

VISCOSITY BEHAVIOR OF LACQUER POLYSACCHARIDE IN AQUEOUS SOLUTION

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ABSTRACT

The dependence of measured viscosity on NaCl concentration (0.1 to 3.0M), pH (range of 2 — 13) and cadoxen composition w_{cad} (from 2% to 100%) for the lacquer polysaccharide in NaCl/cadoxen/H₂O mixture containing HCl or without were obtained. All the viscosity exponents γ in the Mark-Houwink equations under three different solvent condition are close to 0.5. The w_{cad} dependence of reduced viscosity η_{sp}/c confirms the single strand chain of the polysaccharide. As the γ values close to 0.5 and values of unperturbed dimension $\langle S^2 \rangle_0 / M$ and $[\eta]$ much smaller than those for usual linear polymers, these facts suggest that the polysaccharide chains in the aqueous solutions should be dense random coil owing to the highly branched structure.

Recently much attention has been paid to the polysaccharide isolated from the sap of lac trees. The polysaccharide plays an important role in the durability of lacquer films by protecting the polymerized urushiol from oxidative degradation^[1]. Further, it has special biological activities in anti-cancer and immunochemistry^[2]. Oshima et al.^[3] demonstrated that the polysaccharide consists of a $\beta(1-3)$ — linked galactose main chain and a number of randomly distributed side chains mostly having a terminal uronic acid group which is responsible for the biological activities mentioned above. Kumanotani^[1] showed the polysaccharide existing as rather regular aggregates in lacquer film. Our previous reports of light scattering^[4] and osmometry^[5] suggested a spherical random coil for the polysaccharide conformation in aqueous KCl / NaAc solution, but there remained much to be seen for dilute-solution behavior of the polymer.

In the previous work, it was found that aqueous NaCl solution of the polysaccharide were not very stable. After stored for a week, the solute came out as a gelatinous precipitate^[4]. Very recently, we found that a small amount of cadoxen, a solvent for cellulose, was added to an aqueous NaCl solution, the polysaccharide became quite stable. As our previous work on osmometry^[5], the number average molecular weight $\overline{M}_n$ of the polysaccharide in 0.5 M KCl / 10% cadoxen were satisfactorily measured, and their $A_2 \sim \overline{M}_n$ relationship were found to be $A_2 = 0.142 \overline{M}_n^{-0.48}$, which implied the aqueous containing cadoxen was a good solvent for the polysaccharide. It is interesting to investigate the viscosity behavior of the polysaccharide in aqueous NaCl containing cadoxen.

In this paper, described below, the dependence of measured viscosity on NaCl

concentration, pH and cadoxen composition for the polysaccharide in NaCl/cadoxen/H₂O mixture were discussed, clinging to Mark-Houwink equations obtained under three different solvent conditions.

EXPERIMENTAL

Samples

The polysaccharide samples isolated from the sap of lac trees (Vietnam) used were provided by Prof. Kumanotani of Ehime University in Japan. They were one unfractionated sample (unFR) and seven fractionated samples. Their weight average molecular weights $\overline{M}_w$ are listed in Table 1.

Table 1 Data of $\overline{M}_w$ and $[\eta]$ for the lacquer polysaccharide in aqueous NaCl/cadoxen solutions at 30 °C

Samples No.	$\overline{M}_w^4 \times 10^{-4}$	$[\eta] / \text{cm}^3 \text{g}^{-1}$		
		0.01M NaCl / 2% cadoxen (pH=13)	1.0M NaCl / 2% cadoxen / 0.1 M HCl (pH=9.5)	1.0 M NaCl / 2% cadoxen (pH=13)
FR2	13.5	9.96	8.32	7.66
FR3	12.8	9.88	8.08	7.50
FR5	10.1	8.52	—	6.70
FR6	7.52	7.36	6.18	5.79
FR7	6.33	—	5.78	—
FR8	5.85	6.64	5.54	5.08
FR9	5.38	—	—	4.98
unFR	10.9	6.76	6.84	5.95

Solution preparation

NaCl/cadoxen/H₂O mixtures containing HCl or without were prepared with distilled water and spectroscopic grade NaCl according to our previous method^[6]. The polysaccharide dissolved rapidly in the mixture. Aqueous 1.0M NaCl/2% cadoxen/HCl solutions with desired pH from 2 to 13 were obtained by neutralization of initial basic solutions (pH=13) with concentrated HCl. Neither turbidity nor fungus were found in aqueous 1.0M NaCl/2% cadoxen solution at room temperature for three weeks. The reduced viscosity η_{sp}/c for unFR in pure cadoxen remained unchanged for 24 hours, indicating that neither aggregation nor degradation took place in the solution.

