Carbohydrate Research, 99 (1982) 117–127
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

CONFORMATION OF XANTHAN DISSOLVED IN AQUEOUS UREA AND SODIUM CHLORIDE SOLUTIONS

JEFFREY G. SOUTHWICK*, ALEXANDER M. JAMIESON, AND JOHN BLACKWELL
Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106 (U.S.A.)

(Received August 26th, 1981; accepted for publication, September 18th, 1981)

ABSTRACT

Quasielastic light-scattering and other physical-chemical techniques have been used to compare the conformation and intermolecular interactions of xanthan in water, aqueous sodium chloride, and urea solutions. The results showed that xanthan dissolved in 4M urea has a disordered conformation after the solution has been maintained for 3 h at 95° and then cooled to room temperature. This conformation is similar to that previously observed only in solutions having low ionic strength at higher temperatures, following disruption of the ordered, low-temperature form. "Anomalous" behavior is seen for xanthan as a function of ionic strength, in that the hydrodynamic radius increases with increase in ionic strength, whereas a decrease is typical for polyelectrolytes. These observations suggest that aggregation of rod-like chains, similar to that seen for other stiff-chain polymers, occurs for xanthan in salt solutions, where the charged groups of the polyelectrolyte are screened by the salt ions. This aggregation may explain some of the high values reported in the literature for the molecular weight.

INTRODUCTION

The unusual solution-properties of the bacterial polysaccharide xanthan have been utilized in its commercial applications, and have led to extensive, research investigations. Xanthan solutions have high viscosity, which is maintained over a wide range of salt concentrations, pH, and temperature, and is also insensitive to the electrolyte species present. However, the viscosity is very sensitive to shear: with increasing rate of shear, the viscosity decreases rapidly, but it recovers rapidly when the shearing force is removed. These properties have resulted in the use of xanthan as a viscosity-enhancing agent in the food industry, and this polymer also has potential applicability as a mobility-control agent for enhanced-oil-recovery operations.

Xanthan is produced by the bacterium *Xanthomonas campestris*, and has been

---

*Present address: Shell Development Company, Bellaire Research Center, P. O. Box 481, Houston, Texas 77001, U.S.A.

shown to have a pentasaccharide as the repeating unit: the polymer consists of a cellulose backbone [β-(1→4)-D-glucan] with a trisaccharide side-chain attached to every second D-glucose residue; the structure of the side chain is β-D-mannopyranosyl-(1→4)-(α-D-glucopyranosyluronic acid)-(1→2)-β-D-mannopyranoside 6-acetate, and the terminal D-mannose may have[1] a pyruvic acetal group linked to O-4 and O-6. The degree of pyruvylation typically varies[2] from 0.31 to 0.56, and has been shown to depend on the particular, bacterial strain and the fermentation conditions[3,4]. The distribution of the pyruvic acetal groups on the xanthan chain has not yet been determined.

One interesting property of xanthan is that an order→disorder transition occurs when solutions having a low ionic strength are heated; this was first reported[5] as an "anomalous" increase in the viscosity of a "salt-free" xanthan solution, with the midpoint for the transition at 55°. Further studies[6], employing n.m.r. and circular dichroism spectroscopy, showed that the change in properties corresponds to a conformational order→disorder transition, and it was suggested that this involves a change in the orientation of the trisaccharide side-chain. X-Ray studies of the ordered (native) conformation of xanthan are not yet conclusive, but suggest that the most probable model for the ordered conformation of xanthan is a right-handed, 5_1 helix, with the trisaccharide side-chains hydrogen-bonded to the cellulose backbone[7]. It has been proposed that the order→disorder transition involves a disordering of the 5_1 helix, with the side chains being detached from the main chain of the molecule. Other studies[8] have shown that the transition temperature is dependent on the ionic strength of the solution, and that a linear relationship exists when T_m is plotted against the logarithm of the ionic strength.

