



Intrinsic viscosity and viscoelastic properties of xanthan/guar mixtures in dilute solutions: Effect of salt concentration on the polymer interactions

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Received 23 October 2006; accepted 18 March 2007

Abstract

An oscillating capillary rheometer was used to investigate the dynamic viscoelastic and intrinsic viscosity properties of deacetylated xanthan (0.025%), native xanthan (0.025%), guar gum (0.075%), and xanthan–guar mixtures in dilute solutions. Influence of ionic strength on xanthan conformation and interaction with guar gum was elaborated. As the salt concentration increased, a significant ($P < 0.05$) decrease in viscosity (η') and elasticity (η'') values was observed for both native xanthan–guar mixtures and deacetylated xanthan–guar mixtures. In water and 2 mM NaCl solution, the relative viscosity and η'' of both native xanthan–guar mixtures and deacetylated xanthan–guar mixtures were much higher than of those calculated for mixtures assuming no interaction, whereas no pronounced increase was found for polysaccharide mixtures in 40 mM NaCl. The intrinsic viscosities of deacetylated xanthan–guar mixtures in water and 2 mM NaCl were higher, whereas the intrinsic viscosities of native xanthan–guar mixtures were lower than those calculated from the weight averages of the two individually, assuming no interaction. These results demonstrated that intermolecular interaction has occurred between xanthan and guar mixtures in water and 2 mM NaCl, but may not occur in 40 mM NaCl, and mutual incompatibility may occur. The results suggest that the degree of disordering of xanthan played a critical role in xanthan–guar interaction and may explain the differences in η' , η'' , and intrinsic viscosity measurements between 2 and 40 mM NaCl.

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Keywords: Deacetylated and native xanthan; Guar; Synergistic interaction; Ionic strength; Viscoelastic; Intrinsic viscosity

1. Introduction

Xanthan gum is an anionic heteropolysaccharide produced by the microorganism *Xanthomonas campestris*. Xanthan's main backbone consists of (1 → 4) β -D-glucopyranosyl units and is substituted at C-3 on every other glucose residue with a charged trisaccharide sidechain (Jansson, Kennark, & Lindberg, 1975). The trisaccharide chain consists of a D-glucuronic acid unit between two D-

mannose units. Approximately one-half of the terminal D-mannose unit contains a pyruvic acid residue linked via keto group to the 4 and 6 positions, with an unknown distribution. The D-mannose linked to the main chain contains an acetyl group at position O-6 (Garcia-Ochoa, Santos, Casas, & Gomez, 2000). In aqueous solutions, the structure of xanthan undergoes a thermally induced transition from an ordered (helical) to a disordered conformation. This conformational transition depends on ionic strength, nature of electrolyte, pH, and acetyl and pyruvate contents (Holzwarth, 1976; Morris, Rees, Young, Walkinshaw, & Darke, 1977; Baradossi & Brant, 1982; Paoletti, Cesàro, & Delben, 1983; Norton, Goodall, Frangou, Morris, & Rees, 1984). At high temperature and low ionic

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strength, xanthan exists in solutions as a disordered structure, but reduction in temperature and/or addition of salts induces an ordered structure (Norton et al., 1984). In distilled water at 25 °C, the backbone of xanthan is disordered (or partly ordered in the form of a randomly broken helix) but highly extended due to the electrostatic repulsions from the charged groups on the sidechains (Rocheffort & Middleman, 1987). Because the structure is highly extended, the molecules may align and associate via hydrogen bonding to form a weakly structured material. Rocheffort and Middleman (1987) reported that, as the temperature increased, a transition to coil-like configuration occurs, which causes a dissociation of the molecules and a subsequent change in the rheological properties (Rocheffort & Middleman, 1987). When salt is added to the solution at 25 °C, a disorder-order transition occurs in which the backbone takes on a helical conformation, and the charged trisaccharide sidechains collapse down onto the backbone (due to charge screening effects) and stabilize the ordered conformation (Muller, Anhourrache, Lccourtier, & Chauveteau, 1986).

Guar gum is obtained from the seed of the guar plant, *Cyanopsis tetragonolobus*, and has the general structure of galactomannans. Guar gum consists of a main chain (1 → 4) β-D-mannopyranosyl unit substituted at O-6 by single-unit sidechains of α-D-galactopyranose. The ratio of mannose to galactose is approximately 1.6:1, depending on the source and method of extraction (Dea & Morrison, 1975).

A synergistic interaction occurs between xanthan gum and galactomannans in solutions, which results in enhanced viscosity or gelation (Dea & Morrison, 1975; Dea et al., 1977; Morris et al., 1977). Rocks (1971) first reported the synergistic interaction between xanthan and galactomannans. The author pointed out that xanthan gum formed thermoreversible gels when mixed with locust bean gum (LBG), but not with guar gum. Although a few researchers (Kovacs, 1973; Schorsch, Garnier, & Doublier, 1995) invoked the concept of incompatibility to explain the gelation mechanism between xanthan and galactomannans, there is a considerable body of evidence that supports the theory of intermolecular binding between xanthan and galactomannans (Cairns, Miles, & Morris, 1986; Cairns, Miles, Morris, & Brownsey, 1987; Cheetham & Mashimba, 1988, 1991; Cheetham, McCleary, Teng, Lum, & Maryanto, 1986; Cheetham & Punruckrong, 1989; Foster & Morris, 1994; Goycoolea, Foster, Richardson, Morris, & Gidley, 1994; McCleary & Neukom, 1982).

To date, the intermolecular binding mechanism between xanthan and galactomannans is still controversial, and different models have been proposed. The first model was proposed by Dea et al. (1977) and Morris et al. (1977), who reported the synergistic interaction between xanthan and galactomannans, based on a cooperative interaction, depending on the fine structure of the galactomannans. The intermolecular binding may occur between the ordered xanthan and unsubstituted or poorly substituted regions of

the galactomannan backbone (Dea et al., 1977; Morris et al., 1977). The synergistic interaction is strongly dependent on the amount of galactose content (Dea & Morrison, 1975) and galactose distribution to the regions of galactomannans backbone where the galactose units are substituted on one side (McCleary, 1979).

Tako, Asato, and Nakamura (1984) and Tako (1991) proposed a different model, in which the intermolecular interaction occurs between the sidechains of xanthan in the helical form and the backbone of the galactomannans. The authors suggested that the sidechains of the xanthan are inserted into adjacent unsubstituted regions of the galactomannan backbone, which adopts an extended, two-fold, ribbon-like conformation.

