Effects of Added Polysaccharides on the Isotropic/Nematic Phase Equilibrium of κ-Carrageenan

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ABSTRACT: The effects of added ι-carrageenan (IC), guar gum (GG), locust bean gum (LBG), or dextran (Dx) on the isotropic−nematic phase equilibrium of κ-carrageenan (KC) in solutions of 0.1 M NaI were studied. The concentrations of the polysaccharides in the separating phases were determined by NMR, and the phase volumes were observed, at different mixing ratios. All added polysaccharides were enriched in the isotropic phase, but to very different extents. GG partitioned relatively evenly between the two phases, and its effect on the relative phase volumes was very small. Dx was moderately enriched in the isotropic phase. LBG was different from the other added polysaccharides in that already relatively small amounts prevented a macroscopic phase separation, probably due to the increased viscosity. IC was exceptional in that it showed a very strong preference for the isotropic phase. As a consequence, the relative phase volumes were affected on addition of IC, and the nematic phase appeared at a much lower KC concentration than for KC alone. The reason for the exclusion of IC from the nematic phase is not clear, but it is speculated that it could depend on a tendency to form aggregates.

Introduction

The phase behavior of ternary systems containing two types of polymers and a solvent depends on the nature of the polymers and on the interactions between all components. For flexible polymers, the phase separation can be either segregative, where the different polymers are enriched in different phases, or associative, where both polymers are enriched in one concentrated phase.[1] For rigid or semirigid macromolecules, already the binary mixture with a good solvent may separate into one isotropic and one ordered nematic phase above a certain concentration. The nematic ordering, which requires only excluded-volume interactions, has been observed for a wide variety of rodlike particles or rigid polymers in solution, for example charged cellulose crystallites,[2] xanthan,[3] DNA,[4] organophilic boehmite rods,[5] and tobacco mosaic virus.[6]

It was recently shown[7,8] that the helical form of the well-known, gel-forming polysaccharide κ-carrageenan (KC) displays an isotropic−nematic phase equilibrium in certain salt solutions, which act as good solvents for the KC helix.[9] Carrageenans are sulfated, linear polygalactans extracted from certain red marine algae, with a backbone structure of alternating α-1,4 and β-1,3-linked galactose residues. The best known gelling varieties are KC and ι-carrageenan (IC). For both KC and IC, the gelation involves a coil-to-helix transition and a subsequent aggregation of the helices, typically induced by lowering the temperature under suitable solvent conditions. KC and IC are thus very similar, and they differ chemically only by the presence of one additional sulfate ester group on the repeating disaccharide unit for IC. Nevertheless, we recently discovered[10]—quite remarkably—that the small fraction (5%) of IC, which is normally present as a contamination in KC, is strongly excluded from the nematic phase of KC.

The purpose of the present work is to explore in greater detail the response of the KC isotropic/nematic two-phase system to the addition of a second polysaccharide. We present an extended study of the KC/IC system, where the proportions of IC and KC have been varied over wide ranges. For comparison, we also give results for a choice of other polysaccharides, viz. guar gum (GG), locust bean gum (LBG), and dextran (Dx). GG and LBG are both galactomannans, consisting of linear chains of (1→4)-linked β-D-mannopyranosyl units, to which are attached (1→6)-linked α-D-galactopyranosyl groups as single unit side chains. The proportion of α-D-galactopyranosyl units attached to the mannan chain depends on the species from which the polysaccharide is extracted and varies from approximately 20% for locust bean gum (LBG) to 33% for guar gum (GG). Mixtures of GG or LBG with KC are of special interest, since the interactions between these galactomannans and KC have been widely studied. The reason for this is the synergistic enhancement of the gel strength that occurs when KC is mixed with certain galactomannans, notably LBG.[11] Studies have convincingly shown that LBG associates to those aggregates of KC helices that are formed in KC gels,[12,13] whereas the association is weaker or absent for GG. In contrast to most previous studies we here investigate the KC−galactomannan interaction under conditions where KC forms helices, but no gels. Dx, finally, is chosen to represent a polysaccharide without any particular attraction to KC.