The insensitivity of the viscosity to the ionic strength is unusual for polyelectrolytes, which normally exhibit high viscosities at low ionic strengths, due to an expanded-chain conformation caused by charge–charge repulsions. These repulsions are screened at high ionic strength, leading to a more compact conformation and lower viscosities. Whitcomb and Macosko[9] measured viscosities for a 0.1% aqueous solution of xanthan over a range of shear rates and salt concentrations. Plots of viscosity against shear rate obtained at different ionic strengths were very similar, and in fact, addition of salt led to slight *increases* in the viscosity. For very dilute solutions of xanthan, the viscosity does decrease with increasing ionic strength, but the loss in viscosity is not nearly so great as is observed for other polyelectrolytes. These observations suggest that the macromolecule has a relatively rigid, rod-like conformation in solution. Rinaudo and Milas[10] found that increasing the ionic strength for solutions of both xanthan and *O*-(carboxymethyl)cellulose leads to a lowering of the intrinsic viscosity and an increase in the sedimentation coefficient. However, at ionic strengths >0.01M NaCl, the intrinsic viscosity and sedimentation coefficients for xanthan are approximately constant, whereas these parameters for *O*-(carboxymethyl)cellulose continue to change with increase in the ionic strength.

We now present quasielastic light-scattering and viscosity data for xanthan in aqueous urea and sodium chloride solutions. Differences in diffusion coefficients, intrinsic viscosities, and values of the optical rotation suggest differences in molecular conformation and associations.

EXPERIMENTAL

Preparation of solutions. — The urea used was of a standard, reagent grade, obtained from Fisher Scientific Co. A sample of xanthan ("Kelzan") was obtained from the Kelco Co., and purified by the method described by Holzwarth[8]. We had previously[11] determined the molecular weight for this sample to be $\overline{M} = 2.16 \times 10^6$, using our experimental values of D_t° and $[\eta]$, and the Flory–Mandelkern equation; $\overline{M}$ lies between $\overline{M}_w$ and $\overline{M}_z$. Solutions containing 0.45% of xanthan were prepared in de-ionized water prefiltered through 0.1-μm Millipore filters, and then dialyzed for four days against de-ionized water. Aliquots from this stock solution were diluted with 0.1-μm filtered water to the final concentrations. Solutions in 4M urea were prepared by addition of urea to the stock solution; these solutions were heated to 90° and maintained at that temperature for 3 h before being cooled to room temperature. Sodium azide was added to the solutions (except those containing urea) in order to prevent bacterial growth. The final concentration of sodium azide was 3mM (0.02%). All solutions were filtered through 0.22-μm Millipore filters directly into the scattering cells, and centrifuged at ~4500*g* for 30 min immediately prior to data collection.

Quasielastic light-scattering. — Our QELS apparatus was the same as that described previously[12]. The sample cell was immersed in a bath of decahydronaphthalene, whose refractive index almost matches that of glass, in order to lessen stray elastic-scattering. The time correlation function, $C(\tau)$, was derived from measurements of intensity fluctuations in the homodyne component of the scattered light. The data analysis, described in detail elsewhere[11], uses the method of moments, attributable to Brown *et al.*[13], in which the quadratic function

$$\ln|C(\tau)| = -\bar{\Gamma}\tau + \frac{1}{2!}\frac{\mu_2}{\bar{\Gamma}^2}(\Gamma_\tau)^2 \qquad (1)$$

is fitted to the points in the plot of ln $C(\tau)$ against time, τ. The initial slope of the plot ($\bar{\Gamma}$) is an averaged time-constant that is related to the *z*-averaged, translational diffusion-coefficient, D, by the equation

$$\bar{\Gamma} = D\vec{K}^2 \qquad (2)$$

where $\vec{K}$ is the scattering-wave vector. The nonexponential behavior of the correlation function is characterized by the parameter $\mu_2/\bar{\Gamma}^2$, which is a measure of the polydispersity in the sample. The experimental data-points were also weighted, as suggested by Pusey *et al.*[14].

Viscosity. — A four-bulb, variable-shear, capillary viscometer was used to determine the zero-shear, intrinsic viscosity for the xanthan solution in 4M urea, and to collect viscosity data as a function of shear rate for all solutions tested. A limitation to this technique is that very low shear-rates cannot be obtained; however, xanthan in 4M urea was much less shear-thinning than the other xanthan solutions, and an accurate extrapolation to zero rate of shear could be performed. Temperature control of the water bath was achieved with a Haake ED temperature-control unit.

