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Reversible Gel Formation Induced by Ion Complexation. 2. Phase Diagrams

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ABSTRACT: We study the formation of reversible gels induced by addition of borax in aqueous solutions of galactomannans. The number of cross-links can be well controlled by polymer and borax concentrations, temperature, and ionic strength. As theoretically expected we observe that the gelation threshold strongly depends on polymer concentration. Under suitable conditions reversible demixing into concentrated polymer (gel) and dilute phases may occur. This demixing transition can be strongly shifted by the addition of small complexing molecules such as D-mannitol. The important parameter for the onset of demixing as well as for the gelation threshold turns out to be the number of induced intermolecular cross-links per chain. As a consequence, it is possible by an appropriate rescaling to superimpose phase diagrams obtained under various very different conditions. We present a qualitative interpretation of these results in terms of the complexation and the swelling equilibria of the temporary network.

I. Introduction

Polyhydroxy compounds such as galactomannans or poly(vinyl alcohol) form gels in the presence of anions such as borate,[1] titanate[2] or antimonate.[3] The thickening and gelling properties of these systems are widely used in petroleum industry.[4] Most studies focused on rheological properties of dilute aqueous solutions[5,6] and on well-formed homogeneous gels.[7]

The aim of the present work is to describe the conditions for the gelation transition induced by borate ions and to describe phase equilibria in saline solutions of galactomannans. The mechanism of formation of cross-links in this system is relatively simple and is governed by complexation equilibria between borate ions and hydroxyl groups of galactomannan sugar units.[8,9] The number of cross-links may be well controlled by borate and polymer concentrations and temperature. Under suitable conditions, in 1 M NaCl solutions, we observe a striking effect of perfectly reversible demixing into polymer dilute and concentrated phases, even though we are far from θ-conditions. Such a phase transition is not observed in a low ionic strength medium.[10] The demixing can be induced by increasing the number of cross-links in both dilute and semidilute (concentrated) regimes. In dilute solution polymer chains precipitate and then form a dense gel, which is in equilibrium with a very dilute polymer solution. In concentrated solutions (gels) the onset of demixing manifests itself by the progressive expulsion of solvent and by the appearance of an opaque gel, which can later become transparent.

The observed phase separation is analogous to that described for ionic gels[11] and ionomer solutions[12,13] and in some respects to the syneresis in strong chemical gels. The demixing results from the competition between the energy gain when cross-linking occurs and the entropy decrease induced by the increase in local monomer concentration. The quantitative theoretical description of the competition between gelation and precipitation in dilute solutions and near the overlap concentration C^* is delicate.[12–16] In this work we focus on more concentrated solutions, far from the gelation threshold, and discuss the demixing transition in this regime in terms of the complexation and the swelling equilibria of networks. The proposed approach enables us to predict phase behavior at various temperatures and even to explain quantitatively the dramatic effects that ensue when small molecules that complex borate ions are added to the system.

The paper is organized as follows. In section II we describe the materials and our experimental methods of determining phase diagrams. Section III deals with the determination of the overlap concentration C^* of the galactomannan solutions, which is vital to estimation of the minimum concentration for formation of homogeneous gels. We then describe the observed phase diagrams at different temperatures and in the presence of D-mannitol. The interpretation of the phase diagrams is presented in section IV.

II. Experimental Section

Materials. We study guaran and (hydroxypropyl)guaran, galactomannans which are natural neutral copolymers of mannose and galactose with α-D-galactopyranosyl groups branched in 1–6 on a linear chain of 1–4-linked β-D-mannopyranosyl residues. (Hydroxypropyl)guaran is a derivative of guaran where some of the hydroxyl groups have been substituted by hydroxypropyl groups upon ether formation. The molar substitution of our sample is 0.48. (Hydroxypropyl)guaran and guaran were prepared and purified from samples kindly provided by Etudes et Fabrications Dowell Schlumberger, according to a procedure previously described.[8] The galactomannans respectively contain D-mannose and D-galactose units in the molar ratio of 1.2 and 1.3. Weight-average molar weights were estimated by the Zimm method from light scattering data by using a Fica photometer with a 6328-Å He–Ne laser as a light source. The increment indexes dn/dc were measured at 6328 Å with a Brice Phoenix differential refractometer and were 0.155 mL g^{-1} for guaran and (hydroxypropyl)guaran in water and 0.149 mL g^{-1} in 1 M NaCl. The molecular weights were found to be around 2.8×10^6 g for (hydroxypropyl)guaran and 4.5×10^6 g for guaran. Average radius of gyration may be estimated to be respectively around 1900 and 2500 Å. Absolute concentrations of polymers in deionized water (milli-Q system of Millipore) were determined by total organic carbon analysis (DC 80, Dohrmann/Xertex). From light scattering data alone it is difficult to estimate polydispersity, but in ref 17 the polydispersity of a high molecular weight guaran sample is found to be 1.9. Borax ($Na_2B_4O_7{\cdot}10H_2O$), sodium chloride and D-mannitol were commercial materials of analytical grade.

