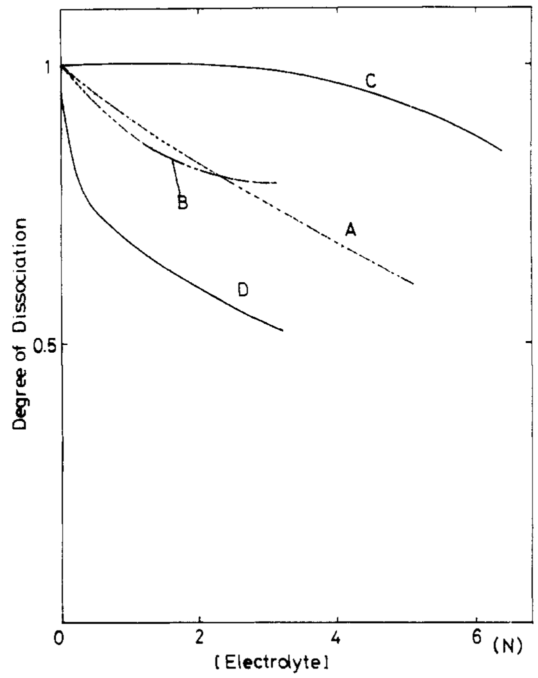

Figure 9. Effect of concentration on the dissociation of sulfonate groups of methanesulfonic acid and poly(ethylenesulfonic acid) at 25 °C: A, *p*-toluenesulfonic acid (dotted curve); B, poly(styrenesulfonic acid) (dotted curve); C, methanesulfonic acid; D, poly(ethylenesulfonic acid).

Lapanje et al.[3] and by Kotin et al.[14] The lower degree of dissociation of HPES compared to HPSS may be due to the phenyl side chains in the latter, which would make the main chains of poly(styrenesulfonate) ions less flexible.

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Registry No. HPSS, 50851-57-5; HPES, 26101-52-0.

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Complex Formation in Polymer-Ion Solutions. 2. Polyelectrolyte Effects

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ABSTRACT: We have studied the effect of electrostatic interactions on ion complexation in polymer solutions. Using a simple self-consistent argument, we show that the complexation constants strongly depend on the ionic strength of the solution and in particular on the complexing ion concentration. We have performed a ^{11}B NMR experimental study of complexation in three different poly(hydroxy compound)-borax systems over a wide range of borax concentration. As theoretically expected, a sharp decrease of complexation constants with increasing borax concentration is observed. This electrostatic effect, specific to macromolecular systems, is absent in corresponding low molecular weight model systems.

I. Introduction

Considerable effort has been devoted to the study of ion complexation by polymer chains over the past 4 decades. Electrostatic repulsion between charged complexes on macromolecular chains plays a major role in various phenomena such as phase separation,[1-2] the swelling of gels,[3] and the rheological properties of semidilute[4] or dilute solutions[5,6] of polymer-ion systems. Electrostatic interactions strongly affect the formation of polymer-ion complexes in many different systems such as polyelectrolyte-metallic ion[7-9] or neutral polymer-anion solutions.[1] The importance of this polyelectrolyte effect in polymer-ion complexation is generally evaluated on the basis of a comparison with the classical complexation picture for small model molecules. In the preceding paper of this series,[9] it has been shown that this classical mass action law scheme is inadequate for dilute polymer solutions when intrachain complexes are formed. The aim of this paper is to present a theoretical analysis of the importance of the polyelectrolyte effect on complex formation in a simple neutral polymer-ion system and to test the predictions for polyelectrolyte effects in poly(hydroxy compound)-borate solutions.

In many situations complexation chemical equilibria between polymers and ions in aqueous solutions may be reduced to the two following successive reactions:

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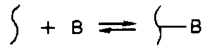
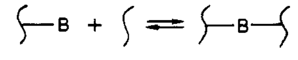

(I)


(II)

where B is the ion. Monocomplexation (reaction I) causes the appearance of a charge on the neutral polymer chains. Dicomplexation (reaction II) leads to the formation of mostly intramolecular cross-links (in very dilute polymers solutions) and both intra- and intermolecular cross-links in semidilute solutions. The number of 1:1 complexes is given by the monocomplexation constant K_1:

$$[\mathrm{BP}^-] = K_1[\mathrm{B}][\mathrm{P}] \qquad (1)$$

where P denotes the polymer site and BP the 1:1 complexes. In the preceding paper[9] it was shown that in dilute polymer solutions the number of 2:1 intrachain complexes also varies linearly with the polymer site concentration:

$$[\mathrm{BP}_2^-] = K_2[\mathrm{B}][\mathrm{P}] \qquad (2)$$

where $[\mathrm{BP}_2^-]$ is the intrachain cross-link concentration. It may be recalled that for small molecules the number of 2:1 complexes is proportional to $[\mathrm{P}]^2$. In addition, it can be argued that in a good solvent, where excluded-volume intractions predominate, intrachain cross-linking leads essentially to small loop formation.[14] In this study we focus on a dilute polymer solution in a good solvent. It is then possible to define a global complexation constant $\tilde{K}$ that yields the total number of complexes or charges carried by the macromolecules:

$$[\mathrm{BP}] + [\mathrm{BP}_2] = \tilde{K}[\mathrm{B}][\mathrm{P}] \qquad (3)$$