Experimental Section

Materials. KC (from *Euchema cottonii*) and IC (from *Euchema spinosum*) were kind gifts from SBI, France. To remove excess salt from the KC sample, it was precipitated in 2-propanol (IPA): One volume of a hot carrageenan solution (1.5%) was poured into two volumes of IPA. The resulting

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precipitate was collected by filtration, washed once with a 40/60 water/IPA mixture, and refiltered. The filtrate was then washed in IPA, filtered, and left overnight at room temperature to dry. The IC obtained from SBI was already precipitated in IPA and was used without this purification step. Both KC and IC samples were converted to the sodium form and depolymerized (by ultrasonication) according to procedures described in a previous study where it was shown that this type of treatment yields a weight-average molecular weight of 7×10^4 g/mol (helix from).[14] GG and LBG were provided by Mayhall Co. (Rhône-Poulenc) and SBI, respectively. According to the manufacturers, the average molar masses were 5×10^4 or 16×10^4 g/mol for low or high molecular GG and 4×10^4 or 10^6 g/mol for low or high molecular LBG. Solutions of 0.5% (low molecular LBG), 5% (low molecular GG), or 1% (high molecular GG) were prepared in Millipore water and then kept under stirring for 24 h at room temperature. The turbid solutions were then centrifuged at 20 000g for 2 h at 22 °C in order to remove the insoluble component. The clear supernatant was diluted with deionized water and dialyzed for 3 days at 4 °C to remove salts. The soluble component was recovered by a slow precipitation into a large excess of ethanol (10:1 by volume). Finally, the galactomannan precipitate was filtered, washed with ether, and dried using a vacuum pump. Dx (from Leuconostoc ssp, Fluka, ref 31391) was used as obtained without further purification. The molar mass of the polymer was approximately 11×10^4 g/mol as stated by the manufacturer.

Sample Preparation. Solutions were prepared by dispersing the dry polysaccharides at the desired ratio and total concentration in 0.1 M aqueous solutions of NaI (or, in some instances, mixtures of CsI and NaI). The composition of the salt mixture is expressed as the molar fraction of the cesium salt ($x_{\mathrm{Cs}} = [\mathrm{CsI}]/([\mathrm{CsI}] + [\mathrm{NaI}])$). Total polymer concentrations are given as weight percent. The polymers were dissolved by heating at 85 °C for at least 30 min while stirring. At this temperature, all studied mixtures were clear, monophasic solutions (the “mother solutons”). Each solution was left at room temperature overnight prior to any measurement. Centrifugation was then carried out at 25 °C with up to 4500g for different lengths of time. To determine the volume of the isotropic phase in the coexistence region, the height of the isotropic phase (h_1) and the height of the entire solution (h_0) were measured with a vernier caliper, and the volume fraction of the isotropic phase was obtained as h_1/h_0.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) measurements were carried out on a DSC30 from Mettler using the TA9000 system for processing the raw data. An aliquot of the solution with an accurately determined mass was sealed hermetically into the DSC pan. For each sample, a reference pan was filled with pure solvent. The two pans were then placed inside the calorimeter, heated to 85 °C, and kept for 10 min to annihilate the thermal history. Then the temperature was lowered to 5 °C at 2.5−10 °C/min, maintained at this low temperature for 5 min, and then raised to 85 °C at the same rate.

NMR. Samples for NMR measurements were prepared in flamed-sealed 5 mm NMR tubes with 5% of the water replaced by heavy water. ^{13}C NMR spectra at 150.85 MHz were recorded on a Varian 600 Unity Plus and Unity Inova spectrometers, equipped with a 14.1 T superconducting magnet and a broadband probe. The temperature was 80 °C and the spectral width 15 kHz. A total of 2048 FIDs were acquired with a recycle delay of 0.6 s. Proton decoupling was achieved using WALTZ-16 and a field strength of 926 Hz.

