

¹³C NMR Study on Gelation of Aqueous Carboxyethylcellulose with Total Degree of Substitution of 0.39 Solution Induced by Metal Cations

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ABSTRACT: The gelation of an aqueous (aq) solution of the sodium salt of carboxyethylcellulose (NaCEC: total degree of substitution $\langle F \rangle = 0.39$) by contacting several aqueous metal chloride solutions was investigated visually and by ¹³C NMR analysis. Diffusion of acidic Ti³⁺ and Al³⁺ into aq NaCEC solution was found to produce CEC gel with high dimensional stability, slightly losing the original transparency of aq NaCEC solution. Purple Ti³⁺ ion was proved to diffuse slower than proton ion. Ca²⁺ was also found to produce CEC gel having a little weaker dimensional stability than those obtained by Ti³⁺ and Al³⁺. It was also affirmed that deuterated hydrogen chloride solution was significantly opaque. Any diffusion of Na⁺ and K⁺ into NaCEC solution produced no gel and aq NaCEC solution remained as solution phase. Analysis on the chemical shift and the half value width of ¹³C NMR peaks obtained for the CEC gel phases in comparison with those of the peaks for the original NaCEC solution revealed that only Al³⁺ and Ti³⁺ produced considerable broadening and splitting of the peaks responsible for the carboxyethyl substituent, but DCl only resulted in a peak shift towards a higher magnetic field with no peak broadening. Chemical shift of C₁ carbon, constituting backbone of NaCEC, of the CEC gels gave different values from gel to gel, showing some difference in configuration of β-glucoside linkage of these CEC gels. Several possible gelation mechanisms were proposed to explain the roles of the cation species and pH value of their solutions used for contacting the aqueous NaCEC solution.

KEY WORDS Carboxyethyl Cellulose / Gelation / ¹³C NMR Analysis / Metal Chloride /

Some aqueous (aq) solutions of naturally occurring polysaccharides and proteins have been known often to show gelation under rather specialized conditions¹: An aq solution of agarose becomes a temperature-reversible (thermotropic) gel² and carrageenan in water was reported to make gel under the existence of cations (Cs⁺, Rb⁺, K⁺, NH₄⁺).³ An aq solution of casein becomes gelatinous by addition of some enzymes⁴. Some anionic cellulose derivatives such as cellulose sulphate and carboxymethylcellulose are also known to produce gel under the coexistence of polyvalent cations⁵. Gelation of aq solutions of these cellulose derivatives has been believed

to be brought about by ionic cross-linking of polyvalent metal cations⁶. However, no direct evidence experimentally supporting this hypothesis has been presented up to now.

In this article, we attempt to disclose a gelation mechanism of an aq solution of sodium salt of carboxyethylcellulose (NaCEC) as an typical anionic cellulose derivative by analysing the changes in chemical shift of ¹³C NMR peaks and in their peak line width of the CEC phases obtained by diffusing various metal cation solutions into aq NaCEC solution.

EXPERIMENTAL

Sample

A NaCEC with total degree of substitution $\langle F \rangle = 0.39$ was prepared as follows: Ten grams (g) of regenerated cellulose (the viscosity-average molecular weight $\bar{M}_v = 12.1 \times 10^4$, calculated from the Mark-Houwink-Sakurada equation for cellulose/cadoxen system established by Brown-Wikström⁷ were recovered from a cuprammonium solution, and dissolved at 0°C into the mixture of 9.1 wt% aq sodium hydroxide (NaOH) solution (220 g) and acrylonitrile (AN) (16 g) cooled beforehand at 0°C. The resultant solution was stirred for about 60 h at 25°C. Then, an addition reaction of AN to the hydroxyl groups of cellulose was interrupted by the addition of a large amount of methanol. The precipitant was separated by paper filter and washed several times with methanol-water (7:3, v/v at 25°C) mixture and finally with acetone, dried *in vacuo* at 60°C for 1 day. $\langle F \rangle$ of NaCEC sample thus obtained was determined from $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in deuterium oxide (D_2O) recorded on NNE mode.