The third model was proposed by Cairns et al. (1986) and Cairns et al. (1987), in which intermolecular binding may occur between the disordered xanthan and galactomannans, and disordering of xanthan helical structure is necessary for gelation. They proposed that xanthan has a disordered, extended, twofold, cellulose-like conformation, rather than a fivefold helix, when interacting with galactomannan. Cheetham et al. (1986) and Cheetham and Mashimba (1988, 1991) proposed that the interaction occurs between the disordered segments of the xanthan chains and galactomannan.

Mannion et al. (1992) suggested that xanthan and galactomannans gelation can be explained by two different mechanisms. One takes place at room temperature, at which the interaction with ordered xanthan gives weaker elastic gels with little dependence on the galactose content of the galactomannan. The second mechanism requires heating of the polysaccharide mixture, and the interaction with heat-disordered segments of the xanthan gives a stronger gel that is highly dependent on the sidechains of the galactomannan. Zhan, Ridout, Brownsey, and Morris (1993) argued that gelation between xanthan and LBG can be explained only by a single mechanism. In agreement with Cheetham et al. (1986) and Cheetham and Mashimba (1988, 1991), they suggested that intermolecular binding involves binding of disordered segments of the xanthan chain to LBG chains in hot mixing, in which the preparation temperature is higher than the transition temperature of xanthan, and in cold mixing, in which preparation temperature is lower. The authors also suggested that the extent of disorder induced in xanthan before mixing is the main factor in the interaction (Khouryieh, Herald, Aramouni, & Alavi, 2006).

To date, much work has been accomplished on the gelling properties of the polysaccharides. The polysaccharide interactions in dilute solutions have been studied to a lesser extent. The objective of this study was to investigate the effect of salt concentration on xanthan conformation and interaction with guar gum in dilute solutions to characterize the interaction mechanism. Intrinsic viscosity and dynamic viscoelastic measurements were used to characterize the synergistic interaction and intermolecular binding for the polysaccharide mixtures.

2. Materials and methods

2.1. Materials

Xanthan gum and guar gum were purchased from Sigma (Sigma-Aldrich, St. Louis, MO, USA).

2.2. Preparation of deacetylated xanthan

Deacetylation of xanthan was achieved by dissolving 0.2% (w/v) of native xanthan in deionized distilled water, and adding 0.025 M KOH and 0.1% (w/v) KCl for 2.5 h at room temperature under an atmosphere of nitrogen. The alkali solution was neutralized with 0.05 M HCl to pH 6.5. The solution was dialyzed against deionized distilled water for 3 d by using a dialyzing tube (Snakeskin TM Pleated Dialysis Tubing, Pierce, Rockford, IL, USA), with a molecular weight cutoff of 10 kDa. The deacetylated xanthan was recovered by lyophilization (Sloneker & Jeanes, 1962).

2.3. Stock solutions preparation

The stock solutions of deacetylated xanthan (0.1%, w/v), native xanthan (0.1%, w/v) and guar gum (0.2%, w/v) were prepared by thoroughly dispersing the required amount of gum in deionized distilled water. The gum solutions were continuously stirred with a magnetic stirrer for 3 h at ambient temperature and were heated for 30 min at 90 °C in a water bath to completely hydrate the gums. Guar gum was centrifuged at 3500 g for 1 h to remove the insoluble particles. The solutions were dialyzed against deionized distilled water for 3 d by using a dialyzing tube (Snakeskin TM Pleated Dialysis Tubing, Pierce, Rockford, IL, USA), with a molecular weight cutoff of 10 kDa. Stock solutions were refrigerated at 4 °C to minimize bacterial growth.

2.4. Preparation of mixed solutions of xanthan and guar gum

To study the interaction between the polysaccharides in dilute domain, the deacetylated and native xanthan gum solutions were diluted with deionized distilled water to a final concentration of 0.025%, whereas the guar gum solution was diluted to 0.075%. The gums were blended at the following ratios: 100% xanthan:0% guar, 80% xanthan:20% guar, 60% xanthan:40% guar, 40% xanthan:60% guar, 20% xanthan:80% guar, and 0% xanthan:100% guar. The final concentrations of the mixtures were 0.025%, 0.035%, 0.045%, 0.055%, 0.065%, and 0.075%, respectively. Freshly prepared xanthan (deacetylated or native) and guar solutions were mixed at 25 °C, and were stirred with a magnetic stirrer for 3 min. To study the effect of salt on the polysaccharides and their interactions, the appropriate amounts of sodium chloride were added to the diluted solutions of deacetylated xanthan, native xanthan, and guar gum, and were completely dissolved to obtain final concentrations

of 2 and 40 mM NaCl. The concentration of each solution was confirmed by the phenol–sulfuric method (Dubois, Giles, Hamilton, Rebers, & Smith, 1956).

2.5. Determination of acetyl and pyruvate contents

The acetyl and pyruvate contents of native xanthan and deacetylated xanthan were determined by the hydroxamic acid (McComb & McCready, 1957) and the 2,4-dinitrophenylhydrazine (Sloneker & Orentas, 1962) methods, respectively.

2.6. Molecular weight determination of polysaccharides

The molecular weights of deacetylated xanthan, native xanthan, and guar gum were determined by high performance size-exclusion chromatography (HPSEC), coupled on-line with a multi-angle laser light scattering detector (MALLS) and a refractive index detector. The MALLS detector was a DAWN DSP laser photometer from Wyatt Technology Corp. (Santa Barbara, CA, USA) and the refractive index detector was a Wyatt optilab DPS interferometric refractometer. A PL aquagel–OH mixed 8- μ m column (Polymer Labs, Amherst, MA, USA) was used. A sample volume of 100 μ mL was injected at a flow rate of 1 ml/min, using 100 mM NaCl as the mobile phase, at a temperature of 30 °C. The dn/dc used for xanthan was 0.145 and for guar was 0.13. The data were analyzed by using Astra software version 4.5 (Wyatt Technology Corp., Santa Barbara, CA, USA).

2.7. Density measurement

The densities of the polysaccharide solutions were determined with a standardized 10-mL pycnometer (Kmax®, Kimble Glass Inc, Vineland, NJ, USA). The mass of the solution was calculated from the weight difference between the empty pycnometer and the filled vessel. The pycnometer was filled with each respective polysaccharide solution and was incubated at 20 °C for 1 h (Equatherm, Lab-Line Instruments Inc, Melrose Park, IL, USA) to equilibrate the sample before density determinations (Yaseen, Herald, Aramouni, & Alavi, 2005).