Optical rotation. — The optical rotations of xanthan solutions at 365 nm ($[\alpha]_{365}$) were measured with a Perkin–Elmer 521 spectropolarimeter. The sample cells had a path length of 10 cm, and were jacketed to allow temperature control by circulating water.

Millipore filtration. — Solutions for filtration studies were prepared as follows. Kelzan was slowly mixed into de-ionized water, with rapid agitation by a Waring Blendor, to afford a 0.6% solution. To this solution was added 0.02% of a proteolytic enzyme obtained from Novo Chemical (Alcalase 1.5P), and the solution was kept for 1 h in a water bath at 50°. (The enzyme is known[15] to degrade residual, bacterial-cell bodies, and this helps to lessen the number of insoluble "micro-gels" by dispersing the polysaccharide chains that are bound to the cell walls of the bacterium.) This enzyme-clarified concentrate was then diluted with de-ionized water to 0.1% of xanthan, and the suspension filtered through a 5.0-μm Millipore filter to remove large, insoluble particulates.

The flow rates of xanthan solutions through Millipore filters of various pore sizes were measured by timing the cumulative flow into a graduated cylinder. A constant pressure-drop (Δp) of 15 lb.in.$^{-2}$ (1.03×10^5 Pa) was applied to the solution with nitrogen from a cylinder. The viscosities of the solutions, before, and after, filtration, were checked with a Brookfield viscometer equipped with a UL adaptor.

RESULTS

Table I lists the $[\alpha]_{365}^{25}$ values for xanthan, and the corresponding, intrinsic viscosity values $[\eta]$ in de-ionized water, 0.3M NaCl, and heat-treated 4M urea solutions. Fig. 1 shows plots of $[\alpha]_{365}$ against temperature for 0.06% xanthan in aqueous solution and for heat-treated, 0.047% xanthan in 4M urea. For the aqueous solution, the optical rotation goes through a sigmoidal change from $[\alpha]_{365}$ −35.8° at 25° to $[\alpha]_{365}$ ~0° at high temperature; the midpoint for the transition is at a temperature of ~55°. These data are very similar to those reported by Morris *et al.*[6] for xanthan

TABLE I

VALUES OF OPTICAL ROTATION AND INTRINSIC VISCOSITY OF XANTHAN IN DIFFERENT SOLVENTS

Solvent	$[\alpha]_{365}^{25}$ *(degrees)*	$[\eta]_{\dot\gamma\to 0}$ *(mL/g)*
H_2O	−35.8 ±0.1	22,400 (ref. 9)
0.3M NaCl	−35.8 ±0.1	7,000 (0.17M NaCl; ref. 16) 8,000 (0.5M NaCl; ref. 17)
4M Urea (heat-treated)	−15.0 ±0.1	2,000

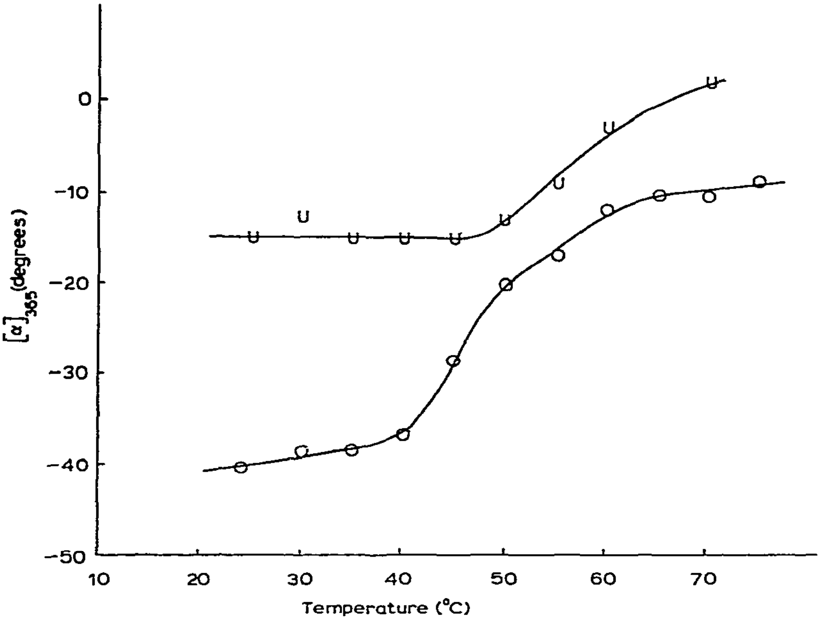

Fig. 1. Specific optical rotation at 365 nm, $[\alpha]_{365}$, plotted against temperature for the following solutions: O, a 0.06% solution of xanthan in 0.02% sodium azide; and U, a heat-treated, 0.047% solution of xanthan in 4M urea. The latter solution had been maintained for 3 h at 90° and cooled to room temperature before measurement of the $[\alpha]_{365}$ value.

