The Effect of Solvent and Ions on the Structure and Rheological Properties of Guar Solutions

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We study the effect of isopropyl alcohol (IPA) and various salts (sodium chloride, sodium thiocyanate, sodium carbonate, and urea) on the rheological behavior and the conformation of aqueous guar solutions. Ultralow angle light scattering, conventional light scattering, and neutron scattering are used to probe the structure of guar over length scales spanning 5 decades, from a few angstroms to several tens of microns. Although both IPA and salts worsen solvent conditions, their effect is very different. Isopropyl alcohol promotes the formation of a network of large-scale structures via intermolecular associations, thus increasing dramatically the elastic response of guar solutions. Salts, on the contrary, affects guar on a local scale, leading to a more collapsed chain configuration, thus to a lower effective volume fraction and to reduced viscosity.

Introduction

Guar[1] is a naturally occurring polysaccharide extracted from the beans of the guar gum plant. The guar molecule consists of a mannose backbone with random galactose substitutions in the ratio 1.6:1. The galactose units solubilize the polymer through steric effects; galactose-poor regions, on the contrary, are less soluble[2] and can associate both intra- and intermolecularly to form partially crystalline complexes.[3,4] Because of these associations, guar possesses remarkable rheological properties[2,5,6] and is widely used to control viscoelasticity in food,[7] personal care,[8,9] and oil recovery[10] industries. In most applications, several additives such as cosolvents or salts are also present in solution, besides guar and water. For example, isopropyl alcohol (IPA) is used in the cosmetic industry for hair sprays and shampoos, while ions are ubiquitous. The presence of these additives can dramatically change the viscoelastic and structural properties of guar solutions, since they affect the quality of the solvent and thus both the chain conformation and the degree of intermolecular associations. Additives, such as IPA, can also be used to precipitate the polymer to extract it from the solvent.[11] However, because the way in which each additive affects the solubility differs, the properties of the end products are not likely to be the same. To fully control the properties of guar solutions in applications it is therefore essential to characterize the structural changes induced by the different additives and to correlate them to the modification of the rheological behavior.

In this paper we report the results of rheological and scattering studies on the effect of IPA and various salts on the viscoelastic properties and the structure of guar solutions in H_2O. Previous work on guar in H_2O showed that association leads to the formation of structures that can vary in size over a wide range of length scales.[3] Therefore, to fully characterize the conformation of guar solutions we use a combination of both conventional and ultralow angle static light scattering (SLS and USALS, respectively) that allow us to probe length scales from a fraction of a micron to hundreds of microns. Additional information on the local conformation of the polymer chain is provided by neutron scattering experiments, for which H_2O was replaced by D_2O to obtain a sufficient contrast.

We find that IPA dramatically changes the rheological properties of guar: while guar in pure H_2O behaves essentially as a viscoelastic fluid[12,13,5] (some loose connections between molecular aggregates being nonetheless present), upon addition of IPA its behavior changes to that of an increasingly stiff gel. Light scattering reveals that this change stems from the formation of structures on length scales of hundreds of microns, while no relevant changes are observed on smaller length scales. The effect of salt on the rheological properties of guar is less pronounced. Three salts were tested at a concentration of 1 M: sodium chloride (NaCl), sodium carbonate (Na_2CO_3), and sodium thiocyanate (NaSCN). All of them reduce, to a different extent, the viscosity of guar suspensions, without altering qualitatively their rheological behavior. Light scattering indicates that no change occurs on the large-scale structure of the suspensions. By contrast, an increase of the fractal dimension—indicative of a less extended state of the polymer— is observed on smaller length scales, thus suggesting that the reduced viscosity be due to a decrease of the effective volume fraction upon addition of salts. The results for NaCl and Na_2CO_3 are in good agreement with expectations from the Hofmeister series,[14] which predicts reduced polymer solubility in the presence of these salts. Sodium thiocyanate is also found to reduce the solubility of guar, in contrast with its “salting-in” behavior in protein solutions. This difference may be due to the different conformation of proteins and guar. Additionally, we performed light-scattering experiments on guar solutions containing urea,

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commonly used as a hydrogen bond breaker to brake polysaccharide aggregates.[13,15] We find for urea the same behavior as for the other salts, thus suggesting that the addition of urea leads to a more collapsed polymer configuration, rather than to the breaking of supramolecular aggregates.