2.8. Rheological properties

The viscous (η') and elastic (η'') components of the polysaccharide solutions and their mixtures were measured as a function of oscillating shear rate by using an oscillating capillary rheometer (Viscoelasticity Analyzer, Vilastic 3, Vilastic Scientific, Inc., Austin, TX, USA). The instrument and theory of measurement are described elsewhere (Thurston, 1960, 1976). The viscoelasticity analyzer is based on the principles of generating oscillatory flow at a selected frequency within a straight, cylindrical, stainless steel tube (0.0504 cm radius and 6.038 cm length). The Vilastic instrument produces an oscillatory flow in a capillary,

and measures the pressure and volumetric flow rate, allowing the determination of both viscous and elastic components of a fluid sample.

The complex coefficient of viscosity (η^*) consists of viscous (η') and elastic (η'') components, and is defined as

$$\eta^* = \eta' - i\eta'' \quad (1)$$

where i is an imaginary number. The η' and η'' are related to dissipated and recovered energy, respectively. Similarly, complex rigidity (G^*) is defined as

$$G^* = G' + iG'' \quad (2)$$

where G' is the storage modulus and G'' is the loss modulus. The complex coefficient of viscosity is related to the complex rigidity modulus by

$$\eta^* = G^*/i\omega \quad (3)$$

or

$$\eta' = G'/\omega \quad \text{and} \quad \eta'' = G''/\omega$$

where the radian frequency $\omega = 2\pi f$, and f is the frequency in Hertz.

The η' and η'' of dilute solutions of xanthan and guar were determined in the shear-rate range $0.8\text{--}30 \text{ s}^{-1}$ at a frequency of 2 Hz. Morris and Taylor (1982) reported that oral perception of solution viscosity correlated well with viscosity measurements at 10 s^{-1} . Thus, all η' and η'' measurements were statistically assessed at 10 s^{-1} . Rheological measurements were carried out at $20 \text{ }^\circ\text{C} \pm 0.1$ by using a temperature-controlled circulating water bath (Haake DC5, Gebr. Haake GmbH, Karlsruhe, Germany). The viscoelasticity analyzer was calibrated with deionized distilled water at $20 \text{ }^\circ\text{C}$ before the verification procedure to further ensure that the rheometer was operating at optimum accuracy.

2.9. Intrinsic viscosity determination

Intrinsic viscosity, denoted as $[\eta]$, is a useful experimental parameter in the study of dilute solutions. Intrinsic viscosity is a measure of the hydrodynamic volume occupied by the individual polymer molecules in isolation (Richardson & Kasapis, 1998). In dilute solutions, the polymer chains are separate, and the $[\eta]$ of a polymer in solution depends only on the dimensions of the polymer chain. Because $[\eta]$ indicates the hydrodynamic volume of the polymer molecule and is related to the molecular weight, it provides deep insights into the molecular characteristics of a biopolymer (Rao, 1999).

One approach to determine the intrinsic viscosity is through extrapolation to infinite dilution, according to the Huggins (1942) empirical expression:

$$\frac{\eta_{sp}}{C} = [\eta] + k'[\eta]^2 C \quad (4)$$

where the specific viscosity (η_{sp}) = $(\eta - \eta_s)/\eta_s = \eta_{rel} - 1$, and the relative viscosity (η_{rel}) = η/η_s . k' is Huggins constant, and η and η_s are the apparent viscosities of the solu-

tion and the solvent, respectively. The extrapolations to zero concentration are usually determined by plotting η_{sp}/C versus C or $\ln(\eta_{rel})/C$ versus C , which would result in straight lines, respectively. Tanglerpaibul and Rao (1987) determined the intrinsic viscosity from the relative viscosity by using the expression:

$$\eta_{rel} = 1 + [\eta]C \quad (5)$$

The $[\eta]$ was obtained from the slope of η_{rel} vs. C plot, which gave straight lines, with linear regression correlation coefficients in the range 0.99–1.0. Chou and Kokini (1987) suggested a similar method for polyelectrolytes, in which the interactions between macromolecules in dilute solutions are not existent, and the second term of the Huggins equation is negligible; therefore, a plot of η_{sp} vs. C is linear.

In this study, the $[\eta]$ was determined for each solution by measuring relative viscosities of polysaccharides solutions within the range $1.2 < \eta_{rel} < 2.0$ at $\gamma = 10 \text{ s}^{-1}$. The intercept of η_{sp}/C vs. C plot in the dilute domain gave the first estimation of $[\eta]$ for guar gum, whereas the slope of η_{rel} vs. C plot gave the first estimation of $[\eta]$ for xanthan and xanthan–guar mixtures.

2.10. Statistical analysis

A two-way factorial design was used for the study of rheological properties. For all polysaccharides samples, three replications were performed. The analysis of variance (ANOVA) and general linear models procedure (GLM) were conducted with Statistical Analysis System (2002–2003) (version 9.1, SAS Institute, Inc., Cary, NC, USA). Comparisons among treatments were analyzed by using Fisher's least significant difference (LSD), with a significance level of $P < 0.05$.

3. Results and discussion

3.1. Characterization of polysaccharides

Values of acetyl and pyruvate contents, and weight average molecular weights for the polysaccharides, are given in Table 1. The molecular weights of native xanthan (2.65×10^6) and deacetylated xanthan (2.36×10^6) were much larger than that of guar gum (1.45×10^6). Some reduction in molecular weight of native xanthan occurred due to the chemical modification. The acetate and pyruvate contents of native xanthan were 3.51% and 0.9%, respectively. Deacetylation of xanthan removed approximately

Table 1
Chemical composition of native xanthan, deacetylated xanthan, and guar gum

Polysaccharide	Acetate (%)	Pyruvate (%)	Molecular weight
Native xanthan	3.51	0.9	2.65×10^6
Deacetylated xanthan	0.32	0.9	2.36×10^6
Guar	–	–	1.45×10^6

91% of the acetate content, but it did not affect the pyruvate content of xanthan.