The effective complexation constant $\tilde{K}$ strongly depends on the ionic strength of the solution and on the free ion concentration. To describe the influence of polyelectrolyte effects on the number of complexes formed on the neutral polymer chain, we represent the chain as a random copolymer with some units bearing charges (complexes). The fraction of charged polymer sites is given by

$$f = \tilde{K}[\mathrm{B}]/(1 + \tilde{K}[\mathrm{B}]) \qquad (4)$$

Two major differences distinguish this system from a classical polyelectrolyte. First, the number of charges on the chain is imposed by the chemical equilibria. Second, free ions always present in the solution partially screen out electrostatic interactions even in the absence of passive salt. As a result, although the conformation depends on the value of the complexation constants, the chains remain flexible. Indeed, in many polymer–ion systems counterion condensation can be neglected since the average contour length d between two charges on the chain is much bigger than the Bjerrum length $Q = e^2/4\pi\epsilon kT$ (typically Q = 7 Å in water at 25 °C): $d > 3Q$. Moreover, extra stiffening of the complexed polymer chain is generally negligible as the electrostatic persistence length, L_e,[11,12] is smaller than Q.[6] Table I gives typical values of characteristic distances for ion–polymer systems.

This paper focuses on such relatively simple situations. In section II we present an analysis of the influence of polyelectrolyte effects on the complexation of ions by a neutral polymer chain. Experimental results on typical systems (poly(vinyl alcohol)–borax and galactomannan–borax solutions) are presented in sections III and IV. Discussion follows in section V.

II. Influence of Polyelectrolyte Effects on Complex Formation: Theoretical Consideration

In polymer solutions, electrostatic interactions are expected to affect complexation chemical equilibria much more strongly than in small-molecule solutions since charges induced by complexation are correlated when they are bound to the polymer chain. As an immediate consequence, complex formation and viscosity in ion-complexing polymer solution is greatly influenced by the addition of passive salt.[6] In the present work we focus on the dependence of the global complexation constant $\tilde{K}$ on the ion concentration, in the absence of added salt.

Table I
Polymer–Ion Complexes: Typical Distances (Angstroms)[a,b]

	free ion concentration [B], M			
	5×10^{-3}	10^{-2}	3×10^{-2}	0.1
dist between charges d	205	105	38	15
Debye length $\kappa^{-1} = (8\pi N_A Q I)^{-1/2}$	44	31	18	10
persistence length[c] $L_e = (Q/4)\kappa^2 d^2$	0.08	0.15	0.3	1

[a] Complexation constant $\tilde{K}$ = 5 L/mol. Monomer length a = 5 Å. Bjerrum length Q = 7 Å. [b] Electrostatic persistence lengths given by Le Bret[13] are for such conditions smaller than 1 Å. [c] References 11 and 12.

The Coulomb interaction energy between two charged complexes on a polymer chain may be approximated by

$$U/kT = Q/b \exp(-\kappa b) \qquad (5)$$

where κ^{-1} denotes the Debye screening length and b is the spatial distance between two charges. The Debye length is related to the ionic strength by $\kappa^2 = 8\pi N_A Q I$, and in the absence of passive salt and for very dilute polymer solutions, the ionic strength is mainly given by the concentration of the free complexing ion: $I \simeq [\mathrm{B}]$. The number n of monomers between two charges induced by complexation depends on the apparent complexation constant $\tilde{K}$. The distance b is then also a function of K, and it can be estimated as the end-to-end distance of a strand of the neutral chain of n polymer units of length a:

$$b(K) \simeq n^{3/5}a \qquad (6)$$

Hence, repulsion between neighboring charged complexes reduces the probability of complex formation:

$$\tilde{K} = K_0 \exp(-\alpha U/kT) \qquad (7)$$

Here, K_0 represents the complexation constant in the absence of electrostatic effects, i.e., in the presence of an excess of added salt. The factor α accounts for the electrostatic energy to be overcome when a new complex is fixed between two already existing charges. The simplest estimate yields $\alpha \simeq 4$.

From eq 5–7 it is therefore possible to calculate self-consistently the complexation constant for each free ion concentration [B] if the number of monomers n between two charges on a chain is known. The simplest situation corresponds to the case when a majority of charges is brought by monocomplexation, for which $n \simeq 1/f$.

