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Dependence of the Stiffness of the Xanthan Chain on the External Salt Concentration

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ABSTRACT: The influence of ionic strength (μ) on the intrinsic viscosity of xanthan is established; extrapolation to infinite ionic strength leads to the relation $[\eta] = 5.66 \times 10^{-4}\ M^1$. The dependence of $[\eta]$ on μ is related to the stiffness of the molecule following the empirical treatment proposed by Smidsrod.[9,10] In this paper, the theory of Odijk[12,13] is introduced to interpret the experimental data and allow for the determination of an intrinsic persistence length equal to 310 Å. The behavior of the xanthan presents many analogies with that of DNA.

Introduction

For a long time now, there have been discussions in the literature concerning the behavior of xanthan in dilute solution. It was suggested to be a rigid rodlike polymer[1] and then more recently to be a wormlike chain characterized by a persistence length from 400 to 1200 Å.[2,3]

In addition to proposing a theoretical model which permits us to understand the behavior of this linear polymer, there remains the problem of whether the conformation is given by a single-helical structure or a double-stranded helix.

We recently reconsidered these questions in our laboratory using electron microscopy[4] and viscosity measurements.[5] The object of this paper is to study the effect of the addition of inorganic salt on the viscosity of dilute aqueous xanthan solutions; from these data it is possible to extrapolate to infinite ionic strength, in order to obtain information about the extension of the xanthan molecule in an effectively uncharged state, the degree of extension being mainly caused by the intrinsic stiffness of the polymer backbone and to a lesser extent by electrostatic expansion caused by the charged groups.

Data will be discussed in terms of the wormlike chain model.

Experimental Section

The xanthan from SHELL Cy was purified as usual;[1] different molecular weights were obtained by sonication;[6] the weight-average molecular weights were determined from light scattering by using Chromatix KMX 6 equipment (θ = 6–7°). The molecular weight distribution was obtained by steric exclusion chromatography.[7] The polydispersity index $\bar{M}_w/\bar{M}_n$ was between 1.2 and 1.4. The viscosity measurements were performed with a Low Shear 30 from Contraves; all the values were extrapolated to zero shear rate. The temperature, adopted for all measurements, was 25 °C. The solutions were prepared by first dissolving the xanthan in water to induce the conformational change followed by addition of NaCl solution to yield the desired ionic concentration. Under these conditions the ordered conformation is stabilized in the renatured form and is controlled by optical rotation measurements. Radius of gyration measurements were carried out in 0.1 N NaCl with a photogoniometer FICA; dn/dc was taken as 0.155 in 0.1 N NaCl.[8]

Results and Discussion

Effect of Ionic Strength on Viscosity. A general property of polyelectrolytes seems to be that over a rather wide range the intrinsic viscosity is very nearly a linear function of the reciprocal square root of the ionic strength. The intrinsic viscosities $[\eta]$ were determined as a function of the weight-average molecular weight for each ionic strength in NaCl solutions.

The ionic strength $[\mu]$ is expressed as the salt content (C_s) which is always much larger than the counterion concentration, which is neglected (i.e., $C_p \ll C_s$).

Table I
Intrinsic Viscosities for Different Molecular Weight Samples of Xanthan at Different Ionic Strengths

	$[\eta]$ for $10^{-6}\bar{M}_w$ of						
μ, N	8.7	3.4	2.6	1.4	0.8	0.64	0.33
10^{-2}	15800	5590	4050	1862	981	598	325
3×10^{-2}	12000	4277	3269	1543	804	550	254
10^{-1}	10000	3683	2910	1415	750	510	302
3×10^{-1}	8714	3100	2405	1170	659	505	227
1	14100	3665	2410		746	550	284
2.5		3784	3012				

Table II
Variation of the Intrinsic Viscosities of Xanthan Samples as a Function of $\mu^{-1/2}$

$\bar{M}_w$	$[\eta]_\mu = [\eta]_\infty + S\mu^{-1/2}$
8.7×10^6	$[\eta]_\mu = 7149 + 857\mu^{-1/2}$
3.4×10^6	$[\eta]_\mu = 2632 + 294\mu^{-1/2}$
2.6×10^6	$[\eta]_\mu = 2173 + 190\mu^{-1/2}$
1.4×10^6	$[\eta]_\mu = 1091 + 78\mu^{-1/2}$
8×10^5	$[\eta]_\mu = 625 + 31\mu^{-1/2}$
6.4×10^5	$[\eta]_\mu = 479 + 12\mu^{-1/2}$
3.3×10^5	$[\eta]_\mu = 270 + 8.6\mu^{-1/2}$

The values of $[\eta]$ are given in Table I. The viscosity decreases as usual for polyelectrolytes. However, above 3×10^{-1} N, increases of $[\eta]$ values are observed, which indicate pseudogel formation. This range of ionic concentration was disregarded in the following. The increase of viscosity is in fact related to strong interchain interaction when the ionic strength increases.