NMR Measurement

First, a 3.75 wt% of the NaCEC solution in D_2O (purity; 99.8%, Merck & Co., Inc., Rahway, U.S.A.) was prepared and 4 g of the solution were carefully put into each NMR sample tube (inner diameter; 10 mm). After degasification each 10 ml of various metal chloride solutions in D_2O (0.3 mol l^{-1}) were slowly added into the tube at 28°C so as to produce a clear interface between the NaCEC and metal chloride solutions and the tube was stood steadily upright allowing the metal chloride to diffuse into the NaCEC phase and finally make the CEC phase gelatinous. The resultant CEC gels or CEC phases introduced by various metal chlorides such as aluminum chloride (AlCl_3), titanium chloride (TiCl_3), ferric chloride (FeCl_3), manganese

chloride (MnCl_2), calcium chloride (CaCl_2), potassium chloride (KCl) and sodium chloride (NaCl) were used for ^{13}C NMR measurement. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra with complete decouple were recorded on a FT-NMR spectrometer (FX-200, JEOL) with 50.15 MHz for ^{13}C nucleus under the following operating conditions: Externally controlled temperature; 30°C, flip angle; 45°, spectral width; 12004 Hz, data point; 8K, pulse interval; 3.182 s, accumulation; more than 16,000 times. Under these operating conditions the Overhauser effect on each ^{13}C nucleus was not ignorable. Nevertheless, changes in chemical shift (δ) and peak line width (measured as half value width of peak $\Delta_{1/2}$) for specific nuclei can be adequately measured owing to a remarkable increase in S/N ratio. The δ was determined as 0 ppm for methyl carbon of sodium 2,2-dimethyl-2-silapentane-5-sulfonate used as an internal reference. $\Delta\delta_{1/2}$ was roughly estimated by approximating the peak area in question as an isosceles triangle having its top at the δ position.

All metal chlorides (guaranteed grade), supplied by Kishida Chemical Co. (Japan), were used without further purification. The amount of each metal chloride employed for gelation of aq NaCEC solution was 4.7 mol/carboxyl residue in NaCEC. Since the acid type of CEC(HCEC) is water-insoluble and some chloride solutions used are highly acidic (for example, AlCl_3 ; pH 3.4, FeCl_3 ; pH 1.3, TiCl_3 ; pH 0.4), NMR measurement was also carried out on the gel-like CEC phase induced by contacting deuterated hydrochloric acid solution (pH 0.1) in D_2O , in order to distinguish the effect of metal ion from that of acid.

RESULTS AND DISCUSSION

Figure 1 shows photographs of the resultant CEC solution phases obtained by contacting various metal chloride solutions at 28°C as a function of contacting time (upper layer, metal chloride solution; bottom layer, resultant CEC

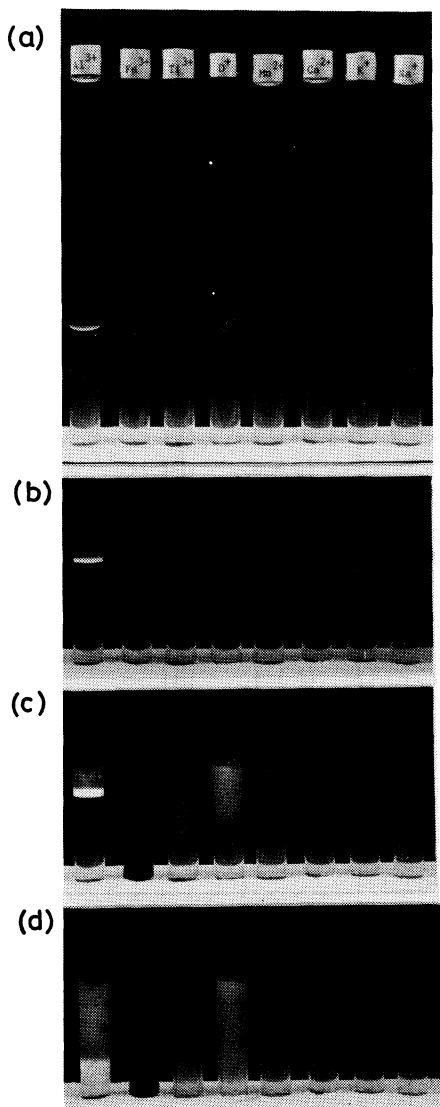


Figure 1. Photographs of the resultant CEC solution phases obtained by contacting various metal chloride solutions at 28°C as a function of contacting time (a) 0 h, (b) 2 h, (c) 8 h, (d) 1 day (Upper layer; metal chloride solution, Bottom layer; resultant CEC phase).

