observation was interpreted as indicating strong interaction between sorbed water and macromolecules.

Hager and Macrury[14] carried out d.s.c. measurements on aqueous poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG) and 50/50 random EG–PG copolymer and, based on the decrease in the heat of fusion of freezable water (according to their terminology, free and freezable bound water) on addition of polymer, they estimated the hydration numbers per monomer residue to be 2.7, 2.3 and 1.5 for PEG, copolymer and PPG, respectively.

Takizawa *et al.*[15] used d.s.c. to investigate the state of water in poly(methyl methacrylate-*co*-*N*-vinylpyrrolidone) (MMA/NVP) membranes with varying water contents. Transition peaks were hardly observable between -60 and 60°C, especially at low water contents, indicating that all the water in MMA/NVP interacts with the polymer[17].

N.m.r. investigations

Carles and Scallan[1] investigated moist cellulose by means of n.m.r., observing not only a broadening of the water peak in the cellulose matrix, but also a spectral shift to higher magnetic field. The shift was attributed to the displacement of the equilibrium between monomeric water and strongly hydrogen-bonded clusters to a higher concentration of the monomeric species[3]. The T_2 of the water proton calculated from the peak width was of the order of 10^{-3} s, which is much shorter than the T_2 of bulk water.

Nyström *et al.*[4] measured T_1, T_2 and D_{self} of H_2O and D_2O in the gel system of cellulose/H_2O using the pulsed n.m.r. technique. The temperature dependence of T_1 and D_{self} can be represented by Arrhenius-type relations; however, T_2 values of H_2O pass through a shallow minimum over the temperature range of 14–44°C.

Uedaira[5] reviewed the theoretical treatment of n.m.r. investigations in relation to the kinetic states of water in

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various polymer systems and argued that the obstruction and compartmentalization effects[26,27] strongly affect the self-diffusion coefficients of water in polymer matrices such as gels and aqueous solutions. The water molecules in polymer matrices are trapped in such small compartments that the observed D_{self} is influenced by collisions with the wall of the compartment. The obstruction effect is caused by the presence of impenetrable polymer chains. Both obstruction and compartmentalization effects should operate even in the absence of interaction between polymer and water.

Duff and Derbyshire[6] determined T_1 and T_2 of water in muscle at various temperatures and calculated the amounts of non-freezable water (according to their terminology, non-freezing water) below 0°C from the intensity of the signal. T_1 was generally at a minimum at -20 to -10°C.

Katayama *et al.*[7,8] studied the states of water in aqueous acrylamide (AA) solutions and poly(acrylamide) (PAA) gels by n.m.r. measurements. Non-freezable water (according to their terminology, unfrozen water) could not be detected in the aqueous solutions but it was found in the PAA gels. They suggest that in aqueous solution AA monomer cannot hold any associated water because of weak hydration and therefore non-freezable water cannot be observed. In the case of the PAA gel framework, weak hydration of the individual polymer residues is linked cooperatively, producing associated water in the gel (spatial effect). They propose the following conditions for the system to hold non-freezable water[8]: (i) the system should include a polymer—exceptions are glycerol and ethylene glycol; (ii) the molecules should contain hydrophilic groups, such as -OH, -COOH, >CO, -CHO, $CONH_2$, >NH, etc.; (iii) the molecules should have a structural specificity of higher order, such as proteins; and (iv) the gel systems should give the spatial effect.

I.r. and Raman investigations

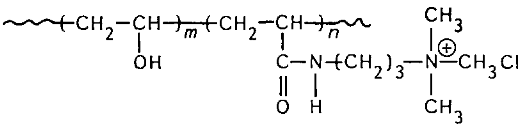
Falk[18] studied the states of water in Nafion by i.r. spectroscopy and observed two bands of water in the OH stretching region, 3660 and 3520 cm^{-1}. The latter band was assigned to the hydrogen bond of water–water or the water–hydrophilic sulphonate group. The former band was assigned to interactions other than the hydrogen bond of water–water or water–hydrophilic moieties. This interaction should be weaker than that of the hydrogen bond.

Scherer *et al.*[21] studied the states of water in cellulose acetate (CA) films at various relative humidities by Raman scattering spectroscopy and discussed the polymer–polymer, polymer–water and water–water interactions. At low relative humidities, monomeric water molecules are present in CA and some of them interact with OH groups of the polymer through hydrogen bonding. With increase in relative humidity, water–water interaction increases and water clusters appear in the CA matrix.

EXPERIMENTAL

Materials

Cationically charged poly[vinyl alcohol-*co*-(*N*-(3-trimethylammoniopropyl)acrylamide chloride)] (PVA-N) was used in this investigation. The polymers were prepared and kindly supplied by Kurarai Co.



$$\sim\!\!\sim\!\left(CH_2-\underset{OH}{CH}\right)_m\!\left(CH_2-\underset{\substack{C(=O)-NH-(CH_2)_3-N^{\oplus}(CH_3)_3\,Cl^{\ominus}}}{CH}\right)_n\!\sim\!\!\sim$$

PVA-N contains 0.23 mol% of charged monomer units; its saponification value is 99.5 mol% and the degree of polymerization is 1620. The polymer was used after Soxhlet extraction with methanol for 16 h.

The 10% aqueous solutions of PVA-N was obtained by dissolving the required amounts of polymer in water at 100°C, gently stirring for 4 h and then allowing to stand for 48 h at 21°C to remove air bubbles completely. The membranes were prepared by casting on clean glass and drying at 21 ± 2°C for one week.

