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Couette flow of dilute solutions of macromolecules: embryo cells and overstability

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The outer cylinder was kept stationary whilst the inner rotated. Weak circulatory motion ('embryo cells') was observed in all the fluids investigated at Taylor numbers Ta less than the critical Taylor number Ta_c. These cells grew with increasing Ta, then burst into vigorous Taylor vortices at $Ta = Ta_c$. In solutions of rigid elongated molecules having concentrations above a minimum concentration, an axial oscillation (overstability?) of the embryo cells was observed. The oscillation did not occur in solutions of flexible folded molecules nor in the solvent. The oscillation was observed over a range $Ta_0 \leqslant Ta \leqslant Ta_c$. For concentrations above the minimum Ta_0/Ta_c decreased with increasing concentration.

Other phenomena of the flow were also studied. It was found for solvent and solutions that the torque on the outer cylinder increased relatively less rapidly with the speed of rotation of the inner cylinder when

$$Ta/Ta_c > 1{\cdot}08$$

than it did when

$$1 < Ta/Ta_c \leqslant 1{\cdot}08.$$

In this latter range there was a torque reduction in the flow of the solutions relative to that in the flow of solvent. At sufficiently high speeds of rotation circumferential waves occurred in the fully developed Taylor cells (at $Ta = Ta_w$) and it was found that when $R_1/R_2 = 0{\cdot}95$ then $Ta_w/Ta_c = 1{\cdot}5$ for the solvent, whereas for the solutions $Ta_w/Ta_c \geqslant 1{\cdot}5$. When $R_1/R_2 = 0{\cdot}90$ then $Ta_w/Ta_c = 1{\cdot}25$, and for the solutions $Ta_w/Ta_c > 1{\cdot}25$. No experiment was done at $Ta > Ta_w$. The normal-stress coefficients of the solution have been evaluated from the results.

1. Introduction

The main motivation for the work, a search for overstability, was described by Jones, Thomas & Thomas (1976). Overstability is not expected unless there is a force other than gravity affecting the motion, for example the temperature gradient in thermal convection, as in the first observation of overstability by Fultz, Nakagawa & Frenzen (1954). In elastic fluids normal-stress differences provide the additional force, and provided these are large enough (minimum elasticity) overstability should occur – see Beard, Davies & Walters (1966). Also, Beard *et al.* expected overstability to be a sensitive test of elasticity, and to be observed even in weakly elastic materials such as dilute polymer solutions. It is therefore relevant to work with such solutions and to measure the other variables which weak elasticity affects. These are the value of the critical Taylor number, the wavenumber, and the torque relative to that in the solvent when Taylor cells are present.

Overstability was expected to manifest itself as an oscillation in one of the properties of Couette flow, but it was not clear which would be the one most affected and be the best to study. Consequently it was decided to study all phenomena occurring in the flow. It is known that the outer cylinder tends to oscillate particularly when secondary motion occurs. Some workers (e.g. Donnelly 1958) have deliberately damped this out, but as we were looking for an oscillation we have noted its amplitude and period, and searched for any change brought about by polymer additives. We have found a jump in amplitude which occurred only in the presence of a solution of rigid elongated molecules, and this we believe coincided with the onset of an axial oscillation of 'embryo cells', which form in the flow before fully developed Taylor vortices form.

Visualization was brought about by suspending ink in the flow which was suitably illuminated. At slow rates the streamlines are circles concentric with the cylinders. Before the onset of Taylor vortices small disturbances occur which show up as thin belts around the cylinder (see Hayes & Hutton 1970; Jones *et al.* 1976); these belts are separated by the same distance l as the thickness of a toroid (cell) in the secondary motion, and for that reason we call them 'embryo cells'. At the critical angular speed the secondary cellular motion appears as fully developed toroidal vortices, the toroids being coaxial with the cylinders. We have made a thorough study of the structure, growth and circulation of the embryo cells, and, as mentioned above, we have found an axial oscillation of the cells when rigid elongated molecules are present in solution, but the oscillation does not occur in solutions of flexible-chain molecules nor in the solvent.

It was also thought that a careful study of the embryo cells and the range of Taylor number over which they form, and over which they change to recognizable Taylor vortices, would be a contribution supplementing recent theoretical work on the onset of vortices. For example Benjamin (1976, 1978) has applied catastrophe theory to the stability of flow, and writes: 'the appearance of a steady cellular motion as Re is gradually increased from zero is a smooth process'. On the other hand, he shows that, as the cylinders are made longer for a given gap width, this smooth process becomes more sharp, and for long cylinders 'the development of cells is rapid over a narrow range of Re'. In our apparatus we saw the weak embryo cells grow smoothly, but then the appearance of *fully developed* strong Taylor cells was sudden; that is, it occurred over a small range of Taylor number which was within the precision of measurement of the number. We report on the precision of measurement in § 2. Other experimental work on the appearance of Taylor cells has been done by Benjamin (1978), and end effects have been considered by Burkhalte & Koshmieder (1973), Blennerhassett & Hall (1979), Hasoon & Martin (1977), Ritchie (1968) and Snyder (1969). No mention was made of embryo cells.

Definitions of symbols

Unprimed symbols will refer to the solvent and primed symbols to the solution. The definitions are the same for each, so only those referring to the solvent are given in (1)–(4). In the experiments the inner cylinder rotated whilst the outer was stationary.

