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Reversible Gelation of Short-Chain *O*-(2,3-Dihydroxypropyl)cellulose/Borax Solutions. 1. A ^{11}B-NMR Study on Polymer–Ion Interactions

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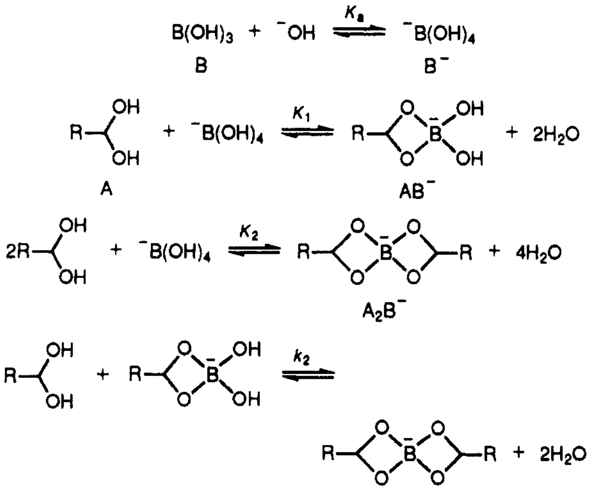
ABSTRACT: The complexation behavior of solutions of borax and *O*-(2,3-dihydroxypropyl)cellulose with a number-average degree of polymerization of about 20 was studied by ^{11}B-NMR spectroscopy. The equilibrium constants of the (ion/diol) 1:1 monocomplexation, K_1, and the 1:2 dicomplexation, K_2, were determined as a function of temperature. A comparison of these results with those obtained for a low-mass model system containing 1,2-propanediol (PG) instead of DHPC has revealed that (i) as in the PG system the complexation in the DHPC system proceeds by the formation of α,β-diol/borate five-membered rings, (ii) both K_1 and K_2 are appreciably larger in the polymer system than in the PG system, and (iii) these differences in both K_1 and K_2 are entropic in origin and are not related to the enthalpy. Possible causes for the differences were discussed. No polymer concentration effect was observed, undoubtedly because of the short-chain and rigid-chain nature of the employed polymers. No or little polyelectrolyte effect was observed for the studied range of borate ion concentrations ($<0.5 \times 10^{-2}$ M).

Introduction

Aqueous solutions of polyhydroxyl polymers such as poly(vinyl alcohol),[1-8] poly(glyceryl methacrylate),[9] and polysaccharides[10-12] form thermoreversible hydrogels in the presence of anionic species such as borate, titanate, and antimonate or metal ions such as Cu^{2+} and Ba^{2+}. These hydrogel systems work as mobility controlled viscous fluids and have found important applications in the fields of, e.g., oil recovery and cosmetics.[13,14] However, the mechanisms of gelation are rarely well understood, and this seems to be prohibiting the development of well-designed hydrogel systems.

O-(2,3-Dihydroxypropyl)cellulose (DHPC), a novel polyhydroxyl polymer that can have more than three hydroxyl groups per anhydroglucose unit,[15,16] forms a thermoreversible gel in the presence of borax. The DHPC/borax system is interesting particularly because the concentrations of cross-linking and other free species can all be determined without ambiguity by ^{11}B-nuclear magnetic resonance spectroscopy (^{11}B-NMR). This kind of information, not always available in other systems, is particularly important in attempting to understand the mechanism of gelation and describe the sol–gel transition in a quantitative fashion.