Before crosslinking, all membranes were kept in a desiccator containing silica gel. They were then swollen in a saturated aqueous Na_2SO_4 solution and crosslinking followed at 25 ± 0.02°C in an aqueous solution containing 20% Na_2SO_4, 1% H_2SO_4 and 0.1% glutaraldehyde. The various degrees of crosslinking were attained by varying the reaction time, thus producing different water contents in the membranes.

The hydrogel membranes thus prepared were kept in distilled deionized water at 21°C, renewing the water every day.

D.s.c. measurements

Water-swollen PVA-N membranes and aqueous PVA-N solutions were used for the experiments. Freezing and melting of water in these polymer systems were investigated by d.s.c. (DSC-10, SSC/575 Thermal Controller, Seiko I. and E. Ltd). Adhering external water was carefully removed from the membranes by wiping with a filter paper. The aluminium pans in which the samples were sealed were pretreated in boiling water for 1 h before use. Each sample weighed approximately 15 mg. The sealed samples were cooled from 300 to 170 K at a rate of 2.5 K min^{-1} and then heated to 300 K at the same rate. The experimental errors in the heat detected in the peak area were ±5%.

The weight of freezable water W_{fz} corresponding to a peak was estimated by the following equation:

$$W_{\mathrm{fz}} = [A_r I R_s]/[H(T)B_s] \qquad (1)$$

where $H(T)$ (mJ mg^{-1}) is the transition enthalpy of water at the transition temperature T, I is the calibration constant (5.698 for our instrument), R_s (mJ s^{-1}) is the range sensitivity, A_r (cm^2) is the peak area and B_s (cm min^{-1}) is the chart speed of the recorder.

For supercooled bulk water the transition enthalpy $H(T)$ is known to be lower than that of bulk water at 273 K, as expressed by[28]:

$$H(T) = H(273\ \mathrm{K}) - \int_{T}^{273\,\mathrm{K}} \delta C_p\, \mathrm{d}T \qquad (2)$$

where δC_p is the difference between the heat capacities of ice and supercooled water.

The amount of non-freezable water can be estimated by subtracting the freezable water from the total amount of water in the polymer matrices.

Pulsed ^1H n.m.r. measurement

The same water-swollen PVA-N membranes and aqueous PVA-N solutions were used. The proton spin–lattice relaxation time T_1 and the spin–spin relaxation time T_2 of water in the polymer matrices were measured.

Before measurements, samples of membranes and solutions were degassed by an aspirator for 2 h. In the case of membranes, after degassing, adhering external water was carefully blotted with a filter paper.

A pulsed n.m.r. spectrometer (Minispec, PC20, Bruker) was used, operating at a frequency of 20 MHz. The spectrometer is equipped with a thermocontroller (Thermolete, BH-41, Yamato Kagaku Co. Ltd), which keeps the temperature within ±1°C in the range from 12 to 44.5°C. T_1 and T_2 of all samples were measured at 12, 25, 35 and 44.5°C. For the confirmation of the reproducibility of the experiment, in the case of membranes the samples were frozen and T_2 was measured again at 44.5°C.

The spin–lattice relaxation times T_1 of water in polymer matrices were obtained by observing the inversion recovery in repeated $180°—t_1—90°$ pulse sequences. The spin–spin relaxation time T_2 was obtained by observing the echo in the Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence, $90°—t_2—180°—t_2$—echo—t_2—$180°$—t_2—echo—. . . , which is called the CPMG method. The relaxation times obtained in this investigation are due to the relaxation mechanisms of single or double mode.

The spin–lattice relaxation time T_1 is calculated by the following equation, which is derived from Bloch's equation:

$$\ln(A_{\mathrm{inf}} - A_{t_1}) = \ln(2A_{\mathrm{inf}}) - t_1/T_1 \tag{3}$$

where A_{t_1} is the magnitude of the recovering vector of magnetization evolved by a 90° pulse at time t_1, and A_{inf} is the value of A_{t_1} when t_1 is long[29].

The spin–spin relaxation time T_2 is calculated as follows[29]. The parameter to be measured by using the CPMG method is the amplitude, $E(t)$, of the echo at time t_1. Its magnitude depends on the spin–spin relaxation time T_2 and the self-diffusion coefficient D_{self}, as shown by the following equation:

$$E(t) \propto \exp\left[-(t/T_2) - \frac{1}{3}\gamma^2 G^2 D_{\mathrm{self}} t_2^2 t\right] \tag{4}$$

where γ is the magnetogyric ratio of the nucleus in resonance (frequency/field), G the magnitude of a steady magnetic field gradient and t_2 the time between 90° and 180° pulses. Within short times, the effect of self-diffusion can be neglected. The relationship between $E(t)$ and T_2 is then expressed by:

$$\ln E(t) = -(t/T_2) + C \tag{5}$$

where C is an arbitrary constant.

According to equation (4), the magnitude of $E(t)$ depends on T_2 and D_{self}, as shown by the first and second terms of the exponential part on the right-hand side of the equation. D_{self} can be calculated accurately when the second term is as large as, or larger than, the first term. In the case when T_2 is small (as for gel samples in this work), the first term is much larger than the second because of the small intrinsic value of G ($G = 2.50 \times 10^{-3}$ T m^{-1}) for the apparatus used. Consequently it is impossible to determine D_{self} with reasonable accuracy. For this reason the determination of D_{self} was neglected.

In the case of the relaxation mechanism of a single mode, the linear relationship between $\ln(A_{\mathrm{inf}} - A_{t_1})$ and t_1 or $\ln E(t)$ and t is given. T_1 and T_2 are thus calculated by a simple least-squares method.

