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Rheology of Aqueous Solutions of an Extracellular Polysaccharide from *Cyanospira capsulata*†

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ABSTRACT

Solution rheology of an extracellular polysaccharide from the cyanobacterium Cyanospira capsulata *has been investigated in water and in aqueous 0·1 M NaCl at 25°C. The study has been carried out within a range of defined experimental conditions aiming at providing both steady-shear and transient rheological behaviour. The behaviour of the polysaccharide solutions is reminiscent of that of concentrated guar for the time-dependent properties alone, while for the rheological effectiveness and for the concentration-dependent properties, similarities with xanthan are found. The whole set of preliminary data are discussed within the framework of molecular viscoelastic theories and some inconsistencies are disclosed. These may be solved eventually when a larger number of data are also obtained on different systems.*

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INTRODUCTION

In the last few years there have been many studies aimed at the structural and physico-chemical characterization of high molecular weight polysaccharidic components secreted in the growth medium by microorganisms (Brant & Marchessault, 1987). This interest is motivated not only by the recognition of the implications of such carbohydrate polymers (exocellular polysaccharides: EPS) in many important biological processes, but also by its increasing use in industrial applications (Stivala *et al.*, 1987; Yalpani, 1987).

The above mentioned interest is strengthened by the common notion that bacterial polysaccharides are characterized by a structural regularity which is seldom present in algal and plant glycans. Indeed, this aspect is related to the peculiar physicochemical properties and the technological performances of the former biopolymers.

From a literature overview, one group of microorganisms almost neglected as glycan producers appears to be that of cyanobacteria, which are photosynthetic procaryotes called blue-green algae by some authors. Cyanobacteria are able to produce several different polysaccharides (Painter, 1983; Bertocchi *et al.*, 1990). Some of them are released and solubilized in the external medium and are described as forming a viscous slime. Our interest towards new bacterial polysaccharides has been greatened due to the fact that glycan is secreted extracellularly by the cyanobacterium *Cyanospira capsulata* (hereafter indicated as CC-EPS). This microorganism was recently discovered and studied by Florenzano *et al.* (1985) and the extracellular polysaccharide was extracted from the culture media and subjected to a preliminary study (Sili *et al.*, 1984).

Although the chemical structure of CC-EPS has not been completely identified (Ballio, pers. communication), some information is already available to motivate a study of the solution properties of this polymer. For instance, the presence of uronic acid has been ascertained and a preliminary physicochemical characterization of its polyelectrolytic behaviour has been achieved (Cesàro *et al.*, in preparation). In particular phenomenological observations on the flow properties of CC-EPS (Sili *et al.*, 1984) stimulated a more detailed investigation. The aim of our study was twofold: (1) to initiate a thorough rheological investigation of the new polysaccharide in aqueous solution under controlled external conditions; (2) to critically compare our data with similar ones for other polysaccharides, taking advantage of studies which have appeared in very recent literature (Morris *et al.*, 1980; Launay *et al.*, 1986; Richardson & Ross-Murphy, 1987*a*, 1987*b*).

The study was stimulated by the observation of some similarities with xanthan (Chauveteau, 1982; Jamieson *et al.*, 1982; Lim *et al.*, 1984; Milas *et al.*, 1985; Cuvelier & Launay, 1986; Rochefort & Middleman, 1987), whose rheological properties have been deeply investigated mainly for the industrial interest in its performance. We wish to report here on the steady-shear and time-dependent rheological behaviour of the exocellular polysaccharide from *Cyanospira capsulata.*

MATERIALS AND METHODS

Samples of crude extracellular polysaccharide from *Cyanospira capsulata* (CC-EPS) have been kindly provided by Professor R. Materassi (Firenze, Italy). The polysaccharide was received as a white powder, soluble in water, forming very viscous opalescent solutions. The samples contained impurities related to the bacterial origin of the polymer such as proteic material (about 6%), nucleic acids and inorganic compounds. The polysaccharide had been purified following a procedure described elsewhere (Cesàro *et al.*, in preparation). In the final step, centrifugation (30 000 rpm, 10°C, 60 min) of the aqueous solution was carried out, and then the solution was extensively dialyzed against bidistilled water and then freeze-dried to produce a white fluffy material. The impurities content after purification was negligible. During the purification process NaN_3 (0·02%) was added to the solution because of its antibacterial activity.

Aqueous solutions of CC-EPS at different concentrations were prepared by dissolving the polymer dispersed in bidistilled water by constantly stirring at room temperature. Particular attention was paid to the preparation of concentrated solutions: in this case stirring at room temperature was prolonged until a homogeneous phase was obtained. Under such conditions it was possible to obtain good reproducibility of experimental data. Solutions of the polymer with defined salts concentration were prepared by carefully mixing equal volumes of a double concentrated CC-EPS aqueous solution with a double concentrated NaCl solution to give the final required polymer concentration and ionic strength. In all cases heating of the solutions was avoided.