phase). Phenomenological change of original NaCEC solution following contact with aq metal chloride solutions differ significantly depending on the metal cation species (including proton ion): (I) Al^{3+} , Fe^{3+} , Ti^{3+} , D^+ , Mn^{2+} , and Ca^{2+} . With proceeding of the diffusion

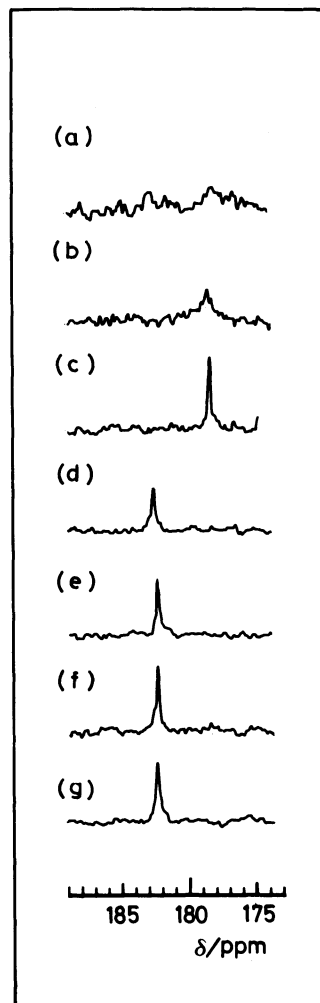


Figure 2. ^{13}C NMR spectra for regions of carboxyl carbon of carboxyethyl cellulose (a) in contact with AlCl_3 solution, (b) TiCl_3 solution, (c) DCl solution, (d) CaCl_2 solution, (e) NaCl solution, (f) KCl solution, (g) not in contact (original NaCEC solution).

of the metal cation (or proton ion) into the original aq NaCEC solution, CEC phase gradually gels slightly losing the original transparency of aq NaCEC solution. (II) Na^+ and K^+ ; Original NaCEC solution retains its solution state and no gelation occurs. Cations in (I) can be divided into two groups, (Ia) Al^{3+} , Fe^{3+} , Ti^{3+} , and D^+ . A clear interface between the gel and the metal chloride

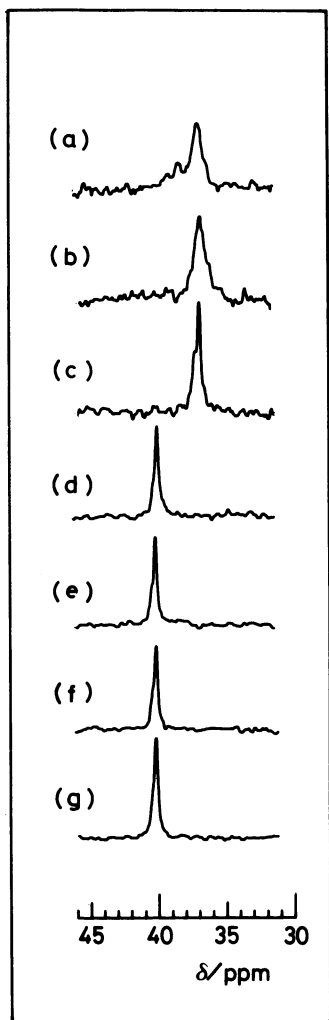


Figure 3. ^{13}C NMR spectra for regions of α -methylene carbon of carboxyethyl substituent of carboxyethyl cellulose (a) in contact with AlCl_3 solution, (b) TiCl_3 solution, (c) DCl solution, (d) CaCl_2 solution, (e) NaCl solution, (f) KCl solution, (g) not in contact (original NaCEC solution).

solution is observed at the final stage of gelation and the gels have high dimensional stability, (Ib) Mn^{2+} and Ca^{2+} . The boundary between the gel and metal chloride solution is obscure and the dimensional stability of the gels is low. Cations in (Ia) further gave different patterns of gelation: Al^{3+} ; A conspicuous white turbid layer with thickness about 2 mm is first produced between the