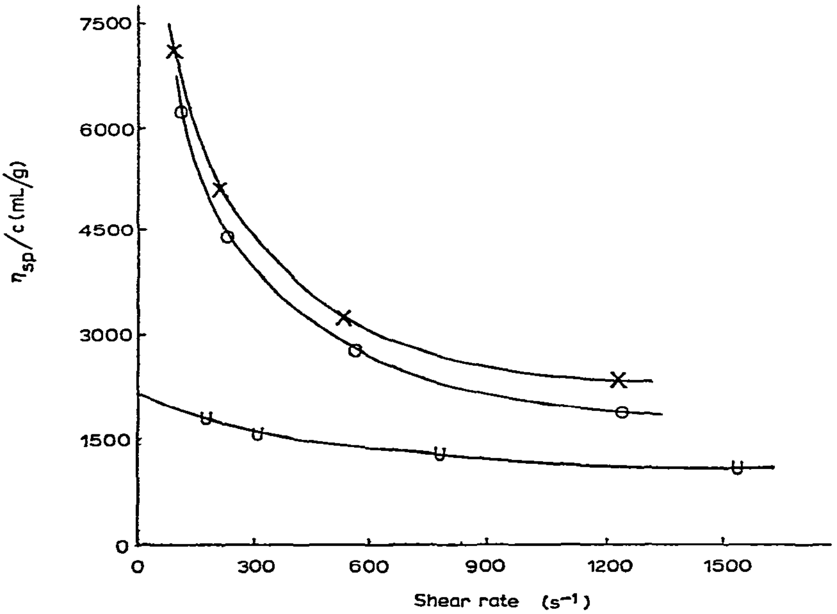

Fig. 2. Plot of η_{sp}/c against shear rate ($\dot{\gamma}$) for 0.025% solution of xanthan in the following solvents: X, 0.01M sodium chloride; O, 1.0M sodium chloride; and U, 4M urea (heat-treated).

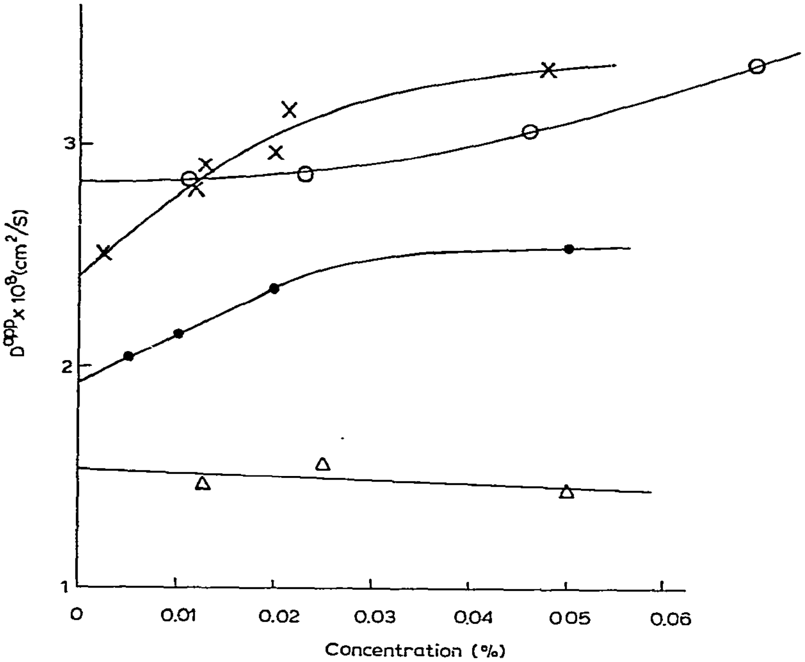

Fig. 3. Apparent diffusion-coefficients (D^{app}) plotted against concentration of xanthan in the following solvents: x, 0.02% sodium azide; ○, 4M urea (heat-treated); ●, 0.3M sodium chloride; and △, 1.0M sodium chloride.