Results and Discussion

Isotropic/Nematic κ-Carrageenan Solutions. At sufficiently high concentrations KC solutions in 0.1 M NaI phase separate into an isotropic and a chiral nematic phase.[7] The influence on the phase equilibria of salt concentration, salt composition, and the molecular weight of KC has been studied previously.[8] For sufficiently low molecular samples, the two phases may be separated macroscopically by centrifugation, yielding two clear liquid phases, separated by a distinct meniscus, where the top phase is isotropic and the bottom phase birefringent. In the course of the present study, we made some additional findings on the KC two-phase system, which provided the reference for the further experiments on mixtures with added polysaccharides.

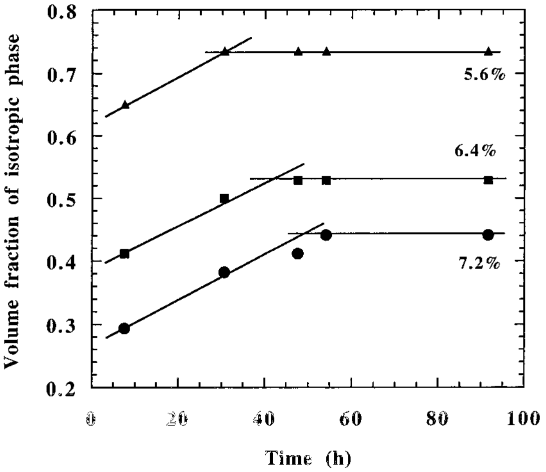

Figure 1. Development of equilibrium phase volumes at 25 °C for 5.6% (triangles), 6.4% (squares), and 7.2% (circles) KC in 0.1 M NaI with the centrifugation time.

Since one of our observables in this study was the relative phase volume, we carefully checked to what extent the macroscopic phases obtained depended on the time of centrifugation. Figure 1 shows representative results obtained for KC at different times of centrifugation. As can be seen, the volume fraction of the isotropic phase became stable only after prolonged centrifugation at 4500g. Not surprisingly, the time required to reach equilibrium depended on the KC concentration; more than 48 h of centrifugation was necessary for the 7.2% sample. To ensure that the macroscopic phase separation had reached equilibrium, a centrifugation time of 72 h at 4500g was used for the most concentrated solutions in further studies.

As reported previously,[7,8] a small volume of a turbid precipitate collected on the bottom of the test tube after centrifugation, in addition to the isotropic and nematic phases mentioned above. Tentatively, we have ascribed this precipitate to some contamination of unknown composition. This suggestion was strengthened by the following investigation: Turbid precipitates from a number of samples were collected in one NMR tube, to which 0.1 M NaI was added. It was noted that the precipitate did not dissolve on heating—the mixed sample was a turbid dispersion even at high temperatures. This should rule out the possibility that the precipitate was another equilibrium phase of KC, since dilute KC is well soluble in NaI—especially at high temperatures. A ^{13}C NMR spectrum run at 80 °C showed only weak signals from a small fraction of KC and some IC. Such signals were expected, since some amount of carrageenan solution was inevitably present with the precipitate taken out for analysis. In the data presented below, we have subtracted the volume fraction of the precipitate from all samples.

Figure 2 shows the relative proportions of the liquid phases at different concentrations. In accordance with previous findings, the volume fraction of the nematic phase does not show a linear dependence on the total

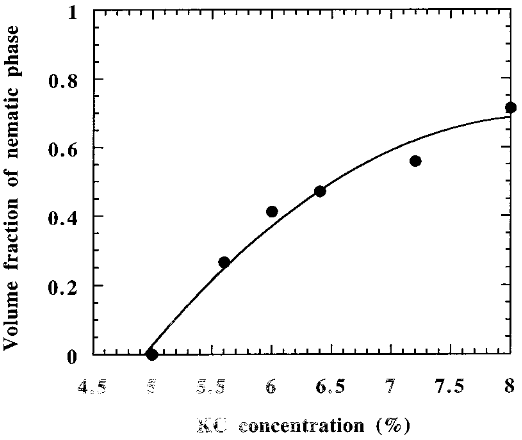

Figure 2. Equilibrium phase volumes at 25 °C for different concentrations of KC in 0.1 M NaI.