The torque G on the outer cylinder increases linearly with the speed of rotation of the inner until the secondary cellular motion sets in, when there is a sudden increase in G; this occurs at a critical value Ta_c of the Taylor number Ta, where

$$Ta = \frac{4R_1^2 d^3}{R_1+R_2}\left(\frac{\Omega}{\nu}\right)^2, \tag{1}$$

in which R_1, R_2 are the radii of the inner and outer cylinders respectively, $d = R_2 - R_1$, Ω is the angular speed of the inner cylinder, and ν is the kinematic viscosity of the fluid. When $d \ll R_2$, the predicted $Ta_c = 3410$ (Taylor 1923). When $Ta < Ta_c$

$$G = C\phi = \frac{4\pi\mu R_1^2 R_2^2 h\Omega}{(R_1+R_2)\,d}, \tag{2}$$

where ϕ is the angular twist in the suspension wire and C is an elastic constant for the wire. μ is the shear viscosity of the fluid and h is the height of cylinder over which the torque is measured.

When $Ta > Ta_c$, the rate of change of G with Ω is greater in the range

$$Ta_c < Ta < 1{\cdot}08Ta_c$$

than it is when Ta satisfies $1{\cdot}08Ta_c < Ta$. Schwartz, Springett & Donelly (1964) observed a transition to a non-axisymmetric mode with azimuthal number $m = 1$ at $Ta = (1{\cdot}03 \text{ to } 1{\cdot}08)Ta_c$. Davey, di Prima & Stuart (1968) predicted a relative reduction in torque when $Ta > 1{\cdot}08Ta_c$; Debler, Füner & Schaaf (1968) found the relative reduction in torque to occur when $Ta > 1{\cdot}2Ta_c$. We denote the value of Ta at which the reduction occurs by Ta_* and we find $Ta_* = 1{\cdot}08Ta_c$, see § 3.2.

It is seen from (2) that ϕP is constant for a given Newtonian fluid when $Ta < Ta_c$, where $P = 2\pi/\Omega$ is the period of rotation of the inner cylinder. Writing $\langle\phi P\rangle$ for the average of several experimental determinations of ϕP when $Ta < Ta_c$, we define $\lambda = \phi P/\langle\phi P\rangle$. The quantity λ is a normalized dimensionless torque. In the range $Ta_c < Ta < Ta_*$, λ satisfies

$$\lambda = 1 + s\left(1 - \frac{Ta_c}{Ta}\right), \tag{3}$$

where s is constant.

For a non-Newtonian fluid we define λ by $\phi P/(\phi P)_c$, where $(\phi P)_c$ is the value as $Ta \to Ta_c$. $\lambda = 1$ when $Ta \to Ta_c$ but, when $Ta < Ta_c$, λ varies as the viscosity of the fluid varies.

When the Taylor vortices form, the thickness l of each one can be measured in visual experiments. The wavenumber

$$\epsilon = \pi d/l, \tag{4}$$

and, when $d \ll R_2$ and $h \gg d$, then $l = d$ (Taylor 1923). As the speed of rotation is increased above critical the visible pattern of flow remains the same until a circumferential wavy disturbance in the vortices sets in at $Ta = Ta_w = 1{\cdot}5Ta_c$, when $R_1/R_2 = 0{\cdot}95$ (see Coles 1965). The rate of increase of G with Ω increases again when $Ta > Ta_w$.

When large polymer molecules are present in solution elasticity affects the values of the quantities. To enable the elasticity to be evaluated we define

$$\Delta = \frac{Ta_c' - Ta_c}{Ta_c}, \quad \bar{\epsilon} = \frac{\epsilon'}{\epsilon}, \quad \bar{s} = \frac{s'}{s}. \tag{5), (6), (7}$$

t (°C)	Kelzan solutions c (p.p.m.)					
	40	20	10	5	3·5	0
15	2·711	2·496	2·397	2·344	2·332	2·276
20	2·319	2·142	2·056	2·011	1·998	1·970

t (°C)	PAM (P250) c (p.p.m.)						
	200	150	100	50	20	10	5
18	2·452	2·347	2·303	2·243	2·190	2·154	2·147

TABLE 1. Kinematic viscosities (in cSt) of various concentrations c of P250 and of Kelzan dissolved in a solution of 25 % glycerol in water (w/w). At $t = 18$ °C a solution of Pusher 700 with $c = 50$ p.p.m. had a kinematic viscosity of 3·604 cSt.

2. Experiments

Two assemblies of concentric cylinders were used: a smaller and a larger. In the larger $R_2 = 3{\cdot}972$ cm, $R_1 = 3{\cdot}782$ cm $(R_1/R_2 = \eta = 0{\cdot}952)$, $h = 50{\cdot}0$ cm, and the length of each guard ring to eliminate end effects was 11·5 cm. The number of cells in the gap within the suspended outer cylinder $(= h/d)$ was 263. In the smaller $R_2 = 1{\cdot}9985$ cm, $R_1 = 1{\cdot}799$ cm $(\eta = 0{\cdot}890)$, $h = 4{\cdot}553$ cm and $h/d = 23$, and the length of each guard ring was 1·98 cm.

The large apparatus was used for torque measurements and the small one for observation of the pattern of flow. The smaller η in the large apparatus increased the sensitivity of the torque measurement, whereas the larger η of the small apparatus was necessary to facilitate photography and the observation of the weak embryo cells. Experimental techniques have been described previously in Jones & Marshall (1969) and Jones *et al.* (1976).

The (Newtonian) solvent for the polymers was a solution of 25 % w/w glycerol in water. This was used because the higher viscosity contributed larger torque at low Ω and because solutions of polymers in glycerol-in-water are reputed to be more elastic than aqueous solutions containing the same amount of polymer. Three polymers were used to make up solutions: a neutral polyacrylamide (P250), an anionic polyacrylamide (Pusher 700), and Xanthan gum ('Kelzan'). The P250 (a flexible folded molecule) or the Kelzan (a more-rigid extended molecule) were used in most experiments. Solutions were characterized by their concentrations and by their kinematic viscosities as determined in the Ostwald viscometer type A (B.S.S.) (table 1). These were the values which were substituted in (1) to calculate Ta'; this procedure is discussed in § 4.