On the other hand, in the case of the relaxation mechanism consisting of two modes[2,30], a linear relationship cannot be expected and the curve obtained should be recognized as being due to the overlap of two straight lines. To obtain the lines from the curve, first the longer T_1 (T_2) value is calculated by the least-squares method using data at a longer time t_1 (t_2). The values of A_{t_1} ($E(t)$) calculated from the longer T_1 (T_2) thus obtained are subtracted from the experimental data. The resultant values are used to obtain the shorter T_1 (T_2) using the least-squares method. The fraction of two species of different mobility can be calculated from the difference of the intercepts on the $\ln(A_{\mathrm{inf}} - A_{t_1})$ and $\ln E(t)$ axes.

RESULTS AND DISCUSSION

D.s.c. measurements

D.s.c. measurements were performed on seven samples of aqueous solutions of PVA-N ($W_t/W_s = 0.860$–0.980) and the same number of PVA-N gel membranes ($W_t/W_s = 0.338$–0.946), where W_t is the weight of water in the solutions or gel membranes and W_s is the weight of the solutions or membranes. PVA-N could not be dissolved homogeneously in water at a lower content than $W_t/W_s = 0.860$ and the water content of PVA-N gel membranes obtained by the method of crosslinking mentioned in the 'Experimental' section could not be lower than $W_t/W_s = 0.3$.

During the cooling cycle (*Figure 1*) one sharp exothermic peak, due to freezing of water, was observed in

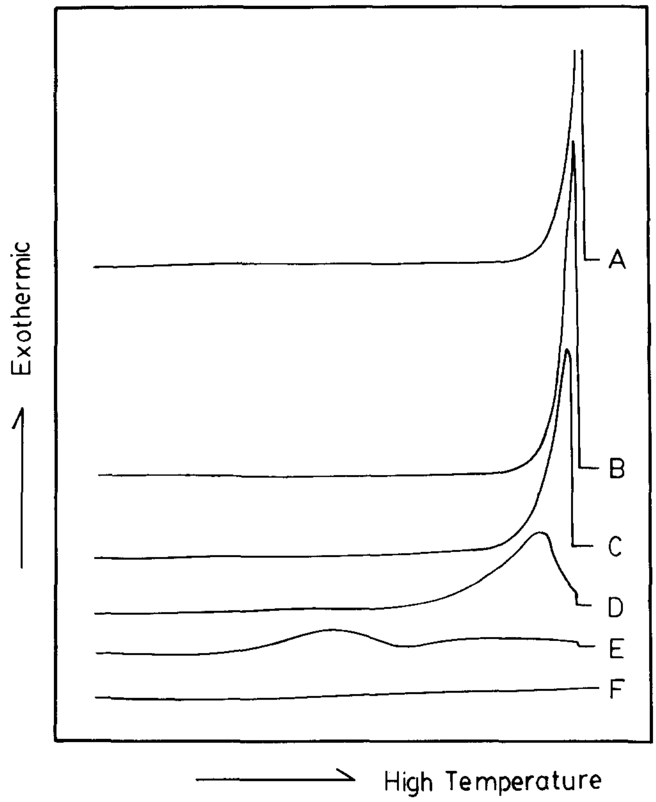


Figure 1 D.s.c. cooling curves of PVA-N aqueous solutions and gels: A, solution ($W_t/W_s = 0.980$); B, gel ($W_t/W_s = 0.946$); C, gel ($W_t/W_s = 0.661$); D, gel ($W_t/W_s = 0.528$); E, gel ($W_t/W_s = 0.393$); F, gel ($W_t/W_s = 0.338$)

Table 1 Phase transition temperatures of PVA-N aqueous solutions and gels

	W_t/W_s						
Solutions	0.980	0.960	0.940	0.920	0.900	0.880	0.860
T_c/K	264.5	252.6	256.0	257.1	255.4	251.6	256.0
T_h/K	273.0	272.6	272.1	271.7	271.2	270.9	270.5
	W_t/W_s						
Gels	0.946	0.859	0.791	0.661	0.528	0.393	0.338
T_c/K	255.9	259.6	256.6	261.6	264.1	261.9/239.8[a]	–[b]
T_h/K	272.3	270.4	270.2	269.1	266.6	247.6/272.0[a]	269.5

[a] Two peaks are observed
[b] No peaks are observed

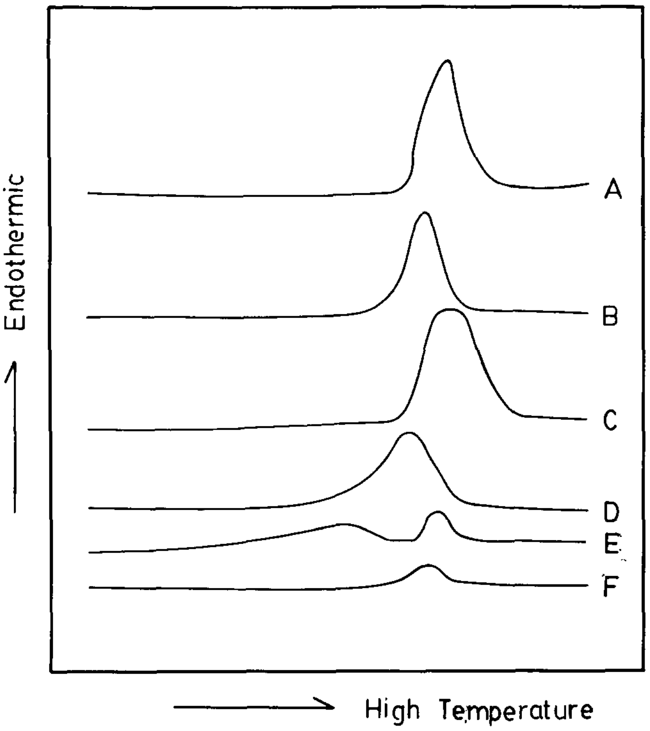


Figure 2 D.s.c. heating curves of PVA-N aqueous solutions and gels: A, solution ($W_t/W_s = 0.980$); B, solution ($W_t/W_s = 0.860$); C, gel ($W_t/W_s = 0.946$); D, gel ($W_t/W_s = 0.528$); E, gel ($W_t/W_s = 0.393$); F, gel ($W_t/W_s = 0.338$)