Viscometry. Viscosity measurements were performed on a Low-Shear Contraves 30 rheometer.

Phase Diagrams. The 5-mL samples were prepared by mixing of appropriate amounts of galactomannan, borax, D-mannitol, and NaCl solutions. The system was vigorously stirred and then allowed to rest in a thermostated bath for 48 h. Absolute concentrations of polymer were determined by total carbon analysis (DC 80, Dohrmann/Xertex). It may be difficult to distinguish between a sol and a reversible gel phase. One may define the gelation threshold as the situation when the biggest temporary cross-linked cluster spans the whole sample volume. To ap-

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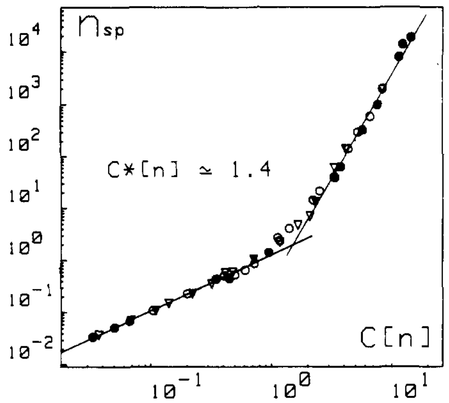


Figure 1. Specific viscosity of the galactomannan samples as a function of reduced concentration $C[\eta]$. The crossover corresponds to the overlap concentration C^*. The slope is about 1.1 in the dilute regime and about 4.0 in the semidilute regime: (○) guaran in pure water; (●) guaran in 1 M NaCl; (▽) (hydroxypropyl)guaran in pure water; (▼) (hydroxypropyl)guaran in 1 M NaCl.

Table I
Intrinsic Viscosities of Galactomannan Samples at 25 °C

sample	$[\eta]$, dL g^{-1}	sample	$[\eta]$, dL g^{-1}
guaran		(hydroxypropyl)guaran	
in H_2O	16.0	in H_2O	13.0
in 1 M NaCl	12.5	in 1 M NaCl	11.0

proximately determine this threshold we used two methods. First, we measured the variation of the viscosity of the galactomannan–borax solution as a function of borax concentration after 24 h of equilibration at the required temperature. At a shear rate of 0.1 s^{-1} a remarkable increase in viscosity indicates the gelation threshold. Beyond this threshold no reproducible viscosity measurement is possible. The second very spectacular and simple method has been inspired by studies of Candau et al. of an irreversible gelation transition.[18] We observed the speckle pattern visible at low scattering angle on a screen placed at a remote distance from the sample lighted by a laser beam. In the sol phase the speckle pattern fluctuated randomly. The movement of speckles was completely frozen above the gelation threshold.

The onset of precipitation can be very slow in dilute solutions. Generally, however, after the sample has been equilibrated during 48 h one can easily distinguish between a homogeneous one-phase sample and a sample in which demixing has occurred.

III. Phase Diagrams

A. Galactomannan Solution Properties. Galactomannans are well-known for their viscous properties. Table I gives the intrinsic viscosities of our samples in pure water and 1 M NaCl solution. It appears that added salt lowers $[\eta]$, which may be explained by a contraction of the polymer chain promoted by enhanced hydrogen bonding between sugar residues.[19] One of the crucial parameters for gelation problems is the critical concentration C^* at which polymer molecules in solution start to overlap. The determination of this critical concentration may be experimentally accomplished by plotting the low-shear (0.02–0.5 s^{-1}) specific viscosity against the reduced concentration $C[\eta]$.[20] A transition in the solution behavior takes place at the overlap concentration C^*, beyond which polymer–polymer entanglements become significant. Figure 1 shows the master plot obtained for our samples. The overlap concentration is then given by the relation $C^* \simeq 1.4/[\eta]$.