Experimental Method

Materials. Unmodified guar galactomannan (LJX-2) was obtained from Rhodia Inc. and purified as described in ref 3. Isopropyl alcohol and salts were obtained from Fluka. Deuterated water and deuterated IPA were obtained from Cambridge Isotope Laboratories. The IPA solutions were made by first dissolving guar in water alone and then by adding the alcohol one drop at a time, so as to present the guar molecule with worsening solvent conditions evenly. The solutions were homogenized by manual shaking. Similarly, salt solutions were prepared by adding the salt to an already dissolved guar solution. All solutions were stored at 6 °C to prevent degradation due to the development of bacteria, except for those containing IPA, a natural bactericide. All samples were tested within a few days of preparation.

Rheological Methods. The rheological behavior of guar solutions was studied by dynamic oscillatory measurements using a stress-controlled Rheometrics Ares rheometer. The apparatus was run in the strain control mode through a feedback loop. A coni-cylinder cell (couette cell, the bob of which has a conical bottom) with a cup diameter of 34.0 mm, a bob diameter of 32.0 mm, a bob length of 33.0 mm, and a gap of 0.05 mm was used. Measurements of the elastic and loss modulii were performed in the angular frequency range $10^{-2} < \omega < 10^2$ rad/s. All measurements were performed in the linear regime, which extends up to 25% strain for guar solution in pure water or with salt, while is reduced to less than 0.1% strain in the presence of IPA. All tests were done at 25 °C.

Scattering Methods. Ultrasmall-angle light scattering (USALS) was performed on a custom-built apparatus that is described in detail elsewhere.[16] The range of accessible scattering vectors q spans almost two decades: $150\ \text{cm}^{-1} < q < 12000\ \text{cm}^{-1}$, where $q = 4\pi n\lambda^{-1} \sin\theta/2$, n being the refractive index of the solvent, λ the in-vacuo laser wavelength, and θ the scattering angle. All data were corrected for stray light contribution as described in ref 17. Static light scattering (SLS) measurements at higher q were performed using a Brookhaven Instruments Corp. apparatus, equipped with a 200SM goniometer and a 9000AT digital correlator. The range of accessible scattering vectors is $30\,000\ \text{cm}^{-1} < q < 300\,700\ \text{cm}^{-1}$. A dust-cutoff routine was used in collecting the data (SLSW software by Brookhaven, dust cutoff = 10, 10−30 repetitions). Small-angle neutron scattering (SANS) was performed on guar in D_2O solutions at the Intense Pulsed Neutron Source at Argonne National Laboratories using the time-of-flight small-angle diffractometer. Large sample cells with a 5 mm path length were used since guar scatters weakly in D_2O. Data for q values ranging from 4.94×10^{-3} Å^{-1} to 2.47×10^{-1} Å^{-1} were collected over 12 h (24 h for the solvents without polymer). All measurements were taken at 25 °C. All data were treated according to methods used by Argonne National Laboratory which correct for solvent and parasitic scattering and place the data on an absolute level using standards. Within the range of polymer concentrations studied here, the amount of H_2O in the bulk (from exchange of hydrogen along the polymer chain with deuterium in the bulk and from residual moisture in the guar powder) is less than 0.1%.

Scattering techniques provide information on the structure of the sample on length scales that vary from a few angstroms (SANS) to several tens of microns (USALS). By combining different techniques, one can therefore obtain a full description of the conformation of macromolecules in solution, from the local chain level to supramolecular associates. A useful concept in describing the structure of macromolecules is the fractal dimension d_f, defined by the scaling law $M \propto l^{d_f}$, where M is the mass enclosed in a "blob" of size l.[18] The fractal dimension can be obtained directly from the scattered intensity profile, since, for a fractal object, $I(q) \propto q^{-d_f}$.[18]

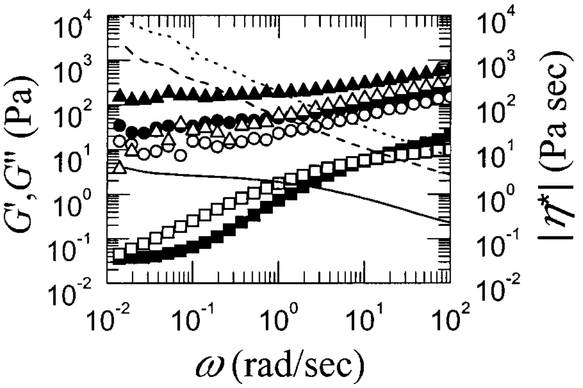

Figure 1. Rheology of concentrated solutions of guar in H_2O (0.46% w/w), in the presence of different amounts of isopropyl alcohol. Solid and open symbols are the storage and loss modulii G' and G'', respectively, lines $|\eta^*|$. Squares and solid line: $c_{IPA} = 0\%$; circles and dashed line: $c_{IPA} = 5\%$; triangles and dotted line: $c_{IPA} = 7.5\%$.

