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Viscosity of locust bean, guar and xanthan gum solutions in the Newtonian domain: a critical examination of the log $(\eta_{sp})_o$–log $C[\eta]_o$ master curves

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The viscosity in the low shear rate Newtonian domain of three biopolymers, locust bean gum, guar gum and xanthan gum was studied as a function of temperature and of polymer concentration in various aqueous solvents. The intrinsic viscosities $[\eta]_o$ of both galactomannans are not modified in the presence of 10 or 40% sucrose. In this case, a master curve relating the Newtonian specific viscosity $(\eta_{sp})_o$ to the reduced concentration $C[\eta]_o$ is obtained and allows (in good agreement with theoretical conjectures), two critical concentrations C^* and C^{**} to be defined, from which the value of the expansion coefficient α may be estimated. For xanthan, as expected for a polyelectrolyte, $[\eta]_o$ depends strongly on salt concentration and on added sucrose and the results did not obey the above-mentioned master curve. However, it is shown that $(\eta_{sp})_o$ depends only on xanthan concentration when $C > C^{**}$, and then it is assumed that chain dimensions have attained their unperturbed values whatever the solvent. Considering that both types of chains, random coils (galactomannans) and semi-rigid (xanthan) should give the same $(\eta_{sp})_o$–$C[\eta]_o$ master curve for $C > C^{**}$ when $[\eta]_o$ is replaced by its unperturbed counterpart $[\eta]_\theta$, a method for estimating $[\eta]_\theta$ for the xanthan sample is proposed. In conclusion, the numerous exceptions to the widely accepted $(\eta_{sp})_o$ vs $C[\eta]_o$ "universal" behaviour are mainly ascribed to significant differences in expansion coefficient values which depend on both the polymer and the solvent. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

To understand the viscous properties of biopolymer solutions in the low shear rate Newtonian domain is of practical value, for example, for predicting their efficiency as thickeners in liquid foods or as stabilizers in dispersed systems. From a more fundamental point of view, it has been shown (Doublier and Launay, 1976) that the "corresponding state principle" (Simha and Zakin, 1960) may be applied to galactomannan samples varying in chain length and in mannose/galactose ratios: in aqueous solution an unique master curve $\log(\eta_{sp})_o$ (zero shear rate specific viscosity) vs log $C[\eta]_o$ (reduced concentration) is obtained. These results have been confirmed (Sabater de Sabates, 1979; Robinson *et al.*, 1982) and extended to other biopolymers (Morris *et al.*, 1981). In the dilute régime ($C < C_{cr}$) the slope of the master curve is in the range 1.2–1.3 and, in the semidilute régime ($C > C_{cr}$), the slope has been found in some cases close to 3.75, a value which may be derived from a theoretical approach proposed by De Gennes (1979). However, the published values of the slopes may vary for random coil polymers in good solvent from 3–4 up to 5 (Launay *et al.*, 1986). Patel *et al.* (1987) have even found a slope equal to 6.3 for guar gum and, more recently, Kapoor *et al.* (1994) have obtained a value of 6.5 for a galactomannan (M/G = 3.5) isolated from a seed of *Cassia nodosa*. However, for xanthan gum, we have shown that two critical concentrations C^* and C^{**}, instead of one (C_{cr}), are manifest on log $(\eta_{sp})_o$ vs log $C[\eta]_o$ plots (Launay *et al.*, 1984, 1986; Cuvelier and

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Launay, 1986).It may be noted that light scattering measurements on xanthan gum lend support to the existence of two critical concentrations whose values are consistent with C^* and C^{**} (Southwick *et al.*, 1981). The opinion has been expressed that this type of behaviour could be extended to other biopolymers (Launay *et al.*, 1986). Thereafter, two critical concentrations have also been found for carboxymethylcellulose (CMC) and hydroxyethylcellulose (HEC) solutions (Castelain *et al.*, 1987). In the intermediate concentration régime ($C^* < C < C^{**}$), the slopes of log $(\eta_{sp})_o$ vs log $C[\eta]_o$ are approx. 2–2.5 (Launay *et al.*, 1986; Castelain *et al.*, 1987).

It has been claimed that random coil polymers obey a universal behaviour expressed through the existence of a unique log $(\eta_{sp})_o$–log $C[\eta]_o$ master curve. Some exceptions (locust bean gum, guar gum, hyaluronate at low pH and high ionic strength) have been attributed to specific molecular interactions creating "hyperentanglements" between chains (Morris *et al.*, 1981). Also, Castelain *et al.* (1987) have obtained non-superimposed results for CMC and HEC in 0.1 M NaCl. However, some doubt has been cast (Launay *et al.*, 1986) on the truly universal character of these plots. In particular, it has been previously demonstrated that the effectiveness of $C[\eta]_o$ as a reduced variable may break down because it does not take into account osmotic compression in good solvents (Simha and Zakin, 1960; Simha and Utracki, 1973). Following the screening principle of De Gennes (1979), Graessley (1980) has described the progressive change in chain dimensions with polymer concentration:

- in the dilute régime ($C < C^*$), polymer coils have "infinite dilution" dimensions
- in the intermediate régime ($C^* < C^{**}$), polymer coils are in contact and progressively shrink as concentration increases
- in the semidilute régime ($C > C^{**}$), polymer coils have reached their limiting size (unperturbed or θ-dimensions). In this régime, polymer chains have to entangle more and more.

In addition, Graessley (1980) has considered that, in good solvents, a third critical concentration Ce ($C^* < Ce < C^{**}$) should exist, the chains at concentrations between Ce and C^{**} having not attained their θ-dimensions but being entangled. Lefebvre (1982) has used these concepts for interpreting the viscous properties in the Newtonian domain of protein solutions in random coil conformation. Castelain *et al.* (1987) have also discussed their results on the critical concentrations of cellulose derivatives along these lines and they have determined Ce from the variation in function of concentration of a characteristic relaxation time deduced from flow curves. This observation is fully compatible with experimental results obtained on xanthan gum (Cuvelier and Launay, 1986).The aim of this work is to compare the viscous properties in the Newtonian domain of three biopolymers, two without charged groups (locust bean gum and guar gum) and a polyelectrolyte (xanthan) and to discuss the results within the theoretical framework presented above.

