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VISCOSITY BEHAVIOUR AND PERSISTENCE LENGTH OF SODIUM XANTHAN IN AQUEOUS SODIUM CHLORIDE

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Zero-shear-rate intrinsic viscosities $[\eta]$ of sodium xanthan in aqueous NaCl at 25°C were determined for five samples ranging in weight-average molecular weight from 2×10^5 to 4×10^6 at salt concentrations C_s between 0.005 and 1 M, at which the polysaccharide maintains its double-helical structure. The measured $[\eta]$ for every sample was almost independent of C_s, in contrast to usual observations on flexible polyelectrolytes. The persistence length q of sodium xanthan was determined as a function of C_s by use of the theory of Yamakawa et al. for $[\eta]$ of an unperturbed worm-like cylinder, and from its C_s dependence the intrinsic persistence length q_0 ($= q$ at infinite ionic strength) was estimated to be 106 nm. This q_0 value was roughly twice as large as that of double-stranded DNA, indicating a high intrinsic rigidity of the xanthan double helix. The electrostatic contribution ($= q - q_0$) to q was only about 10% even at the lowest C_s of 0.005 M. Thus, it was concluded that above $C_s = 0.005$ M, the double-helical structure of sodium xanthan is hardly stiffened by electrostatic interactions between charged groups.

1. Introduction

Xanthan is an ionic polysaccharide produced by the bacterium *Xanthomonas campestris*. It consists of repeating units [1,2] shown in fig. 1, but, in the samples used in our previous work [3–5], only about one-third of the terminal residues of the trisaccharide side chains was pyruvated. With these samples, it was shown that the sodium salt of xanthan dissolves in 0.1 M aqueous NaCl as a rigid double helix behaving like an unperturbed worm-like chain [3–5]. According to the theory of Odijk [6] and that of Skolnick and Fixman [7], the persistence length q of a worm-like polyelectrolyte

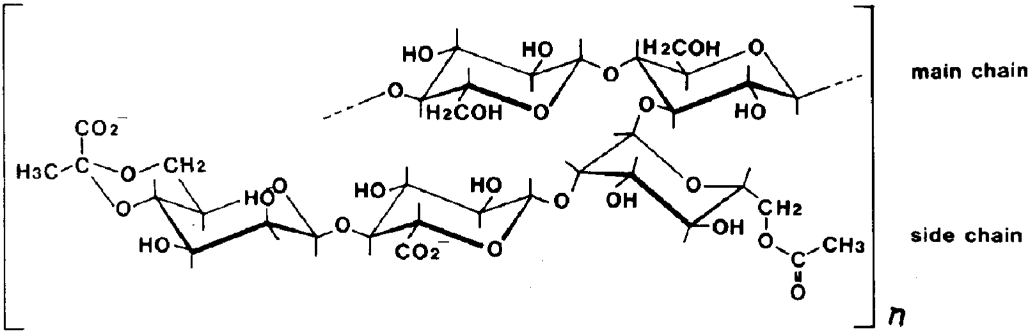

Fig. 1. Repeating unit of xanthan.

in aqueous salt is the sum of two terms, i.e.,

$$q = q_0 + q_{\mathrm{el}} \tag{1}$$

Here, q_0 is the persistence length in the absence of electrostatic interaction and is considered to represent the chain stiffness intrinsic to the backbone of the polyelectrolyte, while q_{el} represents the contribution from electrostatic repulsion of charged groups. The latter vanishes at infinite I (ionic strength of the solvent) so that q_0 can be evaluated by extrapolating experimental q at different I to infinite I.

The present paper describes a viscosity study made to estimate q_0 of the double helix of sodium xanthan in aqueous NaCl at 25°C. A comparison between the experimentally determined I dependence of intrinsic viscosity and theoretical predictions [6–10] is also described.

2. Experimental

2.1. Samples and preparation of solutions

From the samples used in our previous studies [3–5] sodium xanthan X5-6, X3-5, X7-3b and X10-4, were chosen for the present experiment. Their M_w (weight-average molecular weight), $\mathrm{DS}_{\mathrm{pyr}}$ (degree of pyruvation) and σ (charge density expressed in units of elementary charge per unit contour length) [3–5] are listed in table 1.