3.2. Interaction of polysaccharides

To evaluate the synergistic/non-synergistic effect of the xanthan–guar mixtures in dilute solutions, the η_{rel} of polysaccharides and their mixtures were plotted as a function of xanthan fraction at $\gamma = 10 \text{ s}^{-1}$ (Fig. 1a and b). Fig. 1a shows the η_{rel} behavior of native xanthan, guar gum, and their mixtures in water, 2 and 40 mM NaCl at $\gamma = 10 \text{ s}^{-1}$ and 25 °C. Fig. 1b depicts η_{rel} behavior of deacetylated xanthan, guar gum, and their mixtures. In water and 2 mM NaCl, the relative viscosities of both native xanthan–guar mixtures and deacetylated xanthan–guar mixtures were much higher than the relative viscosities calculated for mixtures assuming no interaction, whereas no pronounced increase was found for polysaccharide mixtures in 40 mM NaCl. Such deviations from the values calculated for mixtures assuming no interaction may be explained in terms of specific molecular interactions between xanthan and guar gum. In the 2 mM NaCl, a smaller synergistic interaction was observed, whereas a stronger synergy in the absence of salt was noted. No synergistic interaction was found in 40 mM NaCl. The η_{rel} of native xanthan–guar mixtures and deacetylated xanthan–

guar mixtures varied with respect to polysaccharide ratio. The maximum viscosity synergistic interaction for native xanthan–guar mixtures was observed at a ratio of 60:40, whereas the maximum viscosity synergistic interaction for deacetylated xanthan–guar mixtures was obtained at a ratio of 80:20. These results show the influence of xanthan conformation on the increase of viscosity for the polysaccharide mixtures, reflecting that intermolecular interaction occurred between xanthan and guar gum mixtures in water and 2 mM NaCl, but not in 40 mM NaCl solution.

The viscosity measurements in dilute solutions were further supported by η'' measurements determined by capillary viscometry (Fig. 2a and b). Fig. 2a and b depict the η'' behavior as a function of mixing ratio of native xanthan–guar mixtures and deacetylated xanthan–guar mixtures, respectively, in water and 2 and 40 mM NaCl at $\gamma = 10 \text{ s}^{-1}$. There was very pronounced increase in η'' for both native xanthan–guar mixtures and deacetylated xanthan–guar mixtures in water and 2 mM NaCl, whereas the η'' of the polysaccharide mixtures was diminished in 40 mM NaCl, confirming the viscosity measurements.

To further characterize the intermolecular interaction between the polysaccharides in water and salt solutions, the η' and η'' values in dilute solutions at $\gamma = 10 \text{ s}^{-1}$ were statistically analyzed (Table 2). As shown in Table 2, significant differences ($P < 0.05$) in η' and η'' values were found between water and salt solutions for the native xanthan–guar mixtures and deacetylated xanthan–guar mixtures.

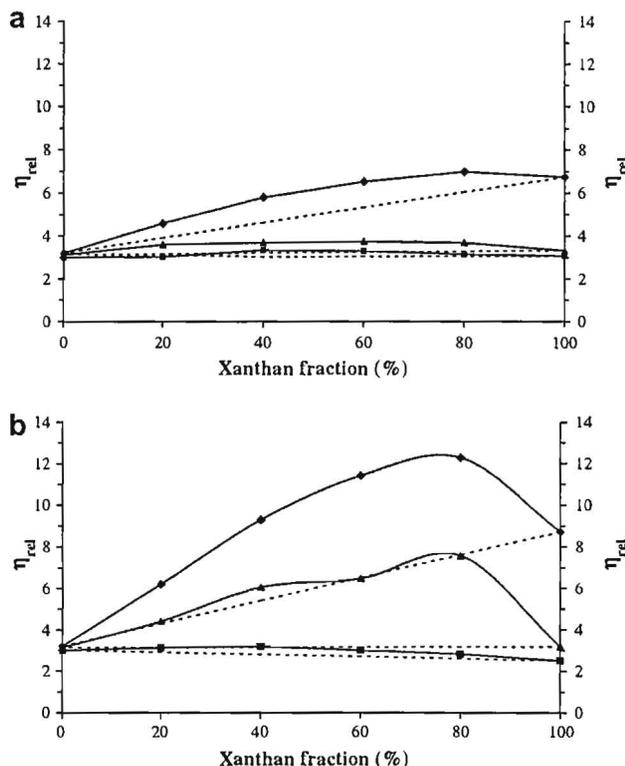


Fig. 1. Relative viscosity (η_{rel}) against xanthan fraction for (a) native xanthan–guar mixtures and (b) deacetylated xanthan–guar mixtures. (◆) water; (▲) 2 mM NaCl; (■) 40 mM NaCl; (---) values calculated for mixtures assuming no interaction.

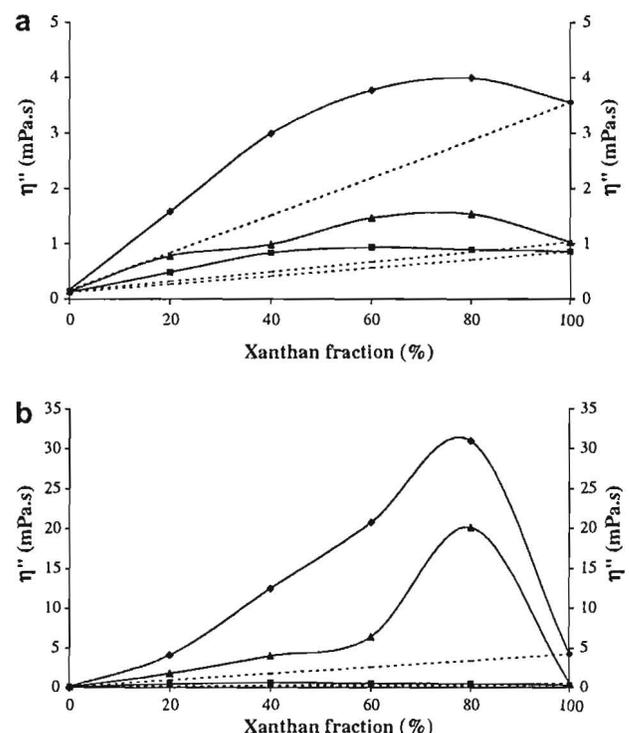


Fig. 2. Elasticity (η'') against xanthan fraction for (a) native xanthan–guar mixtures and (b) deacetylated xanthan–guar mixtures. (◆) water; (▲) 2 mM NaCl; (■) 40 mM NaCl; (---) values calculated for mixtures assuming no interaction.