EXPERIMENTAL

Materials and methods

Locust bean gum (L) and guar gum (G) are considered to behave in solution as random coils (Sabater de Sabates, 1979). The chain of xanthan gum (X) is semirigid in 0.5% NaCl solution and may be described by a worm-like model (Muller *et al.*, 1984). The purified L and G samples were kindly supplied by Meyhall Chemical AG and the food grade X sample by Rhone-Poulenc. Their composition is presented in Table 1. X is in Na-form and is 30% pyruvylated and 100% acetylated. For galactomannans L and G, mannose over galactose ratios (M/G) have been determined with the method previously used by Sabater de Sabates (1979): following 8 h hydrolysis with H_2SO_4 10 N at 100°C in sealed ampulla, neutralization with $BaCO_3$, washing and low pressure drying at 45°C, the sugars were separated on thin layer plates (microcrystalline cellulose TD Baker F112). After extraction in water (85)/acetone (15), mannose and galactose were evaluated with the method of Dubois *et al.* (1951). As classically observed, guar gum is more branched than locust bean gum.

To prepare the gum solutions, samples were thoroughly dispersed in distilled water for 1 h at 20°C, then heated for 1 h at 80°C and cooled at 20°C. When NaCl, HCl or sucrose (10 or 40% w/w) had to be added to them, a mother solution at high gum concentration was first prepared in distilled water, as previously described, then mixed with a solvent containing the required amounts of solutes. Thereafter, these mother solutions were diluted with the appropriate solvent. This method provides more reproducible results than directly dissolving the gum in the solvent, particularly in the presence of sucrose.

Table 1. Composition of locust bean (L), guar (G)and xanthan (X) gum samples

	Water (%)	N (%)[a]	Ash (%)[b]	M/G[c]
L	9.1	0.06	0.14	2.8±0.2
G	7.4	0.05	0.1	1.7±0.1
X	12.0	1.0	7.2	

[a] Kjeldhal, dry basis.
[b] 16 h at 500°C, 1 h at 900°C, dry basis.
[c] Mannose/galactose ratio.

Except for xanthan gum (see below), intrinsic viscosities were determined from efflux times with an Ubbelhode capillary viscometer equipped with a diluting unit (Fica Viscomatic). We have verified that the kinetic energy correction was negligible. Flow behaviour at low shear rates (maximum range 0.017–128 s^{-1}) was studied with a Low Shear 30 Contraves fitted with coaxial cylinders ($r_1/r_2 = 0.92$). No shear rate correction is needed in the Newtonian domain. High shear rate results presented in Fig. 2 have been obtained with additional data determined with double walls cylinders (Contraves Rheomat 30, MSO system $r_1/r_2 = r_3/r_4 = 0.98$) and with a cone-plate viscometer (Ferranti Shirley, cone radius 3.5 cm, cone-plate angle 5.93 10^{-3} radian). No shear rate correction was necessary and a very good superimposition of values issued from the three fixtures has been observed. Intrinsic viscosities and Huggins' coefficients λ were obtained from the Huggins' equation:

$$(\eta_{sp})_o/C = [\eta]_o + \lambda[\eta]_o^2 C \qquad (1)$$

The subscript o means that the specific viscosity η_{sp} (= relative viscosity − 1) is determined in the Newtonian domain.

Intrinsic viscosities

The results are given in Table 2: intrinsic viscosities of galactomannan samples derived from efflux times or from flow curves are almost identical. We have retained the former results because the measurements are considered more precise. On the contrary, a large discrepancy exists for xanthan gum in water: efflux times give much lower values. The maximum shear stress at the wall may be calculated according to Eq. (2):

$$\sigma_{max} = R(\Delta P)_{max}/2l \qquad (2)$$

with R and l radius and length of the capillary, respectively, and $(\Delta P)_{max}$ pressure drop at the beginning of the measurement. When σ_{max} is compared with the critical shear stress associated with incipient shear thinning behaviour, one observes that it is higher, even for diluted xanthan solutions: this leads to underestimated intrinsic viscosities. Therefore, some of the published values on the intrinsic viscosity of xanthan gum have to be considered critically.

It is interesting to note that the hydrodynamic volume of galactomannan coils is not affected by the presence of sucrose, even at a concentration as high as 40%. This observation is at variance with results published by Elfak *et al.* (1977), who have found an approx. 60% decrease in $[\eta]$ for locust bean gum and guar gum in 40% sucrose solution. However, these results have been previously discussed and considered disputable (Launay and Pasquet, 1982). It is also worth mentioning that Michel *et al.* (1984) have obtained the same extrapolated value of the intrinsic viscosity at "infinite" ionic strength (screened electrostatic interactions) for high-methoxyl sodium pectinate in water and with 40 or 60% added sucrose. A limited but significant decrease of $[\eta]_o$ is noted at high ionic strength (2% NaCl) or at low or high pH. In these two latter cases, this effect is probably not attributable to depolymerization or to debranching because the experimental values were stable in the course of the measurements. Therefore, the decrease of $[\eta]_o$ is considered to be due to changes in solvent quality, and these changes also probably explain that Huggins' coefficients vary in the range 0.4–0.9 according to solvent composition. By using a Mark–Houwink relationship established by Sabater de Sabates (1979) for locust bean gum, with about the same level of branching (M/G = 2.9), in distilled water:

$$[\eta]_o = 1.15 \cdot 10^{-4} M_w^{0.8}, [\eta] \text{ in dl g}^{-1} \qquad (3)$$

one gets $M_w = 2.3 \cdot 10^6$ for L. For guar gum, the Mark–Houwink relationship published by Robinson *et al.* (1982) gives $M_w = 1.8 \cdot 10^6$ for sample G.