These samples were dissolved in aqueous NaCl of a salt concentration C_s of 0.005 M, and the solutions were kept at 25°C overnight under stirring to ensure complete dissolution. Aqueous NaCl was then added to prepare solutions of desired C_s. The NaCl used was recrystallized by the standard method. Deionized, distilled water was passed through a mixed-bed ion exchanger (Amberlite IR-120 + IRA-410) just before use.

Table 1

Molecular characteristics of the sodium xanthan samples used

Samples	M_w ($\times 10^{-4}$) [a]	$\mathrm{DS}_{\mathrm{pyr}}$	σ (nm^{-1}) [b]
X5-6	394	0.4	3.0
X3-5	142	0.3	2.8
X9-3	99.4	0.4	3.0
X7-3b	60.3	0.4	3.0
X10-4	20.9	0.4	3.0

[a] In 0.1 M aqueous NaCl at 25°C.

[b] Calculated for the double-helical dimer of sodium xanthan from the relation $\sigma = 2(1 + \mathrm{DS}_{\mathrm{pyr}})/2h$ with a helix pitch h of 0.47 nm per main chain residue [3,5].

2.2. Viscometry

Zero-shear-rate viscosities of aqueous NaCl solutions at 25°C were determined under an argon atmosphere by low-shear four-bulb capillary viscometers for all the samples except the lowest molecular weight sample X10-4, for which use was made of a conventional capillary viscometer of the Ubbelohde type. The measurement was restricted to C_s above 0.005 M, since optical rotation data [11,12] suggested that sodium xanthan does not maintain its double-helical structure at C_s below 0.005 M unless the temperature is lowered below 25°C.

3. Results

Figs. 2 and 3 illustrate the dependence of reduced viscosity η_{sp}/c at zero shear rate on polymer mass concentration c for the highest and lowest molecular weight samples X5-6 and X10-4, respectively. The plots in the former are linear and yield zero-shear-rate intrinsic viscosities $[\eta]$, which are distinctly larger for lower C_s. On the other hand, those in the latter converge to nearly equal intercepts, indicating that $[\eta]$ for sample X10-4 is insensitive to C_s.

The C_s dependence of $[\eta]$ for five xanthan samples is displayed in fig. 4. The curves for the three lower molecular weight samples are substantially horizontal, while those for the two higher molecular weight samples begin to rise slightly with decreasing C_s only below 0.02 M. The filled circles, which represent the data of Rinaudo and Milas [13] for a sodium xanthan sample with $M_w = 2 \times 10^6$, exhibit no substantial ionic strength dependence either, and are consistent with our data. The weak C_s dependence of $[\eta]$ found here differs greatly from that usually observed for flexi-

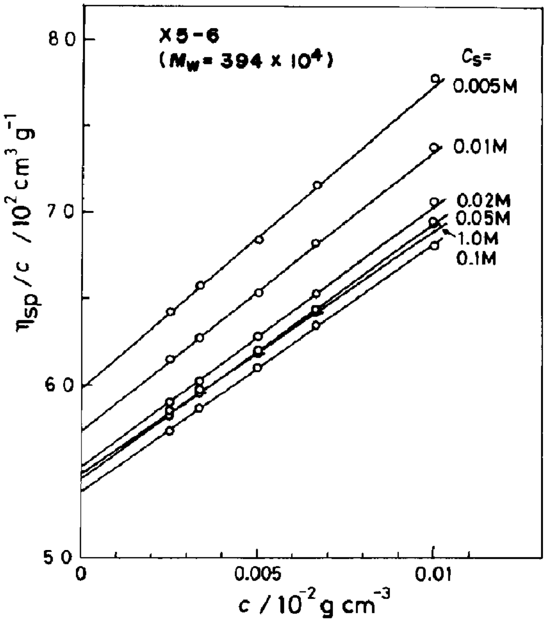

Fig. 2. Concentration dependence of η_{sp}/c for sodium xanthan sample X5-6 in aqueous NaCl of indicated C_s at 25°C.

ble polyelectrolytes, for which $[\eta]$ increases markedly with decreasing C_s.