gel membrane samples of relatively high water content ($W_t/W_s > 0.6$) and all solution samples. In gel membranes with $W_t/W_s < 0.6$ the peak becomes broader as the water content decreases, then separates into two broad peaks ($W_t/W_s = 0.393$) and finally disappears ($W_t/W_s = 0.338$), as shown in *Figure 1*. In all samples except gels with $W_t/W_s = 0.393$ and 0.338, water freezes at temperature from 265 to 250 K as given in *Table 1*. The gel membranes with $W_t/W_s = 0.393$ give two exothermic peaks, which correspond to the two peaks in the cooling thermogram.

During the heating cycle (*Figure 2*) all solutions give endothermic peaks of similar shape. However, in gel membranes a broader peak is observed as the water content is decreased, and at $W_t/W_s = 0.393$ an additional peak forms. The gel membranes with $W_t/W_s = 0.338$ give an endothermic peak; no such peak was detected during the cooling cycle (*Figure 1*, curve F), possibly because it is too small and broad. The melting points of all samples, T_h, given in *Table 1* clearly decrease with decreasing water content. This is attributed to imperfect crystallization of water when the water content is low. The degree of imperfection may depend on the water content and not on whether the sample is a solution or a gel membrane.

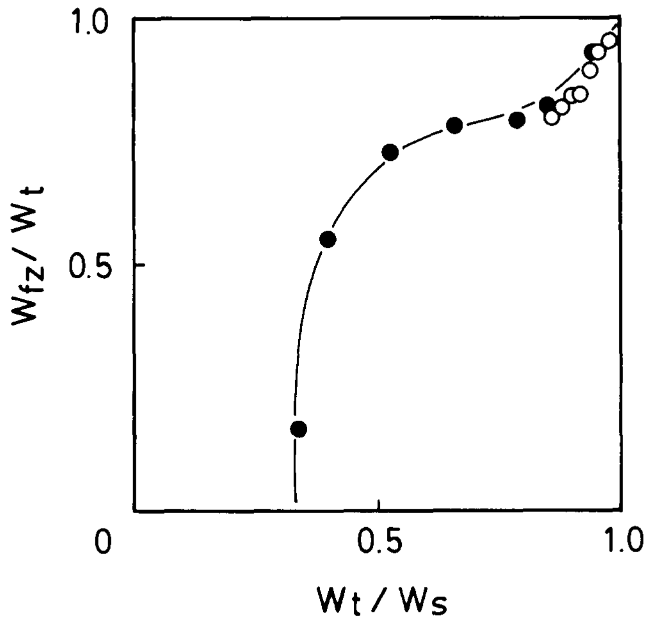


Figure 3 Plot of W_{fz}/W_t against water content: (○) PNA-N aqueous solutions; (●) PVA-N gels

The weight of freezable water, W_{fz}, is calculated from the peak area of the heating curve, using equations (1) and (2). Heating is used because it is clearer for comparison with the cooling curve, especially in the case of gels of low water content. The weight ratios of freezable to total water, W_{fz}/W_t, are shown in *Figure 3*. The value of this ratio is the same for both gels and solutions and decreases with decreasing W_t/W_s. These results will be discussed in detail later, together with n.m.r. data.

Pulsed ^1H n.m.r. measurements

Proton spin–lattice relaxation times T_1 and spin–spin relaxation times T_2, of the same samples as used for the d.s.c. investigation were measured. ^{1}H T_2 measurements at 44.5°C were also carried out before and after freezing. In two samples no difference could be detected in the spin–spin relaxation times, which indicates that the freezing process does not cause any structural change in the polymer matrices.