B. Gelation Threshold and Demixing Transition. The phase diagrams observed at 25 and 10 °C in 1 M NaCl solution are presented in Figure 2. At each temperature we distinguish three zones: homogeneous sol, homogeneous gel, and demixing zone. In the demixing zone the boundary drawn corresponds to a cloud point and not to coexisting phases. For low guaran and borax concentrations, we are below the gelation threshold. A sol–gel transition is observed for $C > C^*$ (C: guaran concentration). At high borax concentration, a syneresis is observed and two phases exist in solution: an opaque polymer-rich region in equilibrium with a dilute-polymer solution. In low concentrated guaran solutions, we may distinguish two steps in the demixing process. First, the solution becomes cloudy and precipitates, then after it rests, two phases are in equilibrium: a small polymer-rich region in the almost pure solvent. Moreover, it is interesting to notice that for $C > C^*$, the concentration of borax needed for the onset of the gel demixing increases only slightly with the concentration of guaran.

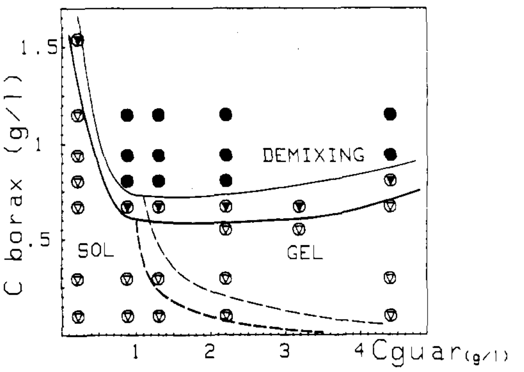


Figure 2. Phase diagrams of guaran–borax 1 M NaCl aqueous solutions at two different temperatures: 10 and 25 °C. The continuous lines denote the conditions of the onset of demixing. The dashed lines indicate the gelation threshold. The demixing and sol–gel transitions require more borax at higher temperature. The full symbols denote samples in which demixing is observed: (○) T = 25 °C; (▽) T = 10 °C.

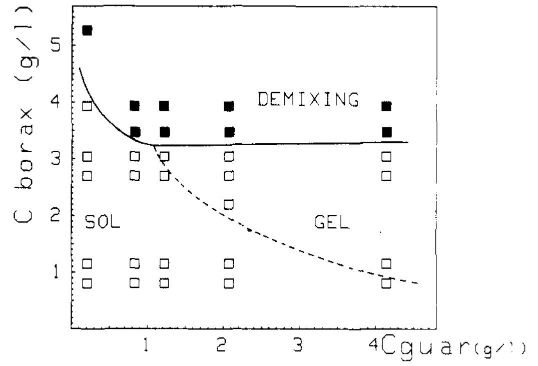
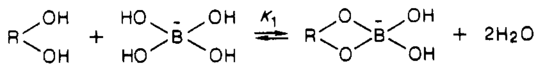


Figure 3. Phase diagram of guaran–borax 1 M NaCl aqueous solutions in the presence of D-mannitol (2×10^{-2} M) at T = 25 °C. The full symbols denote samples in which demixing is observed.

When the temperature is increased more borax is needed to induce both the gelation transition and the demixing (Figure 2). But much more spectacular is the effect of adding a small molecule such as D-mannitol, which is known for its great ability to complex borate ions (see complexation constants reported in Appendix A-c). Figure 3 shows the phase diagram obtained in the presence of a low D-mannitol concentration (2×10^{-2} M). The dramatic changes of the phase equilibria are due to the complexation of borate by D-mannitol, which decreases the number of cross-links in the system. The important shift of the cloud point line and gelation threshold means that D-mannitol is able to fluidify galactomannan–borax gels. Moreover, by adding small amounts of D-mannitol, it is possible to homogenize demixed systems. On the other hand, adding much more borax precipitates again the system. Similar effects are actually expected from any compound able to complex or react with borate ions (other polyols, H_3O^+, ...).

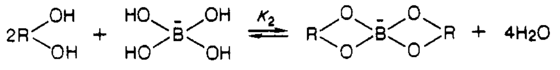
IV. Discussion and Conclusion

(a) Gel Formation. The parameter governing both the gelation transition and the demixing is the number of cross-links formed in the system. In the previous study,[8] galactomannan borate interactions were investigated from stoichiometric and thermodynamic points of view. Reactions between borate ions and hydroxyl groups of galactomannan sugar units lead to monodiol–borate complex formation (reaction I)



(I)

and didiol–borate complexes, i.e., cross-link, formation (reaction II).