All rheological measurements were carried out at 25°C, with a rotational rheometer Haake CV100, which is equipped with the sensor system ZB 15 (Couette type). The inner cylinder used with this coaxial sensor system has the following dimensions: 13·91 diameter, 32·3 mm length; the gap is of 0·545 mm.

Shear-dependent measurements were performed by using triangular and multi-stepwise procedures. According to the former procedure, the shear rate is varied from 0 to a maximum value $\dot{\gamma}$ and, immediately afterwards, is changed from $\dot{\gamma}$ to 0 in a preset time under constant shear acceleration and deceleration. In the second procedure, a sequence of constant shear rate steps is applied, in an alternate mode, each shear rate being maintained for a sufficient length of time for a steady value of the shear stress to be attained. Flow curves were fitted by using a computerized non-linear regression analysis. The Krieger method (Krieger & Yang, 1978) was used for the shear-rates correction.

The analysis of time-dependent properties can be simplified by the application of the single step procedure suggested by Trapeznikov and Fedotova (1954) in the study of the time-dependent behaviour of dispersed systems and subsequently adopted by Komura *et al.* (1964) and by Stratton and Butcher (1973) for investigating the transient properties of polymer fluids. The same shear rate is applied after different rest times and until a steady value of stress is achieved. In such a way the rheological history of the samples is thoroughly defined by the shear rate value and the rest time before the sudden application of shear rate.

RESULTS AND DISCUSSION

Step-wise and triangular procedures

Rheological measurements on aqueous solutions of the extracellular polysaccharide from *Cyanospira capsulata* (CC-EPS) have been carried out at a constant temperature (25°C) on a wide range of concentrations (up to 5 g/litre). In diluted CC-EPS solutions, the results obtained by stepwise and triangular procedures are similar since time-dependent properties are negligible. Therefore, the characterization of the shear-dependent behaviour of these systems is not affected by the choice of experimental procedure. On the contrary, concentrated polymer solutions show appreciable time-dependent properties, and consequently the two different experimental procedures provide different information which cannot be directly compared with each other.

Figure 1 illustrates the results obtained for aqueous 5 g/litre CC-EPS solutions by applying the stepwise procedure. The application of different shear rates determines remarkable, often non-monotonic, variations of shear stress as a function of time.

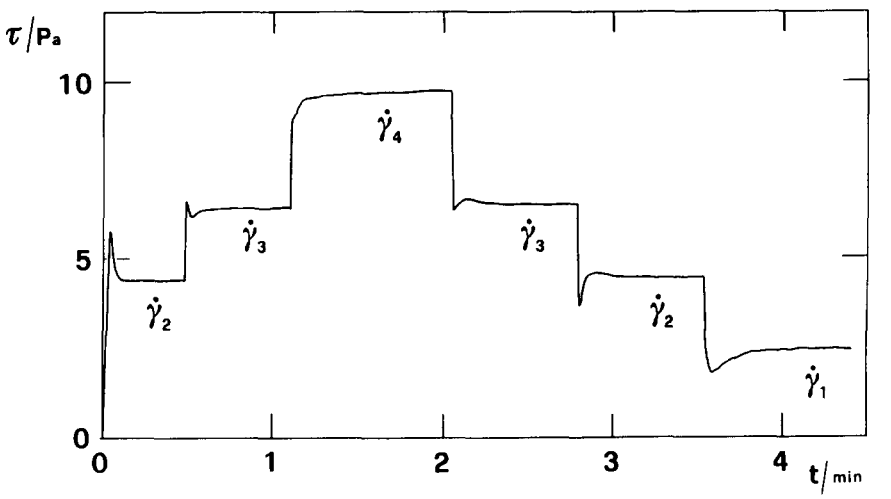

Fig. 1. Example of experimental results obtained with the stepwise procedure. Shear stress, τ, versus time t for a 5 g/litre CC-EPS aqueous solution at different shear rates; $\dot{\gamma}_1$, 0·3 s^{-1}; $\dot{\gamma}_2$, 3 s^{-1}; $\dot{\gamma}_3$, 30 s^{-1}; $\dot{\gamma}_4$, 300 s^{-1}.

The hysteresis cycles, obtained by applying the triangular procedure for concentrated solutions, depend on the previous rheological history of the sample under investigation. Therefore, they cannot be used for a quantitative analysis of shear-dependent behaviour. Thus, the characterization of shear-dependent behaviour of concentrated solutions has been carried out by a stepwise procedure. The stress steady values so obtained are independent of shear history and will be referred to, in order to describe shear properties.

