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Controlled Gelation of Xanthan by Trivalent Chromic Ions

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ABSTRACT

Addition of trivalent chromic ions to xanthan solutions gives rise to gel formation. The dynamic shear storage and loss moduli (0·01–10 rad/s) of xanthan solutions with polymer concentrations ranging from 1 to 7 mg/ml and Cr^{3+} *concentrations ranging from 0 to 50 mM have been studied. It is found that the rate of gel formation is strongly dependent on the* Cr^{3+} *concentration, but to a much smaller extent on the xanthan concentration. The gelation time is less than 1 h for 50 mM* Cr^{3+} *and about 40 h for 2 mM* Cr^{3+}*. It is found that the minimum* Cr^{3+} *concentration needed to give gelation of 1–7 mg/ml xanthan is 1–2 mM.*

INTRODUCTION

Xanthan is the extracellular polysaccharide produced by the microorganism *Xanthomonas campestris* (Jeanes *et al.*, 1961; Rees, 1972; Jansson *et al.*, 1975). This *exo*polysaccharide has been used widely in various industrial prosesses (Sandford & Baird, 1983), but the strong current interest in xanthan is to a large extent stimulated by the large potential for use of this biopolymer as an additive to injection fluids for enhanced oil recovery. Xanthan, and highly viscous polymer solutions in general, are used to improve the sweep efficiency in polymer- or surfactant-flooding (Sandvik & Maerker, 1977) or, in a crosslinked state, as a rock-permeability modifying agent to avoid water-channeling in heterogeneous reservoirs (Hubbard *et al.*, 1986).

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The kinetics of gelation, that is, the time needed to change a xanthan preparation from a viscoelastic fluid to a viscoelastic solid, determines to a large extent how far from the injection well the polymer plug will settle. Several divalent and trivalent metal ions have been reported to either precipitate xanthan or cause gel formation (Doster *et al.*, 1984). Among these, Cr^{3+} is the only one which is added to the polymer commercially, and appears to be one of the most versatile ions with respect to range of gelation times. In the present study, the Cr^{3+}-induced gelation of xanthan was investigated by measuring the dynamic shear storage (G') and loss (G'') moduli.

MATERIALS AND METHODS

Xanthan was obtained as an oilfield grade, dried sample (Kelzan XCD, Kelco Inc., A Division of Merck, San Diego, California, USA). Polymer stock solutions (4·4 mg/ml) were prepared by dispersion of powdered xanthan in 0·1 M NaCl and stirred overnight. Both the stock solution and dilutions thereof were not clear solutions due to large unsolubilized polymer particles. To test to what extent these polymer particles affected the experimental results, we purified an aliquot of the stock solution by the following procedure. The solution was diluted with 0·1 M NaCl to a polymer concentration of approximately 0·3 mg/ml and ultracentrifuged at 90 000 × *g* for 1 h. The pellet contained less than 7% of the total polymer content. The clear supernatant was concentrated by evaporation of water under low pressure (Rotavapor) and then dialyzed against 4 × 1000 ml 0·1 M NaCl for 48 h. The polymer concentration was determined using a colorimetric method (Dubois *et al.*, 1956). The purified sample and a sample diluted to the same polymer concentration from the stock solution showed a difference of less than 5% in the measured dynamic loss and storage moduli, which approximately equals the variation in G' and G'' seen among different dilutions of the stock solution. Therefore xanthan obtained by dilution of the stock solution and not by the more elaborate ultracentrifugation preparation procedure was used in the gelation studies reported here.

The intrinsic viscosity of the purified sample was determined using a Cartesian diver viscometer (Troll *et al.*, 1980). Xanthan solutions with $\eta_{rel} < 2{\cdot}0$, and shear rate from $0{\cdot}2\ s^{-1}$ to $20\ s^{-1}$ were studied. The intrinsic viscosity of the purified sample obtained as (η_{sp}/c) extrapolated to zero polymer concentration and zero shear rate was determined to 7200 ± 250 ml/g in 0·1 M NaCl, at 20·0°C.

Chromium ion stock solutions were prepared by dissolving $Cr(NO_3)_3.9H_2O$ (Merck) in doubly distilled water.