As can be seen in *Figure 4*, in all cases the spin-echo

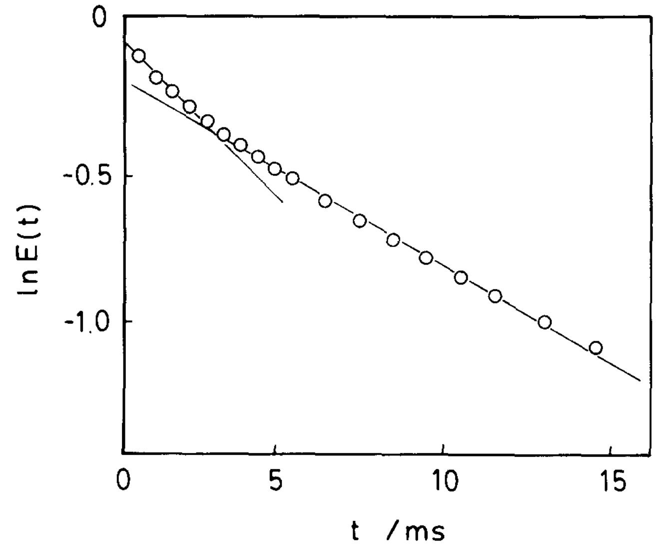


Figure 4 Plot of ln $E(t)$ against time: gel ($W_t/W_s = 0.393$), 25°C

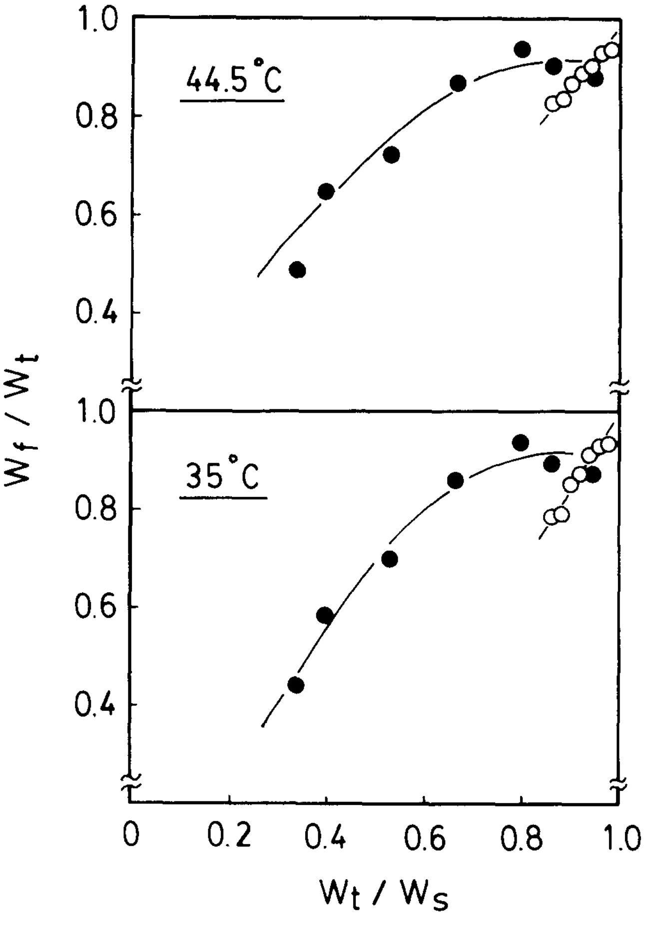


Figure 5 Plot of W_f/W_t against water content: (○) PVA-N aqueous solutions; (●) PVA-N gels

envelope for T_2 consists of two components. However, in all solutions the inversion recovery signal has a single component, whereas some gel membrane samples give two components and some a single component. T_1 goes through a minimum with respect to correlation time τ_c, while T_2 continues to decrease and eventually approaches a limiting value. Spin–spin relaxation was used to analyse the relaxation modes associated with the mobilities of water in the membranes; this led to the classification of two states of water. In *Figures 5* and *6* are shown the weight ratios of free to total water, W_f/W_t, at various temperatures. W_f/W_t decreases with decreasing W_t/W_s just like W_{fz}/W_t in *Figure 3*, but the value W_f/W_t is higher for gel membranes than for solutions. Furthermore, it can be seen clearly that for solution samples the decreasing tendency of W_f/W_t with decrease in W_t/W_s becomes prominent at lower temperatures. Gel membranes show this tendency very little.

T_1 and T_2 of all samples are summarized in *Tables 2* and *3*, respectively. In all cases T_1 and T_2 decrease with decreasing W_t/W_s. As mentioned above, spin–lattice relaxation indicates single or double components depending on the condition of the sample. These results may be interpreted by assuming that both the spin–spin and spin–lattice relaxations are essentially double components for all samples. In the case of solutions and the gel membrane of $W_t/W_s = 0.946$, two of the spin–lattice relaxation times T_1 may be very close, leading to an apparently single component. On the other hand, the gel membrane of $W_t/W_s = 0.393$ gives a single component of spin–lattice relaxation at 12 and 25°C, but double at 35 and 44.5°C (see *Table 2*). The gel membrane with $W_t/W_s = 0.338$ has a single-component relaxation. In these cases two T_1 probably in the minimum region with respect to τ_c and cannot be recognized as two different values. In almost all cases T_1 and T_2 decrease with decreasing temperature.

From inspection of *Figures 7* and *8*, T_2 of free and bound water is at a minimum at approximately 300 K,

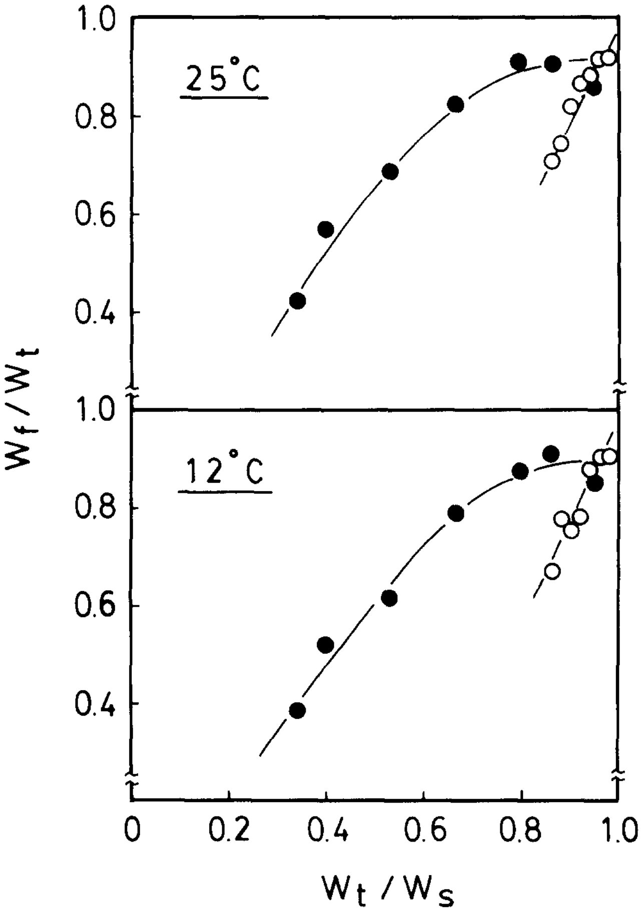


Figure 6 Plot of W_f/W_t against water content: (○) PVA-N aqueous solutions; (●) PVA-N gels