Fig. 5 illustrates the C_s dependence of Huggins' constant k'. For C_s above 0.1 M, the values of k' are normal (≤ 0.5) and almost independent of C_s for any samples. For C_s below 0.1 M, k' for the lowest molecular weight sample increases anoma-

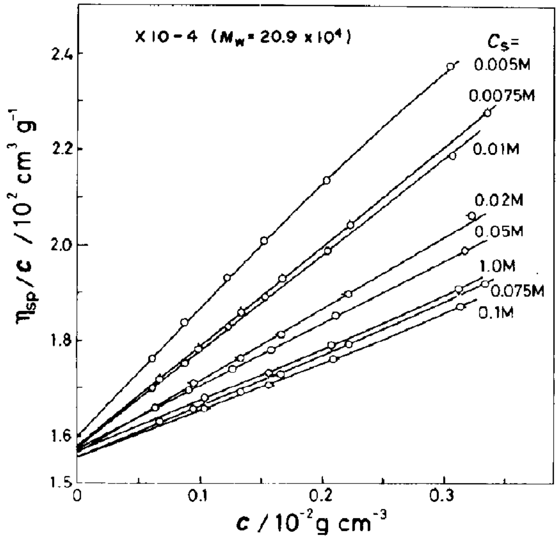

Fig. 3. Concentration dependence of η_{sp}/c for sodium xanthan sample X10-4 in aqueous NaCl of indicated C_s at 25°C.

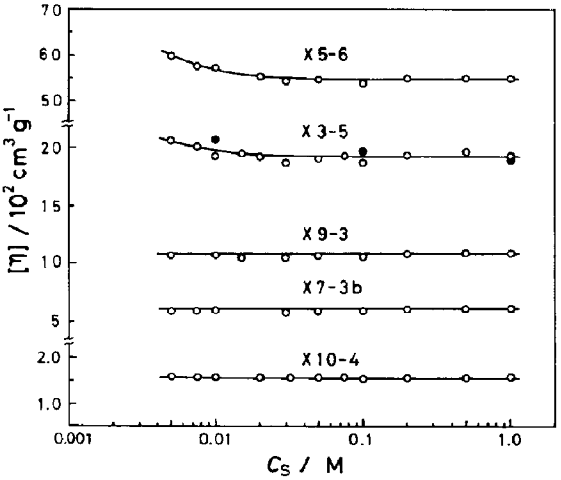

Fig. 4. Ionic strength dependence of $[\eta]$ for sodium xanthan samples in aqueous NaCl at 25°C. (●) Data of Rinaudo and Milas [13].

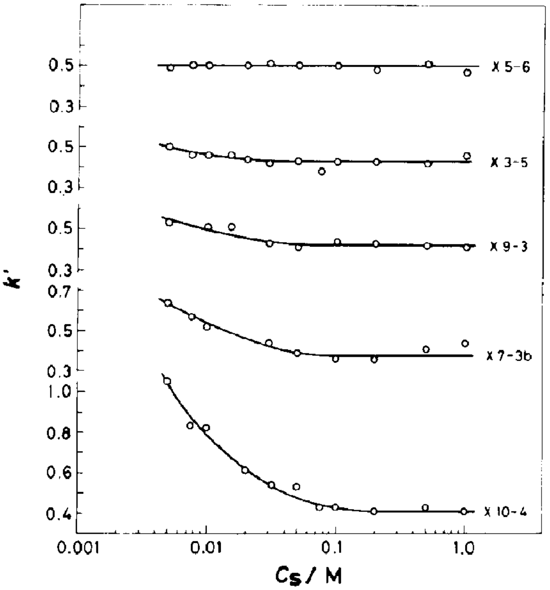

Fig. 5. Values of Huggins' constant plotted against C_s for sodium xanthan samples in aqueous NaCl at 25°C.

lously with decreasing C_s, whereas that for the highest molecular weight sample remains nearly constant. At present, we find no reasonable explanation for this striking M_w-dependent behaviour of k'.

Fig. 6 shows $[\eta]$ at $C_s = 0.005$, 0.01 and 1 M plotted double-logarithmically against M_w. The dashed line has been calculated for the completely rigid double helix of sodium xanthan from the theory of Yoshizaki and Yamamaka [14] with the previously determined values of 0.47 nm [3,5] for the helix pitch h per main chain glucose residue and 2.2 nm [4] for the hydrodynamic diameter d. With an increase in M_w, the three curves fitting the data points for respective C_s deviate progressively from the dashed line, indicating that the xanthan double helix bends more at higher M_w. This is the behaviour expectable for an unperturbed worm-like chain.