In this paper, we shall describe the results of a ^{11}B-NMR study of the DHPC/borax system. We have carried out the experiments in the sol range, using relatively low polymer and borax concentrations in order to obtain a basic understanding of the polymer–ion interactions in this system and avoiding complexities as much as possible. For the same reason, we will use short-chain DHPC's as polymer samples, for which the formation of intrachain loops[9] should be negligible. At low concentrations (<0.1 M), borax is completely dissociated into two boron species, boric acid [$B(OH)_3$] and the borate anion [$^-B(OH)_4$], the equilibrium constant being $pK_a = 9.2$. The complexation reactions with a diol are known to proceed according to[17-21]



$$\underset{B}{B(OH)_3} + {}^-OH \xrightleftharpoons{K_a} \underset{B^-}{{}^-B(OH)_4} \qquad (1)$$

From this point on, $B(OH)_3$, $^-B(OH)_4$, free diol, and diol/monoborate complexes with 1:1 and 2:1 stoichiometry will be abbreviated as B, B^-, A, AB^-, and A_2B^-, respectively. The concentrations of boron species B, B^-, AB^-, and A_2B^- will be determined to evaluate the equilibrium constants K_1 and K_2 (and k_2) as a function of temperature. The results of the polymer system will be compared with those for a low-mass model compound system and discussed. These results form the basis of the discussion about the sol–gel transition of the DHPC/borax system, which is the topic of the forthcoming paper.[22]

Experimental Section

Materials. *O*-(2,3-Dihydroxypropyl)cellulose (DHPC) was prepared by the homogeneous reaction of cellulose with 2,3-epoxy-1-propanol (glycidol) in a 10 wt % LiCl/dimethylacetamide (DMAc) solvent, as described in a previous paper.[16] DHPC was purified by dialysis against deionized water and freeze-dried and then thoroughly dried at 105 °C under vacuum for 24 h before use. Because DHPC has oligo(dihydroxypropyl) (DHP) side chains of indefinite length ($n \geq 0$; Figure 1), its chemical structure needs be characterized by at least two parameters, which are the number of substituted hydroxyl groups per anhydroglucose unit,

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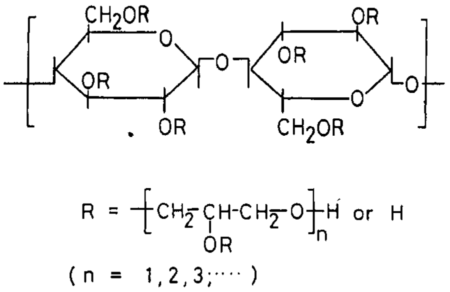

Figure 1. Chemical structure of *O*-(2,3-dihydroxypropyl)cellulose (DHPC).

Table I
Molecular Characteristics of DHPC Samples

sample code	$10^{-4}M_n$[a]	MS	DS	l[b]	DE[c]
DHPC-4	0.8	4.4	1.2	3.7	1.5
DHPC-6	1.2	6.3	1.2	5.1	1.8
DHPC-1	1.2	1.0	0.9	1.1	(1.0)[d]

[a] Values estimated by a poly(ethylene oxide)-calibrated GPC analysis. [b] Mean length of side chains; l = MS/DS. [c] Number of side-chain α,β-diol sites per anhydroglucose unit. [d] Assumed value.

i.e., the degree of substitution (DS), and the total number of glycidol units incorporated into an anhydroglucose unit, i.e., the molar substitution (MS). Two DHPC samples (DHPC-4 and -6) were used for the ^{11}B-NMR measurements, where the numbers in the sample codes indicate approximate MS values (the DS values are practically the same, about 1.2). Sample DHPC-1, in which MS ≃ 1 and DS ≃ 1, was used as a reference sample for the calculation of the DE value (see below). The molecular characteristics of the samples are listed in Table I. The values for the MS, DS, and the average number of α,β-diol end groups (DE) in the DHP side chains per anhydroglucose unit were estimated by the ^{13}C-NMR method.[16]

Sodium tetraborate decahydrate ($Na_2B_4O_7{\cdot}10H_2O$), 1,2-propanediol (PG), and other chemicals, all of reagent grade, were obtained commercially.