Shear-dependent properties

As polymer concentration increases, deviations from Newtonian behaviour become more marked either in the presence or in the absence of salts. In Fig. 2 the dependence of viscosity on polymer concentration is reported at different shear rates in water and in aqueous 0·1 M NaCl. The lower the shear rate values, the more pronounced is the effect of polymer concentration on the solution viscosity. The effects of the addition of salts are negligible at high shear rates and high polymer concentration ($\dot{\gamma} = 300$ s^{-1} and $c_p = 5$ g/litre), while they are appreciable at low shear rates and low polymer concentration ($\dot{\gamma} = 0{\cdot}3$ s^{-1} and $c_p = 0{\cdot}5$ g/litre). This behaviour is not unexpected since the effect of salt concentration on a polyelectrolyte solution vanishes upon increasing

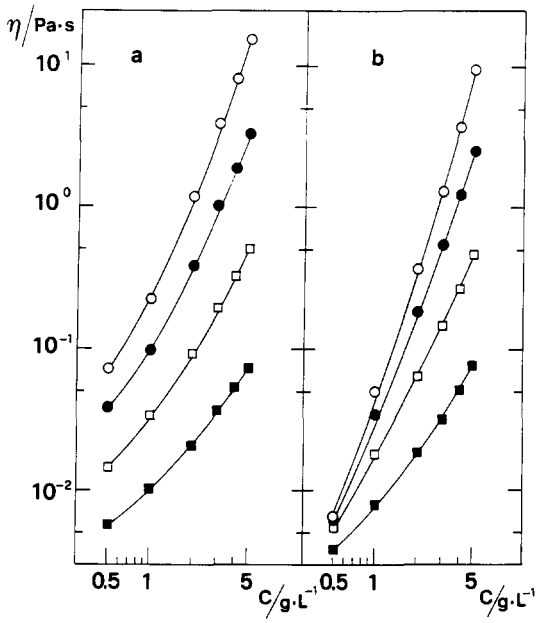

Fig. 2. Steady shear viscosity η as a function of polymer concentration c at different shear rates: ○, 0·3 s^{-1}, ●, 3 s^{-1}; □, 30 s^{-1}; ■, 300 s^{-1} (a, water; b, 0·1 M NaCl).

polymer concentration. On the other hand, all differences are reduced at high shear rates.

Figure 3 reports the viscosity ratio, η_R, defined as the ratio between the viscosity of the polymer solution in the presence and in the absence of salts for the same polymer concentration as a function of concentration and shear rates. In these data, evaluation of the effects of polymer concentration and of ionic strength on shear-dependent properties has been conveniently based upon the raw experimental data obtained directly from the instrument, as it is usually done with Newtonian fluids. Indeed, for non-Newtonian fluids it is necessary to calculate the 'effective shear rate' sheared between rotating coaxial cylinders from the integral equation:

$$\Omega_j = \int_{\tau_{oj}}^{\tau_{ij}} \frac{\dot{\gamma}(\tau)}{2\tau} \, d\tau \tag{1}$$

where Ω_j is the angular velocity and τ_{ij} and τ_{oj} are the tangential stresses at the internal and external cylinder walls, respectively; $\dot{\gamma}(\tau)$ is the unknown quantity. Various methods have been proposed for calculating the effective shear rates, involving different strategies for solving a

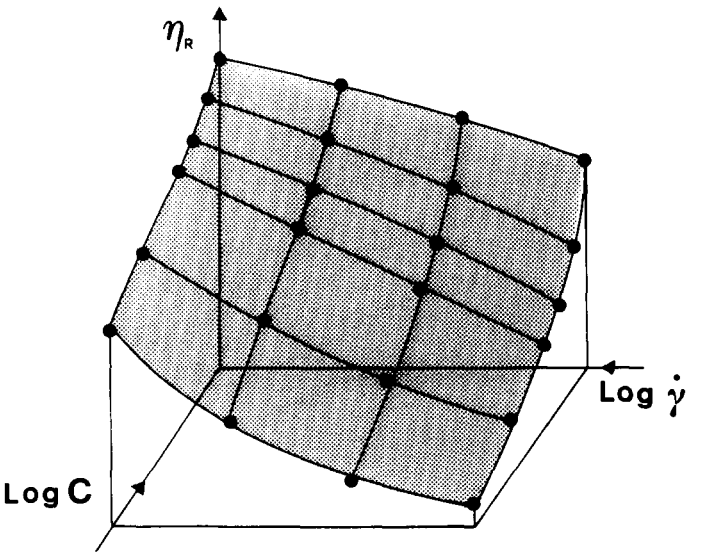

Fig. 3. Viscosity ratio, η_R, (i.e. ratio of the viscosity of polymer salt solution to the viscosity of polymer in pure water) as a function of the polymer concentration and of the shear rate. All conditions are reported in Fig. 2.

system of m integral equations, where m is the number of experimental data. In the present work, the Krieger method has been used which is based on the derivation of both sides of eqn (1) and on the expression of $\dot{\gamma}(\tau)$ as a sum of a convergent infinite series. The series truncation suggested by Krieger and Yang (1978) has been considered here.

Diagrams reported in Fig. 4 and in Fig. 5 are obtained on the basis of shear rate values calculated as described above. They also show that differences in rheological behaviour observed at the two different salt concentrations are apparent at a low polymer concentration regime. In this region the behaviour is slightly shear-thinning and the higher Newtonian plateau is attained only for the lowest concentration of Fig. 5. At higher polymer concentrations, deviations from Newtonian behaviour become stronger and furthermore, neither the higher nor the lower Newtonian plateaux are observed in the flow curves. In the range of shear rates investigated, the data indicate that the performances of CC-EPS (η versus $\dot{\gamma}$ at given c) appear to be comparable with those characteristics of systems showing a strong suspending capability.