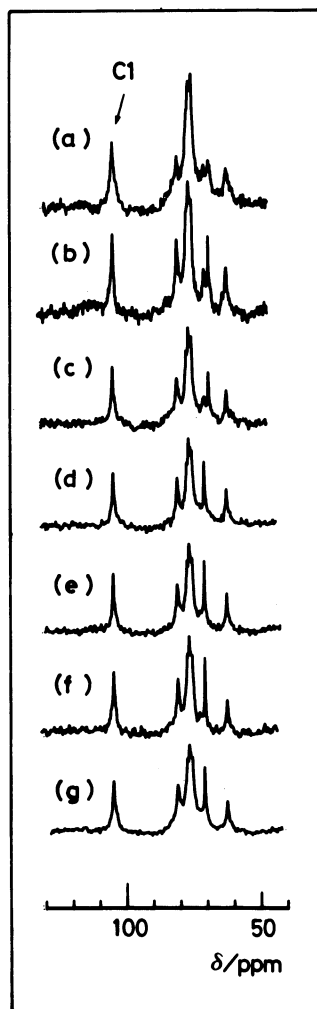


Figure 4. ^{13}C NMR spectra for regions of carbons constituting the cellulose backbone of carboxyethyl cellulose (a) in contact with AlCl_3 solution, (b) TiCl_3 solution, (c) DCl solution, (d) CaCl_2 solution, (e) NaCl solution, (f) KCl solution, (g) not in contact (original NaCEC solution).

NaCEC and Al^{3+} solutions and the layer went down into NaCEC solution phase marking the NaCEC phase slightly turbid gel. Fe^{3+} , Ti^{3+} ; firstly NaCEC phase became slightly opaque gel as D^+ did, but later the gel phase was coloured with intrinsic colour of the cations (Fe^{3+} , brownish orange; Ti^{3+} , purple).

Figures 2, 3, and 4 show ^{13}C NMR spectra for the carbon peak regions of carboxyl

($-\text{OCH}_2\text{CH}_2\overset{*}{\text{C}}\text{OOM}$: M denotes metal or proton), α -methylene ($-\text{OCH}_2\overset{*}{\text{C}}\text{H}_2\text{COOM}$) in carboxyethyl substituent group and backbone ring of CEC molecules in the resultant CEC phases shown in Figure 1C, respectively. The spectra of the CEC phases obtained by contacting Fe^{3+} and Mn^{2+} were omitted in the figures because the above peaks were all considerably broadened owing to the strong paramagnetic nature of the cations. Each figure contains ^{13}C NMR spectrum of the original NaCEC solution in D_2O for comparison. Kamide *et al.*⁸ already gave peak assignment of the spectrum for NaCEC in D_2O showing that carboxyl, β - and α -methylene carbon peaks of carboxyethyl substituent appeared at around 182, 71, and 40 ppm, respectively, and that peaks of the carbons constituting NaCEC backbone were found between 60 and 110 ppm. Careful inspection of Figures 2–4 leads us to the following conclusions: (1) Peak splitting with considerable peak broadening in carboxyl and α -methylene carbon peaks was observed for the resultant CEC gels obtained by contacting acidic Al^{3+} and Ti^{3+} solutions and the δ of the highest field peak in each carbon peak region coincides with the single

carboxyl and α -methylene carbon peaks observed for the CEC gel obtained by contacting D^+ (Figures 2a, b, c and Figures 3a, b, c). (2) α -Methylene carbon peak of the CEC gel obtained by Al^{3+} seems to split into three peaks. (3) No comparably large peak broadening was detected for ring carbon peaks in any CEC gels (Figures 4a, b, c, d). (4) The δ values responsible for carboxyl, β - and α -methylene carbons in carboxyethyl substituent of the CEC gel obtained by contacting D^+ shifted towards higher magnetic field, compared with those for original NaCEC solution in D_2O (Figures 2c, 3c, 4c). (5) The δ of carboxyl carbon for the CEC gel obtained by contacting Ca^{2+} slightly (by about 0.3 ppm) shifted towards lower magnetic field, compared with that of the original NaCEC solution. (6) The contact of Na^+ and K^+ ions with the original NaCEC solution did not cause any appreciable change in δ and $\Delta\delta_{1/2}$ values of NMR peaks for the original NaCEC solution. (7) A small shoulder (at 40.5 ppm) observed as α -methylene carbon peak for the original NaCEC system grew to become an easily detectable peak when D^+ was contacted (Figures 3c, g).