Typical results of torque measurements are shown in figure 1. The values of Ta_c and Ta'_c are determined from the values of P^{-1} at which ϕP suddenly increases. The accuracy with which this can be done was discussed by Jones, Davies & Thomas (1973). They gave 1 % as the best that can be achieved in any one determination. But the apparatus has to be dismantled for cleaning between samples and then the cylinders have to be realigned. Because of the length of the cylinders in the large

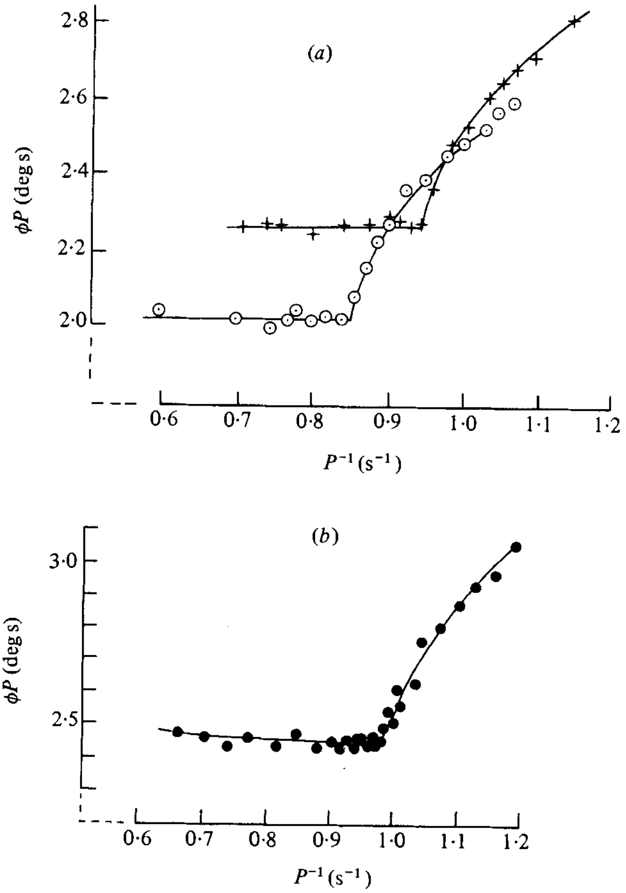


FIGURE 1. (*a*) 100 p.p.m. PAM solution (+) compared with the solvent, (○); (*b*) 80 p.p.m. Kelzan solution. 18 °C.

apparatus alignment is difficult. A misalignment which was detected by observing the gap around the circumference and along the length with a cathetometer, had led to $Ta_c = 3710$. Another setting with a similar but lesser misalignment gave $Ta_c = 3533$. Nevertheless, good reproducibility between alignments and therefore good alignment could be achieved, for example 3399 ± 18, 3400 ± 11, 3382 ± 16 for three runs involving cleaning between runs. Ultimately we took the measured value of Ta_c to be an indicator of satisfactory alignment, requiring it to be within 1 % of 3400.

In the smaller apparatus used for visual experiments alignment was not a problem because of the much shorter cylinders and because the outer (transparent) cylinder was fixed. The appearance of square Taylor cells marked the onset of the secondary motion. The value assigned to Ta_c depends on the skill developed by experience; for example at $Ta = 3312$ square cells were not present in a particular run, but at $Ta = 3457$ they were. So $3312 < Ta_c \leqslant 3457$. There is no extrapolation of sections of a graph to meet at P_c^{-1} as there is in the torque experiment. From successive visual observations the precision of Ta_c could be improved; the value was found to be 3460 ± 75. (Ta_c for the smaller apparatus with $\eta = 0{\cdot}90$ would be expected to be bigger than that found in the larger apparatus with $\eta = 0{\cdot}95$ as established theoretically firstly by Taylor

(1923) and subsequently by others, and as found experimentally – see for example Jones *et al.* (1973).)