Table 2

Effect of ionic strength on the dynamic viscoelastic parameters of native xanthan–guar blends and deacetylated xanthan–guar blends measured at 20 °C and 10 s⁻¹

	Viscosity (mPa s)			Elasticity (mPa s)		
	0 mM NaCl	2 mM NaCl	40 mM NaCl	0 mM NaCl	2 mM NaCl	40 mM NaCl
<i>Native xanthan:guar (%)</i>						
100:0	6.78 ^a ± 0.15	3.33 ^b ± 0.11	3.11 ^c ± 0.03	3.55 ^a ± 0.11	1.03 ^b ± 0.08	0.86 ^b ± 0.01
80:20	7.05 ^a ± 0.05	3.92 ^b ± 0.18	3.23 ^c ± 0.06	3.99 ^a ± 0.21	1.54 ^b ± 0.25	0.90 ^c ± 0.02
60:40	6.57 ^a ± 0.06	3.94 ^b ± 0.18	3.34 ^c ± 0.03	3.77 ^a ± 0.28	1.47 ^b ± 0.32	0.94 ^c ± 0.01
40:60	6.09 ^a ± 0.17	3.72 ^b ± 0.04	3.44 ^c ± 0.04	2.99 ^a ± 0.09	0.99 ^b ± 0.07	0.84 ^b ± 0.05
20:80	4.71 ^a ± 0.06	3.64 ^b ± 0.18	3.20 ^c ± 0.22	1.58 ^a ± 0.02	0.78 ^b ± 0.09	0.48 ^c ± 0.04
0:100	3.24 ^a ± 0.14	3.16 ^{ab} ± 0.14	3.04 ^b ± 0.03	0.16 ^a ± 0.03	0.14 ^a ± 0.02	0.12 ^a ± 0.02
<i>Deacetylated xanthan:guar (%)</i>						
100:0	8.93 ^a ± 0.92	3.25 ^b ± 0.06	2.56 ^b ± 0.05	4.23 ^a ± 0.68	0.54 ^b ± 0.06	0.31 ^b ± 0.03
80:20	12.16 ^a ± 1.54	7.97 ^b ± 0.23	2.88 ^c ± 0.09	30.96 ^a ± 2.66	20.13 ^b ± 2.88	0.49 ^c ± 0.03
60:40	11.81 ^a ± 0.46	6.88 ^b ± 0.51	3.04 ^c ± 0.05	20.75 ^a ± 2.25	6.41 ^a ± 1.35	0.56 ^c ± 0.05
40:60	10.0 ^a ± 0.15	6.11 ^b ± 0.31	3.37 ^c ± 0.01	12.46 ^a ± 0.57	4.03 ^b ± 0.85	0.67 ^c ± 0.01
20:80	6.27 ^a ± 0.49	4.81 ^b ± 0.29	3.17 ^c ± 0.15	4.08 ^a ± 0.52	1.78 ^b ± 0.44	0.47 ^b ± 0.06
0:100	3.24 ^a ± 0.14	3.16 ^a ± 0.14	3.04 ^a ± 0.03	0.16 ^a ± 0.03	0.14 ^a ± 0.02	0.12 ^a ± 0.02

^{a,b,c} Means followed by the same letters in the same row are not significantly different ($P \leq 0.05$). Results are expressed as means ± SD for three replications.

As the salt concentration increased, a significant ($P < 0.05$) decrease in η' and η'' values was observed for both native xanthan–guar mixtures and for the deacetylated xanthan–guar mixtures. The η' of native xanthan significantly decreased as the salt concentration increased, whereas no significant difference was found in the η'' values between 2 and 40 mM NaCl. The η' and η'' values of deacetylated xanthan significantly decreased in salts, compared with values in water solutions, but no significant decrease was found between 2 and 40 mM NaCl. The decrease in η' and η'' values in salt exhibited a typical polyelectrolyte behavior. This decrease with the addition of salt was due to the charge screening of electrostatic repulsions of the trisaccharide sidechains (Muller et al., 1986; Rochefort & Middleman, 1987). The charge screening led to a more compact conformation and caused a reduction in hydrodynamic size of the molecule (Rochefort & Middleman, 1987), hence, lowering the viscosities and elasticities. In contrast, guar gum, which is a neutral polysaccharide, exhibited no significant difference in η' and η'' values between water and salt solutions.

In aqueous solutions, the structure of xanthan undergoes an 'order–disorder' transition from helix to coil structure. This conformational transition depends on temperature, ionic strength of solutions, nature of electrolyte, pH, and acetate and pyruvate contents (Baradossi & Brant, 1982; Holzwarth, 1976; Morris et al., 1977; Norton et al., 1984). Our results show the influence of xanthan conformation on the increase of η' and η'' in water and 2 mM NaCl, reflecting that intermolecular binding between xanthan (native and deacetylated) and guar gum has occurred in dilute solutions. Xanthan is in the disordered conformation in distilled, deionized water at 25 °C, whereas, in salt at 25 °C, xanthan starts to take on an ordered conformation due to charge screening effects. In distilled water at 25 °C, the backbone of xanthan is disordered, but highly

extended, due to the electrostatic repulsions from the charged groups on the trisaccharide sidechains (Rochefort & Middleman, 1987). Because the structure is highly extended, the molecules may align and associate by hydrogen bonding to form a weakly structured material. Therefore, as the temperature increases, a transition to coil-like configuration occurs, which causes a dissociation of the molecules and a subsequent change in the rheological properties (Rochefort & Middleman, 1987). When salt is added to the solution at 25 °C, a disorder–order transition occurs in which the backbone takes on a helical conformation, and the charged trisaccharide sidechains collapse down onto the backbone (due to charge screening effects) and stabilize the ordered conformation (Muller et al., 1986). Mixing the polysaccharides in 40 mM NaCl substantially diminished the molecular associations between xanthan and guar gum, as indicated by the pronounced decreases in the η' and η'' values. The η' and η'' differences in water, 2 mM NaCl, and 40 mM NaCl can be explained in terms of disordering degree of xanthan structure. In water, xanthan is in the disordered conformation. Optical-rotation studies (Lecourtier, Chauveteau, & Muller, 1986; Milas & Rinaudo, 1986; Cheetham & Mashimba, 1988, 1991) have confirmed that xanthan is in the disordered conformation in water at room temperature. Electrostatic repulsions that involve glucuronate and pyruvate in the sidechains are poorly shielded, thus favoring the disordered conformation (Cheetham & Mashimba, 1991). In 2 mM NaCl, xanthan is partly ordered, whereas the molecule is completely ordered in 40 mM NaCl. Muller et al. (1986), using optical-rotation studies, noted a sharp transition in xanthan structure at 10 mM NaCl. Norton et al. (1984) reported that a complete conformational ordering would occur at 25 °C only for salt concentrations in excess of 35 mM. Rochefort and Middleman (1987) observed a gradual transition in the shear viscosity of a 250-ppm xanthan solution, confirming the