Viscosity

Solution viscosities were measured at 30 ± 0.05 °C using a modified capillary viscometer of the Institute of Production and Technology in Tokyo University. Kinetic energy correction was unnecessary. Huggins' plot were used to estimate the intrinsic viscosities $[\eta]$, when η_{sp}/c sharply increase in aqueous 0.01 M NaCl/10% cadoxen and 0.1M NaCl/10% cadoxen, the Fouss equation^[7] were used. All the data were taken within 4 hours after the preparation of solutions.

Potentiometric titration

pH of polysaccharide solutions were determined with concise pH paper. potentiometric titration was carried out on a PXS-5 digital ionic pH-meter. The apparent dissociation constant k_a of the unFR polysaccharide was calculated to be 4.9×10^{-4} from the transition point of the titration curve. The degree of ionization α was evaluated from:

$$\text{pH} = \text{p}k_a + \lg \frac{\alpha}{1 - \alpha}$$

where, $\alpha = [\text{COO}^-] / ([\text{COO}^-] + [\text{COOH}])$, The concentration of carboxylic acid groups was obtained from the structure composition of the polysaccharide^[2].

RESULTS AND DISCUSSION

pH dependence of intrinsic viscosity

The unfilled circles in Figure 1 show $[\eta]$ data plotted against pH for aqueous 1.0 M NaCl / 2% cadoxen / 0-0.2M HCl solutions of the unFR sample. prepared from basic solution to the indicated pH by adding HCl. As pH increases, $[\eta]$ sharply increases up to pH=7 and then decrease. The half-filled circles were obtained from solutions which were brought to the indicated pH by adding NaOH to acidic polysaccharide solutions of aqueous 1.0 M NaCl / 2% cadoxen / 0.2M HCl (pH=2). Their falling on the same curve indicates the reversibility of the observed change in $[\eta]$ with pH.

The filled circles in Figure 1 show that $[\eta]$ increases all the way with the increase of α up to $\alpha=1$ (pH=7). This conforms to normal weak polyelectrolyte behavior that polymer chains expand by electrostatic repulsion among charged groups of polyions^[8]. This behavior is distinctly different from that observed for double helical Xanthan, an ionic polysaccharide, whose $[\eta]$ is almost constant throughout the entire range of α ^[9,10].

Salt concentration dependence of $[\eta]$

Figure 2 illustrates double-logarithmic plots of $[\eta]$ vs. NaCl concentration C_s for the unFR sample in aqueous NaCl / 10% cadoxen and aqueous NaCl / 2% cadoxen. The intrinsic viscosities in both solvents decrease linearly with C_s in the range of C_s from 0.01 to 1.0 M NaCl. This is also typical polyelectrolyte behavior that molecular dimensions reduce with an increase of C_s owing to screening of intrachain ionic interaction^[11]. The intrinsic viscosities in aqueous NaCl / 10% cadoxen are systematically larger than those in aqueous NaCl / 2% cadoxen implying that the polysaccharide chains are more expanded in the former solvent than in the latter solvent. This is probably due to the enhancement in solvent affinity for the sugar units by cadmium diaminoethane in cadoxen, as interpreted by Gadd for cellulose^[12]. To examine the effect of cadoxen on viscosity in more detail, the dependence of reduced viscosity η_{sp}/c ($c = 8 \times 10^{-3} \text{ gcm}^{-3}$) on cadoxen composition W_{cad} for the unFR sample in cadoxen-water mixtures determined. The results showed in Figure 3 indicate that the increase of W_{cad} induces an

increase in η_{sp}/c or hence in chain dimension. This is in contrast with the observed viscosity behavior of xanthan whose $[\eta]$ decreases sharply with an increase in W_{cad} as the result of the dissociation of the double helix to single chain^[13]. At this point, we may say that the lacquer polysaccharide exists in cadoxen-water mixtures as single strand chains. In this connection, we note that the intrinsic viscosities of 8.4 and 6.7 g⁻¹ cm³ previously determined for the unFR sample in 0.1 and 0.4 M aqueous KCl buffer (pH=7.1) respectively^[4], are comparable to 6.78–8.56 g⁻¹ cm³ in 2–100% cadoxen-water mixtures containing HCl (pH=2–12).