However, in many cases the formation of intrachain dicomplexes may complicate the picture. In a good solvent, due to excluded-volume interactions, the dicomplexation leads to the formation of small loops. The effective chemical distance between loops can be estimated as

$$n \simeq (1 - (\tilde{K}_2/\tilde{K})f\lambda)/f \qquad (8)$$

where $\tilde{K}_2$ denotes the dicomplex formation constant defined by (2), $\tilde{K}$ is the global complexation constant giving the total number of charges that are linked to the chain (eq 3), and λ estimates the average number of monomers "lost" in a loop. In the following, we assume that the ratio $\tilde{K}_2/\tilde{K}$ depends only weakly on ionic strength since the formation of a dicomplex from an already existing monocomplex (eq 2) does not introduce a new charge on a chain

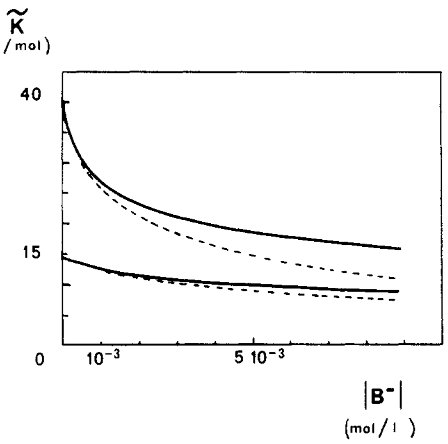


Figure 1. Theoretical influence of the free ion concentration on the apparent value of the polymer–ion complexation constant for two different initial complexation constants K_0 = 40 and 15 L/mol. Thick lines: no loop (e.g., intrachain 2:1 complexes) formation. Dotted lines: loop formation $(K_2/K)\ \lambda = 6$.

and since in most cases the chains are not strongly charged (no stiffening effect). We thus replace the ratio $\tilde{K}_2/\tilde{K}$ by its value K_2/K_0 in the absence of electrostatic effects (determined in the excess of added salt).

The apparent complexation constant $\tilde{K}$ drops sharply when complexing ions are added. The decrease is all the more spectacular when the initial value K_0 is high. Figure 1 shows that for $K_0 \simeq 40$ L/mol, the presence of only 10^{-2} mol/L of free complexing ions in the solution promotes a decrease of $\tilde{K}$ to 15 L/mol. When the formation of intrachain dicomplexes is predominant, the existence of numerous loops reduces the effective distance between charges on the chain (cf. eq 5) and leads to even more important decrease of $\tilde{K}$.

Hence, this simple model indicates that the apparent value of the complexation constant dramatically depends on the number of free ions. In the following sections we test these predictions on poly(hydroxy compound) solutions in the presence of borate ions.

III. Experimental Section

Materials. Borax (or sodium tetraborate decahydrate, $Na_2B_4O_7 \cdot 10H_2O$) at a low concentration in an aqueous solution is totally dissociated into equal amounts of borate ($B(OH)_4^-$) and boric acid ($B(OH)_3$).

Poly(vinyl alcohol) (PVA). The sample (Rhodoviol 4/20, Rhone Poulenc S.A.) is 98% hydrolyzed. This synthetic polymer is dissolved in hot water (80 °C). After cooling, the solution is centrifugated (2 h at 20000*g*). The polymer is then precipitated in ethanol and dried. The intrinsic viscosity of the polymer in water is 28 $mL \cdot g^{-1}$, so that the overlap concentration C^* is around 40 g/L (from the relation $C^* \simeq 1/[\eta]$).

Guar galactomannan is a neutral polysaccharide. Samples were purified according a procedure including dissolution in cold water, centrifugation, and precipitation in ethanol. Two different galactomannan samples were used for viscosity measurements. The high molecular weight sample ($\bar{M}_w \simeq 3 \times 10^6$) was kindly provided by Études et Fabrication Dowell Schlumberger (St-Étienne, France), the low molecular weight sample ($\bar{M}_w \simeq 5 \times 10^5$) comes from Sigma Co.

Depolymerization by mild acidic hydrolysis was performed on the lowest molecular weight purified galactomannan sample. The polymer was dissolved in deionized water (concentration $\simeq$ 5 g/L). The pH of the solution was adjusted to 2.5 with hydrochloric acid. The solution was then heated to 98 °C for 2 h. After cooling, it was neutralized to pH 7 with sodium hydroxide. The galactomannan solution was dialyzed against deionized water (Milli-Q system of Millipore) for several days and finally concentrated by rotary evaporation. The polymer concentration was determined by total carbon analysis (DC 80 Dohrmann/Xertex). From the intrinsic viscosity of the aqueous galactomannan solution, the overlap concentration is estimated to be about 40 g/L.

2,4-Pentanediol (Janssen Chimica) serves as a small model molecule for poly(vinyl alcohol).