^{11}B-NMR Measurements. ^{11}B-NMR spectra were recorded with a JEOL GSX-270 Fourier transform spectrometer operating at 86.55 MHz for ^{11}B nuclei. To avoid the broad signal from the boron incorporated in glasses, measurements were carried out in a 10-mm-o.d. tube made of tetrafluoroethylene. The sample temperature was regulated within ±1 °C. ^{11}B chemical shifts were measured relative to the external boron trifluoride diethyl etherate [$BF_3O(C_2H_5)_2$] with positive values for signals at higher frequency than this reference.

Stock sample solutions were prepared by dissolving an appropriate amount of DHPC or PG in deionized water with stirring at room temperature. A borax solution was added to the sample solution so that the total boron concentration [B_T] became 1.00×10^{-2} M. At the borate concentration used in this study, no polyborate species were detectable.[23-26] After the solution was allowed to stand for 12 h at a desired temperature, its ^{11}B-NMR spectrum was recorded at that temperature.

Other Measurements. ^{13}C-NMR measurements were made on a JEOL GX-400 spectrometer, operating at 100.8 MHz in the proton noise-decoupled mode, using a 10-mm probe and deuterated dimethyl sulfoxide (DMSO-d_6) as solvent. Spectra were recorded with a spectral width of 12.5 kHz, a repetition time of 5 ~ 20 s, and a flip angle of 45°. A total of 10 000–60 000 scans were accumulated.

GPC measurements were made at 25 °C with a Tosoh HLC-803C high-speed liquid chromatograph equipped with a differential refractometer Model RI-8. Hitachi GL-W520, GL-W530, and GL-W540 columns were used with a 0.5% acetic acid solution as eluent. The number- and weight-average molecular weights (M_n and M_w) were estimated on the basis of a calibration curve obtained by using Tosoh standard poly(ethylene oxide)s.

Estimation of the Equilibrium Constants. In a solution of borax/diol compound, two types of complexes with B^- can be formed as shown in eqs 2–4. The equilibrium constants for the individual reactions are given by

$$K_a = [B^-]/([B][OH^-]) \tag{5}$$

$$K_1 = [AB^-]/([B^-][A]) \tag{6}$$

$$K_2 = [A_2B^-]/([B^-][A]^2) \tag{7}$$

$$k_2 = [A_2B^-]/([AB^-][A]) = K_2/K_1 \tag{8}$$

The mass balance equations are

$$[A_T] = [A] + [AB^-] + 2[A_2B^-] \tag{9}$$

$$[B_T] = [B] + [B^-] + [AB^-] + [A_2B^-] \tag{10}$$

where [A_T] and [B_T] are the total concentrations of diol compounds and boron species, respectively.

In the cases of PG and DHPC, the signals due to the monodiol/borate 1:1 complex and the didiol/borate 2:1 complex could be detected as separate signals in addition to the free B/B^- signal (see below). Each spectrum was resolved into these three components by use of a Lorentzian function. Thus the concentrations of the free B/B^- and the complexes can be determined by evaluating the signal areas of the three components. The relative fractions of B and B^- can be estimated according to Sinton.[1] In this way, we could determine the individual concentrations of B, B^-, AB^-, and A_2B^-, with which the equilibrium constants were calculated using eqs 6–8.

Results

Borate Complexation with a Low-Mass Model Compound. 1,2-Propanediol (PG) was used as a model compound of the DHP side chains. The ^{11}B-NMR spectra of PG/borax solutions gave two sharp signals at ≃5.2 and 8.9 ppm, respectively, and a rather broad B/B^- signal showing a decrease in the relative intensity and a downfield shift with increasing PG concentration. The 5.2 and 8.9 ppm peaks were assignable to AB^- and A_2B^-, respectively.[27-29]

In Figure 2a, the concentration ratio of AB^- to B^- is plotted against the diol concentration [A], under equilibrium conditions, and shows a linear relationship between the two quantities. Similarly, the concentration ratio of A_2B^- to B^- is proportional to the square of the diol concentration $[A]^2$, as shown in Figure 2b. The slopes of the lines in parts a and b of Figure 2 give the equilibrium constants, K_1 and K_2, for the mono- and dicomplexations, respectively. The calculated equilibrium constants K_1, K_2, and k_2 for the PG/borax system are given in Table II.