Results and Discussion

The effect of different additives on the rheology of guar solutions of concentration $c = 0.46\%$ (w/w) is probed by oscillatory strain measurements in the linear regime. Figure 1 shows the frequency (ω) dependence of the elastic modulus G', the loss modulus G'', and the complex viscosity $|\eta^*|$ for a volume fraction of IPA, c_{IPA}, of 0, 5, and 7.5%, respectively. In pure water, guar displays a viscoelastic behavior characterized by two crossover times ($\tau_1 = 0.1$ s, and $\tau_2 = 100$ s). Above $\omega = 10$ rad/s G' dominates G'', most likely due to entanglement of the guar chains (the overlap concentration was estimated to be $c^* = 0.19\%$ from intrinsic viscosity $[\eta] = 1/c^{*3}$). No decrease in G'' is observed in this regime, suggesting a broad relaxation spectrum at this time scale. At lower frequencies, the frequency dependence of G' and G'' is weaker than expected for a Maxwellian fluid, for which $G' \propto \omega^2$ and $G'' \propto \omega^1$. Moreover, G' seems to approach a constant value in the low-frequency limit, indicating that there may be a low-frequency plateau below $\omega = 10^{-2}$ rad/s. The presence of a low-frequency plateau in G' would suggest that the system is able to elastically store a small fraction of the stress even over long periods of time (100 s), a feature that has been reported for associating polymers.[19] As many natural polysaccharides, guar is not a homogeneous polymer: while water is a good solvent for most of its segments, some segments poorer in galactose are less soluble and act as intramolecular junctions. Indeed, association in guar solutions has been observed by USALS[3]. The crossover frequency to this low-frequency behavior ($\omega = 0.16$ rad/s, corresponding to a maximum in G''/G') reflects the average molecular weight of the section of polymer chain between two adjacent junctions, and suggests that these junctions are much less numerous than the entanglements.

Upon addition of IPA, the rheological properties of guar solutions change dramatically (see Figure 1). When 5% (by volume) IPA is added, G' dominates over the entire investigated

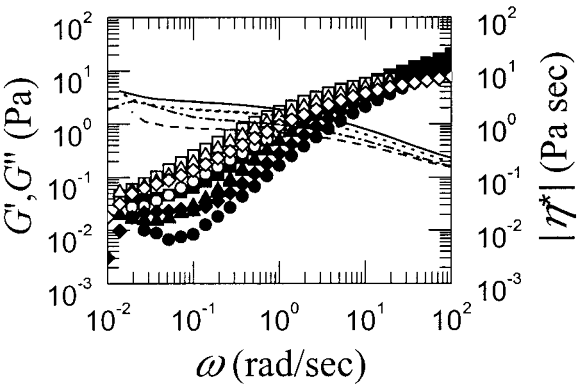

Figure 2. Rheology of concentrated solutions of guar in H_2O (0.46% w/w), in the presence of various salts. Solid and open symbols are G' and G'', respectively, lines $|\eta^*|$. From top to bottom: pure water, 1 M NaCl, 1 M NaSCN, 1 M Na_2CO_3.

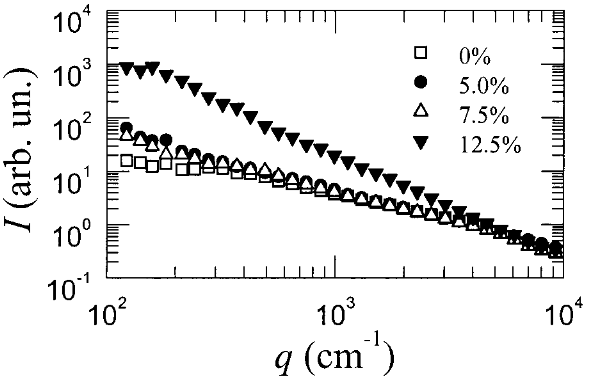

Figure 3. Ultra-small angle scattered intensity vs q for concentrated guar (0.46% w/w) in aqueous solutions of IPA. Curves are labeled by the IPA content (v/v).