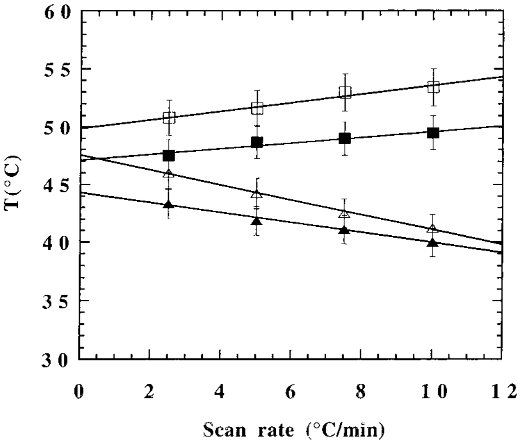

Figure 3. Transition temperatures, as functions of the DSC scan rate, for the isotropic (filled symbols) and nematic (open symbols) phases of a 6.9% sample of KC in 0.1 M NaI. Data refer to both cooling (triangles) and heating (squares) runs.

concentration, and it was not possible to obtain a single-phase nematic sample by direct mixing. This behavior may be due to the fact that KC is polydisperse, which will influence the phase equilibria in the biphasic region. However, as will be discussed below, the main reason for the absence of a single-phase nematic is probably the presence of a small amount of IC contamination in the KC.

The nematic phase of KC only forms—at least for the conditions and compositions investigated so far—when KC is in the helical conformation. We have here made a more detailed study of the thermal stability of the helix conformation in the isotropic and nematic phases of KC. The birefringence of the nematic phase prevents the use of optical rotation for such a study, but DSC is a suitable method. The transition interval, as given by the total width of the DSC peak in the thermograms, was fairly broad (>20 °C), as expected for a degraded carrageenan. The temperature at the peak of the transition, on cooling (T_c, coil → helix) and on heating (T_h, helix → coil), was extracted from the thermograms.

Figure 3 shows the scan rate dependence for the isotropic and nematic phase for a total KC concentation of 6.94%. If T_h and T_c are extrapolated linearly to zero scan rate, there is an apparent thermal hysteresis betwen the coil—helix and helix—coil transitions. The difference is, however, of the order of the error bars and may therfore not be regarded as significant. On the other hand, the transition temperatures in the nematic phase are consistently 2—3 °C higher than in the isotropic phase at all scan rates. The higher transition temperature in the nematic phase should at least partly be due to the higher concentration in this phase (approximately 0.6 percentage units according to previous work[15]). To verify the concentration dependence, solutions in the interval 6.6%—9.9% were measured by DSC at a scan rate of 5 °C/min. Weakly increasing transition temperatures (T_h and T_c) were indeed observed for both phases. The transition temperatures obtained by calorimetry in this work are in good agreement with the temperatures previously determined from rheology at slightly lower concentrations.[16]

On the basis of the total concentrations, the enthalpies of the transitions (the areas under the DSC peaks) were determined to 10 and 15 kJ/mol disaccharide unit in the isotropic and nematic phases, respectively, with no significant concentration dependence in the measured range (6.6%—9.9%). In a recent study on dilute solutions of KC in 0.1 M NaI,[17] the transition enthalpy was found to be 12 kJ/mol, intermediate between our results. Again, the difference in enthalpies found here between the isotropic and the nematic phases should at least in part be due to the fact that the equilibrium concentrations in the two phases are lower and higher, respectively, than the total concentration used in the calculations. The remaining difference could possibly be explained by the preferential enrichment of shorter chains (which presumably form less perfect helices) in the isotropic phase. In summary, our calorimetric data (transition temperatures and enthalpies) allow for the possibility of some additional stabilization of the κ-carrageenan helices in the nematic phase, but the effect is not large.