The PG/borax system was then studied by ^{11}B-NMR as a function of temperature. Figure 3 shows the logarithmic plots for the equilibrium constants K_1 and K_2 against inverse temperature. Each set of data gives a linear relationship. The enthalpy changes ΔH_1 and ΔH_2 and the entropy changes ΔS_1 and ΔS_2 for the AB^- and A_2B^- complexations were calculated from the linear fits by reference to the standard equations

$$K = \exp(-\Delta G/RT) \tag{11}$$

$$\Delta G = \Delta H - T\Delta S \tag{12}$$

where ΔG and R are the free energy change and the gas constant, respectively. The results are given in Table II.

Borate Complexation with DHPC. As already stated, the DHPC's used in this study were synthesized by the reaction of 2,3-epoxy-1-propanol (glycidol) with alkaline activated cellulose in a homogeneous solution. Glycidol reacts not only with the hydroxyl groups of the anhydroglucose units but also with the newly formed hydroxyl

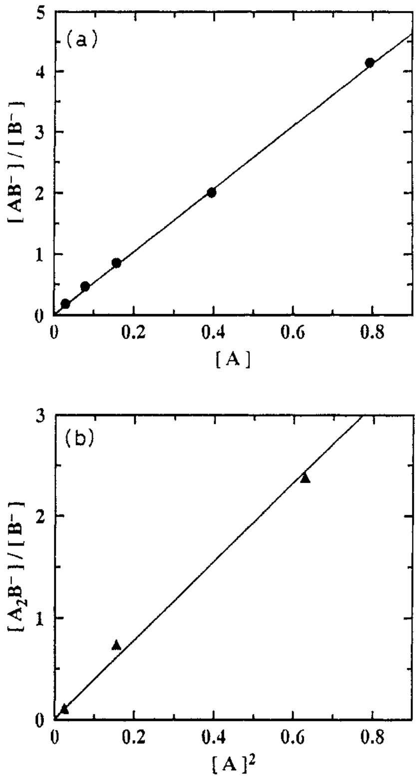

Figure 2. Plots of (a) $[AB^-]/[B^-]$ vs [A] and (b) $[A_2B^-]/[B^-]$ vs $[A]^2$ for the PG/borax system.

groups of the hydroxyalkyl side groups, resulting in poly-DHP side chains. Figure 4 shows two possible structures for the side chain with a "degree of polymerization", l, of 3. In the linear structure (Figure 4a), there are one α,β- and two α,ϵ-diol sites, while in the branched structure (Figure 4b), there are two α,β sites and no α,ϵ site. Other sites are more remote than the α,ϵ sites. In order to clarify the role of the α,ϵ sites, diethylene glycol was studied as a model compound. In contrast to the result for PG, no complexation was observed for diethylene glycol. This indicates that the α,ϵ sites (and probably other more remote sites) make no important contribution to the 2:1 complexation with borate anions.[1] DHPC has other α,β-diol sites with an anti configuration within each individual anhydroglucose unit. A preliminary examination has indicated that anti-positioned α,β-diols in saccharides cannot be complexed with borate anions.[10] Therefore, the complexable diol sites in DHPC may be assumed to be only the α,β-diol groups located at the ends of the DHP side chains.

