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Thermal properties of water insoluble alginate films containing di- and trivalent cations[1]

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Abstract

Water insoluble alginic acid (Alg) films were prepared by replacing the sodium ions (Na^+) of sodium alginate (NaAlg) with di- and trivalent cations, such as Cu^{2+}, Al^{3+}, Fe^{3+}, etc. Dope concentration and degree of substitution (DS) were changed in order to prepare various types of alginate films. Glass transition temperature (T_g), heat capacity (C_p) and C_p difference at T_g (ΔC_p) of the Alg films in the dry state were investigated by differential scanning calorimetry (DSC). With increasing ionic radius of cations, T_g of dry films decreased. In contrast, C_p's of alginate films in the glassy state and ΔC_p increased. The non-freezing water content (W_{nf}) in alginate films in the wet state was also estimated by DSC using enthalpies of melting and crystallization of water. W_{nf} in the films increased with increasing ionic radius. These results indicated that alginate molecules form a more tightly cross linked structure with decreasing ionic radius. Structural change of alginate films during ion exchange was also investigated based on the change of T_g, C_p and W_{nf} values as a function of DS.

Keywords: Alginate films; DSC; Cations

1. Introduction

Alginic acid is a copolysaccharide extracted from brown masse algae consisting of D-mannuronic acid (M component) and L-guluronic acid (G component) [1–3]. Sodium alginate (NaAlg) is one of the representative polyelectrolytes used widely in various in-

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dustrial fields, such as the food and textile industries. Although NaAlg is readily solved in water, water insoluble alginates can be prepared when sodium ions of NaAlg are replaced by di- and trivalent cations. Among various ions, such as Fe^{2+}, Cu^{2+}, Ca^{2+} and Al^{3+}, Ca^{2+} has received particular attention, since it is thought that a unique "egg-box structure" is formed in CaAlg with G components enclosing Ca ions [4,5].

We have studied the thermal properties of water–NaAlg and water–CaAlg systems [6–8] and found that the functional properties of alginate are affected by the presence of bound water. We have also estimated the bound water content in carboxymethylcellulose and cellulose sulfate substituted by various valencies of cations and suggested that the bound water content of polyelectrolyte systems depends strongly on the kind of cations [6,9,10].

In this study, water insoluble alginate films having various cation species and various degrees of substitution (DS) were prepared, and the thermal properties of these films were investigated by differential scanning calorimetry (DSC). The effect of preparative conditions of films such as concentration of dope and ion exchange times, cation species and DS on the glass transition temperature (T_g), specific heat capacity (C_p) and non-freezing water content (W_{nf}) of alginate films were investigated.

2. Experimental

2.1. Sample preparation

Sodium alginate (NaAlg) was commercially obtained from Wako Chemicals Co. Ltd. Molecular weight (Mw) was about 95 000, the degree of polymerization (DP) was about 480, and M/G ratio was from 1.0 to 1.2. Water insoluble alginate films with various cations were prepared by the following method. (1) NaAlg powder was dissolved in water with concentration ranging from 1 to 20 wt.%. (2) Aqueous solutions of NaAlg were cast on glass plates and dried at room temperature. Thus, NaAlg films were prepared. (3) NaAlg films were immersed in aqueous solutions of various metal chlorides, such as $FeCl_2$, $CaCl_2$, $CuCl_2$, $FeCl_3$ and $AlCl_3$ (concentration 1–4%). (4) The films having various degrees of substitution (DS) were prepared by controlling the time for ion exchange (immersing time in aqueous metal chloride solutions). (5) The films obtained were dried in an air oven at 120°C for 30 min. The thickness of the alginate films was from ca. 0.04 to 0.10 mm.

2.2. Measurement

The solubility of the alginate films after ion exchange was tested by observing the film in water for a certain time at room temperature.