Effects of Added ι-Carrageenan. We have previously reported that the small fraction (typically 5—10%) of IC that normally contaminates commercial KC samples is strongly excluded from the nematic phase of KC. Here we have examined this behavior in more detail by studying samples at a fixed total concentration of 8% polysaccharides, but where different proportions of the KC were replaced by IC. The phase volumes were measured for all samples, and a few compositions were selected for analysis by NMR.

Figure 4 shows ^{13}C NMR spectra of the mother solution and the separated isotropic and nematic phases, corresponding to a mixture of 6.0% KC and 2.0% IC in 0.1 M NaI. We will use the notation 6.0KC/2.0IC for this sample and analogous notations for other mixtures discussed below. Note that all spectra were recorded at 80 °C, well above the helix—coil transition temperature, where all samples were isotropic and monophasic, giving isotropic, high-resolution ^{13}C NMR spectra for the carrageenans. Peak assignments may be found in the literature.[18,19] The compositions of the three solutions were clearly very different. The nematic solution gave an almost clean KC spectrum, where the best resolved IC peaks only just exceeded the noise. In contrast, the KC and IC signals from the isotropic phase had roughly the same intensities, and the spectrum of the mother solution was intermediate.

Phase compositions deduced from peak heights in the spectra of Figure 4 and similar spectra from other mixtures are presented in Table 1. In the evaluations, we have used the peak heights of the mother solutions—of known compositions—as references. This was possible

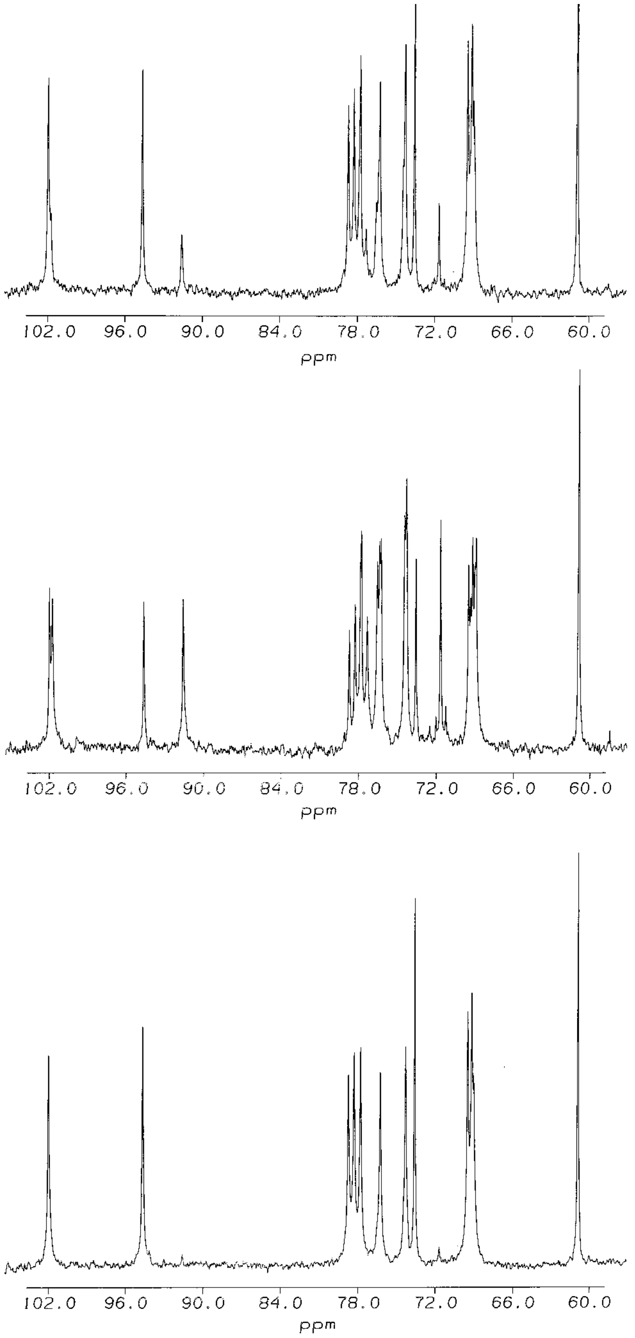

Figure 4. ^{13}C spectra at 80 °C of the mother solution (a, top) and the separated (at 25 °C) isotropic (b, middle) and nematic (c, bottom) phases of a mixture of 6.0% KC and 2.0% IC.