In order to obtain a suitable extrapolation of the zero-shear rate viscosity (η_0) from experimental data it is necessary to resort to non-Newtonian mathematical models. The zero-shear rate viscosity data are used to study the effects of the polymer concentration and of the ionic strength on the solution behaviour.

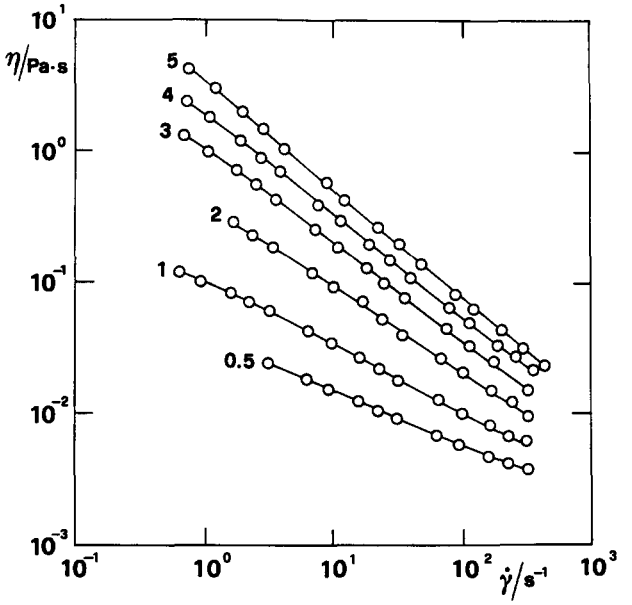

Fig. 4. Steady shear viscosity η for CC-EPS aqueous solutions plotted against shear rates $\dot{\gamma}$. Polymer concentration (g/litre) is indicated on the figure.

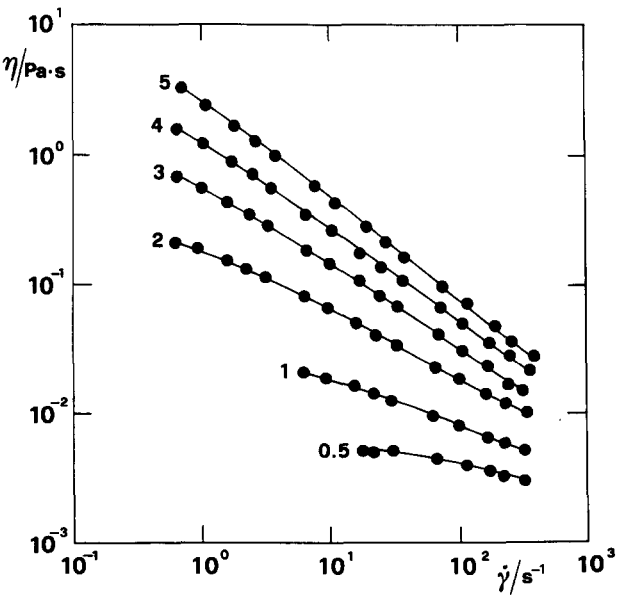

Fig. 5. Steady shear viscosity η for CC-EPS solutions in 0·1 M NaCl plotted against shear rate $\dot{\gamma}$. Polymer concentration (g/litre) is indicated on the figure.

Many equations have been suggested in the literature to fit experimental flow curves. In our case, among several different equations considered, only the three equations proposed by Cross (1965), Carreau (1968) and Sutterby (1966), have been found to provide a satisfactory fitting of the whole experimental data set (Table 1). The models are characterized by three adjustable parameters: η_0, a time constant λ, and a dimensionless exponent n, which represents the power law exponent at high shear rate. Viscosity functions, originally featuring an infinite shear rate viscosity, η_∞, were specialized by setting this limiting value to 0. Table 2 reports the normalized standard error (NSE) values, defined as follows:

$$\mathrm{NSE} = \left[\Sigma_j \frac{[(\eta_{\mathrm{exp,j}} - \eta_{\mathrm{cal,j}})/\eta_{\mathrm{cal,j}}]^2}{(m-1)} \right]^{1/2} \tag{2}$$

where m is the number of experimental data, $\eta_{\mathrm{exp,j}}$ and $\eta_{\mathrm{cal,j}}$ are the experimental and calculated values of η. While the differences in the fitting quality are not significant, the estimated values of η_0 are strongly affected by the choice of the model. Therefore, for a comparison among systems with different polymer concentrations, one must refer to one model only. In our case, the Cross equation represents an appropriate choice, since it fits the data better at higher polymer concentration, while all equations become impracticable at low polymer concentration where η_∞ is not negligible. In addition, the Cross equation has been found to accurately describe not only random coil polysaccharides (e.g. galactomannans (Sharman *et al.*, 1978)), but also stiffer and more ordered

TABLE 1
Non-Newtonian Mathematical Models Used for Zero-Shear Rate Viscosity Extrapolation