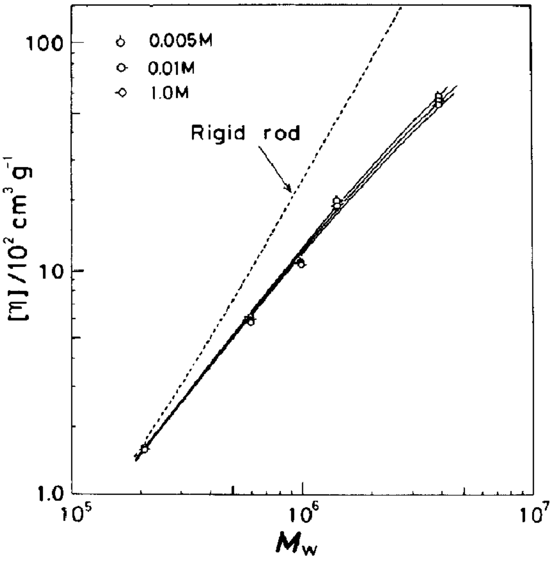

Fig. 6. Molecular weight dependence of $[\eta]$ for sodium xanthan in aqueous NaCl of $C_s = 0.005$, 0.01 and 1 M at 25°C. (— — —) Values calculated for the completely rigid double helix of sodium xanthan from the theory of Yoshizaki and Yamakawa [14] with $h = 0.47$ nm and $d = 2.2$ nm.

4. Discussion

4.1. Rigidity of the xanthan double helix

Bohdanecký [15] showed that the theory of Yamakawa et al. [9,10] for $[\eta]$ of an unperturbed worm-like cylinder can be approximated by

$$(M^2/[\eta])^{1/3} = K + SM^{1/2} \tag{2}$$

with

$$K = 1.516 \times 10^{-8} A_0 M_L \ (g^{1/3}\,cm^{-1}) \tag{3}$$

$$S = 1.516 \times 10^{-8} B_0 (M_L/2q)^{1/2} \ (g^{1/3}\,cm^{-1}) \tag{4}$$

where M is the molecular weight of the polymer, M_L the molar mass per unit contour length, and A_0 and B_0, known functions of $d/2q$ [15]. If the intercept K and slope S of Bohdanecký's plot of $(M_w^2/[\eta])^{1/3}$ vs. $M_w^{1/2}$ at a given C_s are combined with $M_L = 1940$ nm^{-1} corresponding to $h = 0.47$ nm for the xanthan double helix, q can be evaluated as a function of C_s.

The Bohdanecký plots constructed from our data at $C_s = 0.005$, 0.01 and 1 M are shown in fig. 7, and the values of q obtained are summarized in table 2. Above $C_s = 0.03$ M, q stays at 106 nm * and hence this value may be equated to q at infinite ionic strength, i.e., q_0 for the double helix of sodium xanthan in aqueous NaCl at 25°C. This q_0 value is larger by two orders of magnitude than those reported for flexible polyelectrolytes [16,17] and almost twice as large as that for double-stranded DNA [18], indicating a high intrinsic rigidity of the xanthan double helix.

The hydrodynamic diameters d evaluated also from the Bohdanecký plot were about 2.2 nm, almost independent of C_s. This d value agrees with 2.4 ± 0.3 nm estimated previously [5] from $[\eta]$ and sedimentation coefficient data at $C_s = 0.1$ M.

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* This q of 106 nm agrees with the previously estimated q value of 120 ± 20 nm at $C_s = 0.1$ M [5].