The situation is very different for xanthan gum: except in water at low ionic strength, Huggins' coefficients are higher than 1, probably indicating interchain association phenomena (Launay *et al.*, 1986), in agreement with a hypothesis of parallel packing of chain segments in the semidilute régime (Cuvelier and Launay, 1986). Intrinsic viscosity decreases with increasing ionic strength, as expected for a polyelectrolyte. With 10% sucrose, $[\eta]_o$ increases and then decreases with 40% sucrose. Michel *et al.* (1984) have observed a decrease in intrinsic viscosity for high methoxyl pectin in the presence of sucrose, especially at low ionic strength. Several factors are invoked by the authors to explain this effect upon $[\eta]_o$: first, a variation in the dielectric constant of the solvent, or a dehydrating action of sucrose or, less probably, specific interactions between sucrose and xanthan chains.

Temperature effects in the semidilute domain

In the temperature range 5–70°C, Fig. 1 shows that the effect of temperature on the specific viscosity in the Newtonian domain may be described with the empirical Andrade equation:

$$(\eta_{sp})_{o,T} = (\eta_{sp})_{o,T_{ref}} \exp(\Delta H_a/R)(1/T - 1/T_{ref}), \qquad (4)$$

where T_{ref} is the reference temperature and ΔH_a represents the apparent activation energy of viscous flow (J.mol^{-1}). The results are given in Table 3 for polymer concentrations well into the semidilute régime for G and L or at its beginning for X (see Fig. 6): $(\eta_{sp})_o$ is not found to be temperature-independent, contrary to results previously published on guar gum (Doublier and Launay, 1981). However, this conclusion was based on extrapolated η_o values which were

Table 2. Intrinsic viscosities (dl.g^{-1}) and Huggins' coefficients in various aqueous solvents of locust bean gum (L), guar gum (G) and xanthan gum (X) at 25°C determined from efflux times and from flow curves

Gum	L				G				X			
	Cap.[a]		Visc.[b]		Cap.[a]		Visc.[b]		Cap.[a]		Visc.[b]	
	$[\eta]$	λ	$[\eta]$	λ	$[\eta]$	λ	$[\eta]$	λ	$[\eta]$	λ	$[\eta]$	λ
Water	14.1	0.64	13.4	0.89	12.7	0.45	12.7	0.36	87.5	0.05	168	0.68
+10% sucrose	14.4	0.68	13.2	0.92	12.3	0.57	12.6	0.62			205	1.6
+40% sucrose	14.1	0.91			12.6	0.35	12.3	0.63			118	1.5
0.2% NaCl											86	0.81
2% NaCl	9.8	0.55			10.6	0.55					40.5	5.1
20% NaCl											36.8	3.8
HCl 0.2 M	11.1	0.71			10.3	0.74					38	1.7
NaOH 0.2 M	7.5	0.96			7.6	0.77					53.5	1.5

[a] Efflux times (capillary viscometer).

[b] Flow curves (rotational viscometer).

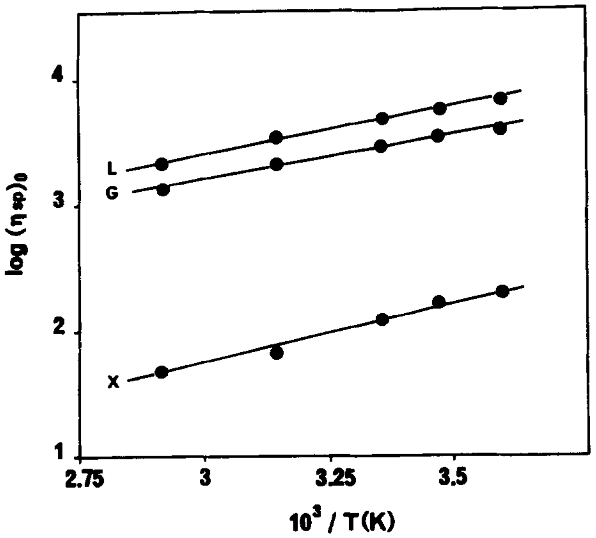

Fig. 1. Variation of the specific viscosity with temperature according to the Arrhenius law: locust bean gum (L, 1%), guar gum (G, 1%) in water, xanthan gum (X, 0.08%) in 2% NaCl.

certainly underestimated (Launay *et al.*, 1986). Therefore, for all three polymers, η_o decreases more than solvent viscosity when temperature increases. In the Newtonian domain, the viscosity of xanthan gum solutions is markedly dependent on temperature, contrary to a frequently expressed opinion, generally based on viscosity measurements at high or, in some cases, at undetermined shear rates. In our experimental conditions it is unlikely that the order–disorder transition of xanthan chain may have occurred upon heating. The transition temperature increases with the ionic strength (Milas and Rinaudo, 1979) and Foss *et al.* (1987) have shown by H-NMR that the thermal transition starts at approx. 80°C with 0.16% NaCl, while a value of 0.19% NaCl for a transition temperature of 80°C may be inferred from the optical rotation measurements of Zhan *et al.* (1993).

Despite the fact that the intrinsic viscosities of xanthan in 0.2 or in 2% NaCl are very different (see Table 2), the corresponding values of ΔH_a are identical, at least in the semidilute régime (Table 3). For galactomannans too, ΔH_a does not seem to depend on ionic strength and, in a narrow range, on polymer concentration. From the results of Patel *et al.* (1987), $\Delta H_a \sim 10\,\text{kJ.mol}^{-1}$ may be calculated for guar gum between 0.9 and 1.1% concentration in water, but higher values ($\sim 20\,\text{kJ.mol}^{-1}$) would be obtained at 1.2% and 1.3% concentration. However, their low shear rate Newtonian viscosities have been extrapolated and further studies on the relationship between polymer concentration and ΔH_a should be undertaken.

Doublier (1975) has shown that the intrinsic viscosity of a guar gum sample ($[\eta]_o = 10\,\text{dl.g}^{-1}$ in water at 25°C) was independent of temperature between 6 and 35°C but that λ decreased. On the contrary, for xanthan, Stokke *et al.* (1992), in agreement with others (Milas and Rinaudo, 1986; Kojima and Berry, 1988), have found that $[\eta]_o$ decreased when the temperature increased from 20 to 70°C. Therefore, the effect of temperature on η_o cannot be solely attributed to changes in $[\eta]_o$ but it may be hypothesized that, at least in the semidilute régime, it also reflects the sensitivity of chain–chain interactions to temperature which would increase in the order G, L, X.