in 5mM sodium chloride, and the transition probably corresponds to conversion of the ordered conformation into a random coil. In contrast, the optical rotation for heat-treated xanthan in 4M urea is constant, at $[\alpha]_{365}$ ~ —15°, up to 50°, after which, there is a steady change to $[\alpha]_{365}$ ~0° at 60°. However, above ~55°, there is a qualitative similarity between the optical rotation–temperature curve for the two solutions: $[\alpha]_{365}$ decreases linearly.

Fig. 2 shows a plot of η_{sp}/c against shear rate ($\dot{\gamma}$) for 0.025% solutions of xanthan in 0.01M and 1.0M sodium chloride, and the heat-treated 4M urea solutions (η_{sp}, the specific viscosity = $(\eta - \eta_o)/\eta_o$, where η_o is the viscosity of the solvent). The sodium chloride solutions display almost identical shear-thinning characteristics, whereas the viscosity of the 4M urea solution is much less sensitive to the rate of shear. Plots of the apparent diffusion-coefficient against concentration for xanthan in water, 0.3M NaCl, 1.0M NaCl, and 4M urea solutions are shown in Fig. 3. The limiting diffusion-coefficients, determined from Fig. 3, and the apparent, hydrodynamic radii determined from the Stokes–Einstein equation are given in Table II, along with viscosity data obtained from the literature, from which it may be seen that xanthan solutions show a decrease in viscosity with added electrolyte, but that, above a critical concentration of electrolyte, this trend is reversed, and additional electrolyte results in increased viscosities. The diffusion coefficients measured show a steadily decreasing

TABLE II

HYDRODYNAMIC AND VISCOMETRIC DATA FOR XANTHAN IN DIFFERENT SOLVENTS

Solvent	η_r (0.02%)	η_r (0.1%)	R_h^{app} *(nm)*	D_t^0
H_2O (de-ionized)	6.5[a]	114[b]	rod 1,500 × 2.0	2.42×10^{-8}
3mM NaCl	2.5[b]	72[b]		
0.17M NaCl	2.5[c]	74[c]		
0.3M NaCl			122.5	1.94×10^{-8}
1.0M NaCl			143.6	1.55×10^{-8}
1.7M NaCl	3.2[c]	139[c]		
4M Urea (heat-treated)	0.46	8.5	80.0	2.80×10^{-8}

[a] Ref. 9. [b] Ref. 18. [c] Ref. 17.

TABLE III

FLOW OF 0.1% XANTHAN THROUGH MILLIPORE FILTERS UNDER A PRESSURE OF 1.03×10^5 Pa.

Volume (mL)	*Time (s)*									
	No salt		*0.01M NaCl*		*0.1M NaCl*		*0.3M NaCl*		*1.0M NaCl*	
	1.2 μm	*0.45 μm*	*1.2 μm*	*0.45 μm*	*1.2 μm*	*0.45 μm*	*1.2 μm*	*0.45 μm*	*1.2 μm*	*0.45 μm*
25	12	19	8	15	11	18	12	18	10	23
50	24	47	21	40	22	44	24	46	20	54
75	38	82	32	72	34	79	37	84	32	100
100	51	132	43	108	45	118	49	131	44	162
125	65	193	55	150	57	166	61	191	56	248
150	78	268	66	197	69	220	73	260	69	350
175	93	365	78	250	82	284	86	347	82	492
200	107	485	91	309	93	356	98	458	95	671
225	121	625	103	360	106	440	110	587	108	892
250	136	771	116	417	118	532	124	732	121	1160
η loss (%)	0	0.6	0	0	0	0	0	2.2	0	2.1

trend with increasing ionic strength. Xanthan in 4M urea solution shows significantly lower viscosity values than the other solutions listed.