Model	*Equation*	*Reference*
Cross	$\frac{\eta}{\eta_0} = \frac{1}{1+(\lambda\dot{\gamma})^{(1-n)}}$	(Cross, 1965)
Carreau	$\frac{\eta}{\eta_0} = [1+(\lambda\dot{\gamma})^2]^{(n-1)/2}$	(Carreau, 1968)
Sutterby	$\frac{\eta}{\eta_0} = \left[\frac{\sin h^{-1}(\lambda\dot{\gamma})}{\lambda\dot{\gamma}}\right]^{(1-n)}$	(Sutterby, 1966)

polymers like xanthan (Cuvelier & Launay, 1986). The values of the Cross model parameters obtained for a series of CC-EPS solutions are reported in Table 3. At high shear rates, the Cross model used turns into the power law (Ostwald & de Waele, 1923), whose exponent n decreases as the polymer concentration increases resulting in similar values both for water and salt systems.

The time constant increases with polymer concentration (Table 3). This is expected, since λ, which has been defined as 'the average time required for the molecules to diffuse enough distance to form an entanglement' (Soong & Shen, 1981), is related to the onset of shear thinning behaviour and it is a function of the density of entanglements in solution. Screening the ionic charges on the polymer through the addition of salt decreases the values of the time constants, especially at low polymer concentration, while at higher concentration λ approaches the values obtained in aqueous solutions. Ionic strength and polymer concentration affect both the intramolecular and intermolecular interactions and therefore the degree of correlation among polymeric chains.

A comparison of the rheological behaviour of a number of polysaccharides has been made by Morris *et al.* (1981). In the log η versus log $c[\eta]$ plot, the results obtained for many systems converge to a single master curve, characterized by a discontinuity at the critical concentration c^*, usually defined as the onset of the coil overlap. It has been noted that, in spite of their different conformational structure and flexibility, a

TABLE 2

Normalized Standard Error (NSE) Values Defined by Eqn (2), for the Two Systems in Water and in Salts Estimated with the Three Models Given in Table 1

Concentration (g/litre)		*NSE* × 10^2	
CC-EPS in water	Cross	Carreau	Sutterby
5	1·40	1·40	1·77
4	2·14	1·89	2·71
3	2·13	2·34	2·66
2	3·44	3·31	3·27
1	2·99	2·59	3·09
CC-EPS in 0·1 M NaCl	Cross	Carreau	Sutterby
5	0·81	1·03	1·25
4	1·25	1·44	1·70
3	3·04	3·42	3·16
2	2·47	2·34	2·48
1	1·18	0·50	1·08

TABLE 3
Values of Cross Parameters η_0, λ, n for CC-EPS Water and Salts Solutions

Concentration (g/litre)	η_0 *(Pa.s)*	λ	n
CC-EPS in water			
5	36·10	17·3	0·17
4	23·00	20·6	0·21
3	10·60	19·4	0·26
2	2·92	16·5	0·34
1	0·46	10·4	0·46
CC-EPS in 0·1 M NaCl			
5	20·80	12·1	0·21
4	6·91	8·0	0·27
3	2·03	4·2	0·32
2	0·58	3·6	0·42
1	0·07	0·8	0·55

similar rheological behaviour is found provided that specific ordered structures are absent (as in, e.g. xanthan). The experimental values of $c^*[\eta]$ given for polysaccharides fall within a range of concentrations (2·5 – 4 g/litre) usually slightly larger than that theoretically defined by the overlapping of the domain of the polymeric coils (Launay *et al.*, 1986). This shift arises from the decreasing chain dimensions upon increasing polymer concentration, which occurs due to the flexibility of the real chain in a good solvent. An opposite effect is generated by the existence of ordered structure and by the chain-chain aggregation as in the pre-gelling conditions.

The diagrams reported in Fig. 6 were obtained by using the η_0 values calculated with the Cross model. The critical concentration for CC-EPS is about 0·36 g/litre at the ionic strength of 0·1 M NaCl, and is higher in aqueous solutions, about 1 g/litre. The intrinsic viscosity in 0·1 M NaCl is $[\eta] = 2$ l/g (Cesàro *et al.*, in preparation), and a value of $c^*[\eta] = 0{\cdot}72$ is obtained. The values of c^* obtained for CC-EPS, in water and in salt solutions, are remarkably lower than those expected for an ideal random coil; therefore, besides the mere overlap between coils, other contributions, for example those briefly mentioned above, can be present. On the other hand, recent theoretical work by Graessley (1980) suggests a value of $c^*[\eta] = 0{\cdot}77$ for ideal random coils, which is very close to that found for CC-EPS but does not correspond with all the other experimental data reported by Morris *et al.* (1981).