For $\mu < 3 \times 10^{-1}$ N, the experimental values agree with the relationship

$$[\eta]_\mu = [\eta]_\infty + S\mu^{-1/2}$$

in which $[\eta]_\mu$ is the intrinsic viscosity for a given ionic strength and $[\eta]_\infty$ the value extrapolated to infinite ionic strength. The equations of these straight lines are given in Table II.

According to Smidsrod's results,[9,10] the values of the slope S show a low dependence of the polymer dimension on ionic strength. A double-logarithmic plot of $S = (\Delta[\eta]/\Delta(\mu)^{-1/2}]$ against $\bar{M}_w$ yields a straight line with a slope of 1.49. According to Smidsrod, the observed molecular weight dependence of S can serve as a parameter of stiffness only if a comparison is made at a given molecular weight. Because intrinsic viscosities at 0.1 N are widely available in the literature and because $[\eta]_{0.1}$ is related to $\bar{M}_w$ by the Mark–Houwink law, Smidsrod used a new empirical relation to compare stiffness of polymers:

$$S = B([\eta]_{0.1})^\nu$$

From Figure 1, we find

$$S = 5.25 \times 10^{-3}[\eta]_{0.1}{}^{1.3}$$

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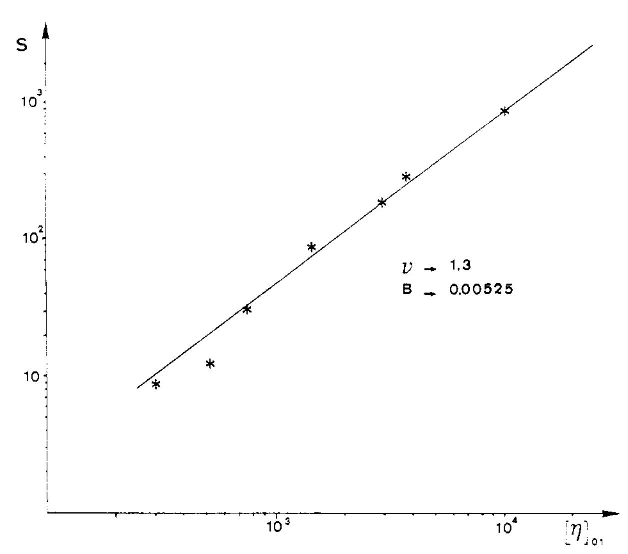

Figure 1. Double-logarithmic plot of S as a function of $[\eta]$ in 0.1 N NaCl.

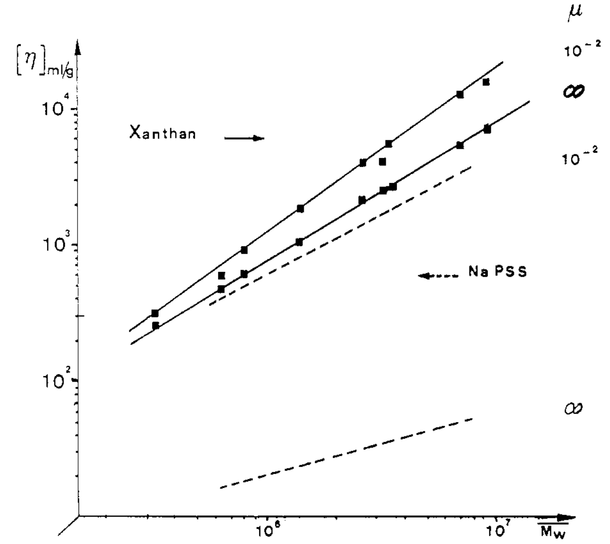

Figure 2. Comparison of $[\eta]$–M plots of xanthan and sodium polystyrenesulfonate at two ionic strengths.

Table III
Mark–Houwink Relations at Different Ionic Strengths

C_s, mol/L	Mark–Houwink relation
10^{-2}	$[\eta] = 3.14 \times 10^{-5} M^{1.26}$
3×10^{-2}	$[\eta] = 4 \times 10^{-5} M^{1.23}$
10^{-1}	$[\eta] = 1.72 \times 10^{-4} M^{1.14}$
3×10^{-1}	$[\eta] = 5.66 \times 10^{-4} M$

The value $\nu = 1.3$ is in good agreement with 1.2–1.4 as observed for different polymers like polyphosphate and DNA.[10]

The difference between the two exponents is of doubtful significance. B constitutes an empirical stiffness parameter equal to 5.25×10^{-3} for xanthan, in agreement with that of DNA (5.5×10^{-3}).