Table III presents the flow times of 0.1% xanthan solutions of different ionic strengths to pass through 1.2-μm and 0.45-μm Millipore filters; also given is the percent of the viscosity that is lost as a result of the filtration. It may be seen that greater differences in the flow rates occur through the 0.45-μm filters than through the 1.2-μm filters as a function of salinity. Addition of 0.01M NaCl to salt-free, 0.1% xanthan solution resulted in an increased flow-rate, but, above 0.1M NaCl, this

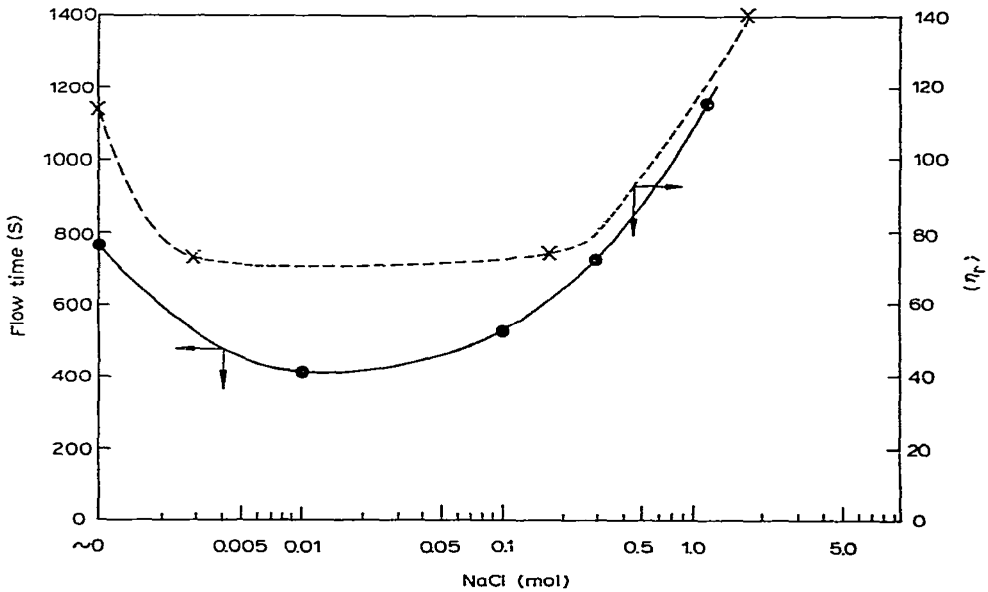

Fig. 4. The zero-shear viscosities (– – – –), and the flow times through 1.2-μm Millipore filters at 1.03×10^5 Pa (——) for 0.1% xanthan solutions, plotted against the number of moles of NaCl in the solutions.

trend was reversed, resulting in lower flow-rates with increasing salinities. Fig. 4 graphically displays this behavior as a plot of the flow time necessary for 250 mL of xanthan solution to pass through the 0.4-μm filters as a function of salinity; also shown in Fig. 4 are the viscosities of 0.1% xanthan solutions that are listed in Table II.

DISCUSSION

*Conformation of xanthan in 4*M *urea solutions.* — The results strongly suggest that, when dissolved in 4M urea, xanthan has a disordered conformation after the solution has been maintained at 95° and then cooled to room temperature. This conformation is similar to that previously observed only in solutions having a low ionic strength, following disruption at higher temperatures of the ordered, low-temperature form; support for this assertion was afforded by the optical rotation and viscosity studies. The higher values for $[\alpha]_{365}$ of xanthan in aqueous or sodium chloride solutions, as compared to the data for 4M urea solutions (see Table I), indicates that a more ordered, secondary structure is present in the aqueous sodium chloride solutions. Moreover, Fig. 1 shows a typical melting-curve for xanthan in water, corresponding to disruption of the ordered, low-temperature form to give the disordered form at a temperature of melting (T_m) above ~55°. The $[\alpha]_{365}$ value for the heat-treated, 4M urea solution is approximately constant between 25 and 50°, and similar in magnitude to those recorded for aqueous xanthan above T_m. Above

55°, $[\alpha]_{365}$ for the urea solution decreases with increasing temperature, behavior that is also observed for the aqueous solutions above T_m. This decrease may be a result of greater conformational flexibility at higher temperatures.