3. Results

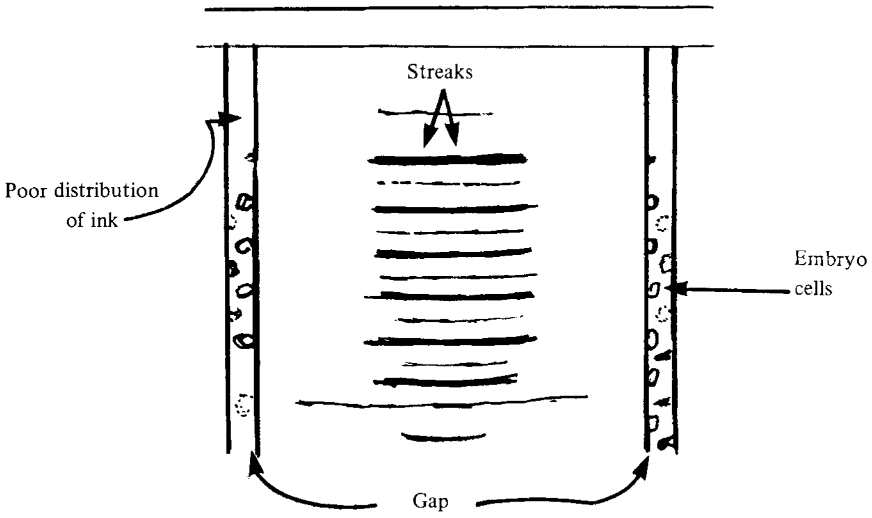
3.1. *Visualization experiments*

In the solvent as Ω was increased from values near zero the ink initially formed lines on the surface of the inner cylinder; subsequently those lines became small cells which extended out a little way into the gap, and which had a stable size and configuration at a given Taylor number. As the dye diffused small cells on the surface of the outer cylinder became visible (figure 2); these alternated in axial position with those on the inner cylinder and they grew larger – as did those on the inner cylinder – as Ω was increased in value. Fluid in the cells on the outer cylinder rotated in the opposite sense to that in the inner cells. These small cells grew from both cylinders until they completely filled the gap and square cells (the Taylor vortices) had formed. The growth of cells in P250 solutions was similar to that in the solvent. However, the growth of cells in Kelzan solutions was quite different. At very low values of Ω the dye formed rings at several places on the inner and outer cylinders, as seen with the solvent and with P250 solutions, then as Ω was increased the ink streaks began to oscillate axially on the surface of the cylinders; the value of Ta' at which oscillation began is designated Ta_0. As Ω was increased further the axial oscillation continued, the streaks gradually altering in appearance with increasing Ω until embryo cells were present which also oscillated axially. Finally the cells became square cells which filled the gap, and these cells *did not oscillate*; the value of Ta' at this transition is designated Ta'_c. The cells then present are the Taylor vortices, and these do not change in appearance with increasing Ω until the circumferential wavy structure appears.

The oscillation of dye streaks caused a mixing of the dye to almost uniform density throughout the gap, thus rendering photography so difficult as to be impracticable. The length of an experiment had to be adjusted to ensure that visual observation of relevant phenomena was possible.

One obvious question is why the oscillation occurs in Kelzan solutions when it does not occur in P250 solutions. Is it molecular shape or chemical interaction? (Kelzan has a glucose backbone and glycerol was present in the solvent.) Two experiments were done to investigate this point. The first experiment concerned the structure of Kelzan itself. Morris *et al.* (1977) and Holzwarth (1976) studied temperature-induced conformational changes in a Xanthan gum chemically similar to Kelzan, in aqueous saline solutions. It was helical or rod-like at temperatures below 24 °C when the concentration of salt was low, and collapsed to a coil at higher temperatures. P250 is coiled in solution, so do Kelzan solutions at $t > 24$ °C behave as P250 solutions? A 20 p.p.m. stock solution of Kelzan was made up, and experiment showed the oscillations at 18 °C, but at 30·6 °C there was no oscillation; square cells were formed at Ta'_c. No oscillation occurred at 18 °C the next day, in the solution which had been heated at 30 °C in keeping with the finding of Morris *et al.* that the time the coiled molecules took to return to their rigid state amounted to 45 days. (We could not keep our solutions at 18 °C for that time because of the difficulty of bacterial growth on the glycerol). The stock solution at 18 °C (which had not been heated to 30 °C) continued

(*a*)



(*b*)

FIGURE 2. (*a*) Photograph of ink in gap at $Ta = 3219$. (*b*) Interpretative diagram. Fluid is water at 18 °C.

to show oscillation in Couette flow. The second experiment concerned polyacrylamide. Pusher 700 is an ionic form of polyacrylamide and as such it exists as an open extended molecule in solution. Three runs were made in the coaxial-cylinder apparatus using a 50 p.p.m. solution of Pusher and an oscillation similar to that in unheated Kelzan solutions occurred in all three. So it would appear that the rod-like shape (or the charge the molecules carry) is related to the oscillation.

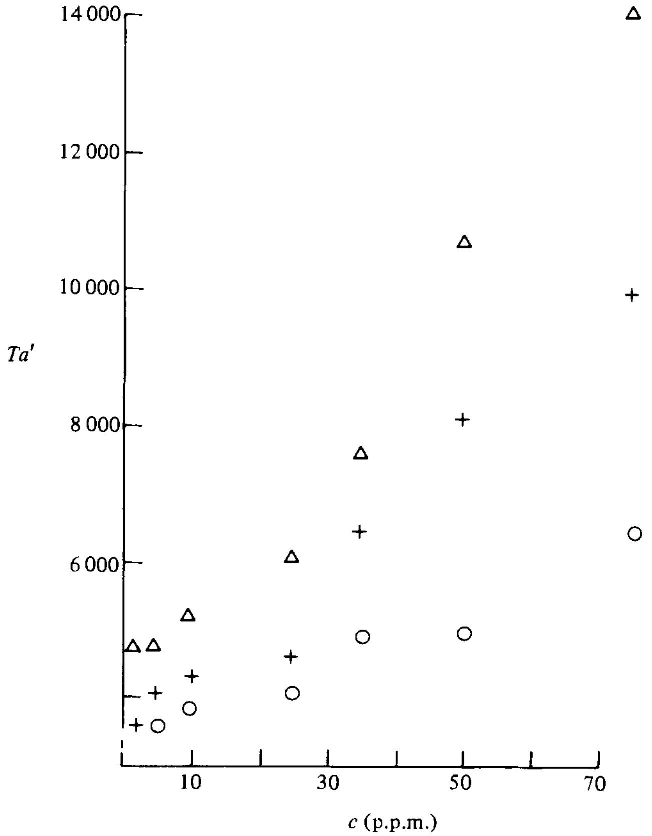


FIGURE 3. Ta_0 (○), Ta'_c (+), Ta'_w (△), for Kelzan solutions at 18 °C. (Visual observation: $\eta = 0{\cdot}90$.)

The concentration determines the value of Ta_0 (figure 3). In the 2 p.p.m. solution that showed no oscillation the dye streaks did not grow into embryo cells as they did in the solvent, but the fully developed square cells (Taylor vortices) formed suddenly at Ta'_c with their boundaries coincident with the dye streaks.

It was possible to measure the period of oscillation of the ink lines and embryo cells, either on the inner cylinder or on the outer cylinder, or somewhere in the gap after the embryo cells had formed. The periods of all these were the same, provided the period of rotation of the cylinder was constant. The period of the oscillation was always twice the period of rotation.