The number of these α,β-diol ends (DE) per anhydroglucose unit was estimated by the ^{13}C-NMR method.[15,16] A representative ^{13}C-NMR spectrum of the DHPC sample is shown in Figure 5 (possible assignments are shown in the spectrum). The strong and sharp peaks designated as P are due to the carbons of the DHP side chains. The signal corresponding to the carbons of the α,β-diol end can be easily assigned on the basis of the chemical shifts of the corresponding carbons in poly(glycidol).[30] The signal designated P_1 is thus assigned to the methylene carbon of the α,β-diol site. The DE was estimated by

$$DE = [P_1]/(1.21[A]) \qquad (13)$$

where $[P_1]$ and [A] denote the integral intensities of the signals P_1 and A, respectively, with the latter corresponding to the C1 carbon. The factor 1.21, which takes account of the difference in integral intensity between the C1 carbon and the carbon atom at the side chain end, was estimated on the basis of the spectrum of sample DHPC-1, whose DE value could be regarded as essentially equal to 1, because MS ≅ DS for this sample (see Table I). This difference in the integral intensity arises from the difference in the spin-lattice relaxation time T_1 between the two carbons.[31] In this study, a rather long pulse repetition time of 20 s was used, but this was still insufficient. The DE values are listed in Table I.

Some representative ^{11}B-NMR spectra for the DHPC/borax solutions are given in Figure 6. Two signals separate from the strong signal from the uncomplexed species can be seen, of which the one at 5.4 ppm is observed even at low concentrations and is assignable to the monocomplexed species (AB^-). The other signal at 9.4 ppm is assignable to the dicomplexed species (A_2B^-). The chemical shift values and the diol-concentration dependence of this system are similar to those of the PG/borax system.

In parts a and b of Figure 7, the data are presented according to eqs 6 and 7, respectively. In each case, a straight line passing through the origin was obtained, the slope of which gave the equilibrium constants K_1, K_2, and k_2 listed in Table II.

^{11}B-NMR data were collected at various temperatures. Figure 8 shows the plots of log K_1 and of log K_2 against inverse temperature. It can be seen that the logarithms of K_1 and K_2 increase linearly with inverse temperature. Numerical results are given in Table II.

Discussion

The ^{11}B-NMR analysis has enabled us to determine the concentrations of the individual boron species in both PG/borax and DHPC/borax systems and thus to evaluate the equilibrium constants K_1 and K_2 in the two systems as a function of temperature. (Tables of ^{11}B-NMR data for the PG/borax and DHPC/borax systems are available upon request to the authors.) The quality of the data presented in Figures 2, 3, 7, and 8 indicates that the numerical results are fairly accurate.

Several points should be noted in comparing the results for the PG system to the DHPC system. First, both systems showed two NMR signals, assignable to the mono- and dicomplexed species, respectively, at nearly the same chemical shift values. This indicates that the complexations in the DHPC system, as well as in the PG system, proceed with the formation of five-membered rings (namely, R = $-CH_2CH_2-$, eqs 2–4). In this regard, PG is an ideal low-mass model compound for DHPC. In fact, it has been observed that the chemical shifts in polymer systems as compared to those in low-mass model systems are not always equal. For example, a 1,3-pentanediol/borax system exhibits two separate resonance signals assignable to the mono- and dicomplexed species, while for poly(vinyl alcohol), the 1,3-diol polymer mixed with borax does not usually offer such a good resolution between the two species, giving rise to certain ambiguities in the interpretation of the data.[1,4,5] In the DHPC system, the diol groups that play a main part in the complexation exist near the ends of the side chains (see above), separated from the main chain by some flexible spacers, and this is likely the reason for the similarities between the DHPC and PG systems.