^{11}B NMR. All NMR spectra were recorded at 20 °C with a Bruker WP 250 spectrometer operating at 80.25 MHz. Boron-11 chemical shifts were referenced to external $BF_3O(C_2H_5)_2$. Species concentrations and stability constants were calculated from the measure of the relative area of each signal. In some delicate cases (PVA–borax solutions), relative areas of two overlapping signals were estimated from a recombination of the spectra, fitting the peaks to Lorentzian functions. Following Sinton[18] we calculate using

$$[B^-] = 2\frac{x}{1+x}p_f C_b$$

where p_f is the relative area of the signal corresponding to the exchange between free borate and boric acid, C_b is the total borax concentration, and

$$x = \frac{\delta_{B/HB} - \delta_{HB}}{\delta_B - \delta_{B/HB}}$$

Here $\delta_{B/HB}$ is the chemical shift of the free borate/boric acid peak, δ_B is the chemical shift of borate alone (δ_B = 0.6 ppm), and δ_{HB} is that of boric acid alone (δ_{HB} = 18.4 ppm).[19]

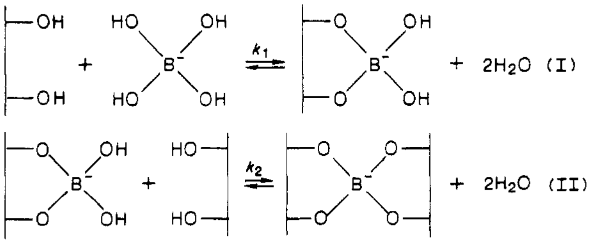
Another method[19] often used for estimating the free borate concentration consists in assuming that only borate ions are complexed, and as borax is a pH buffer, the boric acid concentration does not change during complexation, so $[B^-] = 2(p_f - 0.5)C_b$. The two methods are in good agreement.

Samples were prepared by mixing appropriate amounts of the filtered (0.46 μm) polymer solution and of a borax solution. The final polymer concentration in the sample was low ($<C^*/2$). Solutions were allowed to rest (24 h) before spectra recording.

Viscometry. The viscosity measurements were performed on a low-shear Contraves 30 rheometer. Intrinsic viscosity was determined from the extrapolation of the reduced specific viscosity $[\eta] = \lim\ (C \rightarrow 0)\ (\eta - \eta_0)/\eta_0 C$, where C is the polymer concentration, η the polymer solution viscosity, and η_0 the solvent viscosity.

IV. Experimental Results on Poly(hydroxy compound)–Borate Systems

Interactions between poly(hydroxy compounds) such as poly(vinyl alcohol) and guar galactomannan have motivated numerous studies mainly based on pH and viscometric measurements.[1,5,15,16] More recently ^{11}B NMR investigations allowed a direct observation of the various complexes formed.[17-19] The complexation chemical equilibria involved may be summarized by two reactions: monocomplexation (I) and dicomplexation (II). In a poly(hydroxy compound) chain, two kinds of diol sites can complex borate ions: 1,2-diol sites leading to five-membered ring complexes and 1,3-diol sites leading to six-membered ring complexes.



Our previous study of poly(hydroxy compound)–borate systems showed that it was possible, in the absence of polyelectrolyte effect (i.e., in excess added salt), to define for polymers as for small model molecules a monocomplexation constant $k_1 = [BP^-]/[B^-][P]$, where $[B^-]$, $[P]$, and $[BP^-]$ respectively denote borate, diol site, and monodiol–borate complex concentrations. However, it seems

Table II
2,4-Pentanediol–Borax Aqueous Solution: ^{11}B NMR Data[a]

	boric acid/borate			1:1 complex			2:1 complex	
C_{borax}, M	δ	$\Delta\nu_{1/2}$, Hz	area, %	δ_{BP^-}	$\Delta\nu_{1/2}$, Hz	area, %	$\delta_{BP_2^-}$	area, %
5×10^{-3}	12.7	360	70	1.7	120	28	$\simeq$0.4	$\simeq$2
0.05	11	140	79	1.5	40	19	$\simeq$0.4	$\simeq$2

[a] T = 20 °C, diol concentration = 1.58%.

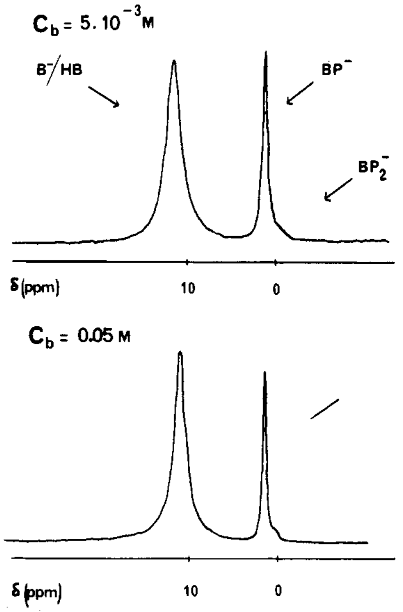


Figure 2. ^{11}B NMR spectra of borax–pentanediol (C = 15.8 g/L) solutions.

that in dilute polymer solution the intrachain dicomplexation step is independent of the diol site concentration, i.e., $[BP_2^-] = k_2[BP^-]$. For dilute poly(hydroxy compound) solutions, it is therefore possible to define a global complexation $\tilde{K}$ that gives the total number of borate complexes formed:

$$\tilde{K} = \frac{[BP^-] + [BP_2^-]}{[B^-][P]}$$

Here we examine the variation of the complexation constant $\tilde{K}$ with the free borate concentration in two systems: poly(vinyl alcohol)–borax and guar galactomannan–borax solutions. Before investigating macromolecular systems, we study small molecules: 2,4-pentanediol serves as a model of poly(vinyl alcohol).