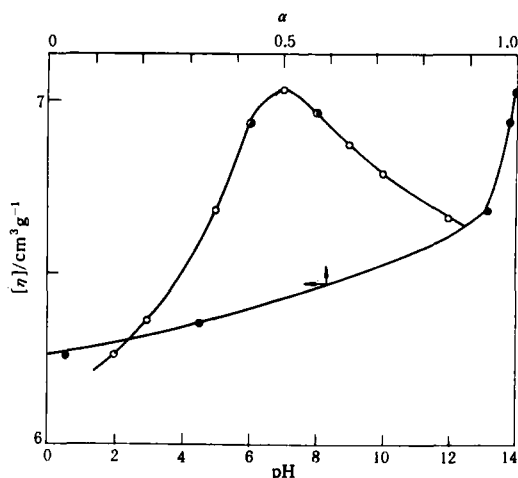


Fig. 1 Plots of $[\eta]$ vs. pH (O and ●) and $[\eta]$ vs. α (●) for the unFR sample in aqueous 1.0M NaCl/2% cadoxen/0–0.2M HCl at 30 °C

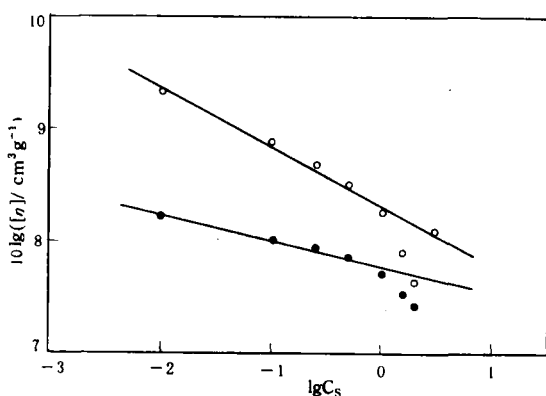


Fig. 2 Plots of $\lg [\eta]$ vs. $\lg C_s$ for unFR sample in aqueous 0.01–3.0 M NaCl/10% cadoxen (O) and aqueous 0.01–2.0 M NaCl/2% cadoxen (●) at 30 °C

Mark-Houwink equation

Figure 4 depicts double-logarithmic plots of $[\eta]$ against $\overline{M}_w$ for the lacquer polysaccharide in aqueous 0.01M NaCl/2% cadoxen (pH=13), 1.0M aqueous

NaCl / 2% cadoxen / 0.1M HCl (pH=9.5), and 1.0M aqueous NaCl / 2% cadoxen (pH=13), and also a double-logarithmic plot of η_{sp}/c vs. $\overline{M}_w$ ($C=4 \times 10^{-3} \text{ gcm}^{-3}$) in aqueous 1.0M NaCl / 2% cadoxen / 0.2M HCl (pH=2). The data in the first three solvents are represented by the following Mark-Houwink equations:

$$\begin{aligned} [\eta] &= 2.19 \times 10^{-2} \overline{M}_w^{0.51} \quad (\text{in } 0.01 \text{ M NaCl / 2\% cadoxen pH=13}) \\ [\eta] &= 2.69 \times 10^{-2} \overline{M}_w^{-0.5} \quad (\text{in } 1.0 \text{ M NaCl / 2\% cadoxen / 0.1M HCl pH=9.5}) \\ [\eta] &= 2.64 \times 10^{-2} \overline{M}_w^{-0.49} \quad (\text{in } 1.0 \text{ M NaCl / 2\% cadoxen pH=13}) \end{aligned}$$

It is to be observed that our $[\eta]$ values are much smaller than those for usual linear polymers when compared at the same $\overline{M}_w$. All the viscosity exponents γ are close to 0.5 which is characteristic of polymers near θ condition. But as above the mixtures used are good solvents for the polysaccharide. Generally, γ for a flexible polymer in a good solvent ranges from 0.6—0.8^[14]. From the fact that the γ values close to 0.5 and the $[\eta]$ values much smaller than those for usual linear polymers, it suggest that the polysaccharide chains in aqueous NaCl / cadoxen should be dense random coils. This must be due to the highly branched structure of the polysaccharide.

Unperturbed dimension

The K_θ of the polysaccharide in the above mentioned solutions were estimated from the $[\eta]$ data according to Stockmayer—Fixman theory^[15].

$$[\eta] / M^{\frac{1}{2}} = K_\theta + C\phi BM^{\frac{1}{2}} \quad (1)$$

where ϕ is the Flory viscosity constant, B , a parameter relevant with the excluded volume; K_θ , a constant related to the unperturbed dimension $\langle S^2 \rangle_\theta / M$ of the polymer by:

$$K_\theta = \phi_0 (6 \langle S^2 \rangle_\theta / M)^{3/2} \quad (2)$$

where ϕ_0 value is assumed as 2.55×10^{23} ; $\langle S^2 \rangle_\theta$, the mean square average radius of gyration under θ condition.