DS of the samples was calculated from the concentration of metal ion in the sample. The concentration of metal ions in the sample was measured using an atomic absorption spectrometer (Polarized Zeeman Atomic Absorption Spectrophotometer, Hitachi 180-80). A certain amount of each sample was weighed and dissolved in concentrated sulfuric acid. A certain amount of water was added to the sulfuric acid solution with the sample in order to obtain a 10 ppm solution and then this dilute solution was measured. The commercial standard solutions of Fe^{2+} and Cu^{2+} were used to obtain calibration curves.

Thermal properties of the films in the dry and wet states were measured using a differential scanning calorimeter (DSC, Seiko Instruments Inc., DSC-220C). The sample films of 4 mm diameter were packed in an aluminum open vessel. Sample weight was about 10 mg. Samples were annealed at 120°C in a DSC sample holder for 10 min. After cooling to room temperature, the sample was immediately heated at 10°C min^{-1} until 140°C. The exotherm attributed to decomposition of the dry sample started from about 160°C [11]. A second heating was carried out after quenching from 140°C to room temperature in order to avoid the effect of residual moisture in the sample. The second run was used for analysis. T_g was defined as the cross point of the baseline and transition line of the glassy and rubbery regions, according to the method reported previously [11,12]. ΔC_p was defined as the difference between the C_p's of the glassy and rubbery states of the sample [11,12].

The C_p of the samples in the dry state was measured by the method of JIS K7123 [13]. A sapphire disk of about 10 mg was used as a standard material of the C_p. The J g^{-1} deg^{-1} was used as the unit of C_p instead of J mol^{-1} deg^{-1}, since the maximum calculation error caused by the difference in molecular weight of the samples having different DS, was 7.1% in the case of Al ions. The non-freezing water sorbed on the alginate film was determined by the method reported previously [14–16]. Water content (W_c) was defined according to

$$W_c = \text{weight of sorbed water/weight of the dry sample (g/g)} \qquad (1)$$

3. Results and discussion

3.1. Alginate films in the dry state

Fig. 1 shows the relationship between the degree of substitution (DS) of alginate samples and replacement time of Fe^{2+} and Fe^{3+}. In the case of Fe^{3+}, DS slowly increased

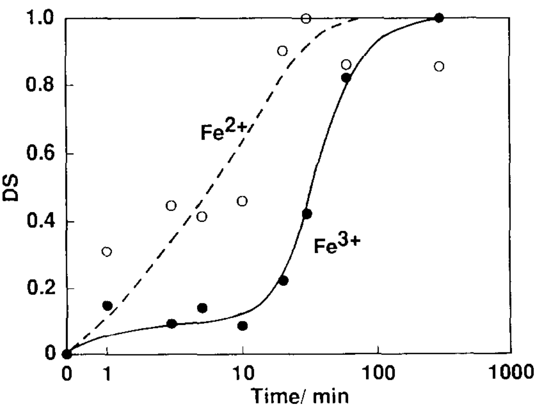

Fig. 1. The relationship between DS of the alginate samples and replacement time of Fe^{2+} and Fe^{3+} ions.

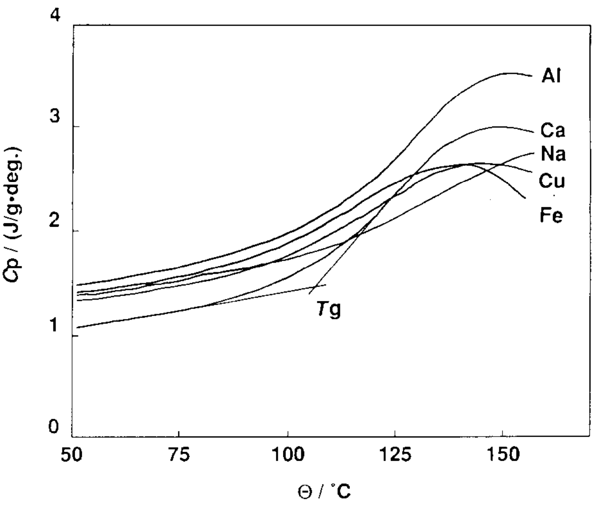

Fig. 2. DSC curves of alginate films with various cations.