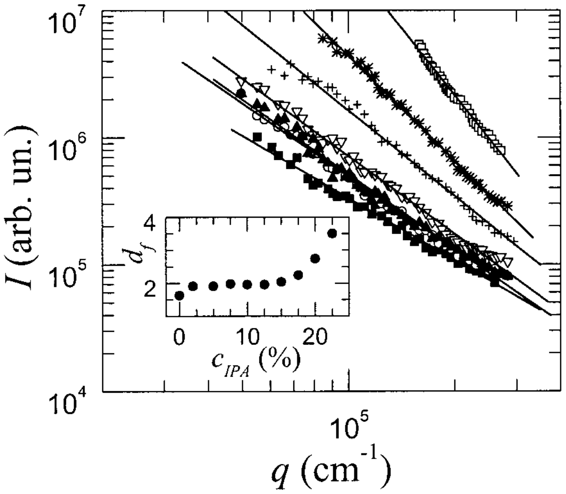

Figure 4. Scattered intensity vs q in the intermediate q range, for diluted (0.038% w/w) guar solutions in H_2O. From top to bottom, the content of IPA is 22.5, 20, 17.5, 15, 12.5, 2, and 0% v/v. Straight lines are power law fits to the data. Inset: IPA dependence of the fractal dimension obtained from the power law fits. (SLS curves for c_{IPA} between 5% and 10% are almost undistinguishable from data for c_{IPA} = 2% and are not shown to avoid crowding the plot).

frequency range and its magnitude increases by several orders of magnitude, reaching 33 Pa in the low-frequency limit. At 7.5% IPA, G' further increases, reaching 150 Pa in the low-frequency limit, and the ratio G''/G' is smaller than for the previous sample, confirming the increased gellike behavior of the material. We note that the addition of a bad solvent increases the number density of nonsoluble segments and thus that of junctions. In the semidilute regime, intermolecular contacts are more likely than intramolecular contacts; thus decreases in the solvent quality are likely to lead to more gellike properties as observed in the present case. Further addition of IPA eventually leads to phase separation. In fact, we find that the elastic properties of guar solutions apparently *decrease* for $c_{IPA} \geq 15\%$ (data not shown), thus suggesting the formation of a non space-filling structure, i.e., precipitation. Indeed we observe macroscopic phase separation at this c_{IPA} for more dilute guar solutions, as discussed below in reference to Figure 4.

The rheological changes upon addition of 1 M of various salts are less dramatic, as can be seen in Figure 2. The overall behavior is closer to that of guar in water alone, while the presence of salt decreases the complex viscosity $|\eta^*|$. The relevance of this effect increases when changing from NaCl to NaSCN, and is maximum for Na_2CO_3, for which $|\eta^*|$ at low frequencies decreases by a factor of 4, compared to that of guar in water alone. The evolution of the complex viscosity suggests a decrease in the effective volume fraction, or a less entangled state of guar solutions upon the addition of salts. As shown by the data reported in Figures 1 and 2, the effect of the addition of IPA and salt on the rheology of guar solutions is very different. To understand the origin of this difference, we investigate the structure of guar solutions by means of light and neutron scattering.