Dynamic loss and storage moduli

Xanthan stock solution was diluted with 0·1 M NaCl to twice the desired final polymer concentration. A solution containing twice the desired final Cr^{3+} concentration was prepared by diluting the chromium ion stock solution with 0·1 M NaCl. Equal volumes of these two solutions were then combined and loaded into the viscoelastometer. Measurements of the dynamic loss and storage moduli were carried out using a gravitational pendulum viscoelastometer (Mikkelsen *et al.*, 1985). The instrument yields viscoelastic properties in shear deformation geometry in the linear viscoelastic regime. The computerized instrument was equipped with a pendulum-cuvette combination having an instrument parameter $C = 6$ dyn/cm^2. Both excitation frequency (ω) dependence of the dynamic loss and storage moduli, and time dependence of G' and G'' at a fixed excitation frequency were recorded. All measurements reported here were carried out at 20·0°C using a Haake DG 8 thermostat circulating water in the sample cuvette walls.

RESULTS AND DISCUSSION

The dynamic shear storage modulus (G') and dynamic shear loss modulus (G'') versus excitation frequency (ω) for various xanthan solutions is shown in Fig. 1. For the 2·7 mg/ml xanthan solution, G'' is about five times as large as G' at excitation frequency $\omega = 0{\cdot}1$ rad/s, whereas $G' \approx G''$ at $\omega = 3{\cdot}5$ rad/s. It was found that increasing the xanthan concentration to 6·3 mg/ml results in a marked increase of both G' and G'', but at the same time both dlog G'/dlog ω and dlogG''/dlog ω were reduced. The frequency where $G' = G''$ shifts towards lower values with increasing xanthan concentration; $G' = G''$ at 0·16 rad/s for 6·3 mg/ml xanthan and at 3·5 rad/s $G' = G''$ for 2·7 mg/ml xanthan. Both the magnitude of G' and G'', and the shift towards lower excitation frequency for the condition $G' = G''$ when the polymer concentration is increased, are in agreement with results reported elsewhere (Cuvelier & Launay, 1986).

The time development of the viscoelastic properties after adding Cr^{3+} to xanthan solutions is shown in Fig. 1(b). Just after mixing, G' is less than G'' for $\omega \approx 0{\cdot}5$ rad/s, and both G' and G'' are strongly dependent on ω. Three hours after mixing, both G' and G'' have increased, but G'' is