The values of the equilibrium constants for the two systems, however, are not the same. As Table II shows, the K_1 of the DHPC system is substantially larger than that for the PG system. The table also shows that the entropy of monocomplexation, ΔS, for the DHPC system is larger than that for the PG system by about 7 J/mol·K, while the enthalpies, ΔH, are the same. Clearly, the mentioned difference in K_1 is entropic in origin and does

Table II
Comparison of Equilibrium Constants[a] K_1, K_2, and k_2, Enthalpies ΔH_1 and ΔH_2, and Entropies ΔS_1 and ΔS_2 of PG–Borax and DHPC–Borax 1:1 and 2:1 Complexations

	equilibrium constants			thermodynamic functions			
compd	K_1 (M^{-1})	K_2 (M^{-2})	k_2 (M^{-1})	ΔH_1 (kJ/mol)	ΔH_2 (kJ/mol)	ΔS_1 (J/mol·K)	ΔS_2 (J/mol·K)
PG	5.6	4.3	0.8	−17.1	−21.5	−43.1	−60.0
DHPC	9.0	21.2	2.4	−16.3	−21.8	−36.4	−47.6

[a] Mean values over all the different diol concentrations examined, T = 25 °C and $[B_T]$ = 0.01 M; $k_2 = K_2/K_1$.

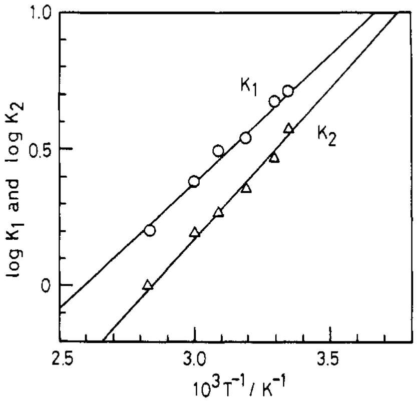

Figure 3. Plots of log K_1 and log K_2 vs inverse temperature for the PG/borax system; $[B_T]$ = 0.01 M, and $[A_T]/[B_T]$ = 80.

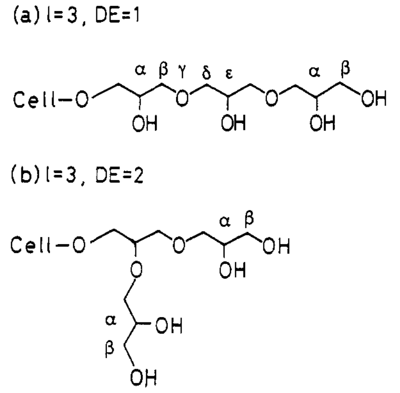

Figure 4. Two possible structures of the DHP side chain with l = 3.

not relate to the enthalpy. It is assumed that the DHPC main and side chains have a certain effect on the structure of the nearby water, causing an uneven distribution of boron ions between the neighboring water and the bulk water. This type of polymer–ion interaction, which is mediated by some kind of water structuring, is believed to be the main mechanism for the separation of small ions by a *neutral* polymer gel.[32]

The difference in the dicomplexation constant K_2 is even more pronounced. It is about 5 times larger in the polymer system than in the low-mass system. Again, the enthalpy ΔH_2 of dicomplexation is about the same in the two systems, while the entropy ΔS_2 is about 12 J larger in the DHPC system than in the PG system. This might be interpreted as originating from the same mechanism discussed above.

Another possible interpretation may be a kind of cooperative effect intrinsic in polymer systems. In a polymer system, the formation of a 2:1 complexation indicates the formation of a cross-link. Once an intermolecular cross-link is formed (in our system, cross-linking occurs mostly intermolecularly, see below), the local concentration of complexable sites near the cross-link would be relatively high; hence, a larger k_2 ($=K_2/K_1$) than in a low-mass system would be expected. Such an effect, however, is likely unimportant in our system, since the