with increasing replacement time until about 30 min, then quickly increased until about 60 min and finally become saturated at 1.0 of DS. The rate of ion exchange of Fe^{2+} was higher than that of Fe^{3+}. This fact suggests that the two-dimensional crosslinking between alginate molecules was easily formed compared with three-dimensional crosslinking. The ion exchange was carried out in a similar manner in other di- or trivalent cation solutions. The solubility of the films in water was tested. The solubility decreased with increasing replacement time.

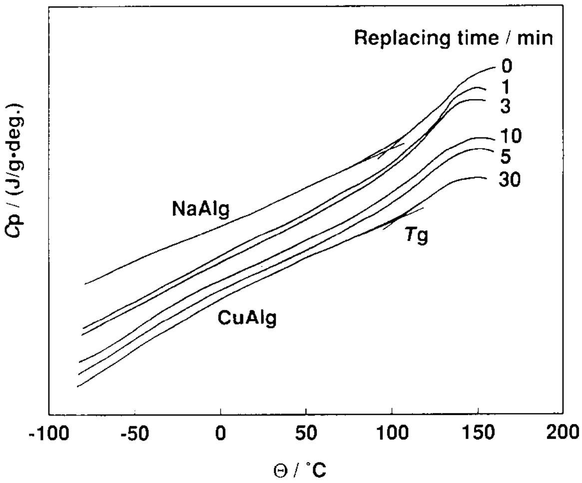

Fig. 3. DSC curves of alginate films with various replacement times in the case of Cu^{2+} ion.

Fig. 2 shows DSC curves of alginate films in the dry state with various cations. The glass transition temperature (T_g) of alginate films was observed as a step-like change in the baseline as shown in this figure. Glass transition was confirmed by heating rate dependency. Main chain motion was also confirmed by dynamic mechanical analysis (DMA) [17]. The tan δ peak attributed to the molecular enhancement of the main chain was observed at about 120°C and the activation energy of the peak was about 350–450 kJ mol^{-1}. The T_g's of these films were observed at about 100–130°C by DSC and the temperature decreased in the order $Al^{3+} > Ca^{2+} > Fe^{2+} > Cu^{2+} > Na^{+}$. The main chain motion is restricted by crosslinkings caused by di- or trivalent cations and also the structural difference of the crosslinking zone may affect the above difference in T_g values.

Fig. 3 shows DSC curves of alginate films with various DSs which are calculated from the results of atomic absorption spectrometry. It was found that T_g increased with increasing DSs, that is, the increase in numbers of crosslinking between alginate molecules depressed the main chain motion.

Fig. 4 shows the relationship between T_g's (Fig. 4A) and ΔC_p (Fig. 4B) of alginate films with various cations and replacement times. T_g of NaAlg was 95.3°C. T_g's of alginates gradually increased with increasing replacement time until 30 min and then leveled off. T_g increase was about 10°C from 95.3°C at time = 0 to 105.7°C at 30 min. The ΔC_p is evaluated as the C_p difference between the glassy and the rubbery states of the sample. The ΔC_p decreased with increasing replacement time. As shown in Fig. 2, C_p's of the glassy state of the samples are similar. In contrast, C_p of the rubbery state is influenced by the DS and species of cations. It is appropriate to consider that C_p of the rubbery state decreased with increasing replacement time. The ΔC_p decrease shown in Fig. 4B is mainly attributed to the decrease of C_p in the rubbery state.

