ELSEVIER

Thermochimica Acta 253 (1995) 137–148

thermochimica
acta

Non-freezing water content of mono- and divalent cation salts of polyelectrolyte–water systems studied by DSC ☆

Tatsuko Hatakeyama [a,]*, Hyoe Hatakeyama [a], Kunio Nakamura [b]

[a] *National Institute of Materials and Chemical Research, 1-1, Higashi, Tsukuba, Ibaraki 305, Japan*
[b] *Otsuma Woman's University, Chiyoda-ku, Tokyo 102, Japan*

Received 8 August 1994; accepted 23 August 1994

Abstract

The number of bound water molecules restricted by mono-, di-, and trivalent cations in polyelectrolytes, such as polystyrene sulphonate, carboxymethylcellulose and alginic acid, was calculated using DSC. The number of bound water molecules decreases with increasing ionic radius in the series of mono- and divalent cations when polyelectrolytes form the liquid crystalline state. However, when polyelectrolytes form rigid junction zones in the presence of cations, the number of bound water molecules is maintained at a constant value regardless of ionic radius. The results indicate that the higher order structure of polyelectrolytes strongly influences the number of water molecules tightly bound by cations.

Keywords: Alginic acid; Carboxymethylcellulose; DSC; Non-freezing water; Polyelectrolyte; Water

1. Introduction

In our previous studies, we established a thermo-analytical method for evaluating the number of water molecules tightly bound with hydrophylic polymers, such as polysaccharides and model polymers of natural compounds [1]. Water molecules

---

* Corresponding author.

☆ Presented (in part) at the International and III Sino-Japanese Symposium on Thermal Measurements, Xi'an, 4–6 June 1994, under the title "Junction Zone Formation of Polysaccharide Hydrogels as Studied by DSC".

SSDI 0040-6031(94)02087-6

are mainly bound via hydrogen bonding with hydrophilic groups, such as the hydroxyl group or the amide group. It was found that water molecules attached to hydrophilic groups [2] show no first-order phase transition. The systems consisting of hydrophilic polymers and tightly bound water molecules form the glassy state by quenching from the liquid state in liquid N_2 atmosphere, and the glass transition is observed by heating [3–6]. This kind of water is categorized as non-freezing water [1]. The amount of non-freezing water markedly increases when ionic groups are introduced in the polymer side chain. This seems to correlate with the fact that the hydration numbers of ionic compounds are larger than those of non-ionic compounds [7]. In our previous studies, it was found that the non-freezing water content in polyelectrolytes decreases with increasing atomic number of the counter ions [8]. It is also known that among ionic compounds, the hydration number increases with increasing ionic charge and with decreasing ionic radius [9].

In this study, the non-freezing water content in various mono- and divalent cation salts of polyelectrolytes in highly concentrated aqueous solutions was evaluated using differential scanning calorimetry (DSC). The intention was to establish the relationships between non-freezing water content and ionic radius of the counter ions of polyelectrolytes using DSC.

2. Experimental

2.1. Samples

The chemical structures of the samples used in this experiment are shown in Fig. 1. Sodium salts of polystyrene sulphonate (PSS) (Scientific Polymer Co.), carboxymethylcellulose (CMC) (Daiichi Kogyo Seiyaku Co.) and alginic acid (Alg) (Kibun Food Chemifer Co.) were chosen as representative polyelectrolytes from synthetic and natural polymers. The sodium ion was substituted by various mono-, di- and trivalent cations by the ion exchange method. The molecular weight (Mw) of CMC is 1×10^5 and the degree of substitution (DS) is shown in Table 1. The Mw of PSS was 7.0×10^4, and the DS was 0.78. The Mw of Alg was 9.5×10^4, the DS was 1.1, and the mannuronic acid to guluronic acid ratio was 1.0–1.2.

The water content of the samples were varied by vaporization after adding an excess amount of deionized and distilled water to the powder samples using a micro syringe. The water content (W_c) of each sample was defined as W_c (g/g) = (water, g)/(dry sample, g). The weight of the dry sample was estimated by heating it to 430 K, the evaporation of water being completed by thermogravimetry. W_c was varied from 0 to 3.0 g/g.