Master curves $\log(\eta_{sp})_o$–$\log C[\eta]_o$: a critical approach

In Fig. 2, locust bean gum and xanthan gum concentrations (1 and 0.2%, respectively) have been selected in such a way that they give the same low shear rate Newtonian viscosity. A striking characteristic of these flow curves is that the viscosity in the shear-thinning domain of the xanthan gum solution is much lower than that of the galactomannan solution (24 times less at $100\,\text{s}^{-1}$, by example). This well-known property of xanthan (Launay *et al.*, 1986) is mainly related to the low critical shear rate $\dot{\gamma}_c$ at the limit of the Newtonian domain: here, approx. $10^{-2}\,\text{s}^{-1}$ compared with $1\,\text{s}^{-1}$ for the galactomannan solution (Fig. 2). This point will be discussed further but we now concentrate on another question: the reduced concentrations $C[\eta]_o$ are not equal (33.6 for xanthan, 14.1 for locust bean gum), in spite of the fact that $(\eta_{sp})_o$ values are identical. This result is confirmed in Fig. 3: in water, the locust bean and guar gum samples give superimposed $\log(\eta_{sp})_o$–$\log C[\eta]_o$ results in the whole concentration range, but not xanthan, except at the lowest concentrations ($C < 0.025\%$). Therefore,

Table 3. Apparent activation energy (ΔH_a) of viscous flow of locust bean gum (L), guar gum (G) and xanthan gum (X)

Gum	Solvent	Concentration (%)	ΔH_a (kJ.mol^{-1})
L	Water	1	14.2
L	+2% NaCl	0.75	14.3
G	Water	0.6	13.2
G	Water	1	13.0
G	+2% NaCl	0.75	12.2
X	0.2% NaCl	0.08	17.2
X	2% NaCl	0.08	17.2

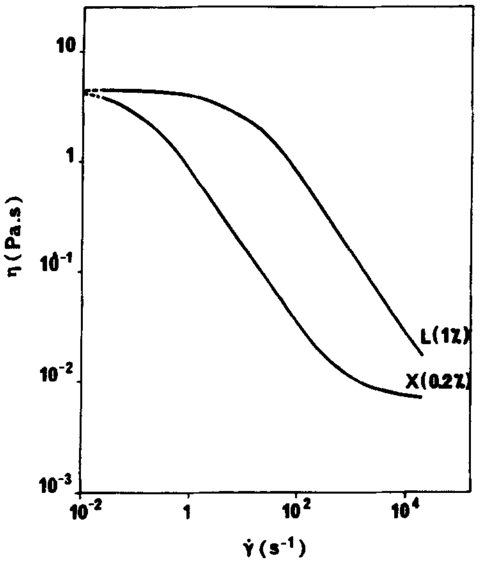

Fig. 2. Comparison of flow curves of locust bean gum (L) and xanthan gum (X) at concentrations 1% and 0.2%, respectively, in distilled water, resulting in the same low shear rate Newtonian viscosity.

before trying to answer this question, it is necessary to examine separately the three concentration régimes.

As previously established (Launay *et al.*, 1984; Cuvelier and Launay, 1986), the existence of two critical concentrations C^* and C^{**} for xanthan gum is manifest in Fig. 3, but it may also be assumed for the galactomannans. This later observation is corroborated if sucrose is added to the solvent: from a careful analysis of the master curve shown on Fig. 4, one gets $C^*[\eta]_o = 0.76$ and $C^{**}[\eta]_o = 3.56$ for both galactomannans in water or in water plus 10 or 40% sucrose. The first critical reduced concentration is equal to the value ($= 0.77$) predicted for flexible random coils from the Fox–Flory equation (Graessley, 1980). Recently, Ganter *et al.* (1992) and Kapoor *et al.* (1994) have found values equal to 2.5–2.6 for two galactomannans from *Leguminosae* seeds and most published values are larger than 2: however, they are based on critical concentrations, C_{cr}, higher than C^* (see Fig. 4).

For both types of galactomannans in water, with or without sucrose, the Newtonian viscosity is completely determined in the whole concentration range by the reduced concentration $C[\eta]_o$ and by the solvent viscosity η_s:

$$\eta_o = \eta_s(1 + f(C[\eta]_o)). \tag{5}$$

In the dilute régime ($C < C^*$):

$$(\eta_{sp})_o = f(C[\eta]_o) = 1.43(C[\eta]_o)^{1.16}. \tag{6}$$

In the intermediate régime ($C^* < C < C^{**}$):

$$(\eta_{sp})_o = f(C[\eta]_o) = 1.75(C[\eta]_o)^{1.9}. \tag{7}$$

In the semidilute régime ($C > C^{**}$):

$$(\eta_{sp})_o = f(C[\eta]_o) = 0.12(C[\eta]_o)^{4.0}. \tag{8}$$

De Gennes (1979) has predicted that η_o would be proportional to $C^{3.75}\ M^3$ for entangled polymer solutions. On the other hand, it has been shown

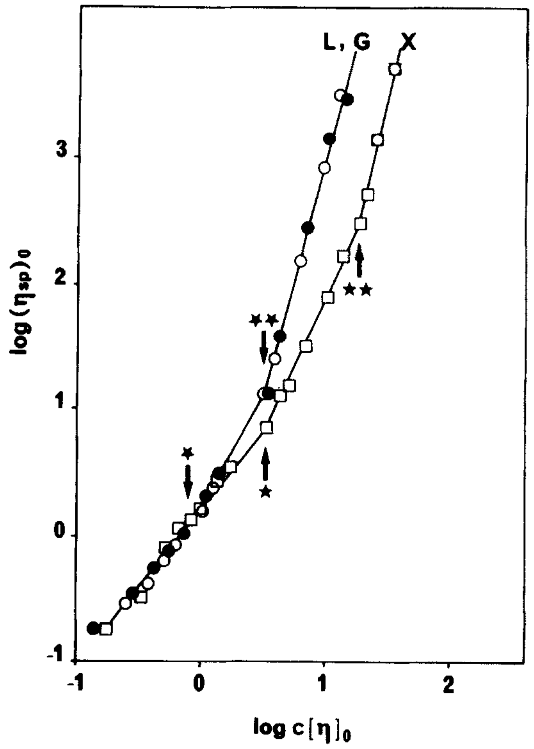

Fig. 3. Master curves obtained in distilled water for the galactomannans (L, G) and for xanthan (X). The corresponding first and second critical concentrations are shown (*, **).