idea of co-existence of ordered and disordered regions in a single chain. They concluded that a complete ordered conformation can be obtained for salt concentrations > 10 mM NaCl. Thus, the highly disordered xanthan was capable of directly interacting with guar gum to form heterotypic structures and a higher synergistic interaction (Zhan et al., 1993; Goycoolea et al., 1994; Morris, Brownsey, & Ridout, 1994; E.R. Morris, 1996; V.J. Morris, 1996). These results support previous studies (Cheetham & Mashimba, 1988, 1991; Khouryeh et al., 2006; Zhan et al., 1993) proposing that intermolecular binding occurred between galactomannans and disordered segments of xanthan.

3.3. Intrinsic viscosities of polysaccharides

The intermolecular binding between xanthan and guar gum was further supported by the intrinsic viscosities of xanthan and guar mixtures (Fig. 3a and b). Fig. 3a and b depict the intrinsic viscosities against the percentage of xanthan fraction at different ionic strengths for native xanthan–guar mixtures and deacetylated xanthan–guar mixtures, respectively. The intrinsic viscosities of deacetylated xanthan–guar mixtures in water and 2 mM NaCl were higher than the calculated values assuming no interaction, whereas the intrinsic viscosities of native xanthan–guar

mixtures were lower than the calculated values assuming no interaction, demonstrating that intermolecular interaction occurred between xanthan and guar gum in water and 2 mM NaCl. If no interaction existed between the two polymers in the mixtures, a linear relationship between intrinsic viscosity and xanthan fraction would be observed, and the intrinsic viscosities for the mixtures would be only the weight averages of the two polymers. Instead, the intrinsic viscosities of the mixtures was out of linearity, suggesting that specific attractive forces were present between the xanthan and guar molecules in water and 2 mM NaCl. In 40 mM NaCl, however, a linear relationship was found between the intrinsic viscosities and xanthan fraction for both deacetylated xanthan–guar mixtures and native xanthan–guar mixtures, suggesting that the intrinsic viscosities of the mixtures were only the weight averages of the two polymers, and that no specific interaction forces were present between the two polymers that would encourage aggregation. The ordered, helical structure of xanthan was stabilized in 40 mM NaCl; thus, the interaction between xanthan and guar gum diminished. The results suggest that the intermolecular binding between xanthan and guar gum may not occur in 40 mM NaCl, and mutual incompatibility may take place under these conditions. These results are in agreement with a previous study conducted by Wang, Wang, and Sun (2002). The discrepancy in the intrinsic viscosities behavior of both deacetylated xanthan–guar mixtures and native xanthan–guar mixtures in water and salts solutions can be explained again in terms of disordering degree of xanthan structure. In 2 mM NaCl, xanthan is partly ordered, whereas the molecule is completely ordered in 40 mM NaCl.

Intrinsic viscosity of polymers is dependent on their molecular weight and chain dimension (Flory, 1953). In dilute solutions, the polymer chains are separate, so $[\eta]$ of a polymer in solution depends only on the dimensions of the polymer chain (Rao, 1999). The strong intermolecular binding between deacetylated xanthan and guar gum can be attributed to the increased chain flexibility of deacetylated xanthan, which may facilitate the interaction with guar gum. The intrinsic viscosities of native xanthan–guar mixtures increased as the xanthan fraction increased in the mixtures. The intrinsic viscosities of native xanthan–guar mixtures were lower than the calculated values assuming no interaction. Because xanthan plays a crucial role in controlling the viscosity of xanthan–guar mixtures, the decrease in intrinsic viscosities of their mixtures can be attributed to the conformational change of xanthan from a helical form to a more flexible form because of binding. Xanthan conformation change outweighed the increase of intrinsic viscosity due to binding of guar gum to xanthan; thus, the dramatic decrease of the intrinsic viscosities of the mixtures was observed. These results suggests that conformational change of deacetylated xanthan may not predominate in controlling the intrinsic viscosity, and that deacetylated xanthan may be in an exact conformation to bind guar gum.

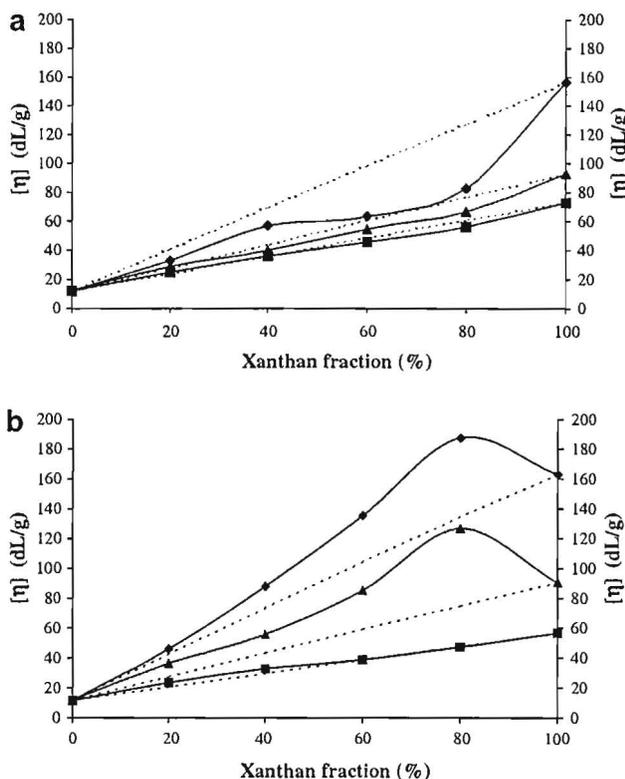


Fig. 3. Plots of intrinsic viscosities against xanthan fraction. (a) Native xanthan–guar mixtures and (b) deacetylated xanthan–guar mixtures. (◆) water; (▲) 2 mM NaCl; (■) 40 mM NaCl; (---) values calculated for mixtures assuming no interaction.