2,4-Pentanediol–Borax Solutions. ^{11}B NMR spectra of 2,4-pentanediol–borax solutions present three peaks (cf. Figure 2 and Table II). The first peak (downfield) is related to the rapid exchange between borate and boric acid. When more complexes are formed, this signal is shifted downfield since only borate ions are taken up by complexation.[15] The two other peaks are very close on the ^{11}B NMR chemical shift scale (as usual for 1,3-diol–borate complexes). However the signal appearing at δ = 1.7 ppm can be assigned to the 1:1 monodiol–borate complex, whereas the peak at $\delta \simeq$ 0.4 ppm (which forms a shoulder on the preceding one) is assigned to the 2:1 didiol–borate complex. At this low polyol concentration, 1:1 complexes largely predominate. Figure 2 shows that the ratio of borate complexes does seem to depend only very slightly on the borax concentration.

Poly(vinyl alcohol)–Borax Solutions. Again, as for model molecules, ^{11}B NMR spectra of poly(vinyl alcohol)–borax solutions show three different signals (Figure 3). In addition to the free borate boric acid resonance peak, two components may be distinguished in the massive signal at about δ = 1.5 ppm. But, conversely to the case of model molecule–borax spectra in similar conditions, the number of didiol–borate complexes is very high and even predominant at low borax concentrations. As the polymer solution is dilute, this means that many loops (or 2:1 intrachain complexes) are formed.

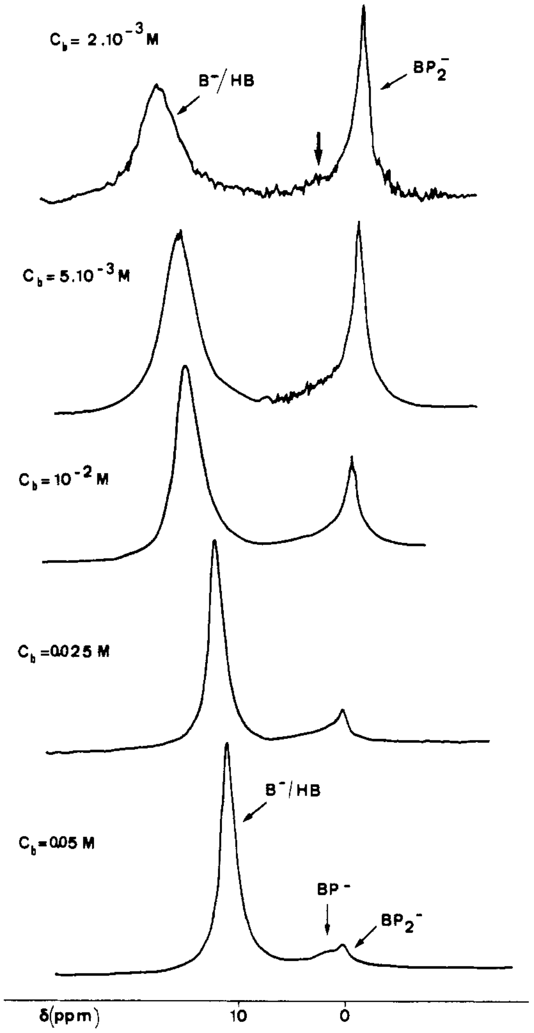


Figure 3. ^{11}B NMR spectra of borax–poly(vinyl alcohol) (C = 15 g/L) solutions. Influence of borax concentration.

The evolution of ^{11}B NMR spectra of the dilute poly(vinyl alcohol) solution with the borax concentration points out two important qualitative effects. First, the relative proportion of complexed borate ions strongly decreases when borax is added (see also Table III). Second, 2:1 intrachain complexes predominate at low borax concentration, but the ratio of 1:1 to 2:1 complexes increases in favor of 1:1 monodiol borate complexes at high borate concentration. It seems, therefore, that the loops in the polymer chain break when the chain becomes highly charged through complexation.

From data reported in Table III it is possible to calculate the value of the apparent global complexation constant $\tilde{K}$ for increasing free borate concentrations. Results plotted

Table III
Borax-PVA Aqueous Solutions: ^{11}B NMR Data

	boric acid/borate ion			complexes				
C_{borax}, M	δ, ppm	$\Delta\nu_{1/2}$, Hz	area, %	$\delta_{\mathrm{BP^-}}$	$\delta_{\mathrm{BP_2^-}}$	$\Delta\nu_{1/2}$, Hz	total area, %	[BP$^-$]/[BP$_2^-$]
				T = 20 °C, Polymer Concentration = 1.5%				
2×10^{-3}	16.2	280	57	≈1.5	0	85	43	≈0.7
5×10^{-2}	14.5	250	62	≈1.5	0	85	38	≈0.85
10^{-2}	13.3	190	71	≈2	0		29	≈1
$2 \times 5.10^{-}$	11.7	150	78	≈1.5	0		22	≈2
5×10^{-2}	10.6	130	86	≈1	0		14	≈6
				T = 20 °C, Polymer Concentration = 1.5%, 0.1 M NaCl				
2×10^{-3}	16.8	280	58	≃2	0	90	42	≈0.6