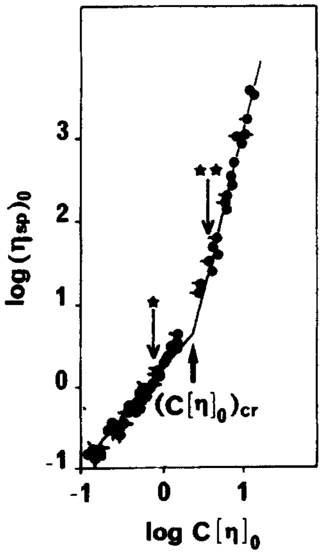

Fig. 4. Master curve for locust bean gum and guar gum in distilled water (●) and in 10 and 40% sucrose solutions (full points with a pipe). Note that the "classical" reduced critical concentration (C_{cr}) is intermediate between C^* and C^{**}.

(Launay *et al.*, 1986) that the exponent in the Mark–Houwink equation $[\eta]_o = K\ M^v$ is $v = 0.8$ for various fractions of locust bean gum, independently of their M/G ratios. Therefore, in the semidilute régime η_o and $(\eta_{sp})_o$ $(\eta_o >> \eta_s)$ should scale as $(C[\eta]_o)^{3.75}$, a theoretical result not far from Eq. (8). Whether the higher slope (4 instead of 3.75) has to be associated with the formation of chain "hyperentanglements", as suggested by Morris *et al.* (1981), is still a subject of debate.

In the dilute régime $(C < C^*)$, $(\eta_{sp})_o$–$C[\eta]_o$ values obtained with xanthan in water are almost perfectly superimposed with the master curve corresponding to galactomannans (Fig. 3). However, this is no longer strictly valid for the other solvents (results not shown, see Launay *et al.*, 1984): in the presence of sucrose or with added NaCl, $[\eta]_o$ has to be replaced by a higher value $[\eta]_s$ to get good superimpositions. Figure 5 shows that the shift factor $[\eta]_s/[\eta]_o$ increases with the interaction parameter λ. This result is in qualitative agreement with Eq. (1), and also with Kramer's, Martin's or other analogous equations (Launay *et al.*, 1986): $(\eta_{sp})_o$ is no longer a unique function of $C[\eta]_o$ if the interaction parameter (λ in Eq. (1)) varies and, in particular, if it takes high values, as is the case for xanthan. Eq. (6) is also valid for xanthan if $[\eta]_s$ is used in place of $[\eta]_o$.

At concentrations higher than C^*, when polymer coils begin to shrink, the curves corresponding to the galactomannans and to xanthan display larger discrepancies (Fig. 3). They are no longer attributable to strong interactions between two chains and now their progressive osmotic compression has to be taken into account.

Effective intrinsic viscosity in the semidilute régime

We have previously shown that a master curve $\log(\eta_{sp})_o$–$\log C[\eta]_o$ is not obtained with xanthan gum in this régime when the solvent properties are modified but that the data are lying on clearly separated lines (Launay *et al.*, 1984). However, when $\log C$ is used instead of $\log C[\eta]_o$, the results almost collapse on a single line, as seen in Fig. 6:

$$\eta_o = \eta_s(1 + 2.35 \cdot 10^6\, C^{4.2})(C \text{ in g.dl}^{-1}). \tag{9}$$

A closer examination of the data at $C > C^{**}$ seems to indicate that they are not perfectly superimposed: to get the same value of η_o would require approx. 25% more xanthan in pure water or in 40% sucrose solution than in any of the other three solvents. However, in comparison, the maximum ratio would be more than 8 between NaCl 2% and sucrose 10% if C was replaced by $C[\eta]_o$ (Launay *et al.*, 1984). Therefore, even if the above-mentioned slight discrepancy is not attributed to experimental uncertainties, it is clear that polymer concentration, and not $C[\eta]_o$, is the governing parameter at $C > C^{**}$. This result corresponds to the theoretical concepts presented in the Introduction. From a critical concentration C^{**} (~0.1%) chain dimensions become independent of concentration and xanthan solutions behave in the same way regardless $[\eta]_o$: the chains have attained a common limiting size $[\eta]_\theta$ and, following De Gennes (1979), the main phenomenon is the decrease in "blob" size as concentration increases. From two other studies on a similar xanthan sample in 0.1 M NaCl, careful determinations of C^{**} have been made, confirming this value: 0.092% (Launay *et al.*, 1984) and 0.11% (Cuvelier and Launay, 1986).

Use of the master curves to evaluate expansion coefficients

On the basis of scaling arguments of De Gennes and coworkers (De Gennes, 1979) the expansion coefficient

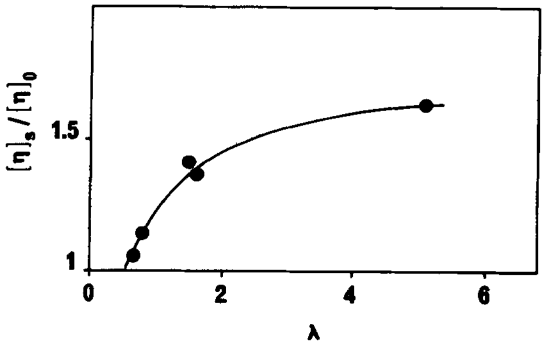

Fig. 5. Superimposition of data points in the dilute régime: shift factor to be used for xanthan in various solvents vs the corresponding values of the Huggin's coefficient.