Dependence of the Intrinsic Viscosity on Molecular Weight. From the set of values given in Tables I and II, the Mark–Houwink relations for different ionic strengths may be established and are summarized in Table III. These last results and Figure 2 demonstrate the low sensitivity of xanthan viscosity on the presence of external salts. The decrease is much lower than for a synthetic polyelectrolyte with a flexible chain; the behavior of sodium polystyrene sulfonate in the presence of NaCl is taken as a comparison.[11]

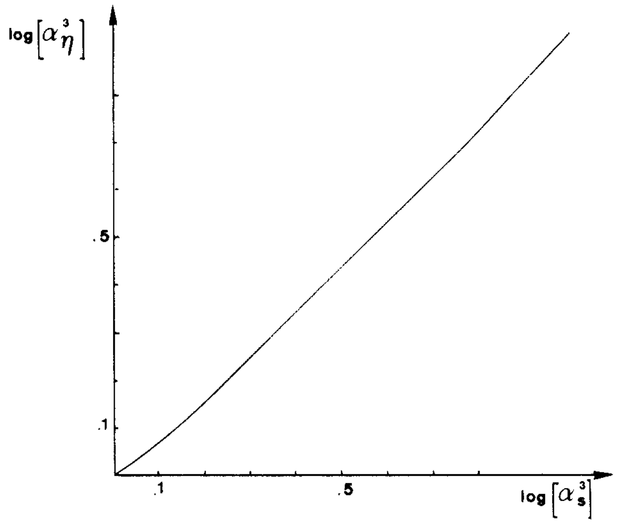

Figure 3. Variation of α_η as a function of α_S from the relation 44 of Weill and des Cloizeaux.[14]

Table IV
Comparison between Calculated and Experimental Values of A_2 for Different Molecular Weights in 0.1 M NaCl

	$\bar{M}_w$		
	8.7×10^6	2.6×10^6	8×10^5
α_s^2	1.238	1.144	1.08
$A_{2\,\mathrm{calcd}}$	9.84×10^{-4}	4.99×10^{-4}	5.84×10^{-4}
$A_{2\,\mathrm{exptl}}$	5.4×10^{-4}	5.3×10^{-4}	5×10^{-4}

The interpretation of this behavior is given by using the treatment proposed by Odijk.[12]

In this model, a wormlike chain is characterized by a total persistance length $L_T = L_p + L_e$, in which L_p is the intrinsic persistence length for the corresponding neutral polymer and L_e the electrostatic contribution. Odijk applied this treatment to interpret the variation of the intrinsic viscosity of DNA with ionic strength.[13] Our interpretation follows the same line, assuming that free draining is not modified when the ionic strength increases, due to the small modification of the hydrodynamic volumes. This means also that $L_T \gg L_e$.

The viscometric expansion factor α_η (with $\alpha_\eta^3 = [\eta]/[\eta]_\theta$; index θ for the unpertubed conditions) is a complicated function of $\alpha_s = R_G/R_{G\theta}$ (R_G is the radius of gyration), which can be derived from the results of Weill and des Cloizeaux by using Figure 3;[14] α_s is obtained from the Yamakawa–Tanaka equation:[15]

$$\alpha_s^2 = 0.541 + 0.459(1 + 6.04 Z_{el})^{0.46}$$

The application of the polymer excluded volume theory is justified, as the contour length is larger than the total persistence length. The value of L_p was chosen such as to give the best agreement between calculated and experimental values of the intrinsic viscosity using the relation:

$$[\eta]_\mu = [\eta]_\infty (L_T/L_p)^{3/2} \alpha_\eta^3$$

in which L_T was calculated for each ionic strength, i.e., each L_e value; the best fit for the different molecular weights tested is obtained for L_p around 310 Å; the experimental and calculated values of $[\eta]_\mu$ are given in Table V and compared in Figure 4. The agreement is good and seems to indicate that an intrinsic value of the persistence length for the xanthan molecule is in the range of 300 Å. In this treatment $[\eta]_\infty$ is assumed to approximate the unperturbed

Table V
Application of Odijk's Model for Different Molecular Weight Xanthan Samples[a]