since all spectra were recorded under identical conditions, with identical sample volumes. For the compositions of the mother solutions, we have also considered the IC impurity in KC (6.6 wt %, according to NMR spectra of the 6.0% KC sample), and we have assumed the existence of a similar contamination of KC in the IC sample. Finally, the presented data for KC/IC mixtures are averages of estimates comparing both the C1 peak of the anhydrogalactose unit and the C4 peak of the galactose unit for the two carrageenans. The trends are very clear. For almost pure KC (sample 6.0KC), the KC concentration is very similar in the two separating phases, as has been reported previously.[7,8] As the content of IC is increased, the compositions of both phases change in the same direction as the average composition, but the changes are much weaker in the nematic phase than in the isotropic phase. Even at high relative contents, IC hardly enters the nematic phase (where the KC concentration remains high) but remains in the isotropic phase, where it becomes strongly enriched.

The strongly unequal partitioning of IC between the two phases is also reflected in the relative phase volumes as a function of KC concentration (Figure 5). Here the results for the mixtures, at a total concentration of 8% (KC + IC), are compared with the phase volumes of KC alone at different concentrations (from Figure 2). Without added IC, the nematic phase is formed at 5% KC and higher, while if IC is present, the nematic phase is formed at least down to 2% KC concentration. We know from the NMR results that IC is excluded from the nematic phase. The increase of the nematic phase volume in the presence of IC is therefore caused by an osmotic compression of the KC by the excluded IC, rather than a formation of a mixed nematic phase.

κ-Carrageenan/Galactomannan Mixtures. In similar experiments, 8% mixtures of KC/GG were prepared in 0.1 M NaI solutions. Birefringence occurred in all samples where the proportion of GG was equal to or lower than 30% GG (sample 5.6KC/2.4GG). These mixtures also phase-separated macroscopically after centrifugation for more than 3 days at 4500*g*. Both the high and the low molecular GG samples were investigated, and the phase separation was quite similar.

NMR results for one particular mixture (6.0KC/2.0GG, containing low molecular GG) are given in Table 1. GG is significantly, but only modestly, enriched in the isotropic phase; it is not nearly as strongly excluded as the IC of the KC/IC sample with a comparable composition. The relative phase volumes are shown in Figure 6. Note that they are quite similar to those observed for KC alone at varying concentrations. Both with and without GG, the nematic phase disappears at around 5% KC concentration. We can thus conclude that the addition of GG has very little effect on the isotropic–nematic phase equilibria. This is in line with the rather uniform partitioning seen in the NMR experiments: GG acts almost like a good cosolvent, which merely dilutes both separating phases to a very similar extent.

Up to now, the KC has been dissolved in a 0.1 M NaI solution, but previous studies on this type of KC preparations have shown that the NaI can to some extent be replaced by CsI, without destroying the nematic phase. Above a molar ratio cesium ions of 0.4 in the 0.1 M salt solution, the isotropic–nematic phase separation could however no longer be obtained, and a birefringent gel was formed instead.[8] Investigations in dilute systems have shown that the molecular origin of this transition is the aggregation of the KC helices into very rigid, superhelical rods, which, in turn, aggregate into larger bundles.[20] It was, furthermore, found that LBG—but not GG—could shift this transition to lower cesium contents, presumably by associating with, and thus stabilizing, the superhelical rods.[21] With this background, we found it interesting to investigate the salt dependence of the interactions of KC with galactomannans also at higher concentrations. We again used a total polymer concentration of 8%, where the proportion of low molecular GG was 25%, and varied the cesium content. Just as for KC alone, a macroscopic phase separation could not be observed for the mixed GG/KC polymers at and above $x_{Cs} = 0.4$, but a strong