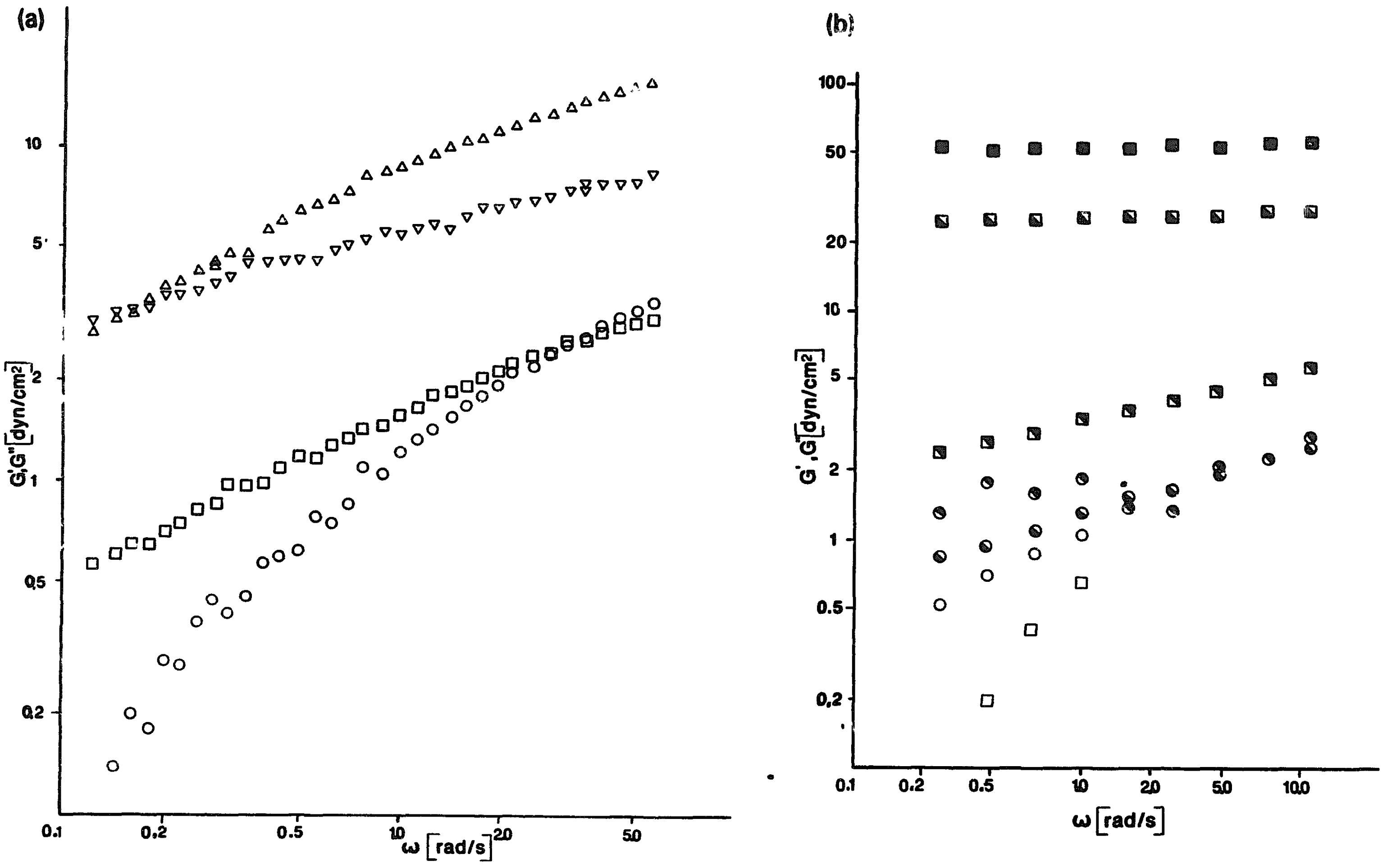

Fig. 1. The dynamic storage (G') and loss (G'') moduli versus excitation frequency (ω) for (a) a solution of purified xanthan in 100 mM NaCl, pH 7, at 20°C containing 2·7 mg/ml (○, □) and 6·3 mg/ml (△, ▽), and (b) 2·0 mg/ml xanthan, 100 mM NaCl, 5 mM [Cr^{3+}], pH 3·5, at 20°C, just after mixing (□, ○); 3 h (▨, ●); 15 h (▨, ●) and 20 h (■) after mixing. Only G' is shown 20 h after mixing.

now only about 25% of G' and the frequency dependence of both G' and G'' is less than just after mixing. After 15 h, G' has increased to about 25 dyn/cm^2, and is only slightly dependent on the excitation frequency in the range experimentally accessible with the gravitational pendulum viscoelastometer (0·01–10 rad/s). Contrary to the ten-fold increase in G' observed from 3 h to 15 h after mixing, only a two-fold increase in G'' was observed during the same period. However, at $t = 15$ h, G'' is less than 8% of G'. The relative uncertainty in G'' is significantly larger at $t = 15$ h than at smaller values of t. The shear storage modulus increases further with time and reaches a frequency independent level of about 50 dyn/cm^2 20 h after mixing (Fig. 1(b)).

The kinetics of gelation was monitored by measuring the time development of G' and G'' at an excitation frequency of 0·126 rad/s. Figure 2(a) shows log G' versus log t for three different xanthan concentrations, all with 5 mM Cr^{3+} and 100 mM NaCl added. Just after mixing, G' depends strongly on the xanthan concentration, because the entanglement contribution to G' depends on the polymer concentration. Fifteen hours after addition of Cr^{3+} it was found that the storage modulus of the xanthan-Cr^{3+} gel is less dependent on the total polymer concentration. However, it would be expected that when the equilibrium network has been established, G' will again be concentration dependent. The shear storage modulus generally consists of two contributions: one from entanglements, G_E, and one due to physical network junctions, G_J (Prud'homme *et al.*, 1983):

$$G' = G_E + G_J \tag{1}$$

At $t = 0$ the modulus $G_J = 0$, which means that $G'(t=0) = G_E$ and $G_J = G' - G'(t=0)$. Figure 2(b) shows the change in G_J induced by the addition of Cr^{3+} to three different xanthan solutions.

Several time constants can be used to characterize the gelation: (a) The time τ_N needed for G_J to reach a given value G_N, where N is the selected value of G_J in dyn/cm^2, and this characteristic gelation time is extracted from Fig. 2(b); (b) a nucleation time τ_{nuc} obtained as the intercept between $G_J = 1$ dyn/cm^2 and the linear part of the log G_J versus log t plot (Fig. 2(b)); (c) the time τ when $G''/G_J = 1$. Figure 2(c) shows tan $\delta = G''/G'$ for the 1 mg/ml and 3 mg/ml xanthan concentrations versus time after addition of Cr^{3+}, and in addition G''/G_J for the 3 mg/ml xanthan concentration. This figure shows the change from a viscoelastic liquid to a viscoelastic solid. τ is obtained for the 3 mg/ml xanthan concentration from Fig. 2(c) at the point where $G''/G_J = 1$. Note that tan δ is smaller for the 1 mg/ml xanthan sample than the 3 mg/ml sample for $t > 15$ h. This indicates that a larger fraction of the chains participate in