				$\bar{M}_w = 8.7 \times 10^6$		$\bar{M}_w = 2.6 \times 10^6$		$\bar{M}_w = 8 \times 10^5$		$\bar{M}_w = 6.4 \times 10^5$	
C_s, N	K^{-1}, Å	L_e, Å	L_t, Å	$[\eta]_{\text{exptl}}$	$[\eta]_{\text{calcd}}$	$[\eta]_{\text{exptl}}$	$[\eta]_{\text{calcd}}$	$[\eta]_{\text{exptl}}$	$[\eta]_{\text{calcd}}$	$[\eta]_{\text{exptl}}$	$[\eta]_{\text{calcd}}$
10^{-2}	30.4	32.3	342.3	15800	16571	4050	4024	931	969	598	714
3×10^{-2}	17.55	10.76	320.8	12000	12036	3269	3050	804	783	550	589
10^{-1}	9.6	3.23	313.2	9920	9376	2910	2560	750	690	510	525
3×10^{-1}	5.55	1.08	311.08	9714	8167	2405	2351	759	656	505	500
$[\eta]_\infty$, mL/g				7149		2173		625		479	

[a] Calculation of intrinsic viscosities for L_p = 310 Å.

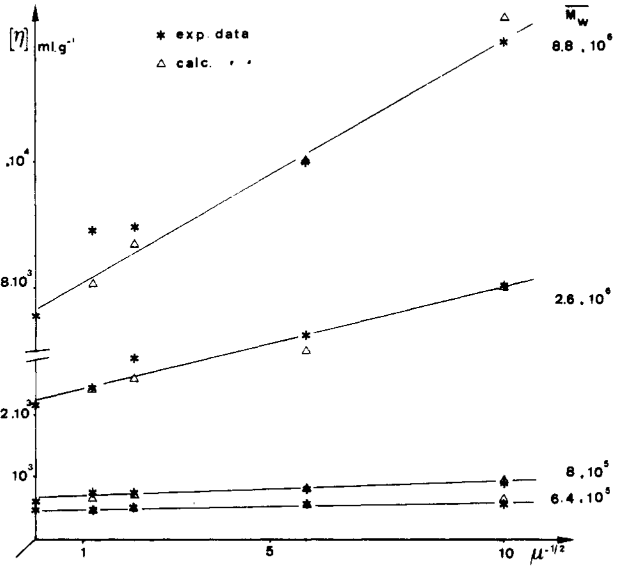

Figure 4. Comparison between calculated and experimental values of intrinsic viscosities as a function of the reciprocal square root of the ionic strength.

value $[\eta]_\theta$. This is demonstrated from A_2 calculations. Second virial coefficients A_2 were determined for two ionic strengths (0.01 and 0.1 N). Extrapolation of our data approaches zero at infinite salt concentration.

In addition, A_2 values can be calculated from the Flory–Orofino relation[16] in 0.1 N NaCl: $A_2 = 16\pi N_A (R_G/3)^{3/2} \bar{M}_w^{-2} \ln [1 + \pi^{1/2}(\alpha_S^2 - 1)/2]$, where R_G is the radius of gyration and N_A Avogadro's number; α_S^2 is taken from the Yamakawa–Tanaka relation.[15]

Calculated and experimental values are in reasonable agreement. This is shown in Table IV.

Conclusion

The experimental results given in this paper show the low sensitivity of the viscosity of dilute xanthan solutions in the presence of external monovalent salt at least at moderate ionic concentrations. For concentrations larger than 3×10^{-1} N, the aggregation process is observed, causing an increase of viscosity. The Mark–Houwink parameters for different ionic strengths were given and the extrapolated values for infinite salt content follow the relation

$$[\eta] = 5.66 \times 10^{-4} M^1$$

This behavior means that the molecule is relatively stiff and in that respect seems to present analogies with DNA.

The determination of an empirical stiffness parameter as proposed by Smidsrod shows a normal value with regard to the rigidity of the xanthan molecule compared with that of DNA. The interpretation of the dependency $[\eta](\mu)$ is suggested in term of the Odijk model; from this treatment, an intrinsic persistence length L_p = 310 Å is found to be valid for the different molecular weight samples in the renatured conformation. For $C_s > 10^{-2}$ the electrostatic L_e contribution is small, compared with L_p, hence the slight variation of $[\eta]$ with ionic strength. This treatment gives a theoretical justification to the empirical Smidsrod parameter.

Finally, the A_2 parameter is found to be zero at infinite ionic strength, and values theoretically calculated with the Flory–Orofino relation are in reasonable agreement with experimental values.

Registry No. NaCl, 7647-14-5; xanthan gum, 11138-66-2.

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