Table 1. Phase Compositions (%) from ^{13}C NMR Peak Heights in 6% KC and in 8% Mixtures of KC with Other Polysaccharides

	isotropic phase				nematic phase			
sample	KC	IC	GG	Dx	KC	IC	GG	Dx
6.0KC	5.4	0.8			5.5	0.0		
6.0KC/2.0IC	3.0	4.8			7.7	0.4		
4.0KC/4.0IC	2.4	5.4			6.0	0.8		
6.0KC/2.0GG	5.6	0.6	2.2		5.5	0.0	1.7	
6.4KC/1.6Dx	5.6	0.7		1.8	6.1	0.0		1.1

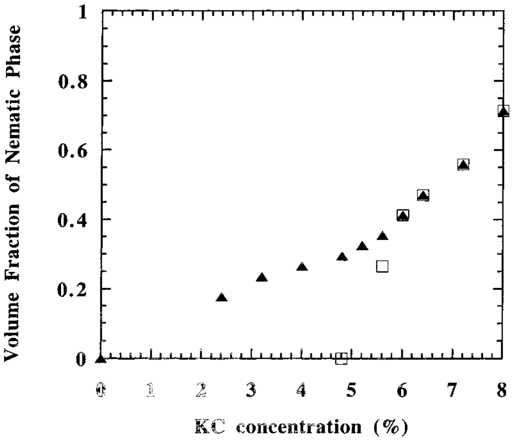

Figure 5. Equilibrium phase volumes (triangles) at 25 °C for 8% KC/IC mixtures of different compositions in 0.1 M NaI. Data for KC alone (squares; from Figure 2) at different concentrations are included for comparison.

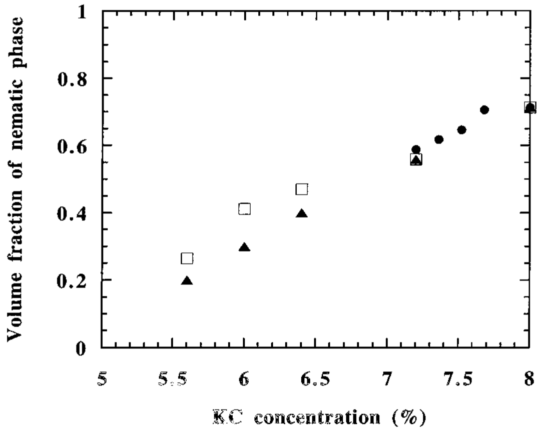

Figure 6. Equilibrium phase volumes at 25 °C for 8% KC/GG (triangles) or KC/LBG (circles) mixtures of different compositions in 0.1 M NaI. Data for KC alone (squares; from Figure 1) at different concentrations are included for comparison.

gel was obtained. The gelling samples were turbid, and the turbidity gradually increased when the cesium content increased. Below $x_{Cs} = 0.4$, a phase separation was observed, and as for KC alone, the volume fraction of the nematic phase increased slightly with increasing cesium content (Figure 7), probably due to an increase in the helical content.[8] Thus, the addition of GG did not notably affect the phase equilibria of the KC in the mixed salts. This supports the conclusion above that GG is "indifferent" to the isotropic–nematic phase equilibrium of KC.