Figure 3 shows the scattered intensity as a function of q for concentrated (0.46% w/w) solutions of guar in H_2O for different values of c_{IPA}. Data were collected with the USALS apparatus, allowing us to probe the structure of the solutions on unusually large length scales, ranging from a few microns to more than 100 μm. For an IPA content less than 7.5% no appreciable differences are noticed with respect to guar dissolved in pure water, except for a slight increase in I for $q < 300$ cm^{-1}. At higher IPA concentrations, however, the rise of the intensity at small q is much steeper, leading to a 50-fold increase at the smallest q probed and indicating the formation of structures on length scales of hundreds of microns. It is worth noting that a similar trend is observed also for diluted guar solutions (0.038% w/w, data not shown), the intensity increasing dramatically at small q vectors when more than 7.5% IPA is added to the solutions. We point out that in rheology a marked difference was found for solutions containing more than 5% IPA, while USALS data exhibit only a significant change at much higher IPA concentrations, which correspond to the onset of phase separation. Since rheology probes the sample on macroscopic length scales, larger than those accessible by USALS, the data suggest that by adding IPA, intermolecular interactions be affected first, leading to the formation of an elastic network. At higher IPA content, the conformation of guar is modified also on smaller length scales, as indicated by USALS measurements. This picture is confirmed by SLS data on diluted (0.038% w/w) guar solutions, shown in Figure 4. At the even smaller length scales probed by SLS, no relevant variations in the scattering profile occur below c_{IPA} = 12.5%, while a rapid increase in both I and d_f (see inset) is observed above this value. (Unfortunately, SLS data on concentrated guar solutions are not available due to experimental difficulties, but the trends at different concentrations are expected to be similar, as observed for USALS). Hence, the transition to the formation of more compact structures (as indicated by a significant change in scattering or rheological properties) occurs at smaller length scales as the IPA concentration increases. For $c_{IPA} \geq 15\%$, the rise in d_f to a value not far from 4 suggests that guar is confined into regions whose surface becomes increasingly smooth (a

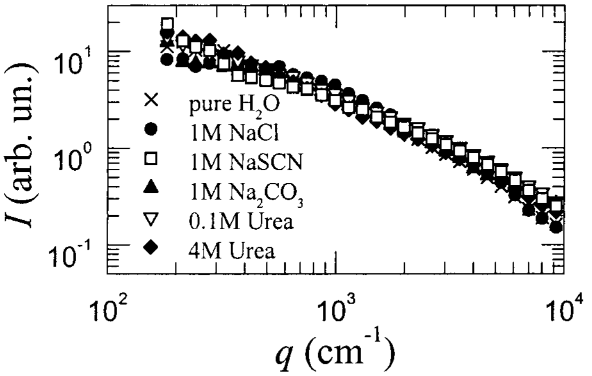

Figure 5. Ultra-small angle scattered intensity vs q for concentrated guar (0.46% w/w) in aqueous solutions of different salts. No significant changes in USALS data are observed upon the addition of salt.

TABLE 1: Fractal Dimension for Diluted Guar Solutions in the Presence of Different Salts, As Measured by SLS

	H_2O	1 M NaCl	0.1 M urea	4 M urea	1 M NaSCN	1 M Na_2CO_3
d_f	1.67	1.73	1.98	2.12	2.22	2.49

value $d_f = 4$—Porod's law—is characteristic of the scattering of two media separated by perfectly smooth interfaces). This is strongly reminiscent of the droplet formation characteristic of the early stages of phase separation in a binary system. Indeed, we recall that macroscopic precipitation is observed in concentrated guar solutions for $c_{IPA} \geq 15\%$.

Figure 5 shows USALS curves for concentrated guar in pure water and in the presence of four different salts: NaCl, NaSCN, urea, and Na_2CO_3. Contrary to the case of IPA, the curves closely follow the scattering profile of guar in pure water and no significant differences are noticed for different salts. This indicates that the addition of salt does not change the large length scale structure of guar solutions. In contrast, the salt effect is considerable at the smaller length scales probed by SLS, as seen in Table 1 where the values of d_f obtained by fitting a power law to the SLS data are reported for dilute solutions of guar. The SLS measurements confirm that water is a good solvent for guar ($d_f = 1.67$), as discussed in ref 3. All the salts that were tested decrease the solvent quality and thus the solubility of guar, as revealed by the increase of the fractal dimension, indicative of a less extended chain conformation. The effect of salt on the solubility of proteins and other biopolymers has been well documented, beginning with Hofmeister in the late nineteenth century.[14] The mechanism is based on the hypothesis that water molecules surrounding nonpolar sections of the molecule are more ordered than in the bulk:[20−22] in the absence of ions water molecules can orient themselves around localized hydrophobic regions of the solute making the molecule soluble. Certain ions enhance this ordering (called structure-making ions) and are said to "salt in" the polymer, whereas other ions break up the ordering (called structure-breaking ions) and are said to "salt out" the polymer. Some studies suggest that this effect be due to entropy: structure-breaking ions are thought to be entropically driven to the proximity of the molecule surface disrupting the local structure there and decreasing the solubility. Trends in the changes in entropy that the ions exhibit when going from gaseous to aqueous phases are correlated to the reported trends on solubility in the oft-cited Hofmeister or lyotropic series.[22] The behavior of guar in solutions of Na_2CO_3 and NaCl follows the one observed for other macromolecular systems. In fact, according to the Hofmeister series, Na_2CO_3 is expected to decrease the solubility of macromolecules, while NaCl generally has a neutral behavior on solubility. Our static light scattering data are in good agreement with this trend. In fact, the addition of NaCl changes only slightly the fractal dimension ($d_f = 1.73$), while Na_2CO_3 increases d_f up to 2.49, indicating that the polymer chain is sensibly more contracted, and thus that the solvent quality is significantly reduced. Sodium thiocyanate, on the contrary, is known to increase the solubility of many proteins. One may expect to observe a similar effect on guar. This is not seen here since $d_f = 2.22$, a value indicative of a chain less extended than in pure water. This difference may be due to the different conformation of proteins and guar. Proteins are globular whereas fully solubilized polymers such as guar have a coil conformation. Hence, with proteins a sheet of water molecules surrounding all parts of the chain is less likely, since geometric restrictions may make it more difficult for ions and water molecules to penetrate inside the protein globule and arrange themselves such as they would in a coil conformation.