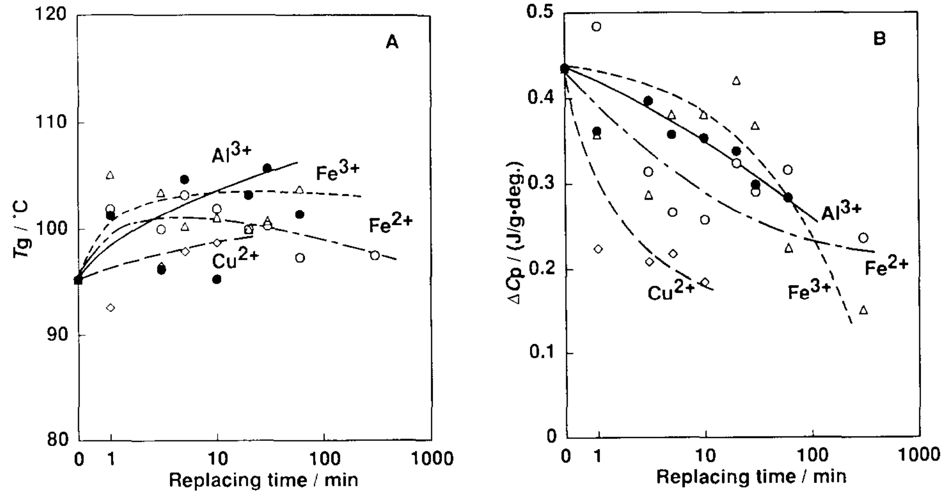

Fig. 4. The relationships between T_g (A) and ΔC_p (B) of alginate films with various cations and replacement times.

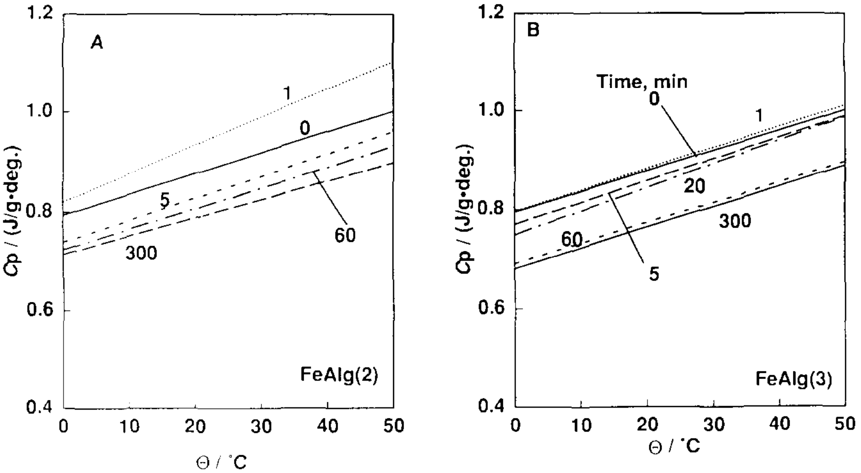

Fig. 5. The C_p's of alginate films in the glassy state replaced by Fe^{2+} (A) and Fe^{3+} (B) for various replacement times.

Fig. 5 shows the C_p's of alginate films in the dry state replaced by Fe^{2+} (Fig. 5A) and Fe^{3+} (Fig. 5B) for various replacement times. C_p in a temperature ranging from 0 to 50°C linearly increased with increasing temperature. The tendency of a decrease in the slope of the C_p lines was clearly observed in the alginates highly substituted by various cations, and also the temperature dependence of the C_p's decreased with increasing DS. It is re-

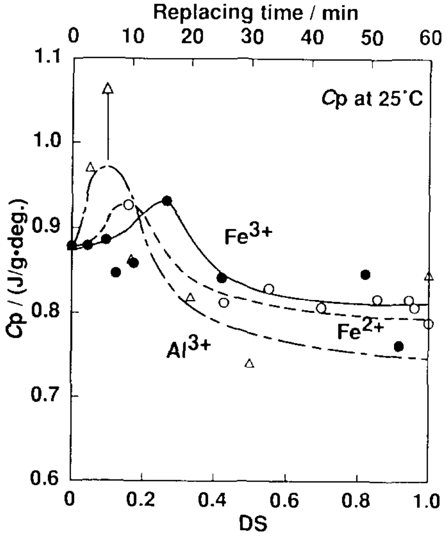

Fig. 6. The relationships between C_p's of alginate films and DS. In the case of AlAlg, the relationship between C_p and replacement time, instead of DS, is shown in the figure.