2.2. Measurements

A Seiko Instrument Co. differential scanning calorimeter DSC 220C and a Perkin-Elmer differential scanning calorimeter, DSC II, both of which were

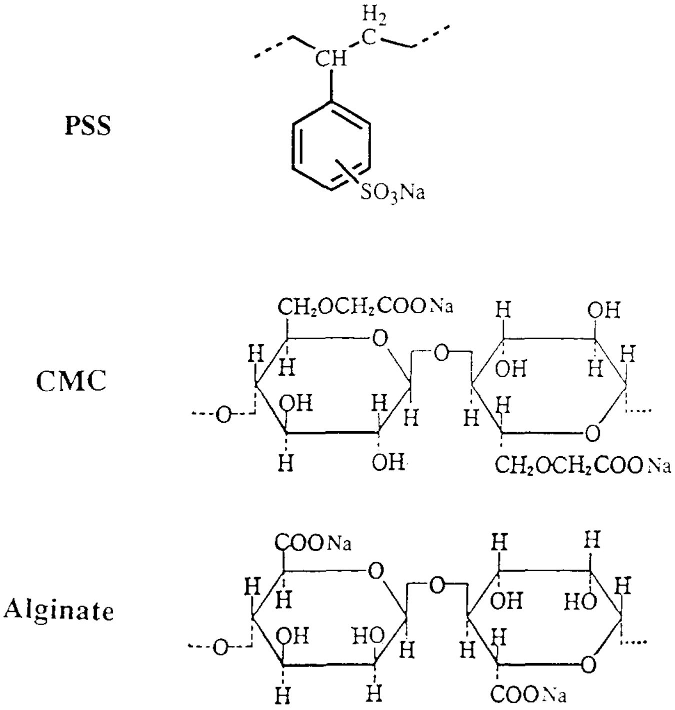

Fig. 1. Chemical structures of the samples in Na forms.

Table 1
Degree of substitution (DS) of various ions of CMCs

Valency	Cation	DS	Valency	Cation	DS
1	Li	0.61	2	Mg	0.59
1	Na	0.60	2	Ca	0.57
1	K	0.59	2	Ba	0.56
1	Cs	0.63	2	Al	0.57

equipped with a cooling apparatus, were used. DSC curves were obtained in the temperature range 120–320 K, sample weights were 3–5 mg, and the scanning rate was 10 K min^{-1}. The temperature and enthalpy of melting of water were calibrated using cyclohexane. The non-freezing water content was calculated by the method reported previously [1].