Table IV
Guar Galactomannan-Borax Aqueous Solutions: ^{11}B NMR Data

						1:1 complexes					
	boric acid/borate			2:1 complex B(P$^-_{1,2}$)$_2$		diol 1,2 (BP$^-_{1,2}$)			diol 1,3 (BP$^-_{1,3}$)		
C_{borax}, M	δ	$\Delta\nu_{1/2}$, Hz	area, %	δ	area, %	δ	$\Delta\nu_{1/2}$, Hz	area, %	δ	$\Delta\nu_{1/2}$, Hz	area, %
					T = 20 °C, Polymer Concentration = 1.62%						
2.10^{-3}	14.0	380	76	8.1	≈3	4.6	160	14	0.5	120	7
5.10^{-3}	12.6	240	78	8.1	≈3	4.5	140	13	0.2		6
10^{-2}	11.9	150	84			4.7	140	11	0.4		5
5.10^{-2}	10.1	100	89			4.6		8	0.4		3
					T = 20 °C, Polymer Concentration = 1.62%, 1 M NaCl						
2.10^{-3}	14.4	480	76	8.1	≈2	4.5	140	15	0.3	120	7

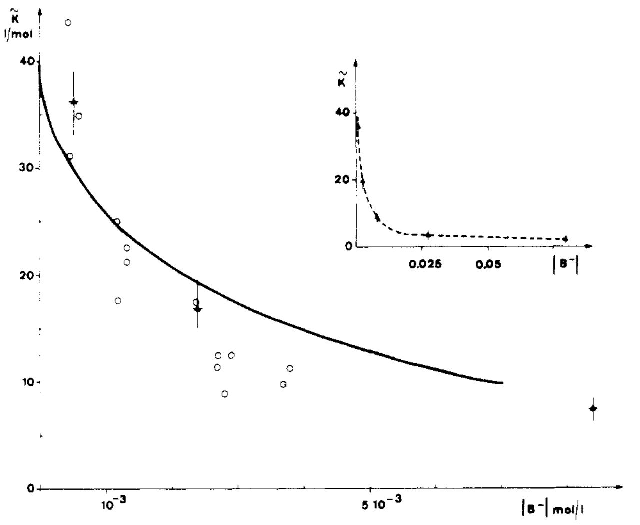


Figure 4. Variation of the apparent complexation constant K with the free borate concentration in PVA solutions: +, data of this work; O, values calculated from Sinton's data;[18] –, theoretical curve (with K_0 = 40 L/mol, K_2/K = 0.6, λ = 24 monomers). Insert: borax concentration ranges from 2×10^{-3} to 5×10^{-2}M (the dotted line is a guide for the eye).

in Figure 4 demonstrate that K decreases dramatically by about a factor of 10 when the borax concentration increases, which attests to the very strong influence of polyelectrolyte effects in polymer complexation equilibria. For comparison, in the case of the 2,4-propanediol model molecule, the monocomplexation constant becomes only slightly smaller in the presence of a high borax concentration. This last effect can be mainly attributed to a change in the activity of the species in aqueous solution at high ionic strength.

Guar Galactomannan-Borax Solutions. The guar galactomannan chain bears 1,2- and 1,3-diol sites.[9] Borate monocomplexation can therefore lead to the formation of two kinds of 1:1 complexes: six- and five-membered rings. Dicomplexation also leads to essentially two kinds of 2:1 complexes. However, 1,2-didiol–borate (five-membered ring) clearly predominates. ^{11}B NMR spectra of guar galactomannan–borax solution allow the distinction between

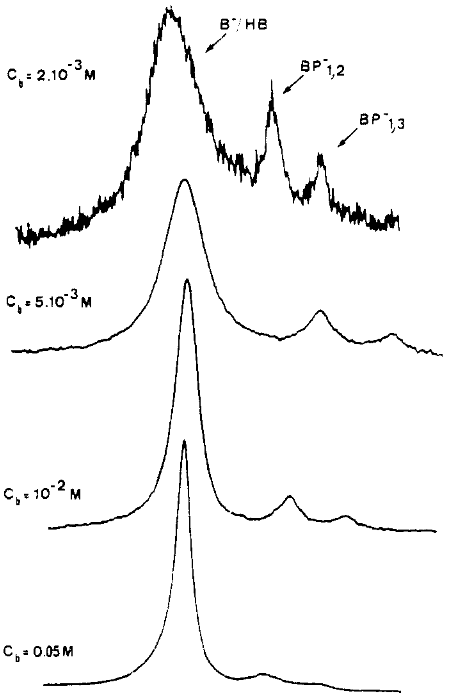


Figure 5. ^{11}B NMR spectra of borax–galactomannan (C = 16.2 g/L) solutions. Influence of borax concentration.