ported that C_p values of polymers are affected by the higher order structure, such as regularity of molecular arrangement [18]. Accordingly it is considered that the variation appearing in Fig. 5 is attributable to the change in the higher order structure of molecular aggregation of alginic molecules moving cooperatively with associated ions.

Fig. 6 shows the relationship between the Cp's of alginate films in the dry state and DS. In the case of AlAlg film, the relationship between C_p and replacement time, instead of DS, is shown in the figure, since the DS measurement of AlAlg was difficult to achieve using atomic absorption spectrometry. The C_p curves show peaks at about 0.15–0.25 and then gradually decrease. The peak observed at around DS = 0.1–0.3 strongly suggests that molecular chains take a more random structure when Na ions are partly exchanged. As shown in Fig. 6, when the ion exchange is completed, C_p decreases suggesting that a tightly arranged molecular structure is established.

3.2. Alginate films in the wet state

Fig. 7 shows the DSC curves of the NaAlg–water system (Fig. 7A) with a water content (W_c) of 0.84, 0.91 and 1.79. DSC curves of the FeAlg(Fe^{3+})–water system (Fig. 7B) with various W_c's are also shown. We have reported that there are three kinds of sorbed water in hydrophilic polymers such as cellulose [15,19,20], polyelectrolytes [21,22] and

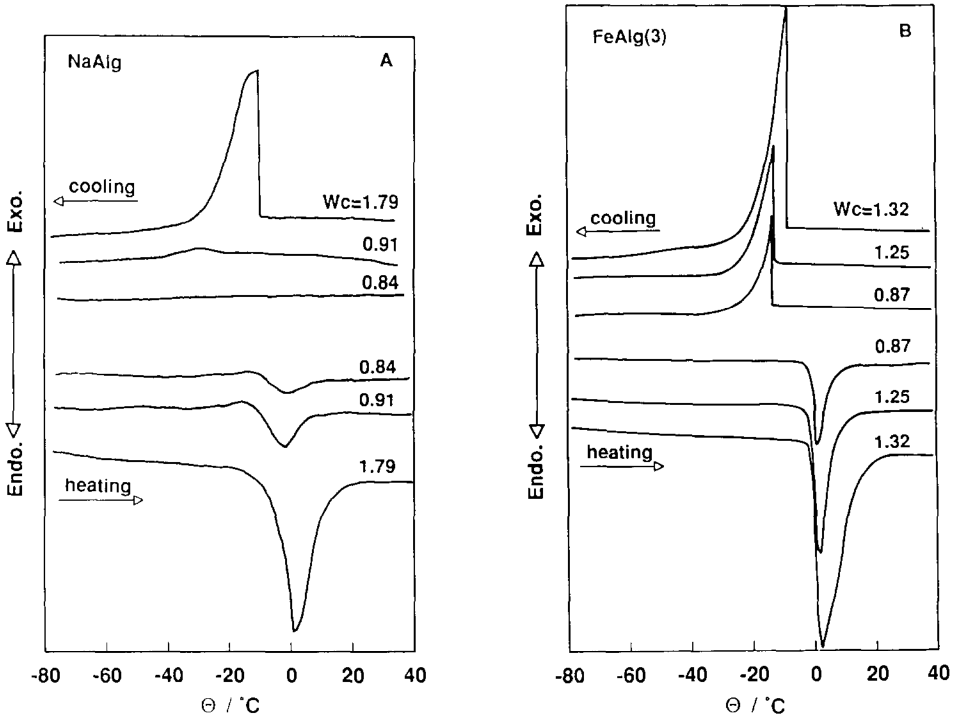

Fig. 7. DSC heating and cooling curves of NaAlg–water (A) and FeAlg–water (B) systems with various W_c.