The large variations in fractal dimension reported in Table 1 for diluted guar solutions reflect the significant changes of the solvent quality when different salts are added. Accordingly, the polymer chains change from a highly swollen state in H_2O alone to an increasingly shrunk state, the most collapsed configuration being that in a 1 M Na_2CO_3 solution. Although there is no guarantee that the same values of d_f would be observed for more concentrated guar solutions, we point out that the trend emerging from SLS data is consistent with the rheological measurements of $|\eta^*|$ shown in Figure 2. In fact, the viscosity decreases when going from pure water solutions to those containing, respectively, NaCl, NaSCN, and Na_2CO_3 (see Figure 2), while the fractal dimension follows the opposite trend, increasing from 1.67 (H_2O) to 2.49 (Na_2CO_3). Guar aggregates with higher fractal dimension are more compact and hence their effective volume fraction is lower. By consequence, one expects the viscosity of such solutions to be lower, which is in good agreement with the observed rheological behavior. Urea is commonly used as a hydrogen bond breaker to reduce the size of polysaccharide aggregates.[13,15] We chose to study guar in the presence of 4 M urea since this is the concentration recommended by Sothwick et al. to ensure hydrogen bond breakage in a similar polysaccharide, xanthan.[15] However, our USALS data indicate that the size of the aggregates hardly changes upon addition of urea, while the fractal dimension measured by SLS significantly increases (from 1.67 in H_2O to 2.12 in 4 M urea). Additional tests at 0.1 M of urea, the concentration used in ref 13, gave qualitatively the same results, albeit the increase of d_f was less pronounced than that at higher urea content. Therefore, we conclude that the addition of urea to guar solutions leads to a more collapsed configuration of the polymer, rather than to the breaking of intramolecular associations.

Collectively, scattering and rheological data suggest that on mesoscopic and macroscopic length scales the effects of IPA and salts on the structure of guar solutions are very different. While a local retraction of the polymer chains is observed in the presence of salts, IPA promotes intermolecular interactions on much larger length scales. To investigate the effect of IPA and ions on the structure of guar on the monomer length scale, we performed SANS experiments. Unfortunately, to achieve a reasonable scattering contrast D_2O solutions are necessary. In previous work,[3] we showed that D_2O is a less good solvent than H_2O, so one should be cautious about extrapolating the results of SANS to aqueous solutions. Nevertheless, we find that the scattered intensity behavior is consistent with what would be