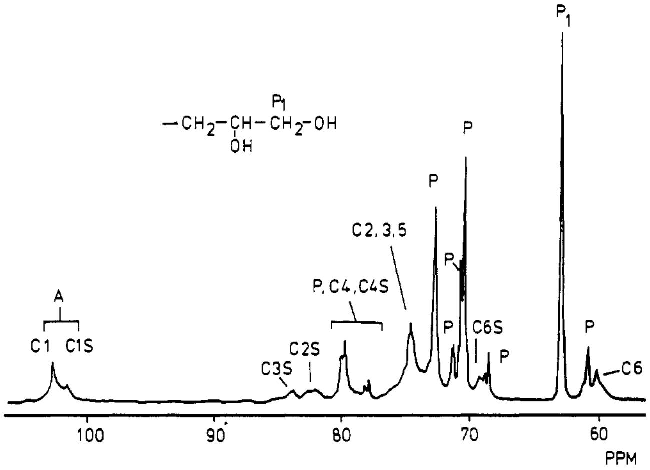

Figure 5. ^{13}C-NMR spectrum of DHPC-1. The strong and sharp peaks designated as P and P_1 are assigned to the carbons of the DHP side chains. The signals from the C2, C3, and C6 carbons bearing a substituted hydroxyl group have been assigned by reference to the chemical shifts of the respective carbons in cellulose derivatives and designated as C2S, C3S, and C6S, respectively.

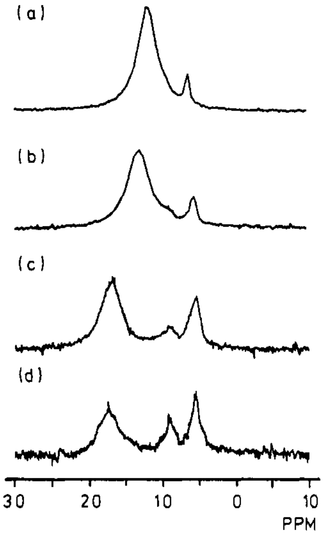

Figure 6. ^{11}B-NMR spectra of DHPC/borax solutions at 25 °C and $[B_T]$ = 0.01 M with (a) $[A_T]/[B_T]$ = 2.1, (b) $[A_T]/[B_T]$ = 4, (c) $[A_T]/[B_T]$ = 28.7, and (d) $[A_T]/[B_T]$ = 43.8.

plot of $[A_2B^-]$ vs $[A]^2$ showed no clear deviation from linearity (Figure 7b). In addition, according to Henderson et al.,[28] who studied borax solutions of several low-mass diols by ^{11}B-NMR, both K_1 and K_2 for the complexation with boron ion increased in the order 1,2-ethanediol < 1,2-propanediol (PG) < 1,1,2,2-tetramethyl-1,2-propanediol (pinacol). In particular, the differences in K_1 and K_2 between PG and the pinacol system were both about the same order of magnitude as observed here between the PG and the DHPC systems. Because these authors used an incorrect assumption to evaluate the B^- concentration and did not study temperature effects, their results cannot be directly compared with ours. Nevertheless, their results do suggest that the "polymer effect"

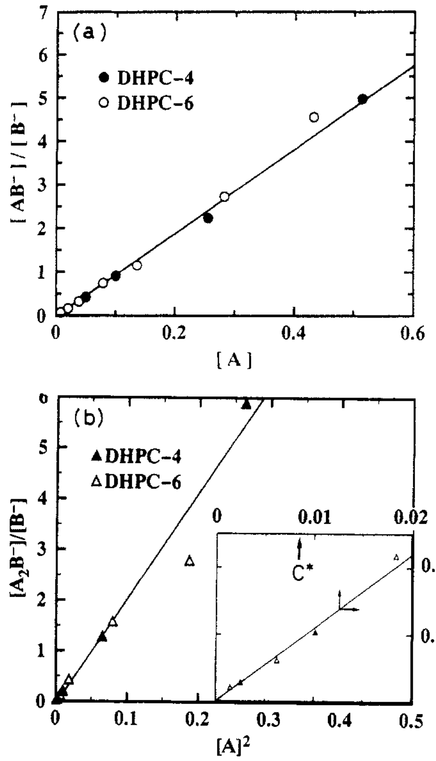

Figure 7. Plots of (a) $[AB^-]/[B^-]$ vs [A] and (b) $[A_2B^-]/[B^-]$ vs $[A]^2$ for the DHPC/borax system. The overlap concentration C^* for DHPC-4 is indicated in the figure.