(II)

These complexation reactions are reversible and exothermic; then when the temperature is raised the cross-link density in galactomannan–borax gels decreases. The association constant $K_1 \simeq 11$ L mol^{-1} has been determined from dialysis experiments on polymer solutions.[8] This value is very close to that obtained for glycoside models.[8,9] The constant characterizing the formation of cross-links has only been measured for models from ^{11}B NMR data, but this determined value of K_2 does not give directly the number of cross-links in polymer solutions. In fact, due to correlation effects present in polymer solutions, the concentration of cross-links may depend on the molecular weight of chains (e.g., in dilute solutions),[13,21] and also the dependence on monomer concentration may be different for polymers and model systems.[13] Still it is important to note that for a fixed galactomannan concentration, the number of cross-links may be expected to be proportional to the amount of free borate ions in solution, as is usual for complexation equilibria. It may also be argued that for semidilute solutions (far from C^*) the number of formed intermolecular cross-links is essentially proportional to the number of monomer–monomer contacts and thus scales like osmotic pressure in a good solvent, i.e., like $C^{3\nu/(3\nu-1)}$ where ν is the swelling exponent relating the radius of gyration and the molecular weight of chains.[22] We will not appeal to the knowledge of the exact value of K_2 in our discussion. However, the temperature dependence of the number of cross-links is governed by the enthalpy of dicomplexation reaction, which to a good approximation is equal to that determined from temperature dependence of K_2 for models.[8] Many features of the observed phase diagram can then be explained by such variation of the number of cross-links as a function of free borate concentration, galactomannan concentration, and temperature. To sum up, in the following discussion we will suppose that the total number of intermolecular cross-links in the semidilute regime scales like

$$N_{\mathrm{tot}} \simeq |B^-|C^{3\nu/(3\nu-1)}e^{-\Delta H/RT} \qquad (1)$$

where $|B^-|$ denotes the concentration of free borate ions and ΔH is the enthalpy of formation of a cross-link.

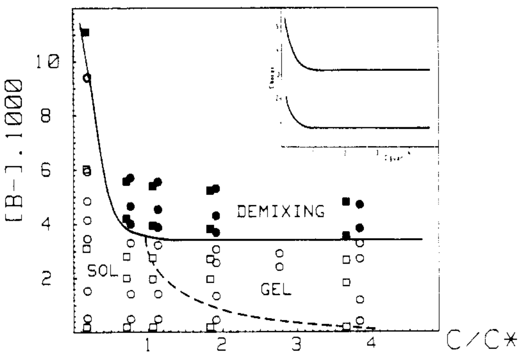


Figure 4. Reduced phase diagram obtained at T = 25 °C, indicating the free borate concentration $|B^-|$ and the overlap ratio C/C^*. The number of cross-links per chain is expected to be proportional to $|B^-|$. In this representation, the limits of stability of a homogeneous phase (full line) and the gelation threshold (dashed line) are nicely superimposed for very different systems. The insert recalls the difference in standard representation (Figures 2 and 3). The symbols are the same as in Figures 2 and 3.

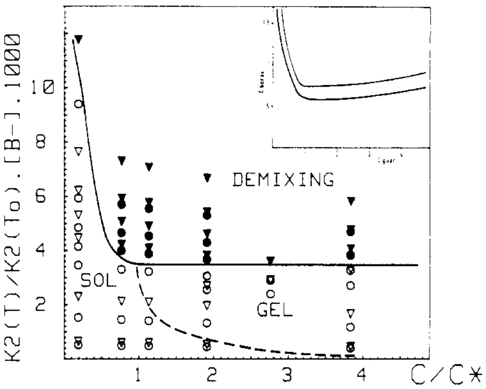


Figure 5. Reduced phase diagrams obtained for systems at two different temperatures T = 25 and 10 °C, indicating the temperature-corrected free borate concentration and the overlap ratio C/C^*. For a fixed galactomannan concentration and the free borate concentration $|B^-|$, the ratio of the number of cross-links at two temperatures T and T_0 is expected to be $K_2(T)/K_2(T_0)$, with K_2 denoting the equilibrium complexation constant. The symbols are the same as in Figure 2, which is recalled in the insert.

All phase diagrams show that the borax concentration necessary to reach the gelation threshold strongly depends on the polymer concentration (Figures 2 and 3). Below the overlap concentration $C^* \simeq 1.1$ g L^{-1}, which was determined by a viscometric method (section III-A), no homogeneous gel spanning over the entire sample can be obtained. Above the overlap concentration, in order to reach the gelation threshold one roughly needs one intermolecular cross-link per guaran chain. Thus the free borate ion concentration necessary to reach the gel point should scale as $C^{-1/(3\nu-1)}$ and should be inversely proportional to the molecular weight of polymer chains. For neutral chains in a good solvent ν takes the Flory value $\nu = {}^3/_5$ and we expect $|B^-|$ at the gelation threshold to vary as $C^{-1.25}$. Our experiments seem to be consistent with these predictions. First, the predicted molecular weight dependence—in conjunction with the hydroxypropyl substitution which reduces the number of sites available for borate complexation—can explain the shift in the gelation threshold between (hydroxypropyl)guaran–borax and guaran–borax systems.[10] Second, the free borate ion concentration is essentially determined by the monocomplexation reaction (see Appendix A) and thus can be calculated quite precisely for different polymer and borax concentrations. When plotted in terms of free borate concentration, all gelation threshold curves get superimposed on one curve that depends only on the galactomannan concentration (Figures 4 and 5). Moreover Figures 4 and 5 seem to indicate that the free borate concentration at the gelation threshold may scale as $C^{-1.25}$. We thus set experiments to study the gel point more precisely. For each concentration of guaran, the free borate concentration needed to reach the gel point was determined