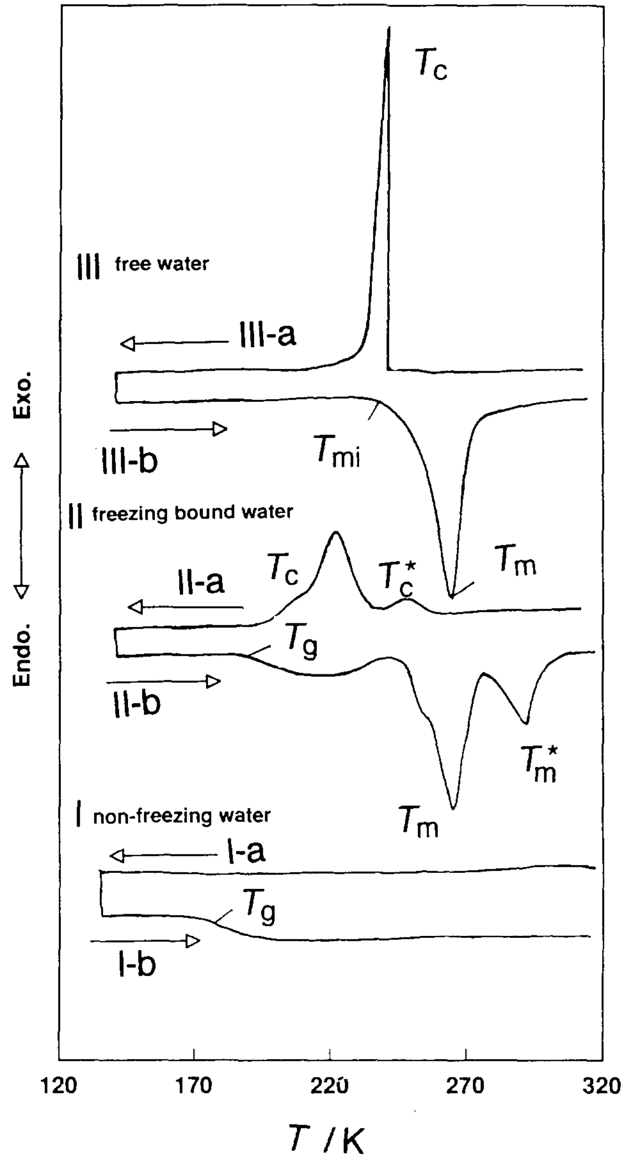

Fig. 2. Schematic DSC curves of water–polyelectrolyte systems used in this experiment: I, non-freezing water; II, freezing bound water ($W_{\mathrm{nf\,max}} < W_c <$ approx. 300 g/g); III, free water. T_g, glass transition; T_m, T_c, melting and crystallization of water; T_m^*, T_c^*, liquid crystal to liquid, and liquid to liquid crystal transition.

3. Results and discussion

PSS is a representative synthetic polyelectrolyte and its physical properties have been investigated by many researchers [10]. CMC is a cellulose derivative produced

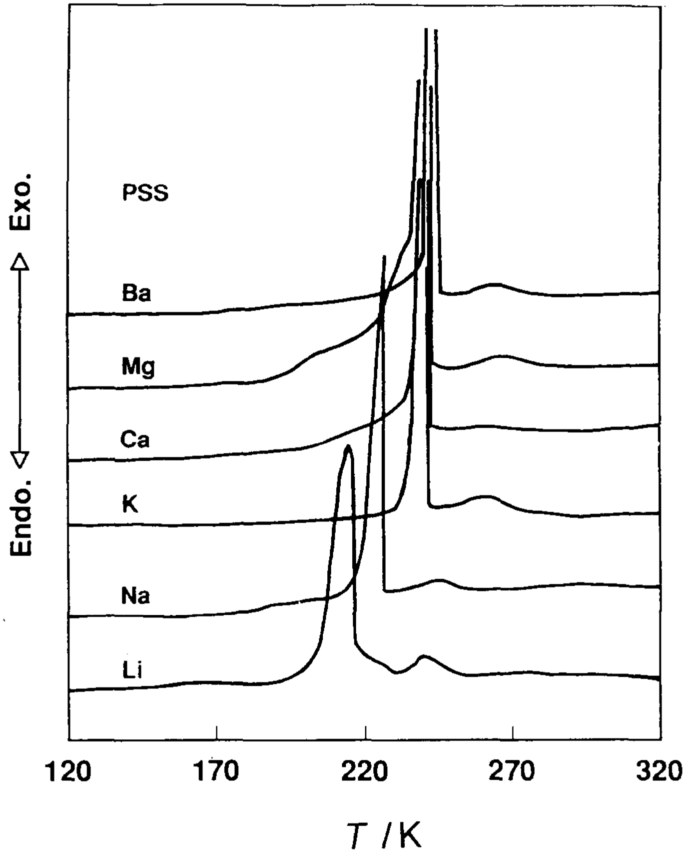

Fig. 3. DSC cooling curves of water–Li-polystyrene sulphonate (LiPSS), -NaPSS, -KPSS, -CaPSS, -MgPSS and -BaPSS. W_c, approx. 1.2 (g/g); heating rate, 10 K min^{-1}.

industrially on a large scale and used in various fields, such as the food and textile industries [11]. Alg is a copolysaccharide consisting of D-mannuronic acid and L-guluronic acid extracted from brown masse algae [12–14]. All the above samples are water soluble when they exist in the form of sodium salts. It is also confirmed that they form lyotropic thermotropic liquid crystals in a highly concentrated aqueous solution in the presence of monovalent cations [3,4,15–19]. Both PSS and CMC are water soluble even in the presence of divalent cations; however, it has been reported that Alg forms a special molecular arrangement in water in the presence of calcium ions, which is called the "egg-box structure" [20,21]. The egg-box model of Alg shows that the Ca ions are wrapped with polyguluronate molecular sequences and form a junction zone of hydrogels of Alg. Fig. 2 shows representative DSC curves of water–polyelectrolytes systems. Curves I-a, II-a and III-a are cooling runs and curves I-b, II-b and III-b are heating runs. When the amount of water in the system is smaller than a characteristic value, no first-order