these various complexes.[14,15] Figure 5 shows the spectra obtained for dilute solutions of a low molecular weight galctomannan. In such conditions, resonance peaks of 1:1 complexes are observed at δ = 4.6 ppm for 1,2-monodiol–borate and δ = 0.4 ppm for 1,3-monodiol–borate. For the lowest borax concentrations, a shoulder on the broad boric acid/borate peak can hardly been distinguished at $\delta \simeq$ 8.1 ppm. This signal is assignable to 1,2-didiol–borate complexes. Its very low area indicates that for such low polymer concentrations ($C \simeq C^*/3$), very few 2:1 complexes (mostly intrachain) are formed. The influence of the borax concentration on the polymer complexation manifests itself by a clear decrease of the complexed borate fraction when the free borate concentration is raised. Taking into account both 1,2-diol and 1,3-

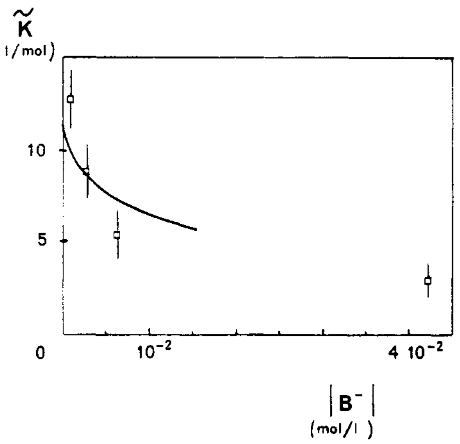


Figure 6. Variation of the apparent complexation constant K with the free borate concentration in galactomannan solutions: +, experimental values; –, theoretical curve (with K_0 = 11 L/mol, K_2/K_0 = 0.1, λ = 30 monomers).

diol–borate complexes,[19] we may calculate the value of the apparent complexation constant $\tilde{K}$ from NMR data (Table IV). Although, less abrupt than in the PVA case (Figure 4), the decrease of $\tilde{K}$ with the borate concentration is remarkable (a factor 2 or 3), as shown in Figure 6.

V. Discussion and Conclusion

From a qualitative point of view, the experimental results are in very good agreement with the theoretical analysis of the influence of polyelectrolyte effect on polymer–ion complexation. Hence, the apparent value of the complexation constant clearly falls off when more complexes are formed on the polymer chain. In addition, this observed decrease is more important when the initial complexation constant is higher: for the guar–borax system $K_0 \simeq$ 11 L/mol and $\tilde{K}$ reaches 30% of this value (for high borate concentration), whereas for the PVA–borax system $K_0 \simeq$ 40 L/mol and $\tilde{K}$ drops to less than 10% of this value!

The decrease of the complexation constant with borate concentration was also qualitatively observed in glycerypolymethacrylate–borate system. But the complexation ability of this synthetic poly(hydroxy compound) K_0 = 3.6 L/mol is smaller than those of poly(vinyl alcohol) or galactomannans, so polyelectrolyte effects are less spectacular.

To discuss more quantitatively these important effects, we have to take into account the formation of loops through intrachain complexation. A delicate point is to estimate the size of the loops. Viscometric measurements offer a simple solution to this problem. In the presence of an excess of passive salt, when all electrostatic effects are screened out, the borate complexation leads to a decrease in the viscosity of a dilute poly(hydroxy compound) solution if 2:1 intrachain complexes are formed. Small loop formation, indeed, is equivalent to a shortening of the polymer chain.

Figure 7 shows that when borax is added to a saline solution of a high molecular weight galactomannan ($M_w \simeq 3 \times 10^6$), the intrinsic viscosity of the polymers decreases to about 30%. For a small molecular weight polymer sample no viscosity decrease is detected (for higher borax concentration, demixing occurs[2]). This observation is consistent with the formation of small loops, since the number of intrachain 2:1 complexes per polymer chain is expected to be proportional to the free borate concentration and to the polymer molecular weight. From the estimation of the value of the intrachain dicomplexation constant $K_2 = k_1k_2$ (cf. reactions I and II), it is possible to get an idea of the average number of loops formed in a polymer chain:

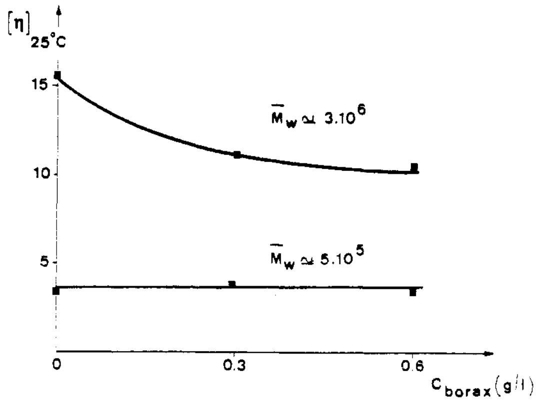


Figure 7. Variation of the intrinsic viscosity of galactomannans in saline (1 M NaCl) solution with the borax concentration (for borax concentrations higher than 1 g/L, dilute galactomannan solutions precipitate).

$$N(\mathrm{BP_2}^-)/N = K_2[\mathrm{B}^-] \qquad (9)$$

where $N(\mathrm{BP_2}^-)$ denote the number of loops per chain and N is the polymerization degree. Moreover, the viscosity is related to the chain radius $\eta \propto R^3$ and in a good solvent $R \simeq N^{3/5}$. From these relations and considering that loop formation reduces the chain length, we obtain the mean loop size λ:

$$\lambda \simeq {}^5\!/_9(\Delta\eta/\eta)/K_2[\mathrm{B}^-] \qquad (10)$$

In the galactomannan case these arguments lead to an estimate of the average loop size of about 50 diol sites, which corresponds to five or six persistence lengths (the characteristic ratio of a galactomannan chain is reported[20] to be $C \simeq 13$).