Table I. Chemical shift expressed in ppm of carbons in substituent of CEC and those for C_1 carbon^a

Ion	$-\text{OCH}_2\text{CH}_2\overset{*}{\text{C}}\text{OOM}$	$-\overset{*}{\text{C}}\text{H}_2\text{CH}_2\text{COOM}$	$-\text{OCH}_2\overset{*}{\text{C}}\text{H}_2\text{COOM}$	C_1
Al^{3+}	183.18 (90)	178.43 (110)	69.05	39.38 38.68 37.28 (43) 104.77 (80)
Ti^{3+}	184.09 (100)	178.58 (50)	69.19	39.43 37.02 (50) 104.75 (40)
D^+		178.46 (9.5)	69.27	37.40 37.05 (11) 104.95 (29)
Ca^{2+}	182.67 (12)		70.92 40.46	40.17 (18) 104.81 (31)
Na^+	182.38 (7.7)		70.95 40.55	40.29 (11) 104.93 (35)
K^+	182.34 (7.1)		70.86 40.46	40.22 (8.8) 104.81 (37)
Blank	182.40 (9.2)		70.91 40.49	40.26 (11) 104.90 (41)

^a (), half value width for the peak; expressed in Hz.

Table I shows the δ (in ppm) and $\Delta\delta_{1/2}$ (in Hz) of the peaks responsible for carboxyethyl substituent of the CEC phases obtained by contacting various cations and the original NaCEC solution. The table also contains the results for the C_1 carbon of the glucopyranose unit constituting CEC backbone. The $\Delta\delta_{1/2}$ of β -methylene was not estimated because the peak tends to be overlapped with other peaks. At least two carboxyl carbon peaks of the CEC gel obtained by Al^{3+} were found at 183.18 and 178.43 ppm and those of the CEC gel obtained by Ti^{3+} were found at 184.09 and 178.58 ppm. α -Methylene carbon peak was at 39.38, 38.68, and 37.28 ppm for the CEC gel by Al^{3+} and at 39.43 and 37.02 ppm for the CEC gel by Ti^{3+} . For the original NaCEC solution carboxyl and α -methylene carbon peaks appeared at 182.40 and 40.26 (main peak) ppm, respectively. These δ values are near the δ values of the lowest field peak of the corresponding split peak regions. The differences of the δ values for carboxyl, β - and α -methylene carbons in carboxyethyl substituent before and after acidification of the NaCEC by D^+ are 4.0, 3.2, and 1.7 ppm, respectively. This explicitly indicates that the magnitude of the shift is larger for the carbons located nearer the carboxyl group. The above results also explain that the change in the chemical shift accompanied by acidification of aq NaCEC solution is brought about by the chemical transformation of $-COONa$ to $-COOH$. For the CEC gels obtained by Al^{3+} and Ti^{3+} solutions, which are fairly strong acid, broad peaks in carboxyl and α -methylene carbon regions appeared at the same δ position (around 178.5 and 37.1 ppm, respectively) as observed for the CEC gel by D^+ . This strongly suggests that these peaks are also responsible for the acid type carboxyethyl substituent. For other resultant CEC phases a salt type carboxyl carbon peak was observed between 182.2 and 183.2 ppm, probably depending on the difference in types of salt.

The order of peak broadening of carboxyl

carbon accompanied by gelation is as follows, judging from $\Delta\delta_{1/2}$ values: $Al^{3+}(90-100) > Ti^{3+}(50) > Ca^{2+}(12) > D^+(9.5)$ (\approx original NaCEC). That for α -methylene carbon is: $Ti^{3+}(50) > Al^{3+}(25-43) > Ca^{2+}(18) > D^+(11)$ (\approx original NaCEC). A significant peak broadening (about 2 times of the original NaCEC solution) on C_1 carbon of CEC backbone was only found for the CEC gel obtained by Al^{3+} . It should be noted here that gelation of NaCEC by Ti^{3+} , Al^{3+} , and Ca^{2+} caused a higher magnetic field shift of C_1 carbon peak, compared with that of original NaCEC solution but the gelation by D^+ gave the reversed shift.