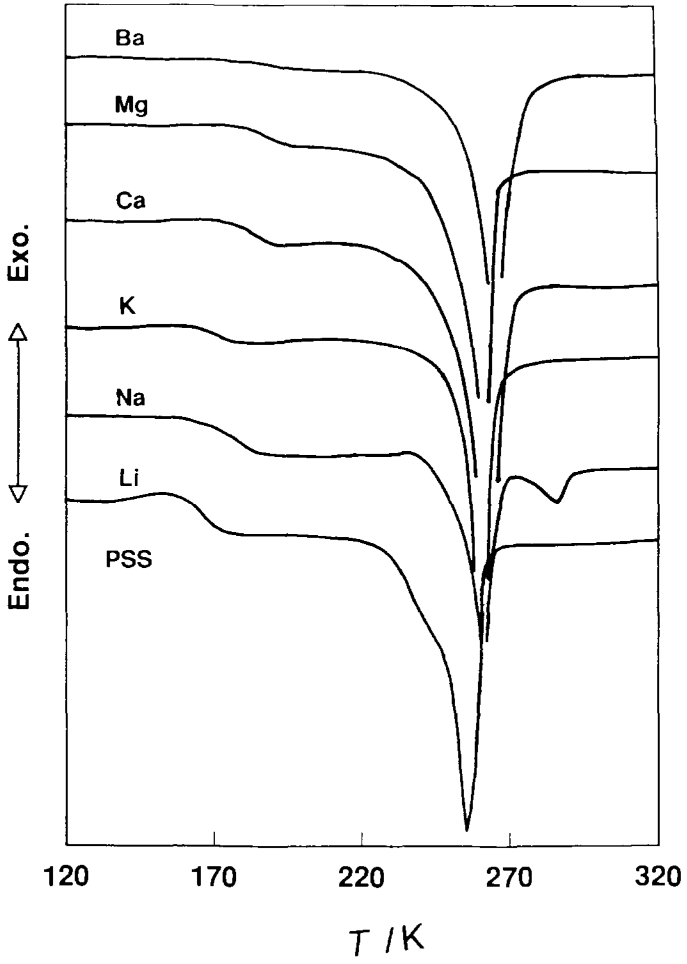

Fig. 4. DSC heating curves of water–Li-polystyrene sulphonate (LiPSS), –NaPSS, –KPSS, –CaPSS, –MgPSS and –BaPSS. W_c, approx. 1.2 (g/g); heating rate, 10 K min^{-1}.

phase transition is observed (curve I); however, as shown in curve I-b, the heat capacity (C_p) gap attributable to the glass transition (T_g) is observed. Water attached closely to the matrix polymer, showing no first-order phase transition, is categorized as non-freezing water (W_{nf}). The maximum amount of W_{nf} depends on the characteristics of each sample.

When W_c exceeds the maximum amount of W_{nf}, a melting peak (T_m) appears, as shown in curve II-b. A melting peak frequently accompanies a sub-melting peak or shoulder on the low temperature side. In the lower temperature side of the melting of ice in the system, a glass transition is observed. The glass transition temperature (T_g) depends on W_c. Another small peak appearing at the high temperature side of the main melting peak is attributed to the transition from the liquid crystalline state to the

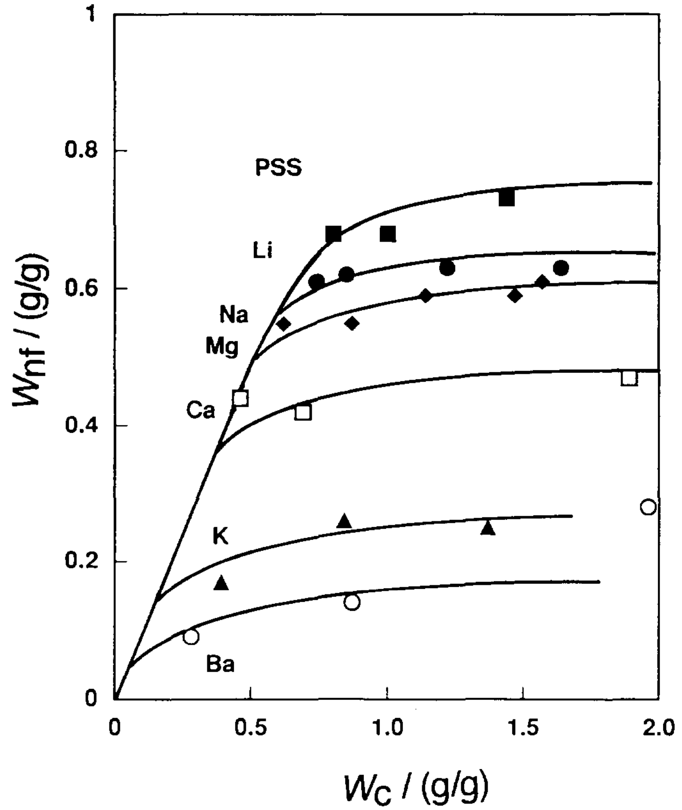

Fig. 5. Relationships between non-freezing water content (W_{nf}) and W_c of PSS with various cations.

liquid state (T^*). T^* was observed for all samples of PSS and CMC, and NaAlg. T^* was not clearly observed in the Alg samples with divalent cations.