Table 3 shows the values of the intrinsic viscosities of deacetylated xanthan, native xanthan, guar gum, and their mixtures in water and salt solutions. The $[\eta]$ of deacetylated and native xanthan decreased significantly ($p < 0.05$) as the salt concentration increased, showing a typical behavior of polyelectrolytes. The charge screening for electrostatic repulsions of the trisaccharide sidechains from NaCl led to a more compact conformation and caused a significant reduction in hydrodynamic size of the molecule. Thus, the $[\eta]$ was decreased. On the other hand, salt exhibited little effect on the $[\eta]$ guar gum due to the non-ionic nature of guar gum. The $[\eta]$ of guar gum decreased slightly with no significant difference as the salt concentration increased.

The $[\eta]$ of deacetylated xanthan in water was higher than the $[\eta]$ of native xanthan. Deacetylated xanthan had a $[\eta]$ of 163 dl/g, whereas the $[\eta]$ of native xanthan was 156 dl/g; however, the difference was not statistically significant ($P > 0.05$). This is consistent with findings reported by Callet, Milas, and Rinaudo (1987), who showed that acetyl and pyruvate contents have no influence on the intrinsic viscosity of xanthan in dilute solution. The $[\eta]$ of guar gum was 12 dl/g. Deacetylated and native xanthan had a much higher $[\eta]$ than guar gum, which can be attributed to the significant difference in their chain stiffness. Xanthan has a stronger chain stiffness than the flexible, random-coil conformation of guar gum, which may increase the chain dimensions, resulting in, a higher $[\eta]$.

3.4. Coil-overlap parameter of polysaccharides

In dilute solutions, the individual polymer coils are separate from each other and are free to move independently. With increasing concentrations, the coils start to overlap and interpenetrate one another. The transition from dilute

Table 3

Effect of ionic strength on the intrinsic viscosity of native xanthan–guar blends and deacetylated xanthan–guar blends measured at 20 °C and 10 s^{-1}

	$[\eta]$ (dL/g)		
	0 mM NaCl	2 mM NaCl	40 mM NaCl
<i>Native xanthan:guar (%)</i>			
100:0	155.7 ^a ± 9.3	92.9 ^b ± 2.7	73.2 ^c ± 1.1
80:20	82.2 ^a ± 2.8	66.0 ^b ± 1.3	56.1 ^c ± 2.2
60:40	63.3 ^a ± 1.4	54.3 ^b ± 0.9	45.3 ^c ± 1.8
40:60	56.9 ^a ± 7.2	39.8 ^b ± 1.4	36.0 ^b ± 1.5
20:80	32.8 ^a ± 2.9	29.2 ^{ab} ± 0.7	25.0 ^b ± 2.5
0:100	12.0 ^a ± 2.1	11.9 ^a ± 0.6	11.7 ^a ± 0.6
<i>Deacetylated xanthan:guar (%)</i>			
100:0	163.0 ^a ± 5.0	90.6 ^b ± 2.3	56.7 ^c ± 3.3
80:20	187.4 ^a ± 5.8	126.6 ^b ± 5.2	47.2 ^c ± 2.5
60:40	135.0 ^a ± 7.3	85.2 ^b ± 1.4	38.7 ^c ± 0.8
40:60	88.0 ^a ± 5.6	55.8 ^b ± 1.1	32.7 ^c ± 0.2
20:80	46.1 ^a ± 2.8	36.4 ^b ± 2.2	23.4 ^c ± 1.6
0:100	12.0 ^a ± 2.1	11.9 ^a ± 0.6	11.7 ^a ± 0.6

^{a,b,c} Means followed by the same letters in the same row are not significantly different ($P \leq 0.05$). Results are expressed as means ± SD for three replications.

solutions to concentrated solutions is usually accompanied by a pronounced change in the concentration dependence of solution viscosity (Morris, Cutler, Ross-Murphy, Res, & Price, 1981; Morris, 1995). The corresponding concentration is called critical or coil-overlap concentration (C^*). For random-coil polysaccharide solutions except for galactomannans, Morris et al. (1981) reported that the slope of double logarithmic plots of η_{sp} against $C[\eta]$ was close to 1.4 in a dilute regime, whereas, in the concentrated regime, the slope increased to 3.3. The C^* transition occurred at a value of $C[\eta]$ close to 4, and the η_{sp} at this degree of coil overlap was invariably close to 10. Guar gum was found to deviate from those observations. The C^* transition of guar gum occurred at a lower value of the coil-overlap parameter $C[\eta] = 2.5$, and the viscosity showed a higher dependence on concentration, with a slope of 5.1 instead of 3.3 (Morris et al., 1981).

In this study, all the polysaccharides systems were studied in the dilute regime. Figs. 4a and b and 5a and b show the double logarithmic plot of η_{sp} against coil-overlap parameter ($C[\eta]$) for native xanthan–guar mixtures and deacetylated xanthan–guar mixtures in 2 and 40 mM NaCl, respectively. There was no change in the slope of the double logarithmic plot of η_{sp} against $C[\eta]$, indicating that no molecular entanglements were obtained, and polysaccha-

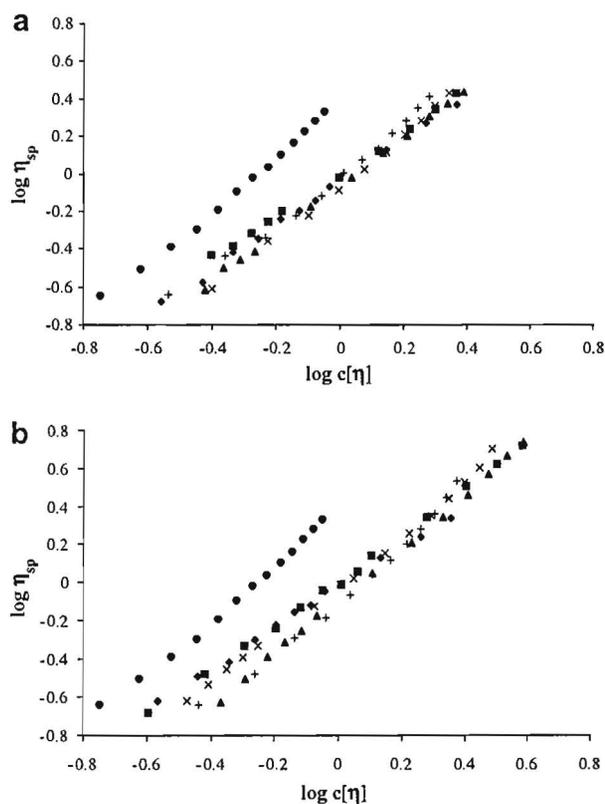


Fig. 4. Double logarithmic plot of specific viscosity (η_{sp}) against coil-overlap parameter ($c[\eta]$) in 2 mM NaCl for (a) deacetylated xanthan–guar mixtures, (b) native xanthan–guar mixtures. Xanthan:guar ratio: (◆) xanthan, (●) guar, (■) 4:1, (▲) 3:2, (×) 2:3, (+) 1:4.