After the Taylor cells had formed the pattern of the flow remained the same with $l \simeq d$ (4), giving $\epsilon = 3{\cdot}18 \pm 0{\cdot}03$, until the wavy pattern was seen. We found $Ta_w = 4402$ and $Ta_c = 3454$, so that $Ta_w/Ta_c = 1{\cdot}27$ (mean of 16 determinations). Similarly, values of Ta'_w/Ta'_c for P250 solutions were between 1·29 and 1·25 respectively for 10 and 20 p.p.m. solutions. Values of Ta'_w for Kelzan solutions are given in figure 3. Ta'_w/Ta'_c ranges from 1·2 to 1·4.

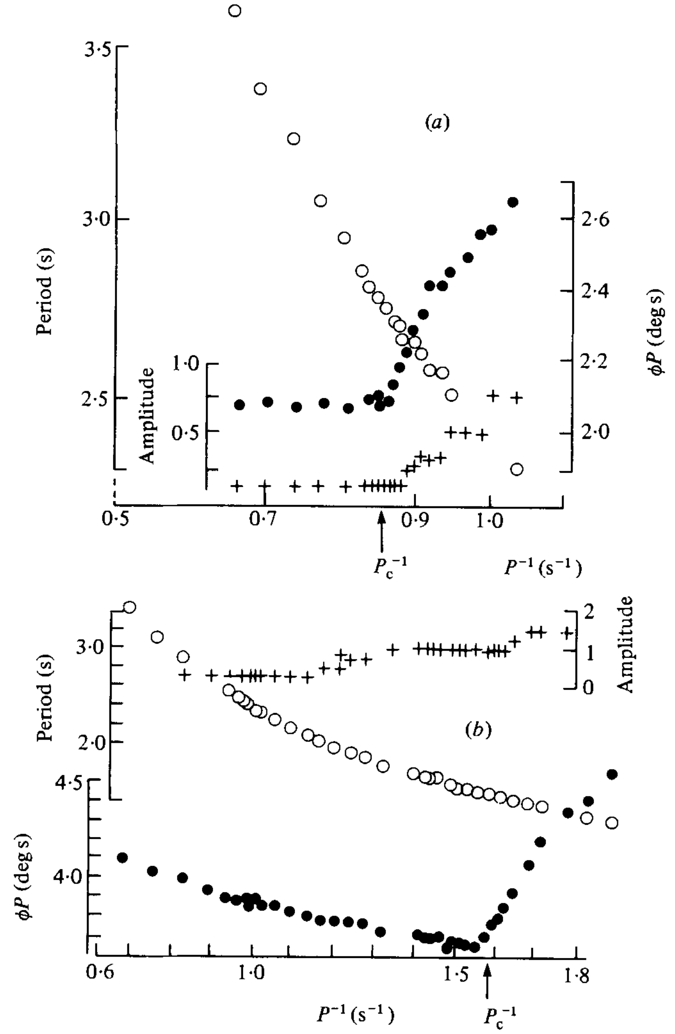


FIGURE 4. Amplitude (+) and period (○) of oscillation of the outer cylinder as a function of frequency P^{-1} of rotation of the inner. ϕP (●) is also shown. (*a*) The solvent (PAM solutions behave similarly); (*b*) an 80 p.p.m. solution of Kelzan. (18 °C.)

3.2. *Measurement of torque*

The magnitude of the torque is determined from the angular twist ϕ in the suspension wire, required to keep the outer cylinder in its zero-stress position. The outer cylinder is not stationary at the zero, however, but oscillates about it; the period and amplitude of the oscillation has been measured (figure 4). For the Kelzan solutions there is a fairly sharp increase in the amplitude at a value of $P^{-1} < P_c^{-1}$. We associate this jump in amplitude with the axial oscillation of the embryo cells, and denoting the value of Ta' at which it occurs by Ta_0 we find this Ta_0 has identical properties with that found from flow visualization. The period of oscillation of the outer cylinder is linearly related to the period of rotation of the inner cylinder, with no change to indicate the occurrence of Taylor vortices nor the occurrence of the axial oscillation of the embryo

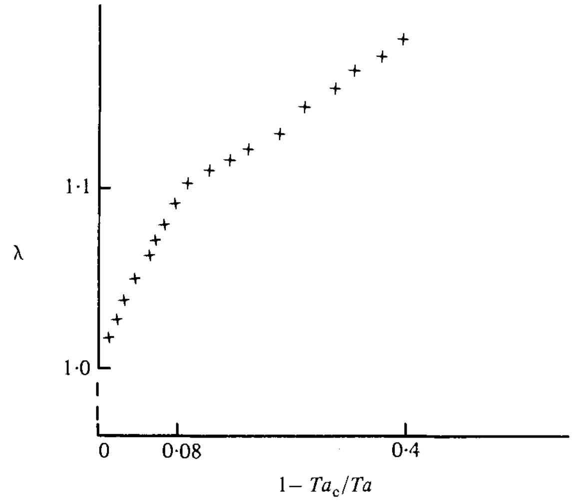


FIGURE 5. Reduced torque as a function of Ta for $Ta_w > Ta > Ta_c$.

cells. The slopes of the lines are the same in all cases, being 2·47 for solvent, 2·34 for P250, and 2·40 for Kelzan.

In Jones *et al.* (1973), where reference was made to embryo cells, there was no record of circulation of fluid within the cells. We attribute that to the difficulty of seeing the circulation. However, since the circulation does occur we would expect the torque to be affected as extra power is required to drive the circulation. There is evidence that is so. Jones *et al.* (1976) compare values for C in (2) found from torsional experiments with those found from flow measurements, and there is a 2 % discrepancy. And in all the experiments although the discrepancies were within experimental error they were all consistently on the side of a small extra torque occurring.