Figs. 3 and 4 show representative DSC cooling (Fig. 3) and heating (Fig. 4) curves of water–PSS systems with various cations and a W_c of approx. 1.2 g/g. The shape of the melting peak is almost the same, regardless of the ionic species. In Fig. 3, the exothermic peaks attributable to the liquid to liquid-crystal transition (T_c^*) and to crystallization (T_c) are observed. In Fig. 4, T_g and T_m are clearly seen, although T^* is not apparent because the enthalpy of transition (3–12 J g^{-1}) is far smaller than the melting enthalpy of ice.

From the melting enthalpy calculated from the melting peak which appears in Fig. 4, the amount of freezing water (W_f) was calculated, assuming that the melting enthalpy of ice in the system is 333 J g^{-1}. Because the total W_c of the system has already been weighed, W_{nf} of the system can be obtained using the relationship.

$$W_{nf}/(g/g) = W_c - W_f \qquad (1)$$

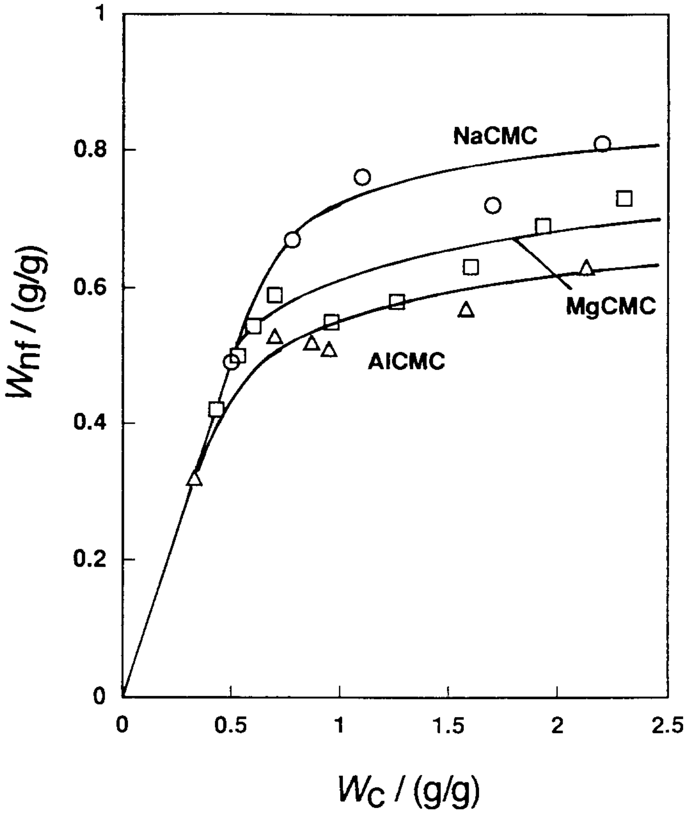

Fig. 6. Relationships between non-freezing water content (W_{nf}) and W_c of carboxymethylcellulose (CMC) with various cations.

Figs. 5, 6 and 7 show the relationships between W_c and W_{nf} of the water–PSS (Fig. 5), water–CMC (Fig. 6) and water–Alg (Fig. 7) system with various ionic species. W_{nf} increases with increasing W_c, reaches a characteristic value, and then maintains a constant value, or increases slightly, for all ionic species. When a similar relationship was established in water–non-electrolyte polymers, W_{nf} values were maintained at an almost constant value after exceeding the critical amount which depends on each polymer [22,23]. Therefore, for the comparison of W_{nf} values among various samples, the W_{nf} value at $W_c = 2.0$ g/g was used as an index.