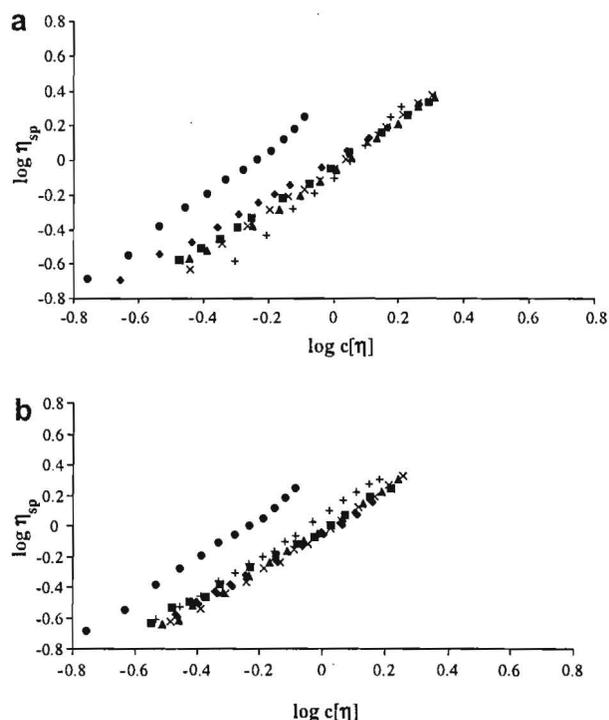


Fig. 5. Double logarithmic plot of specific viscosity (η_{sp}) against coil-overlap parameter ($c[\eta]$) in 40 mM NaCl for (a) deacetylated xanthan-guar mixtures, (b) native xanthan-guar mixtures. Xanthan:guar ratio: (◆) xanthan, (●) guar, (■) 4:1, (▲) 3:2, (×) 2:3, (+) 1:4.

ride mixtures in 2 and 40 mM NaCl were in the dilute domain. The slope values of the double logarithmic plot of η_{sp} against $C[\eta]$ are given in Table 4. As shown in Table 4, the slope of native xanthan and deacetylated xanthan in salt solutions significantly decreased, comparing with the slope in water solutions, whereas no significant change

Table 4
Effect of ionic strength on the slope of native xanthan-guar blends and deacetylated xanthan-guar blends measured at 20 °C and 10 s⁻¹

	Slope		
	0 mM NaCl	2 mM NaCl	40 mM NaCl
<i>Native xanthan:guar (%)</i>			
100:0	1.38 ^a ± 0.02	1.17 ^b ± 0.03	1.11 ^b ± 0.03
80:20	1.51 ^a ± 0.01	1.17 ^a ± 0.04	1.20 ^a ± 0.02
60:40	1.34 ^a ± 0.16	1.28 ^a ± 0.02	1.27 ^a ± 0.02
40:60	1.55 ^a ± 0.02	1.38 ^b ± 0.02	1.36 ^b ± 0.02
20:80	1.69 ^a ± 0.02	1.31 ^b ± 0.04	1.33 ^b ± 0.08
0:100	1.44 ^a ± 0.06	1.41 ^a ± 0.01	1.39 ^a ± 0.01
<i>Deacetylated xanthan:guar (%)</i>			
100:0	1.32 ^a ± 0.05	1.09 ^b ± 0.03	1.17 ^c ± 0.02
80:20	1.22 ^{ab} ± 0.03	1.25 ^a ± 0.05	1.18 ^b ± 0.03
60:40	1.33 ^{ab} ± 0.03	1.38 ^a ± 0.02	1.28 ^b ± 0.03
40:60	1.43 ^a ± 0.07	1.36 ^b ± 0.04	1.33 ^b ± 0.03
20:80	1.35 ^{ab} ± 0.06	1.41 ^a ± 0.04	1.32 ^b ± 0.02
0:100	1.44 ^a ± 0.06	1.41 ^a ± 0.01	1.39 ^a ± 0.01

^{a,b,c} Means followed by the same letters in the same row are not significantly different ($P \leq 0.05$). Results are expressed as means ± SD for three replications.

was observed for guar gum solutions. Our results showed that the slopes of xanthan and guar were lower than those reported by Morris et al. (1981), Cuvelier and Launay (1986), Launay, Cuvelier, and Martinez-Reyes (1997), demonstrating that both xanthan (0.025%) and guar gum (0.075%) were in the dilute domain ($C < C^*$). The slopes for deacetylated xanthan and deacetylated xanthan-guar mixtures were lower than those for native xanthan and native xanthan-guar mixtures, indicating more flexible xanthan due to the deacetylation.

4. Conclusion

Synergistic interactions for both native xanthan-guar mixtures and deacetylated xanthan-guar mixtures in the dilute regime were observed in water and 2 mM NaCl, but not in 40 mM NaCl. A stronger synergistic interaction was noted for deacetylated xanthan-guar mixtures. The results suggest that intermolecular interaction has occurred between xanthan and guar gum mixtures in water and 2 mM NaCl, but may not occur in 40 mM NaCl, and mutual incompatibility may occur. The results suggest that the degree of disordering of xanthan played a critical role in xanthan-guar interaction and may explain the differences in η' , η'' , and $[\eta]$ measurements between 2 and 40 mM NaCl, and hence, the intermolecular interaction that occurred between the backbone of guar gum and the disordered segments of xanthan.

Acknowledgements

This research was supported by the Kansas Agricultural Experiment Station (contribution no. 07-68-J from the Kansas Agricultural Experiment Station, Manhattan, Kansas). The authors would like to thank Dr Scott Bean with USDA-ARS, GMPCRC for his help in determining the molecular weight for the polysaccharides.

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