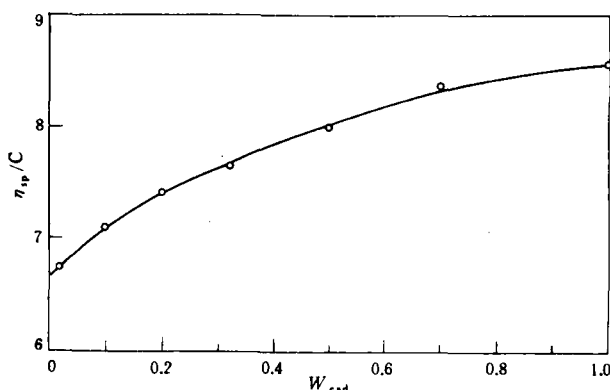


Fig. 3 Cadoxen composition w_{cad} dependence of η_{sp}/c for unFR sample in cadoxen-water mixtures at 30°C

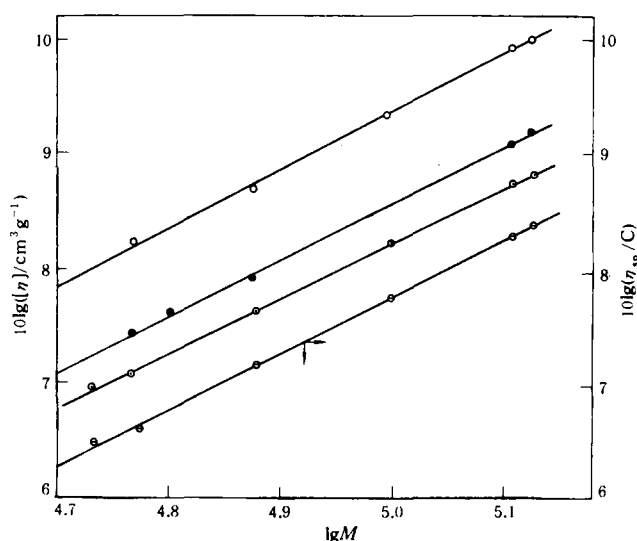


Fig. 4 Plots of $\lg [\eta]$ or η_{sp}/c vs. $\lg M$ for FR samples in listed solvents: 0.01 M NaCl / 2% cadoxen, pH=13 (○) ; 1.0 M NaCl / 2% cadoxen / 0.1 M HCl, pH=9.5 (●) ; 1.0 M NaCl / 2% cadoxen pH=13 (○) ; 1.0 M NaCl / 2% cadoxen / 0.2 M HCl pH=2 (○)

The K_θ values obtained from the plots of $[\eta]/M^{\frac{1}{2}}$ vs. $M^{\frac{1}{2}}$ and the unperturbed dimension $\langle S^2 \rangle_\theta / M$ calculated according to equation (2) are summarized in Table 2. the values of $\langle S^2 \rangle_\theta / M$ are much smaller than those of $7 - 9 \times 10^{-18}$ for general linear polymers^[16-18]. This is a further evidence that the lacquer polysaccharide chain in the aqueous solutions appears to be a dense compact coil.

Table 2 K_θ and $\langle S^2 \rangle_\theta / M$ values of lacquer polysaccharide in aqueous NaCl / cadoxen solutions at 30 °C

Solvents	$K_\theta \times 10^2$	$\langle S^2 \rangle_\theta / M \times 10^{18}$
0.01M NaCl / 2% cadoxen (pH=13)	2.40	3.45
1.0M NaCl / 2% cadoxen / 0.1 M HCl (pH=9.5)	2.27	3.32
1.0M NaCl / 2% cadoxen (pH=13)	2.24	3.29

CONCLUSION

The viscosities of the lacquer polysaccharide in aqueous NaCl/2% cadoxen solutions were measured satisfactorily. The polysaccharide dissolved rapidly in the mixture to form very stable solution. The reduced viscosities of the polysaccharide in cadoxen-water increase smoothly with cadoxen composition suggesting that the polysaccharide chains exist in single strand. The pH dependence of $[\eta]$ for the polysaccharide in aqueous 1.0M NaCl / 2% cadoxen / 0-0.2M HCl indicates the polymer chains reversibly expanded or contracted through electrostatic interaction at pH from 2 to 13. The Mark-Houwink constants γ close to 0.5 and $\langle S^2 \rangle_\theta / M$

values being 3.29×10^{-18} — 3.45×10^{-18} indicate that the lacquer polysaccharide in aqueous NaCl /cadoxen with or without HCl solution adopts dense random coil as a consequence of the highly branched structure^[3].

Keywords:

Lacquer; Polysaccharide; Intrinsic viscosity; Aqueous solution; cadoxen .

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