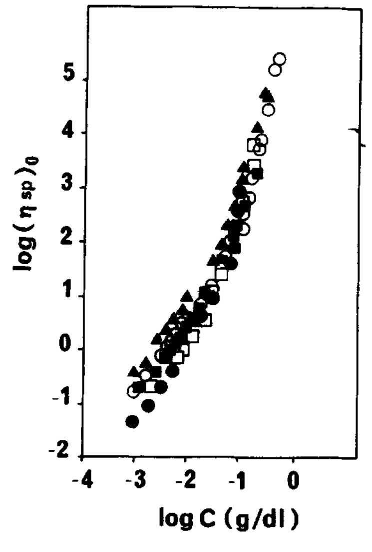

Fig. 6. Xanthan in various aqueous solvents (○, water; □, 0.2% NaCl; ●, 2% NaCl; ▲, 10% sucrose; ■, 40% sucrose): superimposition of the results in the semidilute régime obtained by using non-reduced xanthan concentrations.

α of random coils having a Mark–Houwink exponent $\nu = 0.8$ may be related to C^* and C^{**} by the following equation (Graessley, 1980):

$$\alpha = ([\eta_o]/[\eta]_\theta)^{1/3} = (C^{**}/C^{*})^{0.125}. \tag{10}$$

Equation (10) may be applied to the galactomannan samples in water and in water with sucrose: $C^*[\eta]_o$ has a constant value, close to theoretical predictions (0.77), and it has been shown that $\nu = 0.8$ for locust bean gum. The value $\alpha = 1.21$ calculated from Eq. (10) with $C^{**}/C^* = 3.56/0.76$ is compatible with other results based on light scattering and intrinsic viscosity measurements (Sabater de Sabates, 1979). In θ conditions, intrinsic viscosities equal to 7.2 dl.g^{-1} and 8 dl.g^{-1} for G and L, respectively are obtained. Using these values, α may be determined for the other solvents (Table 4): it decreases in 2% NaCl and 0.2 M HCl and it is almost equal to 1 in 0.2 M NaOH which, therefore, is a θ-solvent for galactomannans if no significant molecular degradation has occurred.

For xanthan, Table 5 shows, on the contrary, that $C^*[\eta]_o$ is not constant when the solvent composition is modified. One even observes an increase in $C^*[\eta]_o$ with $[\eta]_o$ and, except at the highest ionic strength, the first reduced concentrations are much larger than 1. It is hardly to be expected that the equivalent sphere model, on which the theory leading to Eq. (10) relies, may be applied to xanthan chains in the dilute régime: their behavior is considered to be semi-rigid (worm-like) and a value ($\nu = 0.92$) of the Mark–Houwink exponent has been determined in 0.5% NaCl (Muller *et al.*, 1984). However, it may be assumed that a "universal" behavior, as shown in Fig. 6, will be recovered in the semidilute régime, where chain dimensions become independent of concentration (Graessley, 1980). When xanthan chains have just reached their θ-dimensions at $C = 0.1\%$, Eq. (9) gives $\log(\eta_{sp})_o = 2.35$. If xanthan and galactomannan chains behave in the same way in the semidilute régime, their values of $C[\eta]_\theta$ will be identical for the same zero-shear rate specific viscosity. From Eq. (8) one gets $C[\eta]_o = 6.57$ for the galactomannans with $\log(\eta_{sp})_o = 2.35$. Then, using the appropriate value of the expansion coefficient for the galactomannan samples ($\alpha = 1.21$), the intrinsic viscosity of xanthan in θ conditions is given by:

$$0.1[\eta]_\theta = 6.57/(1.21)^3 = 3.71, [\eta]_\theta = 37.1\ \mathrm{dl.g^{-1}}$$

At the end of the experimental concentration domain ($C \sim 0.56$ g.dl^{-1}), the same method gives $[\eta]_\theta = 36.5$ dl.g^{-1}. This discrepancy is not significant, taking into account the approximate character of the method and is mainly due to the small difference between the log–log slopes in the semidilute régime for X, on the one hand, and G and L on the other (4.2 vs 4.0). The mean value $[\eta]_\theta = 36.8$ dl.g^{-1} has been used to calculate α in Table 4. If $[\eta]_o$ is replaced by $[\eta]_\theta$, the reduced concentrations corresponding to the results in Fig. 1 are now in good agreement: 0.2 $[\eta]_\theta = 7.4$ for X and 1 $[\eta]_\theta = 8$ for L. From the values given in Table 4, θ-solvents for xanthan would be HCl 0.2 M and NaCl 20%. This latter result was not unexpected: it is generally admitted that polyelectrolyte chains attain their θ-dimensions at high ionic strength (Launay *et al.*, 1986). Xanthan chains are highly expanded in water and still further in 10% sucrose. If, in place of this method, Eq. (10) is used to calculate α with $C^{**} = 0.1\%$, lower values of the expansion coefficient are obtained, except in 2% NaCl. In addition, the results are not consistent: α increases from 1.19 in water to 1.20 in 0.2% NaCl and to 1.28 in 2% NaCl, corroborating our statement that the equivalent sphere model is not applicable to semi-rigid xanthan chains in the expanded state. When the Mark–Houwink exponent ν is not equal to 0.8, Lefebvre (1982) has proposed an extended form of Eq. (10):

$$\alpha = (C^{**}/C^{*})^{(\nu-0.5)/3\nu}. \tag{11}$$

With $C^{**} = 0.1$ g.dl^{-1} and using the values of α and C^* given in Table 4 and Table 5, Eq. (11) leads to $\nu = 1.20$ in 0.2% NaCl and $\nu = 0.53$ in 2% NaCl: these results are consistent with $\nu = 0.92$ found by Muller *et al.* (1984) for xanthan in 0.5% NaCl. On the other hand, in the absence of counter-ions, the values of ν calculated with Eq. (11) are meaningless: in this case Eq. (11) is not valid for charged chains.