Further evidence that the conformation of xanthan in the 4M urea solution is disordered is found in the shear-dependent, viscosity data (see Fig. 2). The viscosity of the heat-treated, 4M urea solution is less dependent on shear than are those of the aqueous and sodium chloride solutions. Dea *et al.*[18] noted a similar difference in the shear dependence of the viscosity for 1% xanthan solutions at 85° (above T_m, a small shear-dependence) and at 25° (below T_m, a large shear dependence). The relative shear insensitivity of a disordered structure as compared to that of an ordered, rigid, helical structure is therefore observed. Furthermore, the zero-shear intrinsic-viscosity measured for the 4M urea solution (2000 mL/g) is much less than similar viscosities reported for xanthan in water or sodium chloride solutions (see Table I), and this is also consistent with a more random conformation. Wellington[19] has shown that the application of theoretical equations for random coils (employing bond-angle and rotational-angle restrictions) to xanthan only predicts a value for $[\eta]$ of 31 mL/g. Thus, it must be concluded that, even though the helical, secondary structure of xanthan is not present in 4M urea solutions, the xanthan chain still exhibits a degree of rigidity. This disordered conformation present in 4M urea solution is, therefore, not a random coil, but is an extended chain possessing no local, secondary structure. The extended conformation could be stabilized either by the steric interactions of the side chains, or by electrostatic repulsions.

Behavior of xanthan as a function of ionic strength. — The behavior exhibited by xanthan solutions in response to increasing ionic strength is atypical for polyelectrolytes. Normally, polyelectrolyte chains contract in the presence of a salt, resulting in significantly smaller hydrodynamic radii, and lower viscosities, than at low ionic strength. The data collected for the flow of xanthan solutions through Millipore filters, the hydrodynamic radii measured *via* QELS, and the viscosity experiments all point to an *increased* hydrodynamic size which is induced by added electrolyte above a critical value. Fig. 4 suggests that, at low ionic strengths, xanthan shows a typical diminution in viscosity and hydrodynamic volume with added salt, but that at *c* above ~0.02M NaCl, anomalous behavior occurs. It is possible that the cause of this increase in hydrodynamic dimensions at >0.02M NaCl is due to screening of the intermolecular, electrostatic repulsions by the excess of salt ions, leading to a self-association phenomenon. This concept is supported by the fact that the increase in viscosity at 1.7M NaCl (see Table II), as compared to the viscosities at lower ionic strengths, is concentration-dependent, and this would be expected for a self-association mechanism.

Salt-induced aggregation of rigid molecules is energetically more favorable, because the loss of entropy is less for rigid rods than for random coils. Therefore, the self-association of xanthan is not restricted by entropy, and, when the interchain, electrostatic repulsions are shielded, the favorable enthalpic interactions (hydrophobic forces, hydrogen bonding) noted for polysaccharides result in interchain associations.

It is suggested that these associations may result in parallel, side-by-side arrays; in support of this suggestion, it may be noted that Rinaudo *et al.*[20] observed static birefringence attributable to liquid-crystal formation in xanthan solutions. Moreover, salt-induced, side-by-side aggregation has also been observed[21] for solutions of other rigid-rod polymers, namely, poly(*p*-phenylene terephthalamide) (Kevlar), and poly(benzobisoxazole).

The apparent hydrodynamic-radius was not calculated for the xanthan solution of low ionic strength (see Table I), because, at these solution conditions, the molecule more closely approximates a rigid rod than an impenetrable sphere. It has been shown[22] that the behavior of the translational-diffusion coefficient of xanthan in solutions of low ionic strength agrees qualitatively with a theoretical model[23] for the diffusion of rigid rods in semi-dilute solutions. Moreover, the experimental data almost agree with the theoretical predictions if a xanthan rod of length 1.5 μm and width 2.0 nm in salt-free solutions is assumed. A 1.5-μm long, rigid rod for xanthan also agrees with rheological data obtained for salt-free solutions[9].

Therefore, the effect of salinity on xanthan may be summarized as follows. At low ionic strength, the xanthan molecule is a highly extended chain in solution, as a result of intra-chain, electrostatic repulsions. The addition of a small amount of electrolyte shields these repulsions, but, owing to its helical structure and steric-induced rigidity, the xanthan chain undergoes some contraction, and assumes a rigid, worm-like coil structure in solution[24]. At higher ionic strengths, self-association of these worm-like coils occurs.