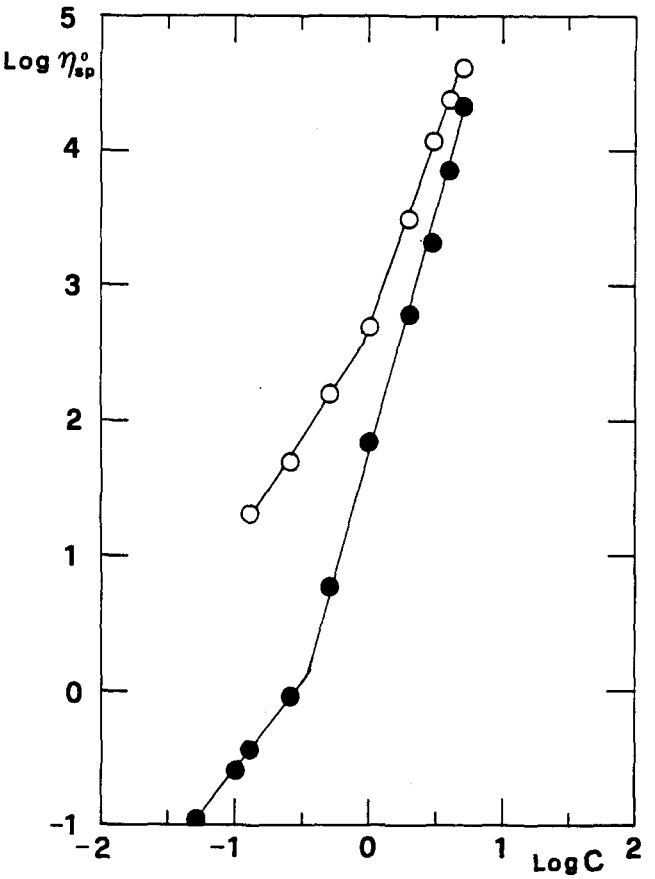

Fig. 6. Concentration dependence of 'zero shear' specific viscosity η^0_{sp} in water (○), and in 0·1 M NaCl (●).

From Fig. 6, the slope of double logarithmic plots at $c < c^*$ is close to 1·4, whereas, at $c > c^*$, in the case of polymer salt solutions the slope is about four, which is higher than the one obtained in aqueous solutions (about three). The slope of the curve for $c > c^*$ in salt solution is seemingly anomalous in comparison with the assertion of Morris *et al.* (1981). This behaviour is similar to that of xanthan (Jamieson *et al.*, 1982; Cuvelier & Launay, 1986). Although this slope has been reported to reflect the topological restrictions of the chains, a merely theoretical approach suggests a value of 3·75 (de Gennes, 1979). From the recent literature values up to, or even larger than, five are not infrequent (Robinson *et al.*, 1982; Enomoto *et al.*, 1984). A change in the value of the slope has to be expected to arise from the thermodynamics of the solution, in addition to the purely topological restrictions. All polymer-

polymer interactions, due to the particular nature of both solvent and polymer components, are responsible for changes in the slope even in the absence of manifest chain association phenomena. It is, therefore, suggested that the higher value of the slope in salt solutions is an indication of the increasing 'poorness' of the solvent with respect to the ionic polysaccharide.

Time-dependent properties

Step-wise experiments were originally planned to find the best operative conditions to study the shear-dependent properties. The results obtained clearly motivated the investigation reported in this section and aimed at characterizing, at least qualitatively, the recovery of non-linear properties after steady-shearing flow. In fact, as shown in Fig. 1, concentrated solutions of CC-EPS in water exhibit a complex time-dependent behaviour. A cursory inspection of Fig. 1 shows that by increasing step-wise the value of $\dot{\gamma}$ a prominent stress overshoot appears at low $\dot{\gamma}$ (3 s^{-1}), while at a higher shear rate (30 s^{-1}) a small overshoot is observed followed by an undershoot. At the highest $\dot{\gamma}$ (300 s^{-1}), both overshoot and undershoot are absent in the step-wise procedure. Upon decreasing shear rate steps, again both undershoot and overshoot appear at intermediate $\dot{\gamma}$ (30 and 3 s^{-1}), while only the undershoot is evident at the lowest shear rate (0·3 s^{-1}). Similar behaviour was also obtained for the CC-EPS 5 g/litre in aqueous 0·1 M NaCl.

An example of stress transients obtained for CC-EPS with a single step procedure (Stratton & Butcher, 1973) at different shear rates and constant rest time (60 s) is reported in Fig. 7. Upon increasing the shear rate, the maximum stress τ_{max} shifts to smaller values of time. In addition, stress transients show overshoot and undershoot at shear rates of 300 and 30 s^{-1}.

Figure 8 reports the stress transient obtained at a given shear rate. It is clear that τ_{max} sensibly increases with the rest time t_r (2 and 60 s) preceding the shear rate application. With the same procedure, stress relaxation data upon the cessation of steady flow are obtained, as shown in the central portion of Fig. 8.