Table 4. Expansion coefficients of locust bean gum (L), guar gum (G) and xanthan gum (X) at 25°C in various solvents

	L	G	X
Water	1.21	1.21	1.66
+ 10% sucrose	1.21	1.21	1.77
+ 40% sucrose	1.21	1.21	1.47
0.2% NaCl			1.33
2% NaCl	1.07	1.14	1.03
20% NaCl			1.00
HCl 0.2 M	1.12	1.13	1.01
NaOH 0.2 M	0.98	1.02	1.13

Orientation of xanthan chains in a shear field

In absence of external ions, the values of C^* $[\eta]_o$ for xanthan are high compared with galactomannans, but they decrease with increasing ionic strength, which may be attributed to the progressive screening of biopolymer charges (Table 5). An other peculiarity of xanthan gum is the very low shear rate, $\dot{\gamma}_c$, where the flow behavior is no longer Newtonian, not only in the semidilute régime, as previously observed (see Fig. 2), but also in the intermediate and in the dilute ones. We have determined on the flow curves the shear rate $\dot{\gamma}_c$, corresponding to $\eta = 0.95$ η_o, and Fig. 7 shows the

Table 5. First critical concentrations C^* and shear rates $\dot{\gamma}_c$ corresponding to the end of the Newtonian domain for $C=C^*$

Polymer	Solvent	10^3 C^* (g.dl^{-1})	$C^*[\eta]_o$	$\dot{\gamma}_c$(s^{-1})
G, C	water			
	+ 10% sucrose	55–61	0.76	$>10^4$
	+ 40% sucrose			
X	water	25	4.2	1.1
	+ 10% sucrose	46	9.4	0.4
	+ 40% sucrose	28	3.3	0.2
	0.2% NaCl	23	2.0	0.6
	2% NaCl	14	0.57	4.6

power law relationships between $\dot{\gamma}_c$,and polymer concentration. In order to compare the values of $\dot{\gamma}_c$ in various solvents in similar conditions of effective polymer concentration, we have determined $\dot{\gamma}_c$ at $C=C^*$ in Fig. 7 (Table 5). The critical shear rates vary between 0.2 and 4.6 s^{-1}, while they are higher than 10^4 s^{-1} for galactomannans. Figure 7 shows that there is no discontinuity in $\dot{\gamma}_c$ vs C at $C=C^*$: this tends to confirm that the main phenomenon arising from C^* is incipient chain collapse, and not the formation of chains entanglements. Therefore, the very low values of $\dot{\gamma}_c$ for xanthan chains, compared with the galactomannans, result from their propensity to be orientated under shear, on account of their extended and semi-rigid conformation. The distribution of orientations in shear flow is a function of the Peclet number $\dot{\gamma}/D_r$, where D_r is the rotational diffusion coefficient (Bohdanecky and Kovar, 1982):

$$D_r = RT/k^+\eta_s[\eta]_oM. \qquad (12)$$

η_s is the solvent viscosity and k^+ a numerical coefficient dependent on the shape of the macromolecule and on the treatment of hydrodynamic interactions. If it is admitted that orientation effects begin to be significant from a Peclet number of approx. 1 (xanthan in 0.5% NaCl, Chauveteau, 1982), taking $k^+=4$ (Bohdanecky and Kovar, 1982), one obtains for xanthan in 0.2% NaCl, with $M=10^6$ or $M=2\ 10^6$ (Cuvelier and Launay, 1986), $\dot{\gamma}=80\,\text{s}^{-1}$ or $40\,\text{s}^{-1}$, respectively. Compared with the highest corresponding value in Fig. 7 ($\dot{\gamma}_c=93\,\text{s}^{-1}$), this result is of the right order of magnitude. Beyond $\dot{\gamma}_c$, owing to progressive chain orientation, the intrinsic viscosity of xanthan begins to decrease, as shown by Chauveteau (1982) and by Stokke *et al.* (1992). On the basis of Eq. (12) it may be assumed that the two main factors responsible for a change in D_r, and hence in $\dot{\gamma}_c$, are chain extension, through $[\eta]_o$, and solvent viscosity: the former may explain why $\dot{\gamma}_c$ is much higher in 2% NaCl than at a lower ionic strength, and the latter why $\dot{\gamma}_c$ decreases with increasing sucrose concentration (Table 5). In addition, Fig. 7 shows that, at finite polymer concentration, orientation under shear is a cooperative phenomenon: the higher the concentration, the lower $\dot{\gamma}_c$, even at $C<C^*$. However, the cooperativity is less pronounced in water than in the presence of external salts: this may account for the lower value of $\dot{\gamma}_c$ in 0.2% NaCl compared with water (Table 5).

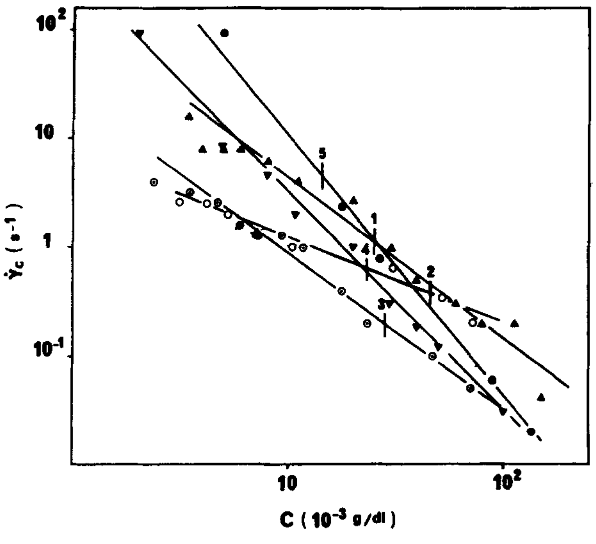

Fig. 7. Critical shear rates associated to the end of the Newtonian domains ($\eta=0.95\ \eta_o$) vs xanthan concentration in various solvents: water (▲, 1), 10% sucrose (○, 2), 40% sucrose (⊙, 3), 0.2% NaCl (▼, 4), 2% NaCl (●, 5). The small bars and the numbers correspond to $C=C^*$ for each solvent composition.