Reference was made in § 2 to the criterion used for the proper alignment of the cylinders. With this fulfilled we found that repeated determinations of Ta_c, without adjustments of the alignment of the cylinders between determinations, yielded different values of Ta_c. For example, out of eight determinations, the lowest value was 3362 and the highest was 3426 – a difference of 1·9 %. However, we cannot conclude that there is any 'inherent imprecision' in the formation of cells arising from a fundamental property of the system itself, since a range of 1·9 % is within the estimated ± 1 % experimental accuracy. The mean value of Ta_c given by the eight determinations was 3392 ± 23 (r.m.s.) – an accuracy of 0·7 %. A similar narrow range of Ta' over which cells develop was observed. The smallest observed value out of ten values of Ta'_c for a solution of 100 p.p.m. P250 was 3439, whereas the largest was 3515 – a difference of 2·1 %. The mean of the ten values was 3489 ± 24. As can be seen there is a significant difference between Ta'_c and Ta_c. This difference gives Δ from (5). Values of Δ are discussed in § 4.

When $P^{-1} > P_c^{-1}$ results are best displayed with torque as a function of Ta_c/Ta. These show that, with three exceptions, the data can best be represented by two straight lines (figure 5) which intersect at $1 - Ta_c/Ta = 0{\cdot}08$. Let this change in slope occur at Ta_*, then $Ta_* = 1{\cdot}086$, which agrees well with the prediction of Davey *et al.* (1968). There is no evidence in our results that polymer additives affect the value of

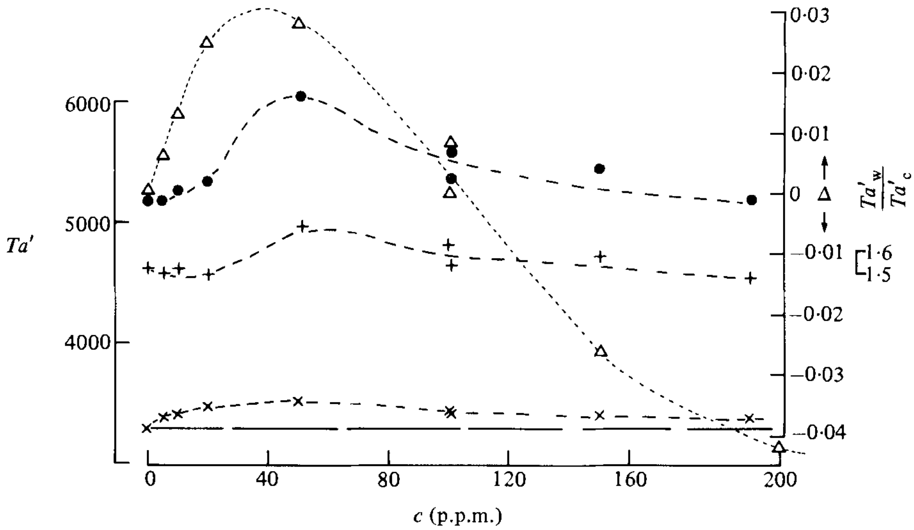


FIGURE 6. Ta'_c (×), Ta'_w (●) and Ta'_w/Ta'_c (+) found using μ'_P, and Δ (△) determined using μ'_T for PAM solutions at 18 °C (see §4). (Large apparatus: η = 0·95.)

Ta_*. (The results could best be represented by one line – no Ta_* – for one run with solvent, one run with 50 p.p.m. P250 and one run with 150 p.p.m. P250.) Identifying s of (3) with the slope of the line in the range $Ta_c < Ta < Ta_*$ it is found that $\bar{s}$ of (7) is unity for small concentrations of P250, whereas it is 0·94 for higher concentrations – which is a relative torque reduction in the polymer solution compared with that in the solvent. Kelzan solutions behave similarly.

As Ω is increased still further the wavy structure in the Taylor vortices occurs. This is accompanied by an increase in the rate of change of torque with angular velocity. Also, at the same time the outer cylinder is pushed into an eccentric position and the vertical plane of eccentricity rotates at about 1·3 times the rate of rotation of the inner cylinder, which is the speed of rotation of the wave. This was referred to as a 'precession' of the outer cylinder by Jones *et al.* (1976). We determined the value of Ω at which this occurred, and hence Ta_w. We did no experiment at higher values of Ω. We found $Ta_w = 5258 \pm 58$ (and $Ta_c = 3392 \pm 7$), mean of seven runs, involving 55 individual measurements of both Ta_c and Ta_w. The figures give $Ta_w/Ta_c = 1{\cdot}55 \pm 0{\cdot}01$, the same value as that found by Coles (1965). In Coles's apparatus $\eta = 0{\cdot}95$, as in our apparatus for torque measurements. (Note that we find $Ta_w/Ta_c = 1{\cdot}25$ when $\eta = 0{\cdot}90$, §3.1.) Values of Ta'_w/Ta'_c for the polyacrylamide solutions are shown in figure 6. Those for 20, 40 and 80 p.p.m. Kelzan solutions were 1·46, 1·32 and 1·42 respectively; these values are discussed in §4.