Some experiments were also performed with LBG, but here it was found that centrifugation for more than 4 days was unable to produce a macroscopic phase separation—even for the low molecular LBG—when the proportion of LBG was above 10%. For lower proportions of LBG, separation of the phases was possible, and the phase volumes were measured (Figure 6). In this small interval—as for the other added polymers—there was no detectable difference from the results for KC alone at the corresponding concentration. The fact that macroscopic phase separation could not be obtained in the mixtures of KC/LBG could be taken as a sign for an association between KC and LBG. However, no such association has been observed in 0.1 M NaI.[21–23] A more probable explanation is that the marked viscosity increase, brought about by the addition of LBG, inhibited the macroscopic phase separation. For KC alone, a strong correlation between increased viscosity and resistance to macroscopic phase separation has been observed.[8]

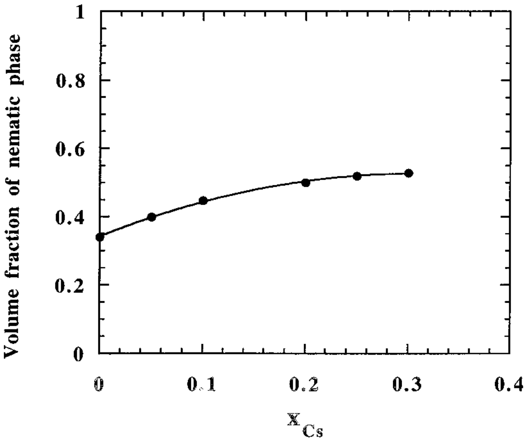

Figure 7. Equilibrium phase volumes at 25 °C for mixtures of 6% KC, 2% GG in 0.1 M NaI/CsI salt mixtures of different compositions.

The κ-Carrageenan/Dextran Mixture. Finally, to compare with an "inert" polysaccharide, we investigated one mixture with the composition 6.4KC/1.6Dx. As seen in Table 1, this mixture behaves rather similarly to the KC/GG mixture and not at all like the KC/IC mixture.

Concluding Remarks

From the results presented above we can conclude that the partitioning of an added polymer between the isotropic and the nematic phase of KC is quite dependent on the type of added polymer. Although there is a general tendency for the added polymer to prefer the isotropic phase, this tendency is quite weak for GG and Dx. The simplest argument that predicts this rather even partitioning is that the phase concentrations in the isotropic/nematic two-phase system are very similar. Thus, although some effective repulsion (preferential interactions between like species) probably exists between the unlike polysaccharides, this repulsion is of similar strength in both phases. A weak partitioning of the added polymer could depend on the small concentration difference between the isotropic and the nematic phase.

There are some theoretical,[24,25] as well as experimental,[26−29] reports in the literature where a preference of the added flexible polymer for the isotropic phase has been noted and explained in terms of the higher flexibility of the added polymer. We note that, for example, the Flory theory is for athermal systems, where there are no preferential interactions. It is impossible for us to separate the two effects (interactions and flexibility) in our systems, since we are comparing different polymers, where neither the flexibility nor the interactions are accurately known. From the molecular structure one would guess that the Dx molecule is more flexible than GG, but the partitioning between the two phases is clearly comparable. This would suggest that the flexibility is not so important.

Clearly, out of the different polymers added, IC is the exception showing a strongly unequal partitioning between the KC phases. This is quite surprising since IC, a priori, is the polymer that should be the most similar to KC. The chemical structures of the two carrageenans differ only by the number of sulfate groups (1 for KC, 2 for IC) per repeating disaccharide unit. Both carrageenans also form double helices, of a quite similar structure,[30] under the salt and temperature conditions where the phase behavior was studied here. Apart from the capacity to form helices, one difference between IC and the other added polysaccharides of the present study is that IC is charged. This should, however, not explain the uneven partitioning. Charged polymers generally partition more evenly than uncharged polymers in biphasic systems, owing to the entropy of mixing of the counterions. Moreover, charged substituents do not in any way prevent nematic ordering; many of the best studied nematogens (DNA, xanthan, TMV, and now KC) are polyelectrolytes.

It does seem significant, however, that IC alone fails to produce a nematic phase under those conditions where KC does so.[8] Unsuccessfully, we have tried both with different molecular weights and different concentrations of iodide salt. At present, we can only speculate why IC avoids the nematic order. One possibility is that the IC helices actually have a larger tendency than KC helices to aggregate in NaI solutions. This difference has been noted by rheological studies[16] which show that IC forms much more gellike systems than KC in 0.1 M NaI.

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