The experimental procedure has been carried out for a range of rest times and concentrations on CC-EPS solutions in water and in 0·1 M NaCl at two different shear rates (3 and 30 s^{-1}). The ratio between maximum stress τ_{max} and steady stress τ_e (τ_{max}/τ_e is known as overshoot ratio maximum) is reported as a function of t_r in Fig. 9. The absolute values of overshoot ratio maximum are numerically lowered by an increase of shear rate as well as by the addition of salt. Independently of

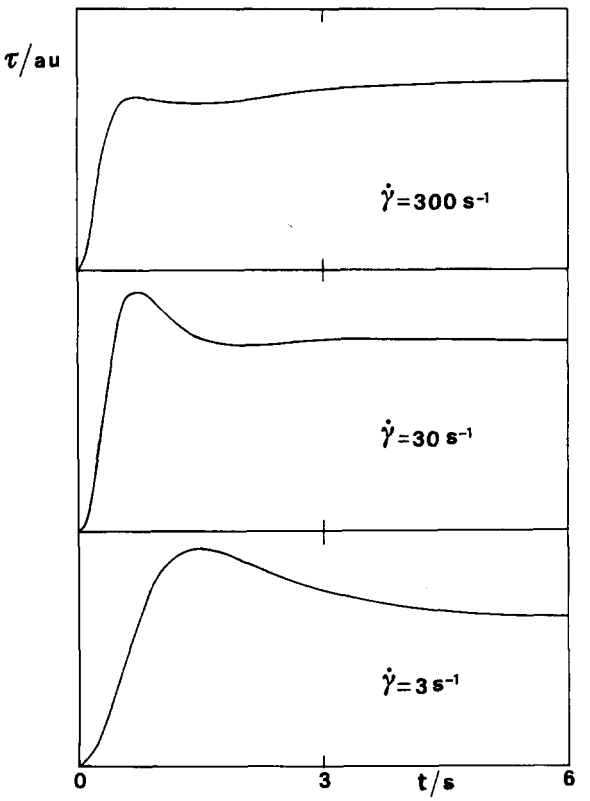

Fig. 7. Time dependence of shear stress for a 5 g/litre CC-EPS solution in 0·1 M NaCl at different shear rates (by the single step procedure). In all cases the rest time is 60 s.

the shear rate applied, τ_{max}/τ_e well approximates the asynthotic value above 300 s. These rest conditions are therefore sufficient to delete almost completely the previous rheological history in the case of CC-EPS concentrated solutions.

According to Stratton and Butcher (1973), the extrapolation of the overshoot ratio maximum value for $t_r \to \infty$ can be used to estimate the entanglement relaxation time t_e. This can be identified with the time required for the stress maximum to reach $(1 - e^{-1})$ of its limiting value. For the 5 g/litre CC-EPS aqueous solution t_e is about 9 s (shear rate 3 s^{-1}). Another relaxation time, t_d, is characteristic of the time scale of the stress relaxation upon the cessation of the steady-flow experiment and it is calculated as the time for the stress to relax to 1/e of its steady-state value. Stress relaxation experiments on 5 g/litre CC-EPS aqueous solution lead to an estimation of t_d of about 1 s (shear rate 3 s^{-1}). The value of t_e, as expected, is significantly larger than t_d.

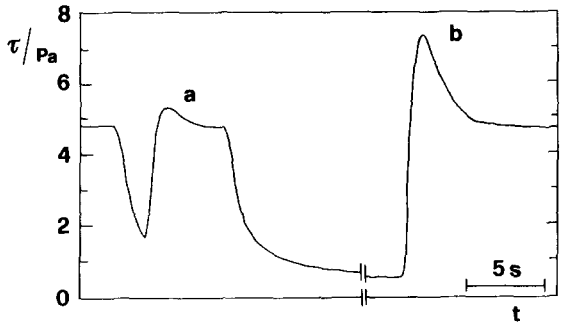

Fig. 8. Time dependence of shear stress for 5 g/litre CC-EPS aqueous solution at different rest times (a, 2 s; b, 60 s). Shear rate is 3 s^{-1}.

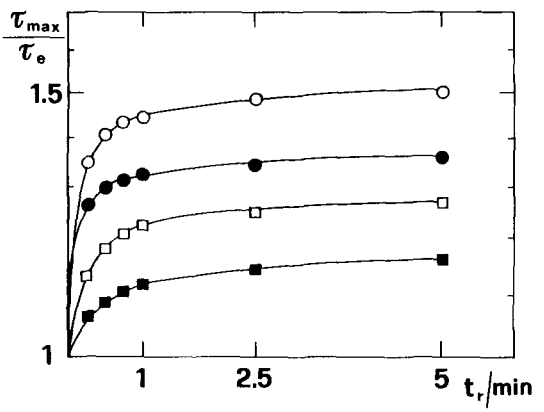

Fig. 9. Shear stress overshoot ratio (τ_{max}/τ_e) as a function of rest time t_r for 5 g/litre CC-EPS solutions at different shear rates (○, ● 30 s^{-1}; □, ■ 3 s^{-1}) and ionic strength (open symbols, water; full symbols, 0·1 M NaCl).

The concentration dependence of the overshoot ratio maximum measured at constant rest time (60 s) is reported in Fig. 10(a). The overshoot effect vanishes upon dilution of the solution and its depletion is larger in 0·1 M NaCl solutions than in water. At high concentration of CC-EPS, the overshoot ratio maximum reaches a plateau in aqueous solutions while in 0·1 M NaCl the plateau is not evident in the range of concentrations investigated. The effect of salt on time-dependent properties is ascribed to the polyelectrolytic character of CC-EPS, consistently with the findings on shear-dependent properties.