4. Discussion

The experimental effort has been directed at establishing the existence of very weak embryo cells at values of $\Omega < \Omega_c$. It is suggested here that the embryo cells are evidence for the slow growth of Taylor cells, as suggested by Benjamin (1978). Arguments in supposing the oscillation is a manifestation of overstability are given

c (p.p.m.) (P250)	5	10	20	50	100	150	200
$\mu'_{\mathrm{T}}/\mu'_{\mathrm{P}}$	1·00	1·00	1·00	1·01	1·01	1·02	1·03
c (p.p.m.) (Kelzan)	20	40	80				
$\mu'_{\mathrm{T}}/\mu'_{\mathrm{P}}$	1·08	1·11	1·26				

TABLE 2. Shear viscosities of various concentrations c of P250 and of Kelzan in a 25 % (w/w) solution of glycerol in water, measured in an Ostwald viscometer compared with those measured in the coaxial cylinder apparatus (η = 0·95) (18 °C)

below. Firstly, however, we discuss the effect of shear thinning on the values quoted in the figures and tables so far given, which were based on measurement of ν in the Ostwald viscometer. It is seen that values of Δ found from (5) are mostly about 0·02 (figure 6), and Ta varies as ν^2, so substitution of accurate values of the viscosity is important. The shear viscosity of many polymer solutions varies with the rate of shear $\dot{\gamma}$. In the large concentric cylinder apparatus at $\Omega = \Omega_{\mathrm{c}}$ and for 5 p.p.m. P250 solutions $\dot{\gamma} = 109\ \mathrm{s}^{-1}$, for the 200 p.p.m. solution $\dot{\gamma} = 126\ \mathrm{s}^{-1}$, and for 80 p.p.m. Kelzan solutions it is $196\ \mathrm{s}^{-1}$. In the Ostwald viscometer the average rate of shear at the wall is $800\ \mathrm{s}^{-1}$ – about four times that in the concentric-cylinder apparatus. From figure 1 it is seen that $\dot{\gamma}$ varies by about 50 % in the primary flow region from the smallest experimental value of Ω to $\Omega = \Omega_{\mathrm{c}}$. Within that range P250 solutions with $c \leqslant 150$ p.p.m. have constant viscosities as indicated by the constant value of ϕP; when $c = 200$ p.p.m. ϕP diminishes by 1 % in the range Ω to Ω_{c}. To compare the shear viscosities

$$\frac{\mu'_{\mathrm{T}}}{\mu_{\mathrm{T}}} = \frac{\langle(\phi P)'\rangle}{\langle(\phi P)\rangle}, \tag{8}$$

the subscript T denoting measurement of torque in the concentric cylinder apparatus. From the Ostwald viscometer

$$\frac{\nu'_{\mathrm{P}}}{\nu_{\mathrm{P}}} = \frac{\mu'_{\mathrm{P}}}{\mu_{\mathrm{P}}} = \frac{t'_1}{t_1}, \tag{9}$$

in which P denotes measurement in pipe flow in the Ostwald viscometer and t_1 is the time to empty the bulb. (The densities of all the solutions and that of the solvent are equal.) As pointed out in § 3.2 the embryo cells are expected to contribute to the torque, and (8) will give an apparent ratio of viscosities. But embryo cells occur in both solvent and solution, and to make progress we assume the embryo cells affect both in proportion to their viscosities. Then for comparison purposes we can write $\mu_{\mathrm{T}} = \mu_{\mathrm{P}}$, and $\mu'_{\mathrm{T}}/\mu'_{\mathrm{P}}$ is then found from (8) and (9) (table 2). The procedure is justified by the fact that the ratio is unity for the most dilute solutions of P250, as would be expected, since the shear dependence of very dilute solutions cannot be detected (the intrinsic viscosities being small). Several experimental runs were made with solvent and solutions such that $\langle(\phi P)\rangle$ and $\langle(\phi P)'\rangle$ were determined to within 0·2 % (r.m.s.). For the shear-thinning Kelzan solutions $(\phi P)'$ at $\Omega = \Omega_{\mathrm{c}}$ is substituted for $\langle(\phi P)'\rangle$ in (8). Values of μ'_{T} can be estimated at any Ω outside the range for which direct readings have been obtained, since plots of $\ln(\phi P)'$ as a function of $\ln \Omega$ are linear.

c (p.p.m.)		Ta_0	Ta'_c	Ta'_w	Δ	$\dfrac{Ta_0}{Ta'_c}$	$\dfrac{T'_w}{Ta'_c}$	$\bar{s}$
20	Using μ'_P	3223 ± 115	3768 ± 4	5515 ± 72	0·11	0·855	1·46	0·87
	Using μ'_T	2763 ± 99	3232 ± 3	4817 ± 63	−0·049	0·854	1·49	0·89
40	Using μ'_P	3257 ± 137	4768 ± 42	6533 ± 322	$0{\cdot}40 \pm 0{\cdot}02$	0·683	1·37	0·81
	Using μ'_T	2696 ± 113	3876 ± 34	5400 ± 266	0·14	0·696	1·39	0·65
80	Using μ'_P	2144 ± 76	5029 ± 18	7157 ± 55	$0{\cdot}48 \pm 0{\cdot}01$	0·426	1·42	0·57
	Using μ'_T	1249 ± 44	3168 ± 11	4731 ± 36	−0·066	0·394	1·49	0·62

TABLE 3. Values of the various Taylor numbers and slopes for Kelzan solutions, determined using the shear viscosity μ'_P as measured in an Ostwald viscometer and using the *in situ* viscosity μ'_T