Fig. 8 shows the relationship between W_{nf} and ionic radius of cations. W_{nf} values decrease with increasing ionic radius in both PSS and CMC, regardless of valency. However, W_{nf} values of Alg are maintained at around 0.9 g/g. As already mentioned, Alg molecules form junction zones via divalent cations. The aggregated Alg molecules are water insoluble and thermally irreversible. From the results shown in Fig. 8, it is clear that W_{nf} values of the highly crosslinked hydrogels are independent of ionic radius, but are influenced by the higher order structure. This

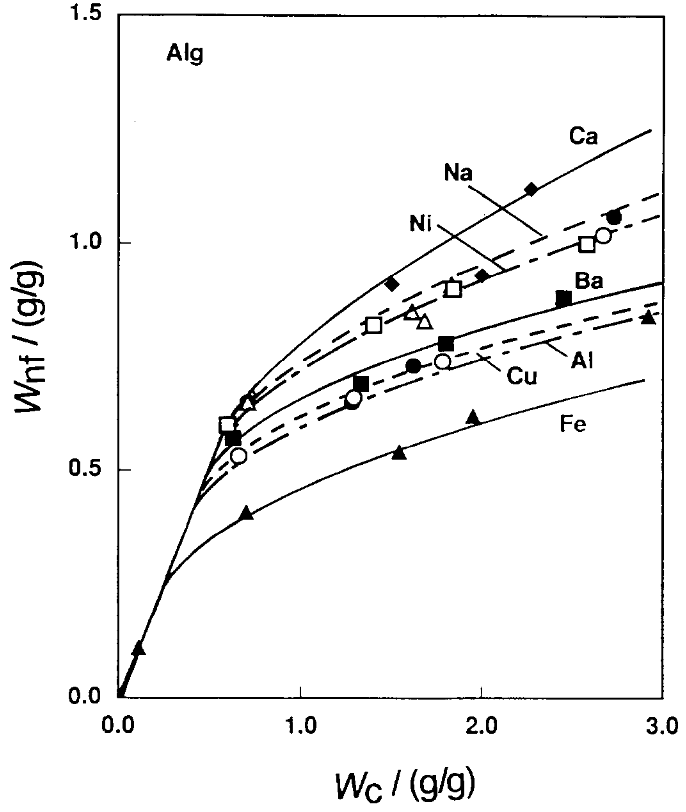

Fig. 7. Relationships between non-freezing water content (W_{nf}) and W_c of alginate with various cations.

is quite a different tendency from that of polyelectrolytes which form a liquid crystalline structure, e.g. PSS and CMC.

Fig. 9 shows the relationships between the number of water molecules attached closely to an ion ($N_{nf/M}$) and its ionic radius. In order to calculate $N_{nf/M}$, it was assumed that one hydroxyl group restricts one water molecule based on our previous results [22,23]. The hydration numbers of non-polymeric electrolytes in aqueous solutions have been determined by various experimental techniques, such as the compression method, nuclear magnetic resonance spectroscopy, X-ray analysis, dielectric measurement, etc. Marcus has collected the reported hydration number values of various ions [24] and the hydration numbers of each ion show an almost constant value, regardless of the structure of the solute molecules in aqueous solution, although the values are widely distributed according to measuring method. For example, the reported value for the hydration numbers of Na ranges from 3.5 to 6. It is suggested that the number of hydrated water molecules decreases with decreasing ionic radius of the ion [9]. When the $N_{nf/M}$ values obtained in this experiment are compared with the reported hydration numbers of mono- and