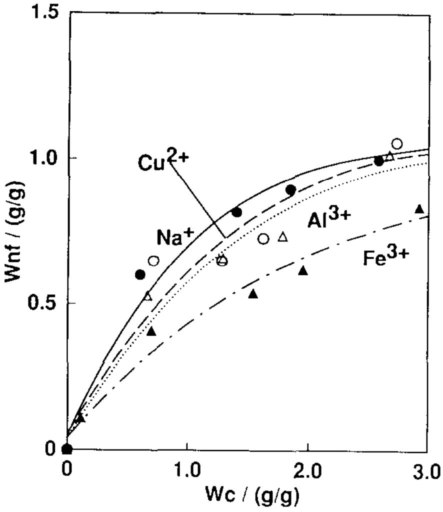

Fig. 8. The relationship between W_{nf} of alginate films with various cations and W_c.

various polysaccharides [23,24]. The bound water content was defined as the sum of non-freezing water (W_{nf}) and freezable bound water content. It was also reported that bound water molecules are strongly restricted by hydrophilic groups and/or networks of higher order structure of the polymers. In the alginate–water systems, freezable bound water was not observed as shown in these figures. Therefore, W_{nf} was calculated.

Fig. 8 shows the relationship between W_{nf} of alginate films having various cations and W_c. W_{nf} increased until about 0.5 of W_c and then gradually leveled off to a certain amount. The amount of W_{nf} depended on the kind of cations. W_{nf} decreased in the order of $Na^+ > Cu^{2+} > Al^{3+} > Fe^{3+}$.

Table 1 shows the ionic radius of cations and W_{nf} of alginate films with various DS. W_{nf} of NaAlg was about 0.823 at W_c of 1.5. When Na ions are replaced by di- or trivalent

Table 1

Ionic radius of cations and W_{nf} of alginate films with various DS

Ion	Ionic radius/Å	DS	W_c	W_{nf}
Na^+	1.16	0.00	1.50	0.823
Cu^{2+}	0.87	0.30	1.32	0.989
		0.93	1.25	0.717
Fe^{2+}	0.75	0.31	1.54	0.982
		0.86	1.43	0.735
Fe^{3+}	0.69	0.15	1.38	0.610
		1.00	1.41	0.503
Al^{3+}	0.67	–	1.26	0.934
		–	1.66	0.667

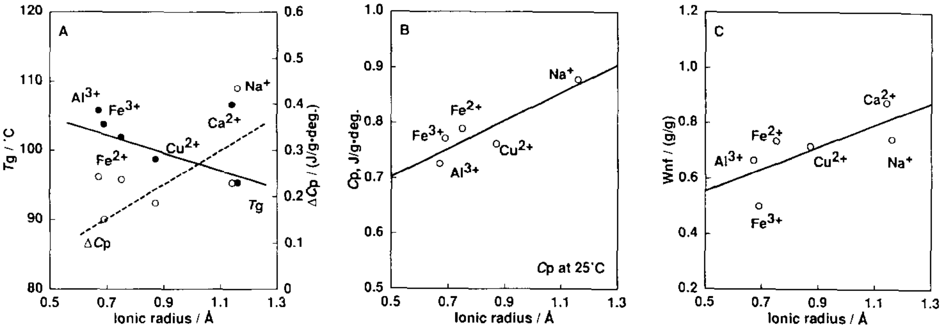

Fig. 9. The relationships between T_g, ΔC_p and ionic radius (A), the relationship between C_p and ionic radius (B) and the relationship between W_{nf} and ionic radius (C) of the cations.

cations, W_{nf} values of alginates with small DS were higher than that of NaAlg. However, W_{nf} values of alginates with large DS were lower than that of NaAlg, as shown in the table. This suggests that the molecular arrangement of alginate gradually changes by the formation of crosslinking during ion exchange.