From the set of experimental responses of Fig. 7 the time required to reach the maximum stress, t_{max}, is a decreasing function of concentration and of shear rate (Fig. 10(b)). In this case the effect of the addition of salt on t_{max} seems to be negligible.

To our knowledge, the only available data in literature on polysaccharides concerning the recovery of non-linear properties after steady shearing flow are those of 3% guar aqueous solutions (Richardson & Ross-Murphy, 1987*a*) and of 1% xanthan aqueous solutions in 0·02 M KCl (Richardson & Ross-Murphy, 1987*b*). In the first case a rest time 'in excess of 10^2 s is necessary to substantially remove shear memory', while for xanthan concentrated solutions, recovery extends to times of 10^4 s. In case of guar, $t_e = 4{\cdot}3$ s and $t_d = 0{\cdot}8$ s have been evaluated, while for xanthan the recovery process is completely different and the estimates of t_e and t_d would have no physical meaning (Richardson & Ross-Murphy, 1987*b*). The authors conclude that, in consistency with other results, xanthan behaviour is typical of that of a weak-gel system, where physical entanglements are less important than chain-chain associative interactions.

It is difficult to make a comparison of our time-dependent results with those obtained for guar and xanthan because of the different experimental setup and conditions. Nevertheless, the data of transient experiments and the estimates of t_e and t_d suggest that the behaviour of CC-EPS at 5 g/litre is qualitatively similar to that observed for guar (at the higher concentration of 30 g/litre).

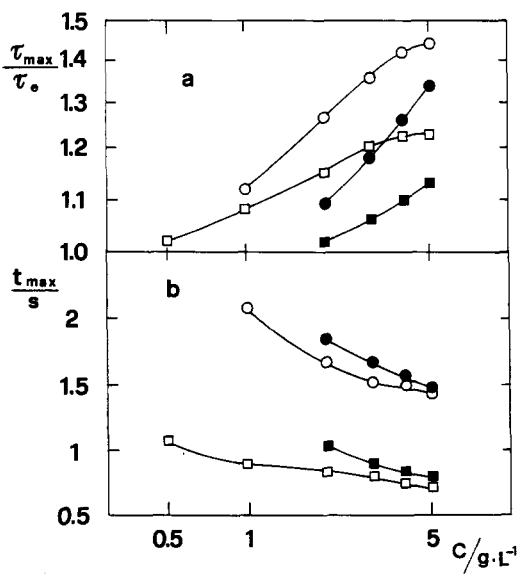

Fig. 10. (a) Concentration dependence of shear stress overshoot ratio (τ_{max}/τ_e) at different shear rates: ○, ● 3 s^{-1}; □, ■ 30 s^{-1} (open symbols, water; full symbols, 0·1 M NaCl). Rest time = 60 s. (b) Concentration dependence of the time required to reach the maximum stress, t_{max}. Symbols and conditions as above.

CONCLUSIONS

Before drawing any final conclusions on the solution rheology of the polysaccharide from *Cyanospira capsulata*, it is important to recall the limits which are imposed by the experimental setup. It has already been emphasized by Richardson and Ross-Murphy (1987*a*, 1987*b*) that a precise knowledge of these limitations is necessary in order to avoid inappropriate conclusions, in particular on the time-dependent properties.

The comparison of the concentration and the time dependence of the viscosity of CC-EPS with that of other polysaccharides is intriguing.

Taking into account the value of $[\eta]=2$ l/g, it turns out that the overlap parameter $c^*[\eta]$ makes the CC-EPS comparable with xanthan. The exponents of the concentration dependence in water and in salt solutions support this conclusion, although no secondary structure seems to be present in CC-EPS under these conditions.

On the other hand, the time-dependent properties of the CC-EPS are reminiscent of those of guar solutions which are 10 times more concentrated (Richardson & Ross-Murphy, 1987*a*) and very different from those of 1% xanthan solutions (Richardson & Ross-Murphy, 1987*b*), suggesting an overall random coil behaviour of CC-EPS. The above mentioned discrepancies between steady-shear and time-dependence behaviour may reveal peculiarities of the system under consideration.

Both the stiffness of the xanthan molecule and the usual working concentration (1–2%) make conceivable cooperative and stable interactions (that is on a long time scale). Meanwhile the flexibility and irregularities of guar chains prevent stable interactions on a long time scale, even at larger concentrations (up to 3%). The most important difference between the two systems is the rank of intermolecular interactions among chain segments. Rheologically relevant intermolecular interactions may also be present in the case of CC-EPS having a polymeric structure characterized by a regular sugar sequence (Ballio, pers. communication) but disordered in conformation (Cesàro *et al.*, in preparation), provided that 'flickering cross-interactions' occur. Whether CC-EPS local stiffness conforms to this view at the low concentration (0·1–0·5%) is at present only an hypothesis which has to be tested with further studies.

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