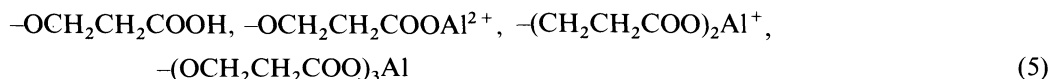
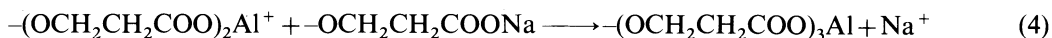
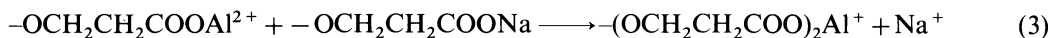
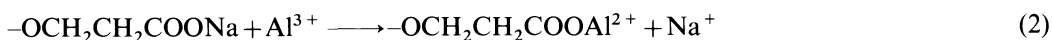
Peak Splitting and Broadening

Judging from the splitting of α -methylene carbon peak in carboxyethyl substituent, the CEC gels obtained by Ti^{3+} and Al^{3+} show at least two types of carboxyethyl groups (highest magnetic field peak, acid type; lowest magnetic field peak, salt type). From the peak area ratio, the fraction of acid type carboxyl was roughly estimated as 65% for the CEC gel by Al^{3+} and about 90% for the CEC gel by Ti^{3+} . The results can be explained by the difference in the acidity of the two metal chloride solutions (pH = 0.4 for Ti^{3+} , pH = 3.4 for Al^{3+}). In fact, phenomenological observation of gelation of NaCEC by Ti^{3+} revealed that coloured Ti^{3+} ion diffused very slowly into the CEC phase, compared with that of D^+ . Salt type carboxyl carbon peak of the gel obtained by Al^{3+} appeared at 183.18 ppm, which is a lower magnetic field than that (182.4 ppm) of the original NaCEC solution. This suggests that partial transformation of $-COONa$ to $-COOAl^{2+}$ might occur. This transformation may include the formation of cross-linking. The partial transformation of $-COONa$ to the corresponding salts is also expected for the CEC gels obtained by Ti^{3+} and Ca^{2+} for the same reason described above. Since the CEC gel obtained by Al^{3+} has three peaks responsible for α -methylene carbon in

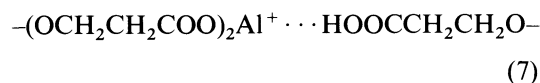
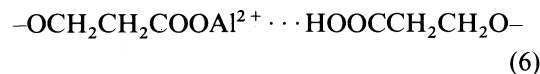
carboxyethyl substituent, another type carboxyl group (for example, higher cross-linked carboxyl by Al^{3+}) can be expected to exist.

Peak broadening is anticipated to occur when the system has nuclei (such as nitrogen) having quadrupole moment or paramagnetic substance such as Fe^{3+} and Mn^{2+} . The CEC systems used here have no nuclei having quadrupole moment. For the latter case, all the NMR peaks should broaden as observed for the CEC gels obtained by Fe^{3+} and Mn^{2+} . In fact, peak broadening of the CEC gels obtained by Ti^{3+} and Al^{3+} occurred on the only specific NMR peak (carbon peaks responsible for carboxyethyl substituent). Therefore, peak

broadening in this case cannot be explained by quadrupole moment and paramagnetic nature. Alternative and acceptable reasoning for the peak broadening of CEC gel is an interchangeable transition between two or more states through dipole-dipole interaction. If the rate of intertransition between these states is very slow, each state can be observed separately by the NMR method, and if the rate is too rapid, only one state which is an intermediate state of the above-mentioned states can be observed by NMR.⁹ This was proved for cyclononane or dimethylformamide.¹⁰ For the CEC gel obtained by Al^{3+} the following states might be interchangeable:



Since the CEC gel obtained by Al^{3+} showed at least three broad split peaks in α -methylene carbon region intertransition between several states shown in eq 5 might be very slow. In such a case, the following cross-linking seems possible:



Ti^{3+} solution is a stronger acid than Al^{3+} solution, and an acidification reaction of $-\text{COONa}$ to $-\text{COOH}$ by TiCl_3 is faster than an ion-exchange reaction of $-\text{COONa}$ to $-\text{COOTi}^{2+}$. The acidified carboxyl group strongly interacts with polyvalent Ti^{3+} lowering the molecular mobility of the carboxyl substituent.

When Ca^{2+} is employed, no peak splitting

takes place because Ca^{2+} solution is not acidic but neutral. The degree of broadening of the carboxyl and α -methylene carbons in the carboxyethyl substituent is significantly low and also the extent of the shifts of these peaks towards lower magnetic field is zero for the α -methylene carbon and negligibly small for the carboxyl carbon, in contrast to Al^{3+} and Ti^{3+} . This indicates that the CEC gel produced by Ca^{2+} has weaker crosslinking than that produced by Al^{3+} or Ti^{3+} , and probably due to low cross-linking density.