Table 2 Spin–lattice relaxation times of PVA-N aqueous solutions (s) and gels (s)

	W_t/W_s							
Solutions (s)	1[a]	0.980	0.960	0.940	0.920	0.900	0.880	0.860
12°C	2.05	1.68	1.61	1.49	1.26	1.10	0.992	0.805
25°C	2.70	2.41	2.15	2.10	1.92	1.66	1.41	1.30
35°C	3.18	2.91	2.67	2.49	2.37	2.18	1.84	1.73
44.5°C	3.92	3.46	3.10	3.08	2.90	2.65	2.33	2.14

	W_t/W_s						
Gels (s)	0.946	0.859	0.791	0.661	0.528	0.393	0.338
12°C	1.23	0.545/0.371[b]	0.296/0.213	0.210/0.174	0.111/9.09 × 10^{-2}	7.98 × 10^{-2}	7.20 × 10^{-2}
25°C	1.57	0.710/0.519	0.418/0.298	0.246/0.182	0.112/9.80 × 10^{-2}	7.83 × 10^{-2}	7.55 × 10^{-2}
35°C	1.89	0.940/0.646	0.470/0.258	0.279/0.205	0.133/0.105	0.103/7.94 × 10^{-2}	7.02 × 10^{-2}
44.5°C	2.46	1.04/0.735	0.646/0.413	0.284/0.222	0.165/0.147	9.03 × 10^{-2}/7.72 × 10^{-2}	6.29 × 10^{-2}

[a] Bulk water
[b] Two-component relaxation

Table 3 Spin–spin relaxation times of PVA-N aqueous solutions (s) and gels (ms)

	W_t/W_s							
Solutions (s)	1[a]	0.980	0.960	0.940	0.920	0.900	0.880	0.860
12°C	2.38	2.05/1.54[b]	1.96/1.49	1.68/1.34	1.65/1.15	1.38/1.05	0.925/0.628	0.916/0.614
25°C	2.99	2.54/1.81	2.21/1.57	1.94/1.44	1.42/1.09	1.03/0.780	0.923/0.698	0.902/0.618
35°C	3.58	2.76/1.96	2.47/1.96	2.39/1.88	2.12/1.32	1.96/1.19	1.43/0.913	1.34/0.871
44.5°C	3.93	2.93/2.18	2.86/2.30	2.67/1.82	2.51/1.62	2.22/1.31	1.82/1.04	1.46/0.887

	W_t/W_s						
Gels (ms)	0.946	0.859	0.791	0.661	0.528	0.393	0.338
12°C	676/522[b]	179/118	67.9/48.6	61.2/34.2	34.7/17.3	20.0/6.42	15.6/2.49
25°C	712/526	219/160	83.2/59.2	68.7/38.8	38.6/19.3	21.2/5.94	19.7/3.50
35°C	943/691	367/205	125/90.9	83.4/49.0	43.7/22.6	22.9/7.05	17.4/3.56
44.5°C	1.18 × 10^3/848	319/229	181/115	111/60.3	58.8/29.5	27.6/10.6	18.4/5.01

[a] Bulk water
[b] Two-component relaxation

in the solution samples of $W_t/W_s = 0.860$–0.920, while T_1 has no minimum in the experimental temperature range. Similar results for T_2 were reported by Nyström *et al.*[4] for cellulose gels. They interpreted the minimum as being the consequence of exchange of water protons with exchangeable protons of the polymer chains. In the PVA-N system, proton exchange between water molecules and OH groups in PVA-N can be assumed. In the case of solutions of $W_t/W_s = 0.860$–0.920, such an effect on the spin–spin relaxation can be expected.

As shown in *Figure 9* for gels of $W_t/W_s = 0.393$, T_1 is approximately constant in the temperature range 285–300 K. For the gel membrane $W_t/W_s = 0.338$, T_1 increases with decreasing temperature. According to the Bloembergen–Purcel–Pound (BPP) theory[31], the spin–lattice relaxation time has a minimum value when τ_c is expressed as:

$$\tau_c\omega = 1/\sqrt{2} \qquad (6)$$

where ω is the resonance frequency (2 × 10^7 Hz). Thus τ_c can be calculated as $\tau_c = 3.5 \times 10^{-8}$ s at minimum T_1. In the case of the gel membrane of $W_t/W_s = 0.393$, T_1 is assumed at a minimum at 285–300 K (*Figure 9*). In the case of the gel membrane of $W_t/W_s = 0.338$, the minimum is assumed to be above 320 K, whereas for the gel membrane of $W_t/W_s = 0.528$, the minimum is below 285 K. The correlation times of bulk water at 285, 303 and 323 K are 4.7×10^{-12}, 2.7×10^{-12} and 1.9×10^{-12} s, respectively[31]. Using these values, it can be estimated that the mobility of water in the gel membrane of $W_t/W_s = 0.393$ is restricted at least 7.4×10^3 times, compared with bulk water at 283 K. For the gel membrane of $W_t/W_s = 0.338$ the ratio seems to exceed 1.8×10^4.