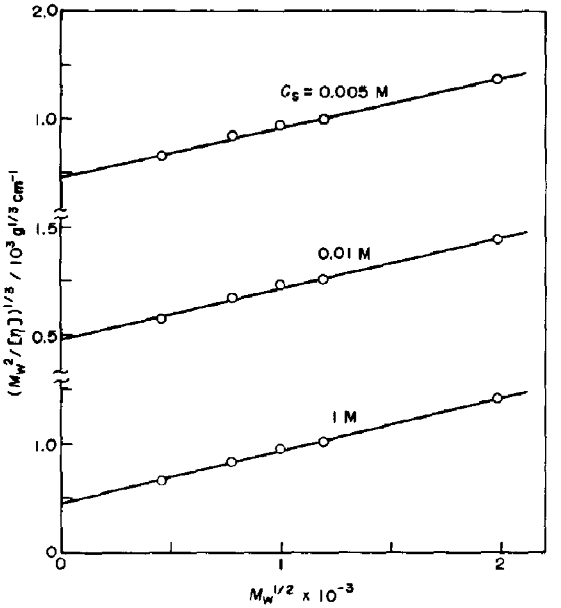

Fig. 7. Bohdanecký plots for sodium xanthan samples in aqueous NaCl at indicated C_s.

4.2. *Electrostatic contribution to the persistence length*

The fourth column of table 2 presents the values of q_{el} calculated from eq. 1 with $q_0 = 106$ nm and the q values in the second column. At any C_s, q_{el} is much smaller than q_0 and makes only an almost negligible contribution to the total persistence length q. Thus, it may be concluded that in the range of C_s studied, electrostatic repulsion of charged groups has almost no influence on stiffening of the double-helical structure of sodium xanthan.

Table 2

Values of q, q_0 and q_{el} for sodium xanthan in aqueous NaCl at 25°C

C_s (M)	q (nm)	q_0 (nm)	q_{el} (nm)
0.005	12_0		14 [a]
0.01	11_3		7 [a]
0.03–1	10_6		0
Infinite I		10_6	

[a] These values are not very accurate, since $q \sim q_0$.

The relation $q_{el} \ll q_0$ found above implies that $[\eta]$ of the xanthan double helix in aqueous NaCl is determined substantially by q_0 unless the molecular weight is too high or C_s is too low. In other words, the very weak dependence of $[\eta]$ on C_s observed in fig. 4 is a reflection of the high intrinsic rigidity of the double-helical structure.

4.3. *Comparison between theory and experiment*

The Odijk-Skolnick-Fixman expression [6,7] for q_{el} of a wormlike polyelectrolyte in aqueous 1-1 electrolyte is

$$q_{el} = 1/4\kappa^2 Q \quad (\text{for } \sigma Q \geqslant 1) \tag{5}$$

Here, Q and κ are, respectively, the Bjerrum length (= 0.714 nm for water at 25°C) and the reciprocal of the Debye length defined by

$$\kappa^2 = 8\pi Q N_A C_s/1000 \tag{6}$$

with N_A being the Avogadro constant (C_s is expressed in units of mol l^{-1}). It should be noted that eq. 5 has been derived on the basis of the Debye-Hückel approximation to the Poisson-Boltzmann equation and the Manning theory [19] for ion condensation. Le Bret [8] numerically calculated q_{el} for a charged toroid with a radius of a_t and a dielectric constant D, using the complete Poisson-Boltzmann equation, and tabulated the calculated q_{el} values as a function of σ and κa_t for $D/D_0 = 0$ and ∞ (D_0, dielectric constant of water). Fixman [20] also carried out a similar calculation and obtained essentially the same results as those of Le Bret.

The theoretical predictions of Odijk [6], Skolnick and Fixman [7] and Le Bret [8] can be compared with our $[\eta]$ vs. C_s relations for xanthan samples if their theories are combined with that of Yamakawa et al. [9,10] for $[\eta]$ of an unperturbed worm-like chain. In fig. 8, theoretical and experimental values of $[\eta]$ for sample X5-6 (panel A) and those of $[\eta]_{0.005}/[\eta]_\infty$ (subscript 0.005 refers to $C_s = 0.005$ M and subscript ∞ to infinite I) (panel B) are plotted against log C_s and log M_w, respectively. Here, the average of $[\eta]$ at $C_s \geqslant 0.03$ M was taken as experimental $[\eta]_\infty$, and the theoretical $[\eta]$ values were calculated with $M_L = 1940$