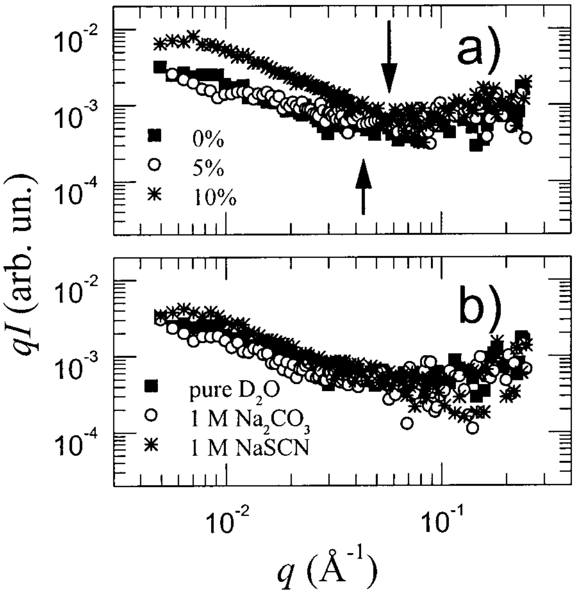

Figure 6. Neutron scattered intensity vs q for concentrated (0.5% w/w) guar solutions in D_2O. (a) the effect of IPA (curves are labeled by c_{IPA}); (b) the same data, plotted as $qI(q)$ vs q. The arrows show q_{pl} for $c_{IPA} \leq 5\%$ (bottom arrow) and for $c_{IPA} = 10\%$ (top arrow), respectively; (c) no significant changes are observed in the scattering profile upon addition of Na_2CO_3 and NaSCN.

expected for H_2O solutions, as discussed in the following. Figure 6 a shows SANS data, plotted as *qI vs q*, for 0.46% (w/w) guar in D_2O with $c_{IPA} = 0$, 5, and 10%, respectively. At low q, the intensity decays as a power law, with an exponent close to that measured by SLS. The crossover to a q^{-1} behavior occurs at a scattering vector q_{pl} of the order of the inverse of the persistence length. While no difference is found between the pure D_2O and the 5% IPA solutions, for $c_{IPA} = 10\%$ q_{pl} shifts to larger q vectors (see arrows in a)) and the low-q decay is steeper. These features indicate a smaller persistence length, consistently with the less extended chain conformation (larger fractal dimension) observed in light scattering, which we attribute to a decreased polymer solubility for increasing IPA concentration as discussed in reference to Figures 1, 3, and 4. The effect of salt on the small length scale structure of guar is much less pronounced, similarly to what is observed at larger length scales by light scattering and rheology. As shown in Figure 6 b, a slight increase of the fractal dimension at the smaller scattering vectors probed by SANS (2.06 instead of 1.91) is observed only in the presence of Na_2CO_3, the salt which causes the highest increase of d_f in the intermediate q regime probed by SLS. For all salts tested, no appreciable difference is seen in q_{pl}.

An important factor in setting the structure and the rheological properties of guar in the presence of additives is the order of addition of the polymer and the additive when preparing the solution. To exemplify this issue, which has relevant practical and industrial consequences, we show in Figure 7 a USALS data for a diluted guar solution in 1 M Na_2CO_3. When salt is added to an already dissolved guar solution, the data look similar to that of a concentrated solution (only shifted to lower intensity, compare to Figure 5), which were made the same way. By contrast, when guar is added to a salt solution, the low-q intensity increases by more than 2 orders of magnitudes, indicating structure formation at large length scales. The data suggest that guar dissolves in a manner that depends on the solvent quality it is initially presented with. When dry guar is dissolved in pure water (a good solvent), it extends its chains freely, while when it is added to a salt solution it sees much less favorable conditions for dissolving and collapses locally before having the chance to extend fully as in pure water. A similar trend is observed in rheological measurements on concentrated guar in 1 M Na_2CO_3. As can be seen in Figure 7 b, the elastic modulus and the viscosity increase significantly for the solution where the salt is added first. This indicates a more connected network, both locally and at macromolecular length scales. The problem seems to be one of kinetics. While thermodynamically one expects that both sample preparations would eventually yield the same solution structure and hence the same rheological properties, this appears not to be the case, at least on the time scale of a few months. We recall that even in good solvent conditions aggregated (or crystallite) regions do exist.[3] In less good solvent conditions, these regions are even more likely to exist, and will be harder to break up.