DISCUSSION

The intrinsic viscosity of locust bean gum and guar gum is unchanged in the presence of sucrose, as expected for non-ionic polymers, but contrary to previously published results (Elfak *et al.*, 1977). The existence of two critical concentrations, C^* and C^{**}, is demonstrated for both galactomannans as well as for xanthan. They are related to the beginning and to the end, respectively, of a progressive coil shrinkage phenomenon brought about by increasing space occupancy. In addition, theoretical conjectures predict that polymer chains attain their unperturbed dimensions at $C=C^{**}$. At least in the semidilute régime, it is hardly to be expected that the decrease in $(\eta_{sp})_o$ with increasing temperatures for galactomannans and for xanthan may be solely attributable to a reduction in intrinsic viscosity. First, some results tend to indicate that, contrary to xanthan, the intrinsic viscosity of guar gum does not depend on temperature. In addition, at these concentrations, chains should have collapsed to their θ-dimensions. Therefore, another cause has to be put forward. The slopes (S) of the master curves at $C > C^{**}$ do not always have exactly the value predicted following De Gennes (1979), even when the Mark–Houwink exponent is equal to 0.8: by example, for the galactomannan samples $S = 4.0$ instead of 3.75. Depending on the biopolymer and on the solvent, the slopes may range approximately from $S = 3.3$ to $S = 5$ (Launay *et al.*, 1986). If these differences are meaningful, and not due to experimental uncertainties, their origin is a very interesting question. It has been claimed that slopes higher than 3.3 could be explained by the creation of "hyperentanglements" (Morris *et al.*, 1981). More precisely, it has been recently proposed that, in addition to purely topological entanglements, further intermolecular associations could be formed between unsubstituted regions having, like the galactomannans, linear backbones of (1–4) diequatorially linked sugars (Goycoolea *et al.*, 1995). however, we have also found a rather high slope ($S = 4.2$) for xanthan, confirming previous results (Launay *et al.*, 1984; Cuvelier and Launay, 1986). Therefore, a more general explanation is required and these facts place a limit on the universal character of the master curve. Amongst the factors which could have a direct or an indirect effect on the slope, temperature may be taken into consideration. The change in the value of the slope corresponding to the observed decrease of $(\eta_{sp})_o$ between 5 and 70°C may be calculated. For example, for the guar sample at 1% concentration, assuming that the proportionality term in Eq. (8) is not modified and replacing $[\eta]_o$ by its unperturbed value, one obtains $\Delta S = 0.56$. If a linear variation of S with temperature is admitted, this will give $S = 4.2$ at 5°C and $S = 3.6$ at 70°C, well within the range of published experimental values for galactomannan samples. Therefore, the strength of the contacts between segments belonging to two chains may increase their entanglement probability, and then could explain the observed differences in the values of S. Further work should be undertaken to check this hypothesis.

We have shown that biopolymer solutions will not give superimposed $\log(\eta_{sp})_o$–$\log C[\eta]_o$ master curves if the two following conditions are not met: in the dilute domain ($C < C^*$), $(\eta_{sp})_o$ will be higher than expected if $\lambda > 0.5$–0.6, and beyond C^*, superimposition will not hold for different biopolymers, or for the same biopolymer in different solvents, when the expansion coefficients are not closely similar. The equivalent sphere model may be used to calculate the expansion coefficients of galactomannans. If the chains attain their unperturbed dimensions in the semidilute régime ($C > C^{**}$), for a given xanthan sample $(\eta_{sp})_o$ will be a function of concentration alone, practically independent of the solvent used, whereas its intrinsic viscosity varies strongly with the ionic strength or the sucrose content of the solvent. Based on this "universal behavior" assumption in the semidilute régime, the expansion coefficients of xanthan in various solvents may be estimated, despite the fact that the equivalent sphere model is not applicable in the dilute régime, owing to the the extended and semi-rigid chain conformation of xanthan. This conformation also explains the much easier orientation in a shear field of xanthan chains compared with galactomannans.

For xanthan, the calculated values of the expansion coefficient are based on the result estimated for the galactomannan samples using Eq. (10): thus, they cannot be considered as absolute but their relative magnitude is probably meaningful. If $\alpha = 1.30$ is retained for galactomannan instead of $\alpha = 1.21$, $[\eta]_\theta = 29.9\,\mathrm{dl.g^{-1}}$ will be calculated for xanthan: thus, even in 20% NaCl, the chain would still be somewhat expanded ($\alpha = 1.07$). In any case, Eq. (10) is not applicable to xanthan but possibly in its extended form (Eq. (11)) to the presence of counterions.

A final point deserves examination: the values of C^{**} are equal to 0.1, 0.25 and $0.28\,\mathrm{g.dl^{-1}}$ for X, L and G, respectively, i.e. they are approx. two orders of magnitude lower than those obtained by Graessley (1980). This means that these random coil biopolymers are much more expanded in water than the synthetic polymers in good solvent (polystyrene/toluene and polybutadiene/tetrahydrofurane) studied by Graessley (1980). In water (pH 7, 0.1 M NaCl) Castelain *et al.* (1987) have found $C^{**} = 1.8$ and $0.43\,\mathrm{g.dl^{-1}}$ for a low and a high viscosity carboxymethylcellulose and $C^{**} = 0.64\,\mathrm{g.dl^{-1}}$ for a hydroxyethylcellulose sample. It may be asserted that C^{**} depends on the type of polymer, in particular on its intrinsic rigidity, on its molecular weight and on the solvent quality. Kok and Rudin (1982), using a different theoretical approach, have tabulated critical concentrations C_x at which the macromolecular coils reach their unperturbed dimensions: they range from 0.1 to more than $8\,\mathrm{g.dl^{-1}}$. This adds a further limitation to the "universality" of the master curve $(\eta_{sp})_o$ vs $C[\eta]_o$. We assume that this universal character will be recovered in a large part if $C[\eta]_\theta$ is used in place of $C[\eta]_o$ but the master curve will not always start at the same value of $C[\eta]_\theta$: if $C^{**}[\eta]_\theta = 2$ for both galactomannans, a value not far from the theoretical predictions of Kok and Rudin (1982) for flexible coils ($C_x[\eta]_\theta = 1.23$), we get $C^{**}[\eta]_\theta \sim 3.7$ for xanthan. In addition, the variations in slope frequently observed in the semidilute régime remain an open question.

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