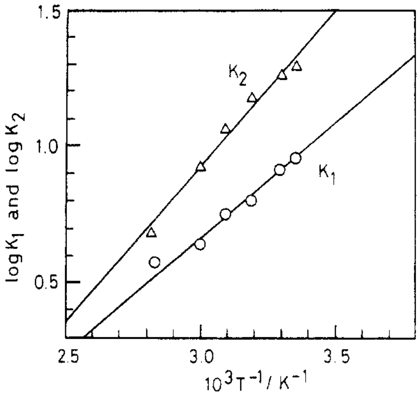

Figure 8. Plots of log K_1 and log K_2 vs inverse temperature for the DHPC-6/borax system; $[B_T]$ = 0.01 M, and $[A_T]/[B_T]$ = 28.3.

may not be the main cause for the large k_2 or K_2 observed in the DHPC system.

Pezron et al., who studied poly(glyceryl methacrylate)/borate solutions by the ^{11}B-NMR method, observed that, at concentrations lower than the overlap concentration, the concentration ratio of the 2:1 complex against the 1:1 complex was almost constant, independent of polymer concentration. This is because 2:1 complexes are formed intramolecularly. At higher concentrations, the ratio increased with increasing polymer concentration, indicating an increase in intermolecular 2:1 complexes. For this reason, they could not evaluate the equilibrium constant of the dicomplexation without ambiguity. In contrast, the DHPC/borax system studied here shows no indication of intramolecular cross-linking. A lower concentration region of the plot given in Figure 7b is magnified in the inset of the figure. The approximate overlap concentration C^* of DHPC-4 is estimated on the basis of the intrinsic viscosity value $[\eta]$ with[11] $C^* = 1.4/[\eta]$ as shown by the arrowhead in the inset. Clearly, the proportional relationship holds even at concentrations well below C^*, indicating that no intramolecular cross-links are formed.

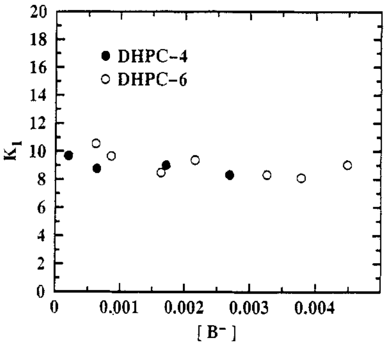

Figure 9. Plot of K_1 vs $[B^-]$ for the DHPC-4/borax system (filled circles) and DHPC-6/borax system (open circles) at 25 °C.

This is quite understandable in light of the molecular characteristics of the DHPC samples. According to Pezron et al.,[9] intramolecular cross-linking or loop formation requires at least 20–25 monomer units in poly(vinyl alcohol) and at least 50 units in galactomannan, a stiffer chain. The persistence length of DHPC should be similar to those of alkylcelluloses, typically about 10 nm,[33] and hence its Kuhn segment length should be about 20 nm or about 40 units in terms of its degree of polymerization, DP. The number-average DP's of the DHPC samples used here are about 20, which is too short to all allow for intramolecular loop formation. This in fact is the main reason why we have chosen the short-chain DHPC's as polymer samples.

Finally, we comment on "polyelectrolyte effects" on the complexation. Pezron et al.[4] have shown theoretically and experimentally that the ion complexation constants in polymer systems strongly depend on the complexing ion concentration $[B^-]$. Figure 9 shows the plot of K_1 against $[B^-]$ for the DHPC/borax system. In the studied range of $[B^-]$, K_1 may be regarded as approximately constant. (In fact, it may appear to decrease slightly with increasing $[B^-]$ and that much of a decrease seems to be consistent with the result of Pezron et al. for the galactomannan system.) Clearly, experiments covering a wider range of $[B^-]$ are needed to discuss the polyelectrolyte effects in this system.

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