States of water in polymer matrices

According to the n.m.r. results, the amount of bound water depends on whether the samples are gel membranes or solutions. In addition, T_1 and T_2 of solutions are different from those of gel membranes even when the weight fraction of water is approximately the same (*Figures 7* and *8*), the mobilities of free and bound water

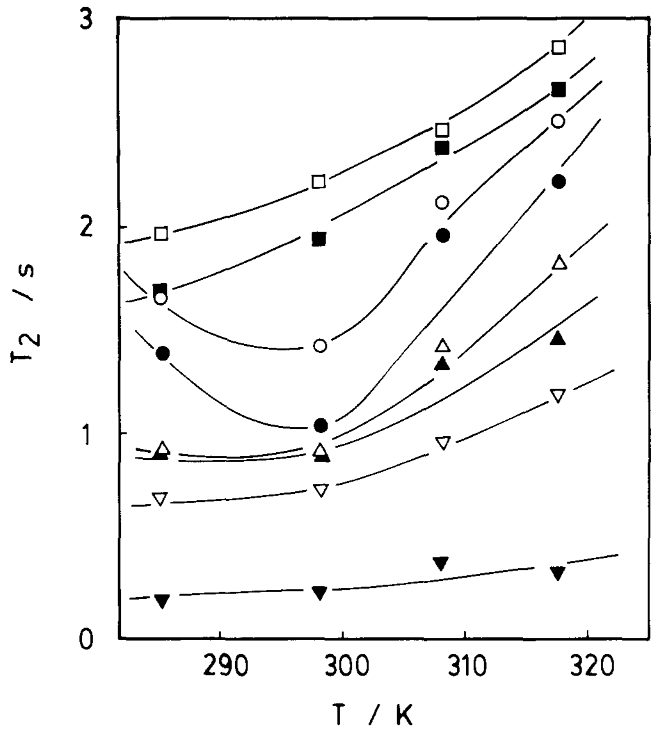


Figure 7 Spin–spin relaxation times T_2 of free water plotted against temperature: (□) solution ($W_t/W_s = 0.960$); (■) solution ($W_t/W_s = 0.940$); (○) solution ($W_t/W_s = 0.920$); (●) solution ($W_t/W_s = 0.900$); (△) solution ($W_t/W_s = 0.880$); (▲) solution ($W_t/W_s = 0.860$); (▽) gel ($W_t/W_s = 0.946$); (▼) gel ($W_t/W_s = 0.859$)

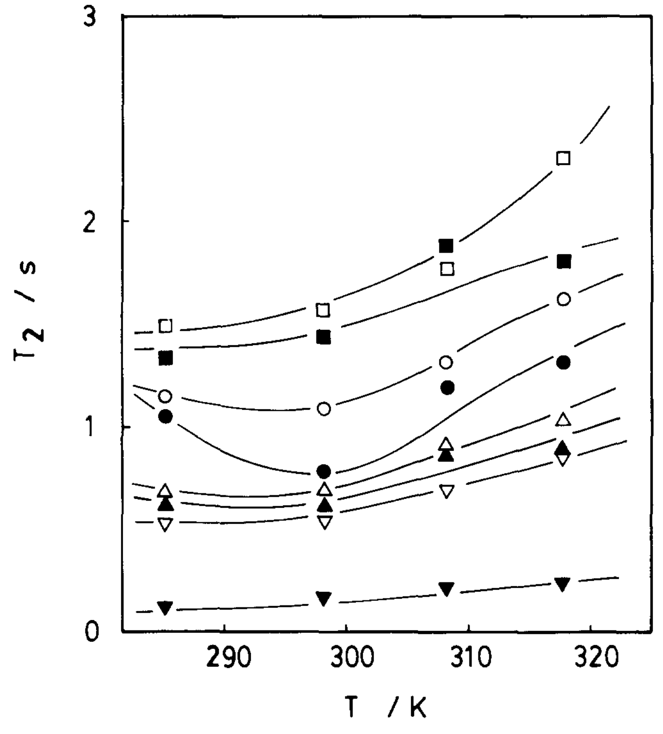


Figure 8 Spin–spin relaxation times T_2 of bound water plotted against temperature: (□) solution ($W_t/W_s = 0.960$); (■) solution ($W_t/W_s = 0.940$); (○) solution ($W_t/W_s = 0.920$); (●) solution ($W_t/W_s = 0.900$); (△) solution ($W_t/W_s = 0.880$); (▲) solution ($W_t/W_s = 0.860$); (▽) gel ($W_t/W_s = 0.946$); (▼) gel ($W_t/W_s = 0.859$)

depending on the condition of the samples. On the other hand, the amount of non-freezable water is independent of the condition of the sample. This may be interpreted as follows.

The mobility of free and bound water and their ratio estimated by the relaxation technique depend on the temperature, water content and mobility of the polymer. Because of crosslinking and crystallization, the mobilities of polymer chains in the gel membranes are restricted, compared with solutions, whereas the amount of non-freezable water depends only on the water content. In polymer matrices the polymer chain is likely to hinder the freezing of water.