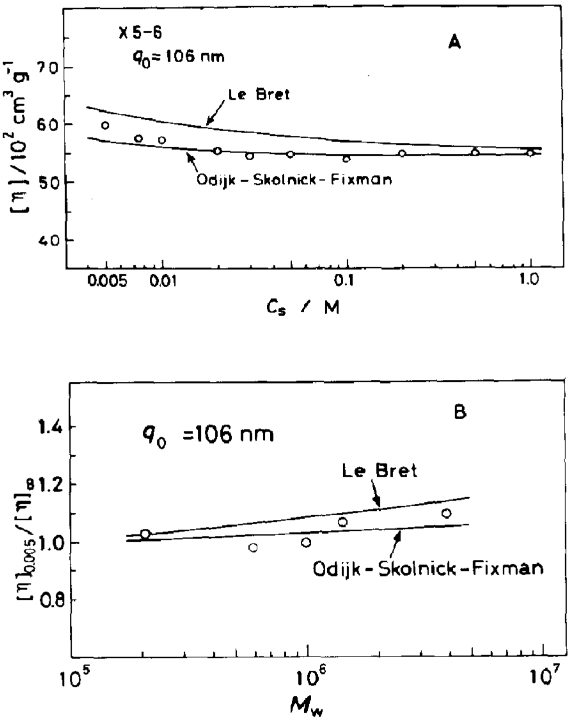

Fig. 8. Comparison between the measured [η] (circles) for sodium xanthan and the values (curves) calculated from the theories of Odijk [6], Skolnick and Fixman [7] and Le Bret [8] for q_{el} combined with that of Yamakawa et al. [9,10] for [η]. $[\eta]_{0.005}$, [η] at $C_s = 0.005$ M; $[\eta]_\infty$, [η] at infinite ionic strength.

nm^{-1}, $d = 2.2$ nm and the q values obtained by substituting Odijk-Skolnick-Fixman's or Le Bret's theoretical q_{el} and our experimental q_0 of 106 nm into eq. 1; in evaluating Le Bret's q_{el} values, D/D_0 and a_t were assumed to be 0 and 1.1 nm ($= d/2$), respectively.

It can be seen in fig. 8 that both Odijk-Skolnick-Fixman's and Le Bret's theories combined with that of Yamakawa et al. describe fairly accurately the experimental C_s dependence of [η] and the molecular weight dependence of $[\eta]_{0.005}/[\eta]_\infty$. A similar agreement was found for the C_s dependence of $\langle S^2 \rangle^{1/2}$ (radius of gyration) of double-stranded DNA by Mandel and Schouten [21], who compared the experimental data with eq. 5 combined with Benoit and Doty's expression [22] for $\langle S^2 \rangle$ of an unperturbed worm-like chain.

5. Concluding remarks

The agreement between theory and experiment shown above (fig. 8) does not always prove the theories of Odijk [6], Skolnick and Fixman [7] and Le Bret [8] for q_{el}. The reason is as follows. As mentioned in section 4, [η] of the xanthan double helix in aqueous NaCl is determined essentially by q_0 in the range of C_s studied. In fact, even at $C_s = 0.005$ M (the lowest C_s studied), Odijk-Skolnick-Fixman's and Le Bret's q_{el} values, which are 6.5 and 18 nm, respectively, are much smaller than 106 nm for q_0. Hence the large difference of these q_{el} values results in a relatively small difference in q, and hardly affects either [η] vs. log C_s or $[\eta]_{0.005}/[\eta]_\infty$ vs. log M_w curve (see fig. 8). Thus, double-helical sodium xanthan in aqueous NaCl at 25°C is intrinsically too rigid to be used for a critical test of the q_{el} theories.

It seems from the above consideration that flexible polyelectrolytes are more advantageous for an experimental check of the q_{el} theories. However, this is not always true, since [η] or $\langle S^2 \rangle$ of such polymers should be appreciably perturbed by excluded-volume effects for which no rigorous way of correction is yet established. To avoid this complexity, Mandel and Schouten [21] used a low molecular weight DNA with $M_w = 3 \times 10^5$ in their light scattering study cited above, and found that $\langle S^2 \rangle^{1/2}$ in the range of C_s studied ($C_s \geqslant 0.005$ M) did not differ greatly from that at infinite I, i.e., it is essentially determined by q_0. Hence, we cannot say that the agreement between theory and experiment found by these authors has lent support to the q_{el} theories. In conclusion, the current polyelectrolyte theory for the persistence length has yet to be checked with well-characterized stiff polyelectrolytes.

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