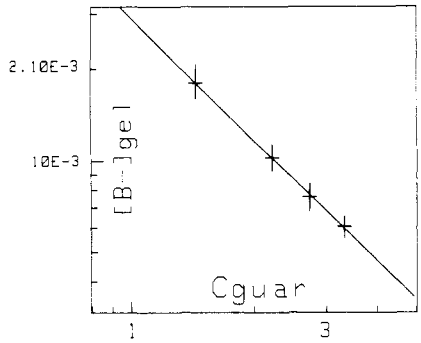


Figure 6. Logarithmic plot of the concentration of free borate ions at the gelation point versus galactomannan concentration. Symbols serve as error bars.

by measuring the viscosity of the sample at $\gamma = 0.1\ \mathrm{s}^{-1}$ when incremental amounts of borax were added to the solution. At some concentration of borax, a big increase in viscosity indicates the gel point. Figure 6 shows logarithmic plots of the free borate concentration $|\mathrm{B}^-|$ necessary to obtain a gel, as a function of concentration. The characteristic exponent is found to be -1.3 ± 0.1. It should be remarked, however, that the precision of determination of the exponent is limited. Similar strong dependence on monomer concentration has been observed for irreversible gelation[23] and also has been predicted for that case.[24]

(b) Demixing. Much more striking is the fact than when plotted in appropriate variables, cloud curves observed in very different conditions can be superimposed on one master curve over the whole range of polymer concentrations (Figures 4 and 5). It is very intriguing and important from a practical point of view to observe that in the semidilute regime the borate concentration necessary to induce demixing seems to be only very slightly dependent on galactomannan concentration. The superposition of data seems to indicate that the parameter governing the onset of demixing for a given monomer concentration is the number of cross-links per chain. In Appendix B, we show how this observation allows an estimation of the enthalpy ΔH of formation of a cross-link by borate ions in a (hydroxypropyl)guaran solution. This estimation of ΔH is obtained from values of the demixing threshold at different temperatures. A good agreement with values determined for glycoside model reactions is found.

The demixing transition is related to the formation of interchain didiol–borate complexes which act as temporary tie-points. The complexes induce in the polymer solution some additional monomer correlations which favor monomer contacts and are equivalent to interchain attractions. When the borate ion concentration increases, the probability of interchain contacts through the dicomplexation reaction is high enough to induce phase separation. Similar phase separations have been observed in ionomer solutions and in hydrogen-bonding systems for which theoretical models have been developed.[12,13,16,25] Although in our system the bonding mechanism is more complex as it involves not only polymer (and solvent) but also ions, one can simply adapt the same mean-field Flory approach. In concentrated, complexed solution, the free energy density can be approximated as[12,25]

$$\left.\frac{F}{kT}\right|_{\mathrm{cm}^3} \simeq \frac{1}{2}vC^2 + \frac{1}{6}w^2C^3 - UK_2C^2|\mathrm{B}^-| \qquad (2)$$

The first two terms represent the free energy density of a concentrated polymer solution. Here v and w^2 denote respectively the excluded volume and third monomer virial coefficient. The last term represents the attractive effect of dicomplex formation which is assumed to be proportional to the free energy kTU gained by the formation of a cross-link, which in a mean-field approximation is proportional to $|\mathrm{B}^-|C^2$. In the above approximation, the monomer correlations imposed by complexation lead to the same effect as lowering the solvent quality: they decrease the effective excluded-volume parameter. The onset of demixing correspond to the spinodal when the osmotic compressibility diverges, i.e. $\partial\pi/\partial c = 0$ or $\partial^2F/\partial C^2 = 0$. We assume that the monomer and free borate concentration fluctuations may be decoupled. This yields $|\mathrm{B}^-|$ at the demixing transition:

$$|\mathrm{B}^-|_{\mathrm{dem}} = \frac{v}{2UK_2}(1 + w^2C/v) \qquad (3)$$

This result nicely explains our experimental observations. The free borate concentration needed to provoke the demixing weakly depends on the polymer concentration (Figure 5). Indeed in a good solvent the term w^2C/v is on the order of the monomer volume fraction and gives negligible contribution to (3). Moreover, for typical values $v \simeq (6\ \text{Å})^3$, K_2 of the order of $10\ \mathrm{L}^2/\mathrm{mol}^2$, and $U \simeq \Delta H/RT \simeq 5$, we find $|\mathrm{B}^-|_{\mathrm{dem}}$ of about 1.5×10^{-3} mol/L, which is a very reasonable estimation of the demixing threshold. Expression 3 also accounts for the shift of the borate concentration necessary for the onset of demixing as a function of the temperature (Figure 5). In fact $K_2 \simeq \exp(-\Delta H/RT)$ and so $|\mathrm{B}^-|_{\mathrm{dem}} \simeq \exp(\Delta H/RT)$. It should be stressed that well beyond the overlap concentration, the demixing threshold is expected to be independent of the molecular weight of the chains. This simple model may also be used to predict the polymer and supernatant phases by adding when necessary translational entropy terms to (2) and considering all the complexation equilibria.

Although the above crude mean-field approach accounts qualitatively for the experimental observations, it has an essential conceptual drawback as it treats the excluded volume and complexation-induced correlations on an equal footing, i.e., as small perturbations of ideal chain solutions. Actually, even at the demixing threshold, the average chain length between two tie-points can be estimated to be long and thus swollen. The importance of excluded volume effects has been pointed out and discussed by Cates and Witten[13] for association phenomena in dilute solutions of ionomers. Analogously, for our system one can expect that excluded-volume interactions predominantly influence the formation of complexes and the situation might then be in many respects similar to irreversible gelation. At a given concentration, the maximum number of interchain tie-points cannot exceed the natural number of interchain contacts in the semidilute solution without provoking the demixing (syneresis). Hence when the free borate concentration is small the number of cross-links per chain is low. The average distance of a strand of a chain between two cross-links, R_x, is then bigger than the correlation length ζ which scales like $\zeta \simeq C^{-\nu/(3-1)}$. For a permanent network, this would mean that the gel is more concentrated than in the swelling equilibrium. If more borax is added, more cross-links are formed and the distance R_x decreases but the correlation length does not change. At some point, when the distance R_x becomes smaller than ζ the number of interchain contacts imposed by cross-linking would be higher than the overall natural number of interchain contacts corresponding to the given guaran concentration C. The system is expected to demix in order to match the number of cross-links and natural interchain contacts. In the dense phase, the polymer concentration increases and the free borate concentration decreases until the equilibrium is reached. Hence, in the first approximation the

Table II
(Hydroxypropyl)guaran–Borax Gel Demixing[a]

temp, °C	borax concn, g/L	$\lvert B^-\rvert_{dem}$, M	temp, °C	borax concn, g/L	$\lvert B^-\rvert_{dem}$, M
50	5.5	2.60×10^{-2}	37.5	4.5	2.11×10^{-2}
41	4.75	2.23×10^{-2}	30	4.1	1.90×10^{-2}

[a] (Hydroxypropyl)guaran concentration, 5.44 g/L.

onset of demixing corresponds to the situation where the temporary cross-linked network is in its swelling equilibrium, i.e., has a concentration

$$C \simeq (M/p)^{-3\nu+1} \tag{4}$$

for which ξ is essentially on the order of R_x. Here M is the polymer molecular weight and p denotes the number of intermolecular cross-links per chain. From (1) and (4) we thus find that the free borate concentration for which demixing appears should scale as

$$\lvert B^-\rvert_{dem} \simeq e^{\Delta H/RT} \tag{5}$$

In this picture, $\lvert B^-\rvert_{dem}$ is then independent of the molecular weight of precursor chains, of the guaran concentration, and even of the exact value of the swelling exponent ν. The above picture might explain the observed reduced phase diagrams at concentrated solutions and a very weak dependence of cloud points on guaran concentration. Relation 5 also implies a possibility of superposition of phase diagrams at different temperatures (Figure 5). The above discussion indicates a need for a statistical model that takes into account both excluded-volume effects and complexation equilibria in order to fully understand the observed phase diagrams. However, we feel that some of our results can be useful for studying other systems in which cross-linking is induced by complexing reactions, e.g., for poly(acrylamide)–Cr^{3+} or (hydroxypropyl)guar–titanate systems.[2,26] Our main conclusion is that the important parameter for both the sol–gel transition and the onset of demixing is the number of cross-links per chain. This implies that the phase diagrams obtained in completely different situations can be reduced to one "universal" phase diagram by an appropriate scaling of variables for all polymer concentrations. The interpretation of the reduced phase diagram far from the gel point indicates that the concentration of free binding ions should be essentially constant at the demixing threshold and it should be confirmed for other systems whether its order of magnitude can be roughly estimated from the equilibrium swelling degree of networks when the complexation constants of monomers are known or alternatively from the compensation of excluded volume by the energy gain when complexation occurs. This latter picture may be more adequate when the quality of the solvent is lowered by addition of a nonsolvent.[25]