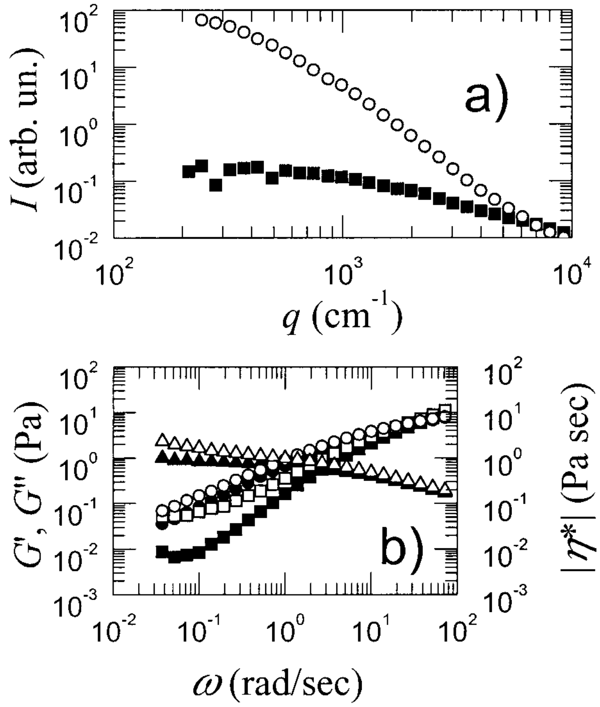

Figure 7. The effect of the order of addition of guar and salt during the preparation of a 1 M Na_2CO_3 solution of guar. Open symbols: guar is added to a salt solution; solid symbols: salt is added to a guar solution. a): USALS *I vs. q* for diluted (0.038% w/w) guar solutions. b): rheology data for concentrated (0.46%) guar solutions. Squares and circles are G' and G'', respectively; triangles are $|\eta^*|$.

Conclusions

The rheological properties and the conformation of guar in H_2O were tested as a function of solvent quality. In particular, the effects of isopropyl alcohol and that of various salts were studied. Guar in H_2O behaves essentially as a viscoelastic fluid, besides for the presence of a weak low-frequency plateau of G', hinting to a loose network due to intermolecular associations. When increasing amounts of IPA are added, the rheological behavior of the solution changes dramatically to that of a solidlike gel. Ultralow angle light scattering measurements show that the development of the elastic response of the solutions is concomitant to the growth of intermolecular associates on length scales of hundreds of microns. On smaller length scales, on the contrary, no relevant changes are observed in the structure of guar, until the precipitation point is approached. In fact, the fractal dimension only increases slightly before rapidly approaching the value $d_f = 4$ in proximity of the precipitation point. Therefore, rheology and scattering data collectively suggest that the remarkable rheological properties of guar in the presence of even small amounts of IPA be due to the enhancement of intermolecular association, rather than to a local change in chain conformation.

The influence of the salt is quite different. Four different salts were tested—NaCl, NaSCN, urea, and Na_2CO_3. They have a similar, moderate influence on the rheological properties. In fact, the rheological behavior does not change qualitatively and only a slight decrease of the complex viscosity is observed upon addition of salt. Scattering measurements indicate that virtually no changes occur in the large length scale structure of solutions, while the variation in solvent quality is reflected, to a different extent for each salt, by an increase in the fractal dimension, indicative of a more collapsed state of the polymer chains. Scattering data and rheology measurements are consistent, since less extended polymers occupy a smaller effective volume, thus leading to a lower $|\eta^*|$. The scattering profiles in the presence of sodium chloride and sodium carbonate agree with the predictions based on the Hofmeister series: NaCl has almost no effect on solubility while Na_2CO_3 shows a “salting out” effect. The behavior of guar in the presence of NaSCN, on the contrary, is in sharp contrast to that of protein solutions. In fact, for guar we observe a salting out effect with NaSCN, while sodium salicilate is usually reported to increase the solubility of proteins. This difference may stem from the different structure of proteins and other macromolecules, like guar, which have a more extended coil conformation.

A possible explanation for the decreased solubility of guar in salt solutions is the disruption of the sheath of the water molecules surrounding the chain because of the presence of the salt ions. Additional experiments investigating the effect of temperature would further test this hypothesis, since temperature will also cause the water molecules to lose much of their ordering[23] around the guar solute and ions, thus affecting the conformation and resulting rheological behavior. Likewise, similar tests on other macromolecules such as poly-ethylene-oxide would provide insight into how common the behavior seen here with guar is among water-soluble polymers in general.

We mentioned that the order of addition of the polymer and the additive (salt or IPA) is important in determining the final structure of the solution. Also important are the rate at which the additive is incorporated in the guar solution and the way the solution is mixed (e.g., with a mechanical stirrer, by using a rotating wheel, or by manually shaking). The differences in the solution properties and structure according to the preparation method demonstrate how difficult it is for the system to reach thermodynamic equilibrium. They also have important practical implications in applications and highlight the difficulties in the determination of the molecular weight of the polymer by light scattering or other methods such as gel permeation chromatography.

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