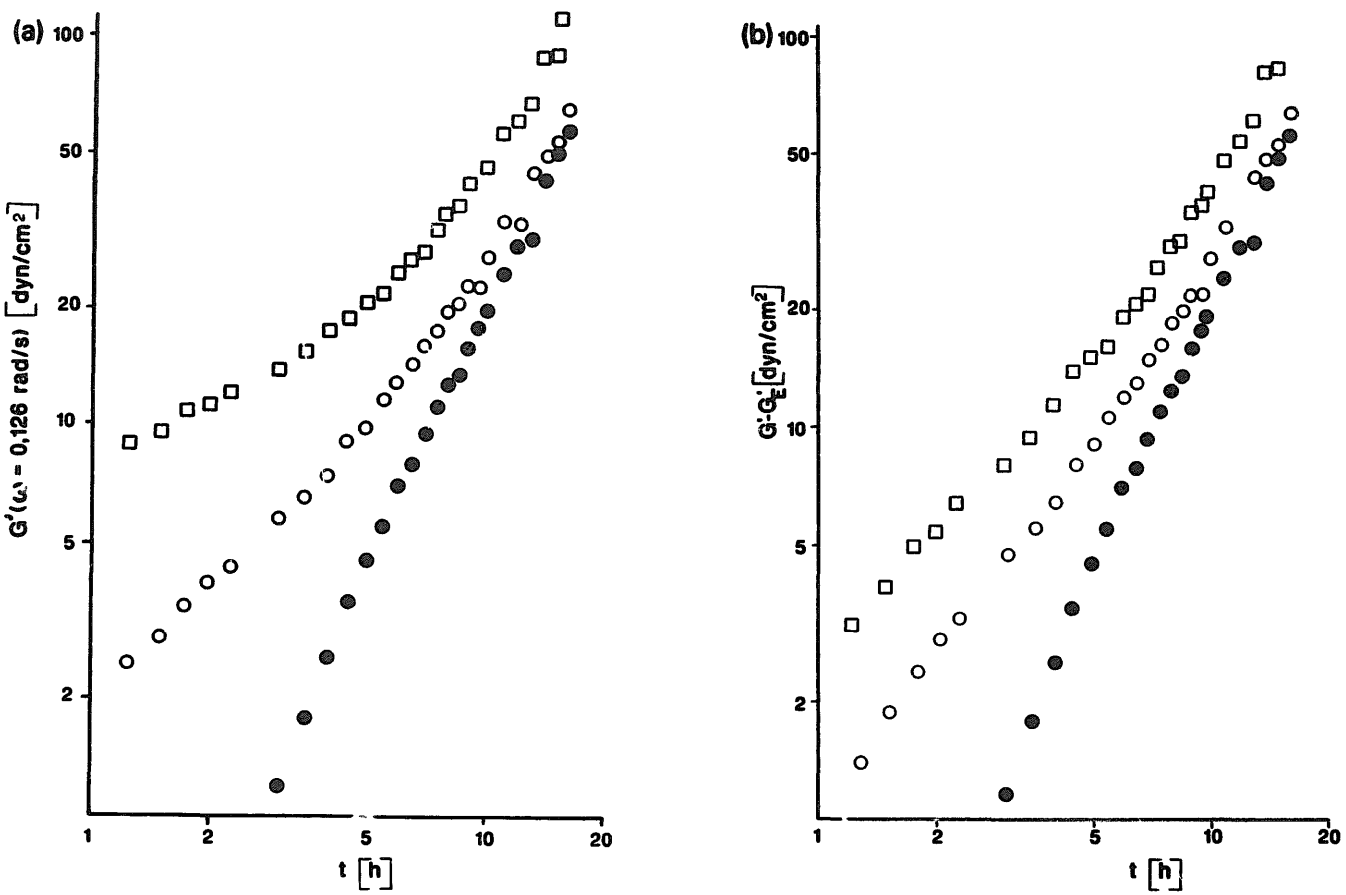

Fig. 2. (a) The dynamic storage modulus G' at $\omega = 0{\cdot}126$ rad/s versus incubation time t for 1 mg/ml (●), 3 mg/ml (○) and 5 mg/ml (□) xanthan in 100 mM NaCl, 5 mM Cr^{3+}, pH 3·5 at 20·0°C. (b) The net storage modulus (see text) $G = G' - G'_E$ at $\omega = 0{\cdot}126$ rad/s versus incubation time t for 1 mg/ml (●), 3 mg/ml (○) and 5 mg/ml (□) xanthan at 100 mM NaCl, 5 mM Cr^{3+}, pH 3·5, at 20·0°C. (c) The loss tangent tan $\delta = G''/G'$ at $\omega = 0{\cdot}126$ rad/s versus incubation time t for 1 mg/ml (▽), 3 mg/ml (○) and G''/G_l at $\omega = 0{\cdot}126$ rad/s for 3 mg/ml (□) xanthan in 100 mM NaCl, 5 mM Cr^{3+}, pH 3·5, at 20·0°C.

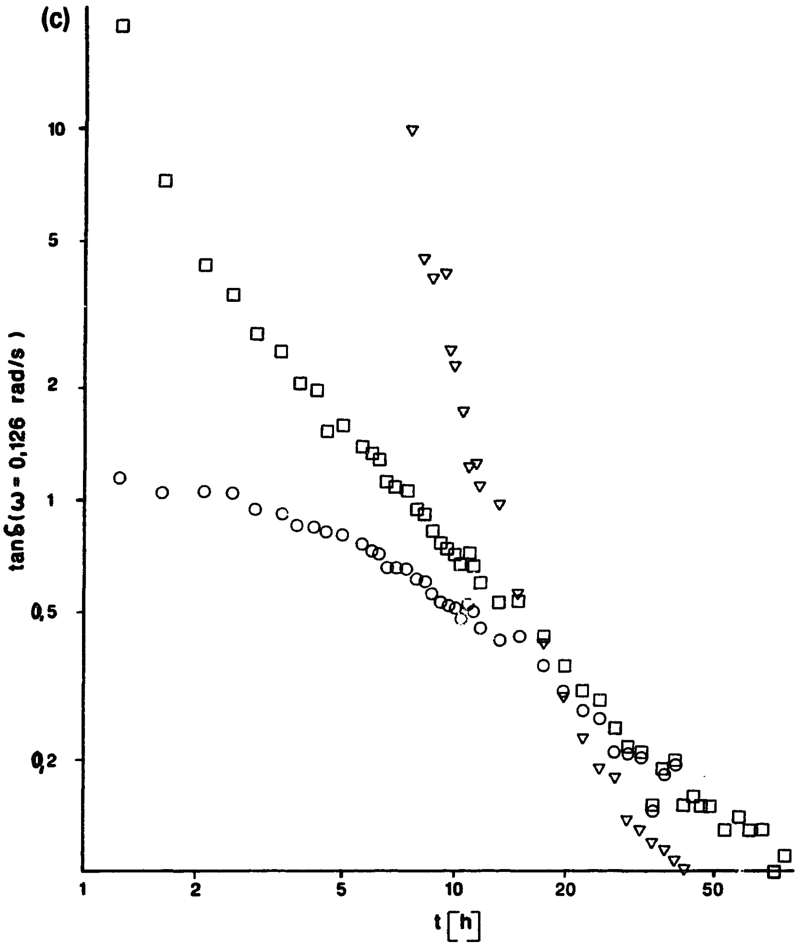

Fig. 2. — *contd.*

the elastic network at 1 mg/ml than 3 mg/ml even though G' is higher for 3 mg/ml than for 1 mg/ml.

The defined gelation times are dependent on the excitation frequency, but dependencies of the gelation times upon polymer and ionic cross-linker concentrations are expected to be frequency independent. Figure 3 shows $1/\tau_{\text{nuc}}$ and $1/\tau_{10}$ at excitation frequency $\omega = 0{\cdot}126$ rad/s versus xanthan concentration. The two time constants shows a small, similar polymer concentration dependence. There is no indication of a lower critical xanthan concentration needed for formation of a continuous network in this concentration range. However, it is noted that the xanthan concentrations used are all well above the overlap concentration c^* where the xanthan molecules in solution begin to interact geometrically: $c^* = 4/[\eta]$ where $[\eta]$ is the intrinsic viscosity (Morris *et al.*, 1981). For the xanthan used $[\eta] = 7200$ ml/g (see Materials and Methods) which yields $c^* \approx 0{\cdot}56$ mg/ml.