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Appendix A. Chemical Equilibria and Mass Balance Equations

(a) Guaran–Borax Phase Diagrams in 1 M NaCl Solutions. In the simplest scheme the following equilibria and association constants are involved:

$$B^- + G \overset{K_1}{\rightleftarrows} BG^- \qquad K_1 = \frac{\lvert BG^-\rvert}{\lvert B^-\rvert \lvert G\rvert} \tag{A-1}$$

$$BG^- + G \overset{k_2}{\rightleftarrows} BG_2^- \qquad k_2 = \frac{\lvert BG_2^-\rvert}{\lvert BG^-\rvert \lvert G\rvert} \tag{A-2}$$

$$B^- + 2G \overset{K_2}{\rightleftarrows} BG_2^- \qquad K_2 = \frac{\lvert BG_2^-\rvert}{\lvert B^-\rvert \lvert G\rvert^2} \tag{A-3}$$

where B^- is the free borate ion and G is guaran expressed in sugar units. Mass balance equations are given by

$$C_B = \lvert B^-\rvert + \lvert BG^-\rvert + \lvert BG_2^-\rvert \tag{A-4}$$

$$C = \lvert G\rvert + \lvert BG^-\rvert + 2\lvert BG_2^-\rvert \tag{A-5}$$

where C_B is the total borate concentration and C denotes the total guaran concentration. Because in our phase diagram $\lvert G\rvert$ is on the order of 5×10^{-2} M or less and the constant k_2 is on the order of unity,[8] it is clear that borate–guaran dicomplex concentration $\lvert BG_2^-\rvert$ can be neglected in eq A-4 and A-5. Knowing K_1, C_B, and C, $\lvert B^-\rvert$ is then easily calculated by using eq A-1.

(b) Guaran–Borate Complexation Constants. From dialysis experiments performed at 23 °C, the monocomplexation constant K_1 was determined and found to be in the range of the association constants values measured for glycoside models from ^{11}B NMR data.[8] From the familiar thermodynamic relations

$$K_1(T) = K_1(T_0) \exp\left[-\frac{\Delta H_1}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{A-6}$$

and taking $\Delta H_1 = -7.8$ kJ/mL from the study of glycoside models, we get estimations of the guaran–borate monocomplexation constants $K_1 = 11.1$ L/mol, at $T = 25$ °C, and $K_1 = 13.3$ L/mol, at $T = 10$ °C.

The guaran–borate dicomplex formation constant K_2 was not directly measured. It seems reasonable to write

$$K_2(T) = K_2(T_0) \exp\left[-\frac{\Delta H_2}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{A-7}$$

where ΔH_2 is the enthalpy of cross-link formation. For model molecules $\overline{\Delta H_2} = -14$ kJ/mol. Schultz and Myers[7] showed that in the case of poly(vinyl alcohol)–borate systems (very similar to galactomannan–borate systems), $\overline{\Delta H_2}$ obtained for models is a good approximation to ΔH_2 for polymers.

In the phase diagram on Figure 5, $K_2(T)/K_2(T_0)\lvert B^-\rvert$ is thus plotted as the ordinate with $K_2(T)/K_2(T_0) = 1$, at $T = T_0 = 25$ °C, and $K_2(T)/K_2(T_0) = 1.3$, at $T = 10$ °C obtained from (A-7) with $\overline{\Delta H_2}$ instead of ΔH_2.