The decrease in $\Delta\delta_{1/2}$ values of the carboxyl and α -methylene carbon peaks by contacting Na^+ or K^+ might be due to the dilution effect (*i.e.*, a decrease in polymer concentration in the system) because aq NaCEC solution remains as a solution.

The $\Delta\delta_{1/2}$ values of the carboxyl and α -methylene carbon peaks of the CEC gel obtained by contacting DCl solution are equal to

those of the original NaCEC in D₂O. A formation of a gel phase of NaCEC solution when contacted with DCl cannot be explained by the mechanism proposed for gelation induced by Al³⁺ and Ti³⁺.

Inspection of Table I leads to the conclusion that diffusion of metal ions, except for Al³⁺, into aq NaCEC solution does not cause detectable change in the $\Delta\delta_{1/2}$ of C₁ carbon peak, which is a measure expressing the mobility of backbone glucopyranose chain of CEC. However, even in the Al³⁺ case, the increase in $\Delta\delta_{1/2}$ of C₁ carbon peak was found to be much smaller than those observed for the peaks responsible for the carboxyethyl substituent. This means that mobility of the backbone chain in CEC gel phase is not so different from that in original NaCEC in D₂O.

Distribution of Substitution

A close inspection of the spectrum of original NaCEC in D₂O reveals that α -methylene carbon envelope consists of two peaks, which become distinctly separated when DCl in D₂O was in contact with the NaCEC solution (see Figures 3e, f). The peak ratio of the substituted- to the unsubstituted-C₆ carbon peaks (72.8 and 62.9 ppm, respectively) and the same ratio of the substituted -C₂ plus -C₃ envelope (around 83.9 ppm) to the C₁ carbon peak (104.9 ppm) enables us to estimate $\langle\langle f_6 \rangle\rangle / \langle\langle f_2 \rangle\rangle + \langle\langle f_3 \rangle\rangle$. Here, $\langle\langle f_k \rangle\rangle$ denotes the probability of substitution at C_k ($k=2, 3,$ and 6) position. The value thus determined ($=2.25$) agrees well with the peak ratio of two peaks at 40.22 and 40.46 ppm for original NaCEC in D₂O. This means that the main peak at 40.26 ppm is assigned to the α -methylene carbon of carboxyethyl substituent attached to C₆ position and small peak at 40.46 ppm is assigned to that attached to C₂ and C₃ positions of the glucopyranose unit. Thus, $\langle\langle f_6 \rangle\rangle$ and $\langle\langle f_2 \rangle\rangle + \langle\langle f_3 \rangle\rangle$ of the sample used in this study were found to be 0.27 and 0.12, respectively.

Gelation of CEC

Gelation of NaCEC induced by contacting Al³⁺ and Ti³⁺ does not accompany a significant peak broadening of the carbons constituting the NaCEC backbone but broadens the carbon peaks of substituent. This strongly suggests that gelation of NaCEC proceeds neither by the formation of double helix reported for κ -carrageenan nor by the formation of egg-box type cross-linking reported for alginic acid.^{2,3,11,12} which causes the strong restriction of molecular motion of backbone molecules. The backbone molecular chain in CEC gel obtained in this case is relatively mobile and only the side chain (substituent) takes part in the cross-linking probably through ionic bond (see Figure 5). However, a slight but direct cross-linking between glucopyranose units through some force may be anticipated for the CEC gel obtained by Al³⁺ because of slight increase in the $\Delta\delta_{1/2}$ of C₁ carbon peak. For these gels the molecular chain in the so-called network is regarded to have almost the same molecular mobility as in the solution state.

Gelation of NaCEC by contacting DCl does not accompany any peak broadening, only giving rise to a change in the chemical shift of the carbons constituting carboxyethyl substituent by acidification. In other words, carboxyl groups in the gel are completely displaced by proton and dissociation of the acid type of carboxyl groups is strongly restricted. Furthermore, during the gelation of NaCEC change in the molecular mobility did not take place. The NaCEC solution used in this study can be classified as a semi-dilute solution and the molecular chains in the solution are considered to be adequately entangled with each other. On the other hand, the NaCEC sample used here was found to be insoluble in acid solution and to be precipitated from its aqueous solution by addition of acidic solution. Acidic solution is thought to be a kind of poor solvent against NaCEC, although accompanying a change in counter ion in carboxyl part as