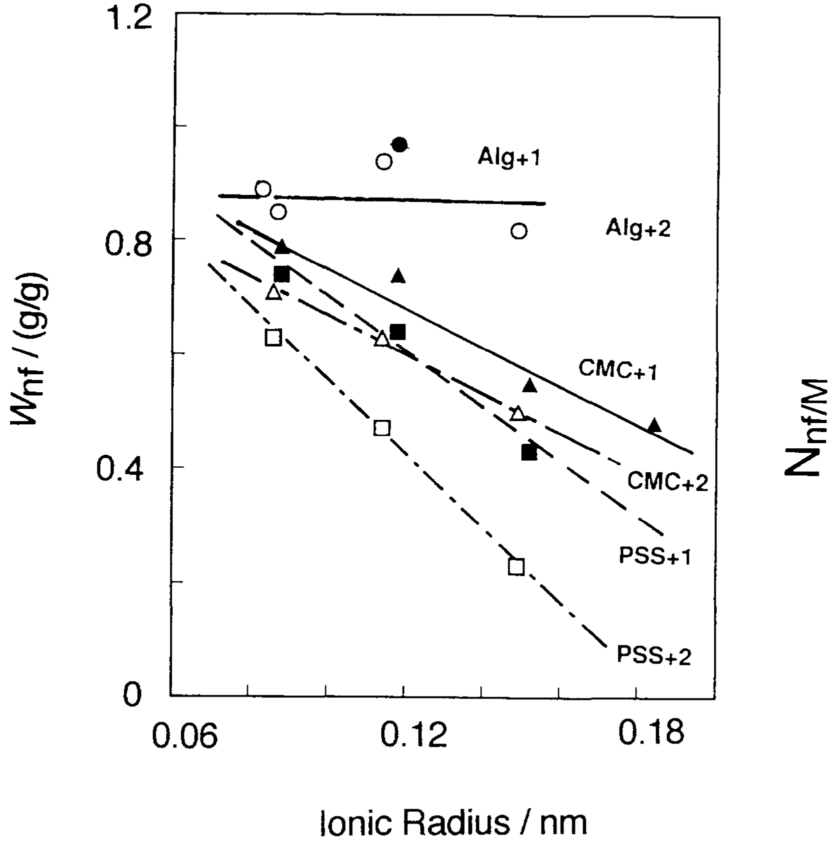

Fig. 8. Relationships between W_{nf} and ionic radius of the samples.

divalent cations of non-polymeric electrolytes, the calculated values are almost twice as high. This strongly suggests that the number of water molecules which are restricted by cations is influenced by the higher order structure of matrix polyelectrolytes. At the same time, the fact that $N_{nf/M}$ values of CMC are larger than those of PSS in both mono- and divalent cations suggests that the hydroxyl groups located near the cations also contribute to the increase in the number of water molecules. When the values obtained are compared with those of low molecular electrolytes, the concentration of solutes must be taken into consideration, i.e. $N_{nf/M}$ values in this experiment were calculated in a highly concentrated aqueous solution (up to 3.0 g/g), whereas reported values were obtained in a dilute solution (approx. 200 g/g). When DSC is used, it is necessary to choose a concentrated W_c range, because experimental error increases when W_{nf} is determined in dilute aqueous solutions. At the same time, values in a high W_c range are useful because many hydrophlic polymers are used in high concentrations in industrial applications.

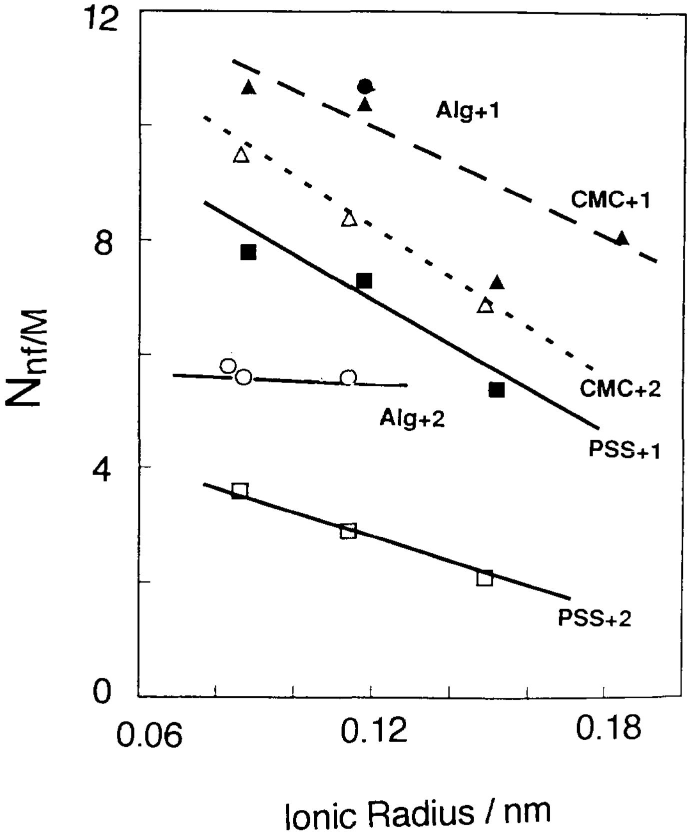

Fig. 9. Relationships between the number of water molecules attached to a cation ($N_{nf/M}$) and its ionic radius.