(c) Guaran–Mannitol–Borax Solution. With the addition of D-mannitol the following equilibria compete with equilibria A-1 and A-3 written above:

$$B^- + M \overset{K_M}{\rightleftarrows} BM^- \qquad K_M = \frac{\lvert BM^-\rvert}{\lvert B^-\rvert \lvert M\rvert} \tag{A-8}$$

$$B^- + 2M \rightleftarrows BM_2^- \qquad K_{MM} = \frac{\lvert BM_2^-\rvert}{\lvert B^-\rvert \lvert M\rvert^2} \tag{A-9}$$

$$B^- + G + M \rightleftarrows BGM^- \qquad K_{MG} = \frac{\lvert BGM^-\rvert}{\lvert B^-\rvert \lvert M\rvert \lvert G\rvert} \tag{A-10}$$

In this more complex system the complete mass balance equations are

$$C_B = \lvert B^-\rvert + \lvert BM^-\rvert + \lvert BM_2^-\rvert + \lvert BG^-\rvert + \lvert BG_2^-\rvert + \lvert BGM^-\rvert \tag{A-11}$$

$$C = |\mathrm{G}| + |\mathrm{BG}^-| + 2|\mathrm{BG}_2^-| + |\mathrm{BGM}^-| \qquad (\text{A-12})$$

$$C_\mathrm{M} = |\mathrm{M}| + |\mathrm{BM}^-| + 2|\mathrm{BM}_2^-| + |\mathrm{BGM}^-| \qquad (\text{A-13})$$

where C_M denotes the concentration of D-mannitol. The formation constants of borate–mannitol complexes, K_M and K_MM, are reported in the literature. We used the values obtained in ref 27 from ^{11}B NMR data at 25 °C: $K_\mathrm{M} = 1060$ L/mol and $K_\mathrm{MM} = 16 \times 10^4$ L^2/mol^2. They are in good agreement with values determined from pH[28] or calorimetric studies.[29] We can estimate K_MG, the constant of formation of mixed mannitol–guaran–borate complex, to be about $K_\mathrm{MG} \simeq K_\mathrm{M}k_2 \simeq K_1K_\mathrm{MM}/K_\mathrm{M}$. The two procedures lead to $K_\mathrm{MG} \simeq 1600$ L^2 mol^{-2}. Because of low concentrations of free D-mannitol and free galactomannan sites, the concentrations $|\mathrm{BMG}^-|$ and $|\mathrm{BG}_2^-|$ are small and the mass balance equations may be simplified

$$C_\mathrm{B} \simeq |\mathrm{B}^-| + |\mathrm{BG}^-| + |\mathrm{BM}^-| + |\mathrm{BM}_2^-| \qquad (\text{A-14})$$

$$C_\mathrm{G} \simeq |\mathrm{G}| + |\mathrm{BG}^-| \qquad (\text{A-15})$$

$$C_\mathrm{M} \simeq |\mathrm{M}| + |\mathrm{BM}^-| + 2|\mathrm{BM}_2^-| \qquad (\text{A-16})$$

We calculate the free borate concentration $|\mathrm{B}^-|$ from the above equations (A-1), (A-2), (A-9), and (A-14)–(A-16).

Appendix B. (Hydroxypropyl)guaran–Borax Gel Demixing

To estimate the cross-linking free enthalpy the following experiments were performed. A set of six (hydroxypropyl)guaran–borax samples were prepared and successively thermostated at four temperatures: 30, 37.5, 41, and 50 °C. The concentration of (hydroxypropyl)guaran was $C = 5.4$ g/L (i.e., $C/C^* \simeq 5$). The free borate concentration, which ranges from 1.8×10^{-2} M to 2.5×10^{-2} M, was calculated as in Appendix A, but taking into account that hydroxypropylation reduces the number of glactomannan sugar units available for complexation.[30] At each temperature, the light scattered at $\theta = 30°$ was measured for all the samples. The cloud point corresponds to the borate concentration at which the scattered light intensity diverges. It was then possible to determine with good accuracy the borate concentration necessary to induce the demixing transition for each temperature (see Table II).

From relation 3 or 5 we get

$$\ln\left(|\mathrm{B}^-|_{\mathrm{dem}\,T}/|\mathrm{B}^-|_{\mathrm{dem}\,T_0}\right) = \frac{\Delta H}{R}\,\frac{T_0 - T}{T_0T} \qquad (\text{B-1})$$

where $|\mathrm{B}^-|_{\mathrm{dem}\,T}$ is the free borate concentration when demixing appears at the temperature T (and concentration C). Plotting the experimental values of Table II, we obtain an estimation of the cross-linking free enthalpy. We find $\Delta H_2 = -12.8$ kJ/mol. This value is in a good agreement with complexation free enthalpy reported for glycoside models, e.g., $\overline{\Delta H_2} = -14$ kJ/mol for methyl α-D-galactopyranoside–borate complexes.

Registry No. Borax, 1303-96-4; guaran, 9000-30-0; (hydroxypropyl)guaran, 39421-75-5; sodium chloride, 7647-14-5; D-mannitol, 69-65-8.

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