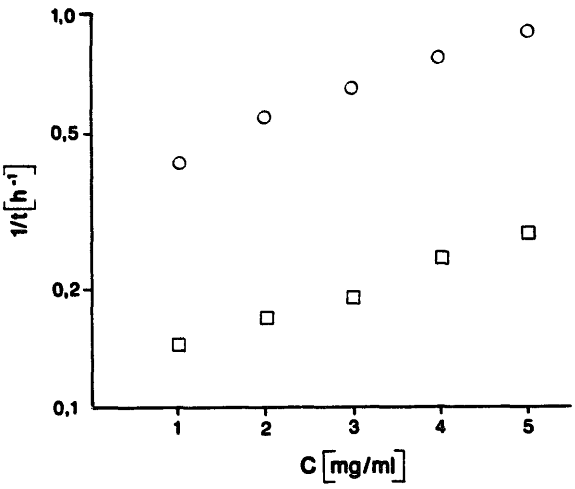

Fig. 3. Inverse time constants $1/\tau_{nucl}$ (○) and $1/\tau_{10}$ (□) (see text) versus xanthan concentration for gelation of xanthan in 100 mM NaCl, 5 mM Cr^{3+}, pH 3·5, at 20·0°C.

Effect of Cr^{3+} concentration

Figure 4 shows the Cr^{3+} concentration dependence on the kinetics of gelation for a 2 mg/ml xanthan solution ($\omega = 0{\cdot}126$ rad/s). At this xanthan concentration $G'(\omega = 0{\cdot}126) \approx G_J$. We find that the concentration of chromic ions affects strongly the rate of gelation. Reducing Cr^{3+} from 10 mM to 2·5 mM results in an increase in τ_{10} from about 2 h to 28 h. However, the slope of dlog G'/dlog t is essentially independent of the chromic ion concentration. Least square fit of log (τ_{50}) versus log c yields an estimate of $\xi = \Delta\log(\tau_{50})/\Delta\log c = -1{\cdot}9$, which is close to an inverse second power dependence (Fig. 5(a)). τ_3 is shifted towards higher t, but shows a similar dependence on the chromic ion concentration as τ_{50} (Fig. 5(a)). At low chromic ion concentrations, the gelation times become very long and are in the order of days. Figure 5(b) shows $-\log \tau_{50}$ versus chromic ion concentration, and indicates that there is a lower, critical chromic ion concentration needed to form a gel. This concentration is in the range 1–2 mM for 1–7 mg/ml xanthan. Using the degree of pyruvate substitution of 0·34 determined by ^1H NMR, we find that 1 mg/ml xanthan corresponds to 1·34 mM bound charges which is of the same order of magnitude as the indicated lower critical chromic ion concentration for gel formation. However, if every chromic ion participates in a network junction, it is expected that sub-stoichiometric amounts of Cr^{3+} would also crosslink xanthan solutions. The theory for rubber-like elasticity of crosslinked random coil type polymers is well established: G_J is given as the density of network strands multiplied by kT where k is the Boltzmann constant and T is the absolute temperature (Treloar, 1975).