From the above results, it is shown that the number of tightly bound water molecules restricted by cations can be calculated using DSC. The number of bound water molecules decreases with increasing ionic radius in the series of mono- and divalent cations when polyelectrolytes form the liquid crystalline state. However, when polyelectrolytes form junction zones by association with cations, the number of water molecules is maintained at a constant value, regardless of ionic radius. The results indicate that the higher order structure of polyelectrolytes strongly influences the number of water molecules tightly bound by cations.

References

[1] T. Hatakeyama, K. Nakamura and H. Hatakeyama, Thermochim. Acta, 123 (1988) 153.
[2] K. Nakamura, T. Hatakeyama and H. Hatakeyama, Polymer, 24 (1983) 871.

[3] T. Hatakeyama and H. Hatakeyama, Polym. Adv. Technol., 1 (1990) 305.
[4] T. Hatakeyama and H. Hatakeyama, in W. Glasser and H. Hatakeyama (Eds.), Viscoelasticity of Biomaterials, ACS Symp. Ser. 489, Am. Chem. Soc., Washington, 1990, p. 350.
[5] H. Yoshida, T. Hatakeyama and H. Hatakeyama, in W. Glasser and H. Hatakeyama (Eds.), Viscoelasticity of Biomaterials, ACS Symp. Ser. 489, Am. Chem. Soc., Washington, 1990, p. 217.
[6] K. Nakamura, T. Hatakeyama and H. Hatakeyama, Polym. J., 23 (1983) 253.
[7] B.E. Conway, in Ionic Hydration in Chemistry and Biophysics, Elsevier Sci. Pub. Co., Amsterdam, 1981, Chapt. 34.
[8] K. Nakamura, T. Hatakeyama and H. Hatakeyama, in J.F. Kennedy, G.O. Phillips and P.A. Williams (Eds.), Wood and Cellulosics, Ellis Horwood Pub., Chichester, 1987, p. 97.
[9] K. Miyajima, in M. Nakagaki (Ed.), Structure and Properties of Water, Nankodo Pub., Tokyo, 1974, Chapt. 5.
[10] For example, R.A. Weiss, J.J. Fitzgerald and D. Kim, in L. Salmen and M. Htun (Eds.), Properties of Ionic Polymers, Natural and Synthetic, STFI-Meddelande, Stockholm, 1991, p. 187.
[11] G.I. Stelzer, E.D. Klung and R.L. Davidson (Eds.), Handbook of Water-Soluble Gums and Resins, McGraw-Hill Book Co., New York, 1980, Chapt. 4.
[12] E.D.T. Atkins, I.A. Nieduszynski, W. Mackie, K.D. Parker and E.E. Smolko, Biopolymer, 12 (1973) 1865.
[13] E.D.T. Atkins, I.A. Nieduszynski, W. Mackie, K.D. Parker and E.E. Smolko, Biopolymer, 12 (1973) 1879.
[14] A. Huang, B. Larsen and O. Smidsrod, Acta Chem. Scand., 21 (1967) 691.
[15] T. Hatakeyama, N. Bahar and H. Hatakeyama, Sen-i Gakkaishi (J. Soc. Fiber Sci. Technol., Japan), 47 (1991) 417.
[16] K. Nakamura, T. Hatakeyama and H. Hatakeyama, Sen-i Gakkaishi (J. Soc. Fiber Sci. Technol., Japan), 47 (1991) 421.
[17] T. Hatakeyama, K. Nakamura, H. Yoshida and H. Hatakeyama, Food Hydrocolloids, 3 (1989) 301.
[18] H. Hatakeyama and T. Hatakeyama, in L. Salmen and M. Htun (Eds.), STFI-Meddelande, Stockholm, Properties of Ionic Polymers, Natural and Synthetic, 1991, p. 123.
[19] T. Hatakeyama, K. Nakamura, H. Yoshida and H. Hatakeyama, Food Hydrocolloids, 3 (1989) 301.
[20] D.A. Rees and E.J. Welsh, Angew. Chem. Int. Ed. Engl., 16 (1967) 691.
[21] D.A. Rees, Adv. Carbohydr. Chem. Biochem., 24 (1977) 214.
[22] K. Nakamura, T. Hatakeyama and H. Hatakeyama, Text. Res. J., 51 (1981) 607.
[23] K. Nakamura, T. Hatakeyama and H. Hatakeyama, Polymer, 24 (1983) 871.
[24] Y. Marcus, Ion Solvation, John Wiley, London, 1985, Chapt. 5.