Finally, the relevance of these salt-induced, self-association findings to the discrepancies in the molecular weights for xanthan reported in the literature may be noted. Values of 2×10^6 (refs. 10, 11, and 19) and 12×10^6 (ref. 25) have been reported; however, the higher molecular weights reported had been obtained by sedimenting xanthan molecules in a density gradient of high salinity (0.7–1.4M NaCl). The high ionic strength employed in such a technique could induce self-associations, and result in an erroneously high value. We consider that unassociated xanthan chains have a molecular weight of 2×10^6.

ACKNOWLEDGMENT

One of us (J.G.S.) expresses thanks to S. L. Wellington for several helpful discussions.

REFERENCES

1 P.-E. Jansson, L. Keene, and B. Lindberg, *Carbohydr. Res.*, 45 (1975) 275–282.

2 P. A. Sandford, P. R. Watson, and C. A. Knutson, *Carbohydr. Res.*, 63 (1978) 253–256.

3 M. C. Cadmus, S. P. Rogovin, K. A. Burton, J. E. Pittsley, C. A. Knutson, and A. Jeanes, *Can. J. Microbiol.*, 22 (1976) 942–948.

4 M. C. Cadmus, C. A. Knutson, A. A. Lagoda, J. E. Pittsley, and K. A. Burton, *Biotech. Bioeng.*, 20 (1978) 1003–1014.

5 A. Jeanes, J. E. Pittsley, and F. R. Senti, *J. Appl. Polym. Sci.*, 5 (1961) 519–526.

6 E. R. Morris, D. A. Rees, G. Young, M. D. Walkinshaw, and A. Darke, *J. Mol. Biol.*, 110 (1977) 1–16.

7 R. Moorhouse, M. D. Walkinshaw, and S. Arnott, *Am. Chem. Soc. Symp. Ser.*, 45 (1977) 90–102.

8 G. Holzwarth, *Biochemistry*, 15 (1976) 4333–4339.

9 P. J. Whitcomb and C. W. Macosko, *J. Rheol.*, 22 (1978) 493–505.

10 M. Rinaudo and M. Milas, *Biopolymers*, 17 (1978) 2663–2678.

11 J. G. Southwick, H. Lee, A. M. Jamieson, and J. Blackwell, *Carbohydr. Res.*, 84 (1980) 287–295.

12 J. G. Southwick, M. E. McDonnell, A. M. Jamieson, and J. Blackwell, *Macromolecules*, 12 (1979) 305–311.

13 J. C. Brown, P. N. Pusey, and R. Dietz, *J. Chem. Phys.*, 62 (1975) 1136–1144.

14 P. N. Pusey, D. E. Koppel, D. W. Schaefer, R. D. Camerini-Otero, and S. H. Koenig, *Biochemistry*, 13 (1974) 952–960.

15 S. L. Wellington, *Enzyme-Filtration Clarification of Xanthan Gum Polymer Solution*, U.S. Pat. 4,119,491 (1978).

16 G. A. Pope, K. Tsaur, R. S. Schechter, and B. Wang, *SPE/DOE Symp. Enhanced Oil Recovery, 1st*, SPE 8826 (1980) 159–174.

17 S. L. Wellington, (1981) personal communication.

18 I. C. M. Dea, E. R. Morris, D. A. Rees, E. J. Welsh, H. A. Barnes, and G. Price, *Carbohydr. Res.*, 57 (1977) 249–272.

19 S. L. Wellington, *Am. Chem. Soc. Symp. Ser., Polymer Preprints*, 22(2), (1981) 63–66.

20 M. Rinaudo, M. Milas, and R. Duplessix, *IUPAC Symp. Macromol., 26th*, Preprints Makro Mainz, II (1979) 800–803.

21 C. P. Wong, H. Ohnuma, and G. C. Berry, *J. Polym. Sci., Polym. Symp.*, 56 (1978) 173–192.

22 J. G. Southwick, A. M. Jamieson, and J. Blackwell, *Macromolecules*, (1981) in press.

23 M. Doi and S. F. Edwards, *J. Chem. Soc. Faraday Trans. 2*, (1978) 560–570.

24 G. Holzwarth, *Am. Chem. Soc. Symp. Ser.*, 150 (1980) 15–23.

25 G. Holzwarth, *Carbohydr. Res.*, 66 (1978) 173–186.