3.3. *Effect of ionic radius*

Fig. 9 shows the relationships between T_g, ΔC_p and ionic radius (Fig. 9A), the relationship between C_p of alginate films at 25°C and ionic radius (Fig. 9B) and the relationship between W_{nf} of alginate films and ionic radius (Fig. 9C) of the cations. T_g decreased, and ΔC_p increased with increasing ionic radius. C_p and W_{nf} also increased with increasing ionic radius of cations. These results show that crosslinkings are tightly formed between alginate molecules by cations with short ionic radius.

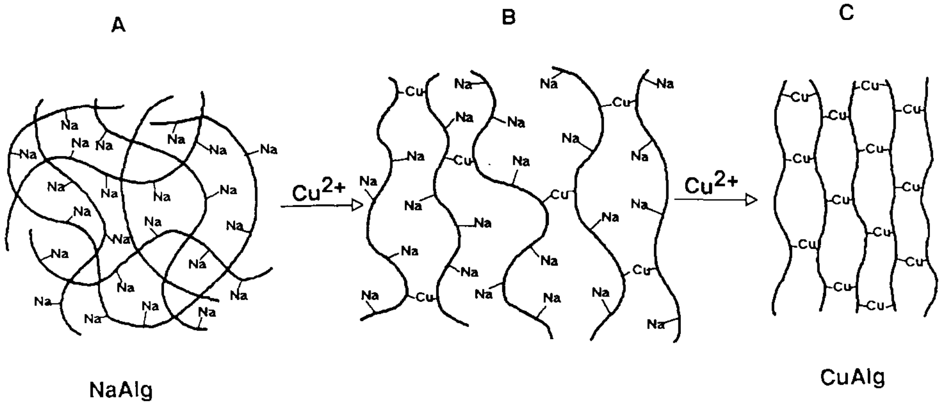

Fig. 10. The schematic illustration of the molecular arrangement of alginate subjected to the controlling ion exchange.

Fig. 10 shows a schematic illustration of the molecular arrangement of the alginates subjected to controlled ion exchange. Exchange from NaAlg to CuAlg is shown as an example. From the results of T_g, C_p and W_{nf} of NaAlg, it is reasonable to consider that the NaAlg takes a more random structure than those of alginates substituted with di- and trivalent cations (Fig. 10A). When Na ions are partly substituted with Cu ions, NaAlg molecules have a more bulky arrangement (Fig. 10B). The peak observed in the relationship between C_p and DS (Fig. 6) is well explained by this structure. When the crosslinking is fully established, a tightly arranged structure as shown in Fig. 10C is organized. Variation of W_{nf} values can also be explained when the above structure is assumed. As shown in Fig. 9, when the ionic radius is small, the structure shown in Fig. 10C, becomes tighter; C_p and W_{nf} values decrease and T_g increases.

4. Conclusion

The following conclusions are obtained from the above results. Water insoluble alginate films are prepared by replacing Na ions with di- and trivalent cations except for Mg^{2+} ions. The T_g of alginate films having various cations decreased in the order $Al^{3+} > Ca^{2+} > Fe^{2+} > Cu^{2+} > Na^+$. The C_p of the alginate films in the glassy state showed a maximum peak in the low DS region and then decreased. The C_p's of alginate films replaced by various cations decreased in the order of $Na^+ > Fe^{2+} > Fe^{3+} > Cu^{2+} > Al^{3+}$. The W_{nf} decreased in the order of $Na^+ > Fe^{2+} > Cu^{2+} > Al^{3+} > Fe^{3+}$. The values of T_g, C_p and W_{nf} of alginate films depend strongly on the ionic radius of the cations.

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