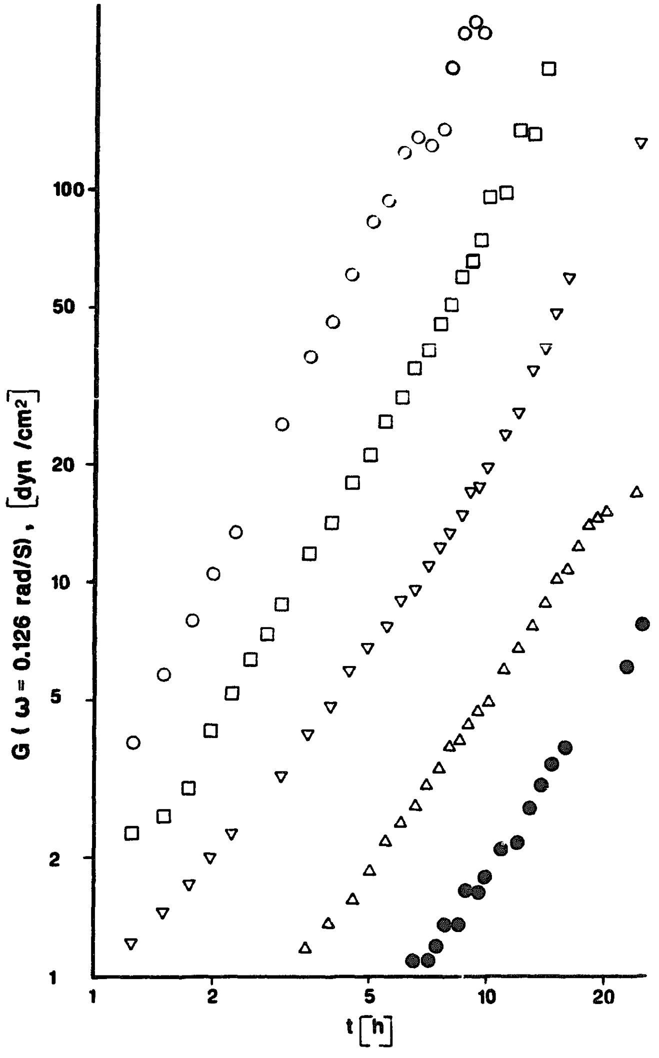

Fig. 4. The dynamic storage modulus G' at $\omega = 0{\cdot}126$ rad/s versus incubation time t for 2 mg/ml xanthan in 100 mM NaCl and 2·5 mM Cr^{3+} (●), 3·5 mM Cr^{3+} (△), 5 mM Cr^{3+} (▽), 7 mM Cr^{3+} (□), and 10 mM Cr^{3+} (○), respectively, at 20·0°C and pH 3·5.

The deformation free energies of polysaccharide gels are often of energetic rather than entropic origin, and the G' is empirically found to be 3–10 times that predicted for rubber-like elasticity (Clark *et al.*, 1983). The average molecular weight between network junctions, M_c, can then be calculated, taking correction for dangling ends into account (Treloar, 1975):

$$G_J = (KcRT/M_c)(1 - 2\,M_c/M_w) \qquad (2)$$

where K is the empirical factor ranging from 3–10, R is the molar gas constant and M_w is the polymer molecular weight. M_c is then obtained from:

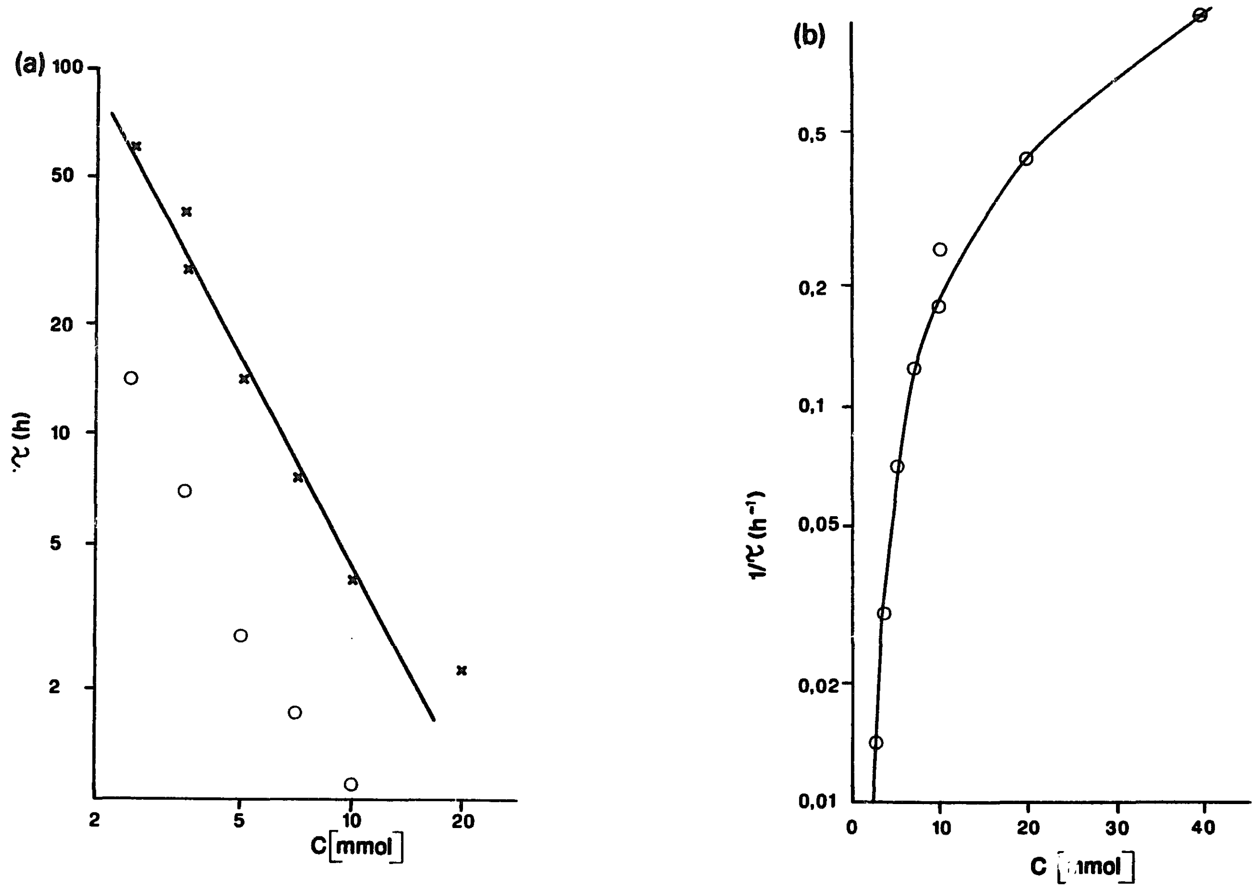

Fig. 5. (a) Log τ_3 (○) and log τ_{50} (X) versus log [Cr^{3+}] for 4 mg/ml xanthan gel in 100 mM NaCl, pH 3·5 at 20·0°C. The straight line is obtained by least square fit of log τ_{50} versus log [Cr^{3+}] for [Cr^{3+}] < 12 mM. (b) Inverse gelation time $1/\tau_{50}$ versus [Cr^{3+}] for 4 mg/ml xanthan in 100 mM NaCl, pH 3·5, 20·0°C.

$$M_c = (KcRT/G_J)(1 + KcRT/G_J M_w) \tag{3}$$

Figure 6 shows calculated M_c versus xanthan concentrations at $G_J = 100$ dyn/cm^2 for $K = 1$, 3 and 10. In the calculations, $M_w = 5 \times 10^6$ a.m.u. was estimated from the observed $[\eta] = 7200$ ml/g and the intrinsic viscosity–molecular weight relation reported by Sato *et al.*, (1984) was used. This yields an average spacing between crosslinks in the order $0{\cdot}5 - 1{\cdot}5 \times 10^6$ (Fig. 6), which is several orders of magnitude larger than the molecular weight of the pentasaccharide repeat unit of xanthan. Together with our finding of an apparent critical concentration for chromic ions, which is of the same order of magnitude as the xanthan pentasaccharide concentration, this suggests that either there are several ions involved in every junction or a large fraction of the ions are not involved in junction formation.

CONCLUSION

This study shows that a large range of gelation times for xanthan solutions can be obtained by varying concentrations of Cr^{3+} crosslinking

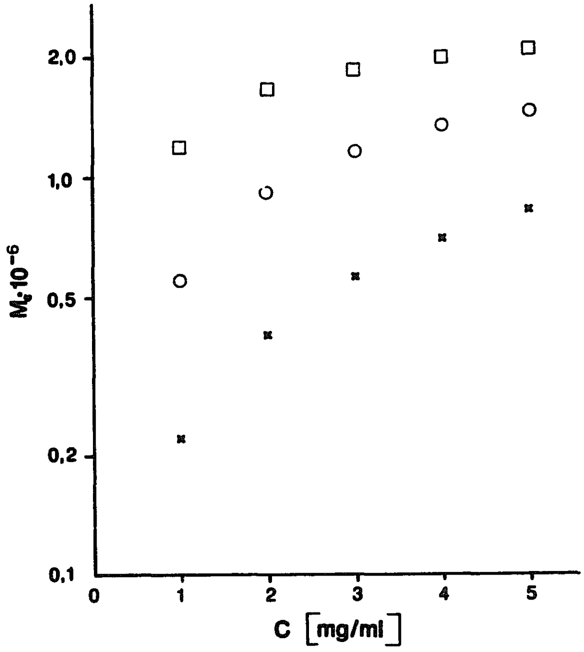

Fig. 6. Calculated average molecular weight between junctions, M_c, versus xanthan concentration (eqn 3) assuming that $K = 1$ (X), 3 (○) or 10 (□) with an equilibrium storage modulus of 100 dyn/cm^2.

agent. Increasing the Cr^{3+} concentration above 50 mM leads to precipitation of xanthan and a heterogeneous structure, using the present metal ion introduction procedure. Introduction of the metal ion at this high concentration by dialysis may yield gels and not precipitates. However, gelation times will be more difficult to measure because of the diffusion controlled introduction of the metal ion in the polymer solution. At the other extreme of Cr^{3+} concentrations less than 2 mM, gelation times in the range of days or more may be expected (based on extrapolation in Fig. 5). This large range of gelation times makes the Cr^{3+}–xanthan system versatile and a possible candidate as a permeability modifying agent of heterogeneous oil reservoirs.

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