We have studied the states of water in PVA gel membranes by i.r. spectroscopy[32] and concluded that the hydrogen bonds of water in the membrane are weaker than those in bulk water. The hydrogen bonds of water

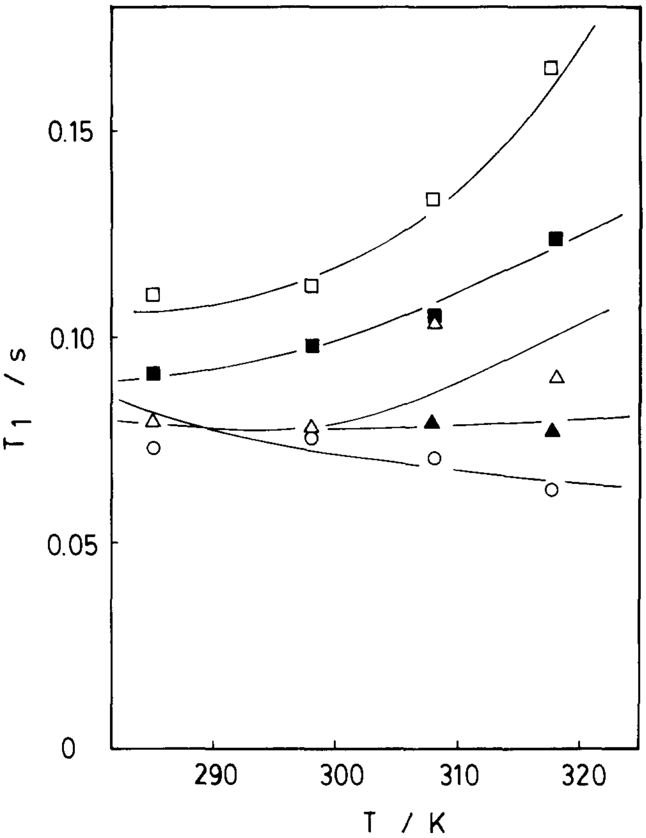


Figure 9 Spin–lattice relaxation times T_1 plotted against temperature: (○) gel ($W_t/W_s = 0.338$); (▲, △) gel ($W_t/W_s = 0.393$); (■, □) gel ($W_t/W_s = 0.528$)

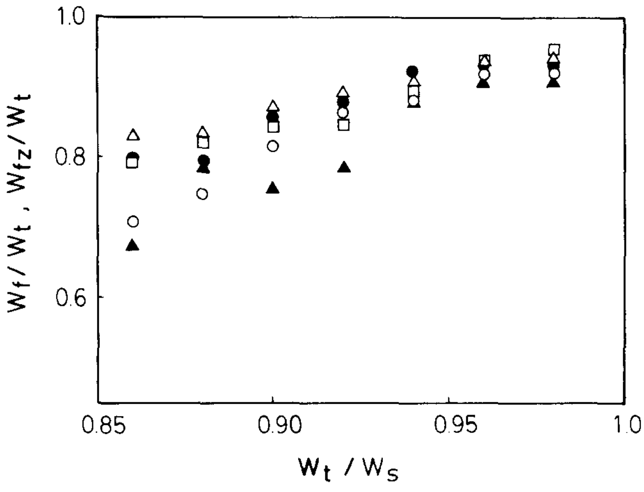


Figure 10 Plots of W_{fz}/W_t and W_f/W_t against water content of aqueous PVA-N solutions: (▲) 12°C (n.m.r.); (○) 25°C (n.m.r.); (●) 35°C (n.m.r.); (△) 44.5°C (n.m.r.); (□) d.s.c.

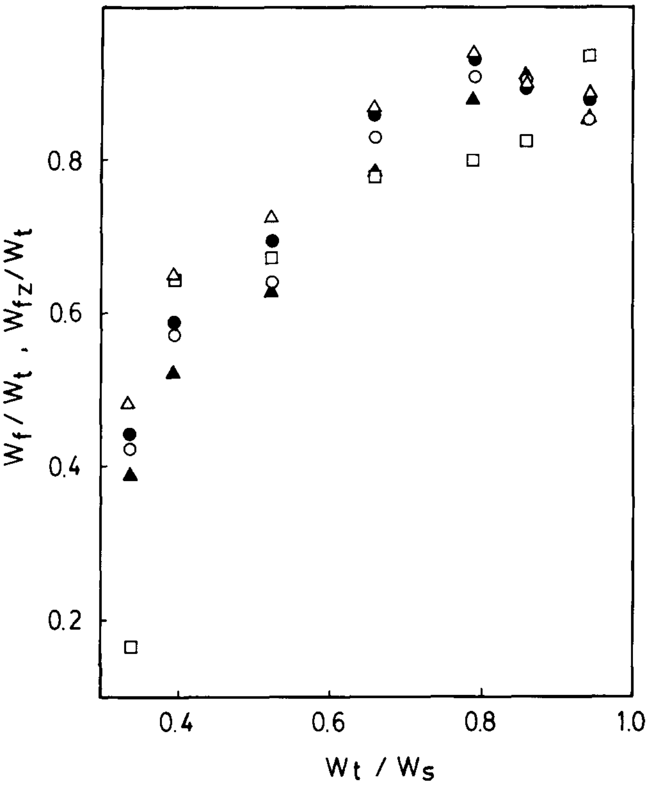


Figure 11 Plots of W_{fz}/W_t and W_f/W_t against water content of PVA-N gel: (▲) 12°C (n.m.r.); (○) 25°C (n.m.r.); (●) 35°C (n.m.r.); (△) 44.5°C (n.m.r.); (☐) d.s.c.

in the PVA-N matrices are likely to be weaker than in bulk water. Katayama and Fujiwara[8] proposed the formation of a cooperative hydrogen bond in associated water in the polymer (spatial effect). The relaxation time of water in the polymer matrix should be shorter because of this cooperative interaction. Water in polymer matrices can be divided into two classes, depending on the difference in the degree of association. Bound water is affected strongly by the polymer, but free water is only slightly affected by the polymer through bound water.

As mentioned previously, bound water is not necessarily identical with non-freezable water. As shown in *Figure 10*, W_f/W_t and W_{fz}/W_t are approximately the same for solution samples; and in the case of gel membranes, as shown in *Figure 11*, W_f/W_t and W_{fz}/W_t are approximately the same in the medium region of the weight fraction of water.

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