Similar viscosity measurements in PVA solutions yield a loop size of 20–25 monomers, which corresponds to about six persistence lengths (C = 8.3).[21] However, it should be stressed that such measurements are particularly delicate for poly(vinyl alcohol) because in saline solutions this polymer undergoes phase separation very readily in the presence of very small amounts of borax. This is related to the high values of the complexation constants in this system. It may also be worth noticing that for another complexing system, PVA–Cu^{2+}, it was concluded[21] that no intrachain complexes can be formed for a polymer chain shorter than 20 monomers ($\mathrm{DP_n}$ = 20), which seems to confirm our estimation of loop size on the PVA chain. In Appendix A, we develop a little further the relation between loop formation, polymer stiffness, and competition between intrachain and interchain cross-links in semidilute solutions.

^{11}B NMR spectroscopic data and viscosity measurements therefore yield an estimate of values of microscopic parameters such as K_0, K_2, and λ. Hence, it is possible from 6, 7, and 9 to calculate the decrease of the complexation constant with the ionic strength in a poly(hydroxy compound)–borate solution.

Figure 6 shows that the agreement between the theoretical curve and experimental data in the galactomannan case is reasonably good. We recall that on this relatively rigid polysaccharide chain, few intrachain loops are formed.

Agreement between experiment and theory is also satisfactory for PVA–borax solutions. Figure 4 shows results of the present study and values of constant calculated from the data reported by Sinton.[18] It clearly shows that in this system it is necessary to take into account polyelectrolyte effects even (or especially) when very small amounts of borate ions are present in the solution. Moreover Sinton's results were obtained at different polymer concentrations and molecular weights of PVA. This seems to confirm that the borate complexation is independent of the chain molecular weight and concentration in the dilute regime (i.e., $C < C^*$).

In conclusion, this study provides spectroscopic evidence of the considerable influence of electrostatic repulsion on complexation between polymers and ions. The proposed theoretical approach describes this polyelectrolyte effect quantitatively. This analysis on a poly(hydroxy compound)–borate system may be useful for the understanding of complexation phenomena in more complex systems (e.g., polyelectrolyte–metallic ions).

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Appendix: Competition between Intrachain and Interchain Complex Formation

The variation of the size of loops induced by intrachain complexation with the polymer rigidity seems to be an interesting effect. In a dilute poly(hydroxy compound) solution, a borate ion fixed on a chain by monocomplexation will tend to react with a neighboring site born on its own chain rather than with another macromolecule. In a semidilute polymer solution the situation is clearly different. A 1:1 complex can react with another diol site without distinguishing whether this unit belongs to the same or to another polymer chain. In this problem of competition between intrachain and interchain complexation, the average size of a loop, λ, emerges as the important length. For a polymer concentration C_0 corresponding to a blob size of g monomers[22] of the order of λ, interchain complexation should become greatly favored. Since g scales with the monomer concentration as $g \simeq C^{-5/4}$, the limit concentration should scale as

$$C_0 \simeq \lambda^{-4/5} \qquad \text{(A1)}$$

In this approach the ratio of the concentration of interchain to intrachain cross-links is given by

$$\text{inter/intra} \simeq (C/C_0)^{5/4} \qquad \text{(A2)}$$

Actually these arguments are in principle applicable to all systems for which gelation is induced by vulcanization.

Expression A2 yields instructive orders of magnitude for practical systems. For instance, in a galactomannan solution λ is around 50 monomers, which gives C_0 of about 4%. In solutions of poly(vinyl alcohol), a flexible polymer, one finds C_0 of about 8%. Such values mean that even when a gel is formed (e.g., interchain complexation occurs), intrachain complexes are largely predominant. For example, for a PVA solution at $C = 2\%$, we can estimate the ratio of inter- to intrachain tie points to be about 18%. (It is useful to recall that for a solution of PVA of $\overline{M}_w = 100\,000$, C^* is about 1%.) The existence of a large amount of intrachain loops at the gel point seems to be fully consistent with observations reported on glyceryl–polymethacrylate–borax,[9] polyacrylamide–Cr(III)[23] systems, or chemically cross-linked polystyrene solutions.[24] It seems that the loop size increases with the polymer chain persistence length. The simple approach proposed here could be useful to estimate the ratio of interchain and intrachain cross-links in other gelling systems.

Registry No. PVA, 9002-89-5; borax, 1303-96-4; galactomannan, 11078-30-1; 2,4-pentanediol, 625-69-4.

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