It is possible now to discuss the effect of shear thinning on Taylor numbers and on the slopes of curves. Ta'_c and Ta_0 can be recalculated with appropriate values of μ'_T substituted for μ'_P in the equations. To substitute μ'_T in the calculation of Ta'_w and s' requires the assumption that the rate of shear determining the viscosity is that in the primary flow and any effects due to secondary flow can be neglected; the logarithmic curves referred to above can then be used to find the appropriate values of μ'_T. Values are given in table 3 and in figure 6. Points to note are: (i) in figure 6 the initial increase in Δ with concentration followed by a fall-off to negative values of Δ at higher concentrations – Giesekus (1972) found a similar maximum in Δ as a function of concentration for 'Praestol 2935' (a polyacrylamide) dissolved in dimethylformamide in water; (ii) the significant differences between Ta_w/Ta_c and Ta'_w/Ta'_c, and the significant 'torque reduction' demonstrated by values of $\bar{s}$, each suggesting that contributory factors other than shear viscosity are affecting the flow. In previous works elasticity has been considered as a factor, the normal-stress coefficients (related to the material constants) being the relevant quantities to consider. Applying the second-order fluid model, curves such as those presented by Jones *et al.* (1973) may be used to find the constants. Results for polyacrylamide solutions show that the second normal-stress coefficient decreases rapidly at first as the concentration increases, but then more slowly, whereas the first normal-stress coefficient increases slowly at first, then more rapidly (figure 7*a*). From figure 7(*b*) it is seen that the predicted changes in $\bar{\epsilon}$ are less than 1 %, undetectable in our experiments. Kelzan solutions are shear-thinning, and therefore the second-order model is inappropriate. However, placing values of Δ and s/s' found from μ'_T on figure 7(*a*) shows that the normal stresses are much larger for the Kelzan solutions than for the polyacrylamide. (Results for the 80 p.p.m. solution, which is off the scale of the diagram, give $-\alpha_2 \simeq 75\ \text{mg m}^{-1}$ and $\alpha_1 + 2\alpha_2 \simeq -3{\cdot}0\ \text{mg m}^{-1}$.) A value of $\bar{\epsilon}$ of 0·92 is predicted for the 40 p.p.m. Kelzan solution from figure 7(*b*). This agrees well with the value of 0·93 found by Jones *et al.* (1973) for aqueous solutions of Kelzan. The values of α_1 and α_2 found from these experiments (glycerol solution was the solvent) are very similar in magnitude to those found in previous work with water as solvent. So the reputed large elasticity of polymers dissolved in glycerol/water compared with water alone, does not seem to be justified.

In their paper on overstability, Beard *et al.* (1966) use a simple Maxwell model

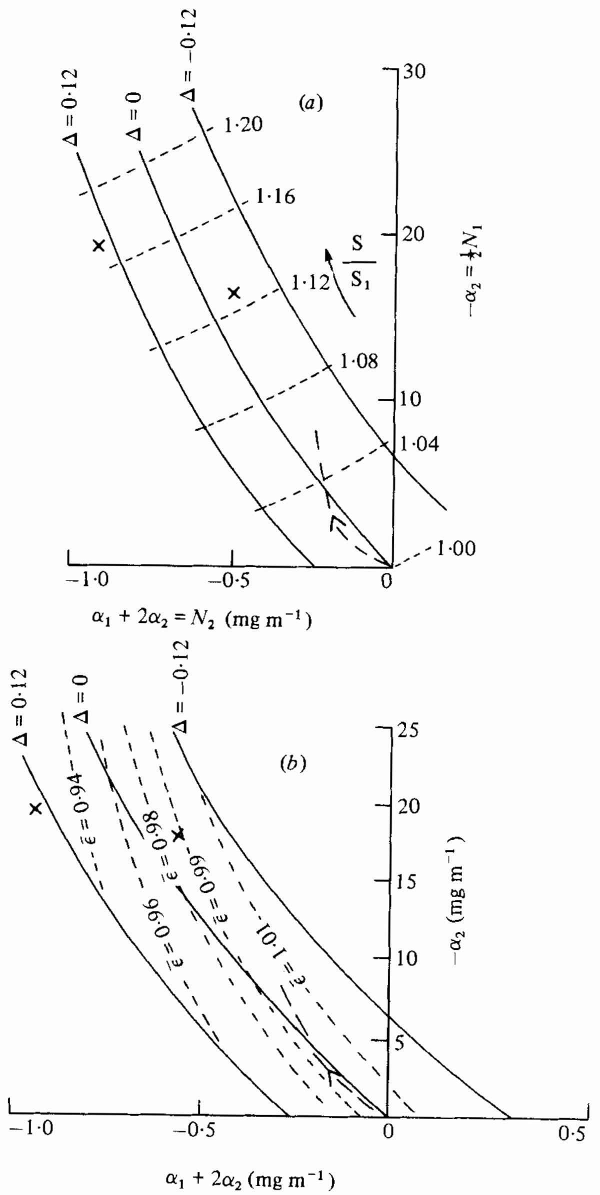


FIGURE 7. (*a*) Experimental values of Δ and s/s' (dashed line) for P250 superposed on theoretical stability diagram; arrow indicates increasing concentration; N_1 and N_2 are respectively first and second normal-stress coefficients; crosses × for 20 and 40 p.p.m. Kelzan solutions. (*b*) Values of N_1 and N_2 from (*a*) superposed on diagram of $\bar{\epsilon}$ and Δ.

with one elastic constant. This too has a constant shear viscosity. However, setting this aside and supposing that the oscillation seen in Kelzan is due to overstability, then comparing Ta_0/Ta'_c as observed with that predicted by the theory shows that the dimensionless elastic constant denoted by k by Beard *et al.* ranges from 0·2 to 0·5 as the concentration ranges from 20 to 80 p.p.m. The elastic constant $\alpha = k\rho d^2$ therefore ranges from 800 to 2000 mg m^{-1}. This is an order of magnitude bigger than that found from values of Δ and $\bar{s}$. On the other hand, these larger values are very similar to values estimated from flow in bent pipes, as discussed by Jones (1979).

Finally, is the oscillation of the embryo cells 'overstability'? It appeared at lower values of Ta_0 as concentration increased, as predicted by the theory of overstability, and there did seem to be an optimum value of concentration (< 5 p.p.m.) below which no oscillation appeared, as might be expected from the theoretical prediction that overstability only occurs when $k \geqslant 0{\cdot}13$. Also $Ta_0 < Ta_c'$ as predicted. However, the period of the oscillation was not constant (as might be expected of a liquid property) but was linearly related to the period of rotation of the cylinder. So the question remains an open one.

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