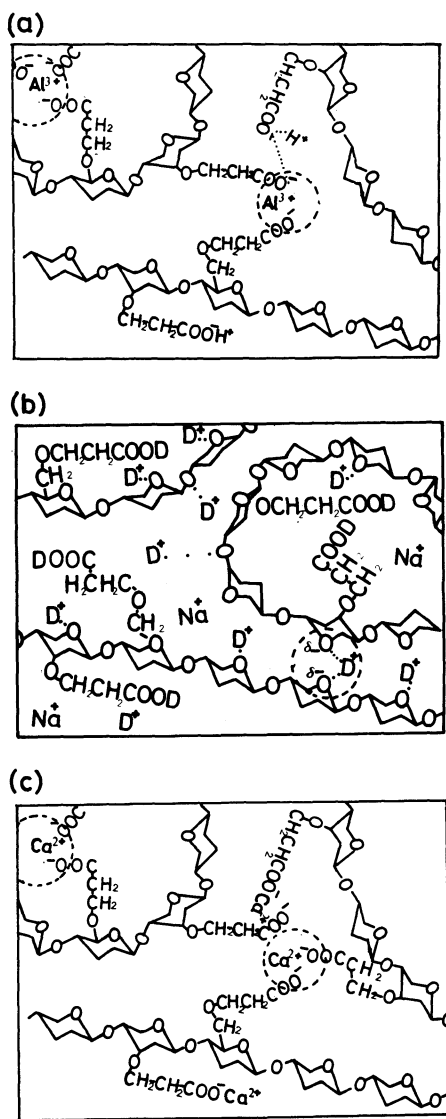


Figure 5. Model structure of CEC gel containing (a) AlCl_3 , (b) DCl , (c) CaCl_2 . The region surrounded by broken line represent cross-links in the gel.

shown in eq 1. The gelation, observed when DCl is in contact with NaCEC solution, seems to be induced by the so-called micro-phase separation during which the partly precipitating CEC molecules entangle each other accommodating water, D^+ and Na^+ steadily into the molecular space. In this case the excess

sive proton ions may serve as a kind of very weak cross-links which link directly glucopyranose units (see Figure 5b).

Ca^{2+} produces another type of CEC gel in which a part of Ca^{2+} is involved in cross-linking of carboxyethyl substituent and the gel has no free acid type of the substituent (see Figure 5c).

The CEC gels obtained here give different chemical shifts for C_1 carbon in the backbone glucopyranose unit. The reason for this is probably due to the difference in configuration of β -glucoside linkage (*i.e.*, $-\text{C}_1-\text{O}-\text{C}_4-$). A direct interaction of cations with ether oxygen or an inclusion of cations to the interaction between ring (hemiacetal) oxygen and C_3-OH (or $\text{C}_3\text{OCH}_2\text{CH}_2\text{COOM}(\text{H})$) in the neighbouring unit or in different molecular chain may cause configurational change in β -glucoside linkage (see Figure 5). These interactions give the possibility that even univalent cation may cause a kind of cross-linking. Thus, such interactions may give a possible basis for gelation of aq solution of an anionic cellulose derivative by univalent cation (for example, aq solution of sodium salt of cellulose sulfate by K^+ or in this study the CEC gel by D^+). But, the existence of such an interaction shown in Figure 5 is not proved at present.

Summarizing, an aqueous solution of sodium salt of carboxyethylcellulose (NaCEC : total degree of substitution $\langle\langle F \rangle\rangle = 0.39$) was proved to produce gels by contacting polyvalent cations and acid but the gelation processes were significantly different from each other. Analysis on the chemical shift and half value width of ^{13}C NMR peaks obtained for the CEC gel phases in comparison with those of the peaks for the original NaCEC solution revealed that only Al^{3+} and Ti^{3+} produced considerable broadening and splitting of the peaks responsible for only the carboxyethyl substituent, but DCl only resulted in peak shift towards higher magnetic field with no peak broadening. The chemical shift of C_1 carbon, constituting the backbone of NaCEC , of the

CEC gels gave different values from gel to gel, showing some difference in configuration of C₁-O-C₄ linkage (β -glucoside linkage) of these CEC gels.

Tentative gelation mechanisms were proposed to explain the roles of the cation species including protons in their solutions used for contacting the aqueous NaCEC solution.

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