Instability in Couette flow of solutions of macromolecules

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(Received 8 August 1961 and in revised form 8 December 1961)

In Couette flow between coaxial cylinders, ring-shaped vortices, illustrated schematically in figure 1, develop at a Reynolds number which depends strongly on the geometry of the system, as treated analytically for Newtonian fluids by Chandrasekhar (1958). The problem was first considered by Taylor (1923) who, examining simple (micromolecular) liquids, arrived at an equation for the critical Reynolds number Re_i above which instability (vortex formation) would occur when the inner cylinder rotates and the outer is stationary, and when the gap is small compared to the radius. The Taylor equation is

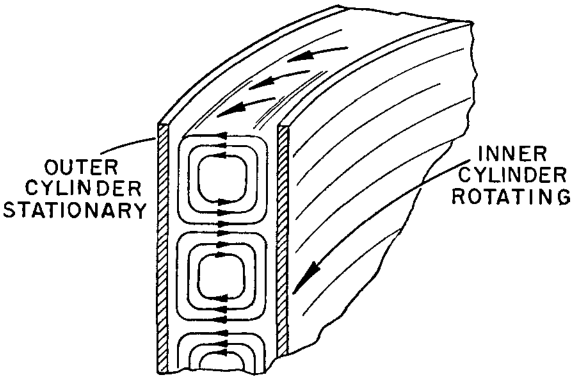

FIGURE 1. Taylor vortices in liquid between coaxial cylinders, with the inner cylinder rotating, the outer being stationary.

$$Re_i = \frac{Uh}{\eta/\rho} = 41{\cdot}8\left(\frac{r_1}{h}\right)^{\frac{1}{2}}, \tag{1}$$

where U is the peripheral velocity of the surface of the inner cylinder, h the width of the annular gap $= r_2 - r_1$, r_1 the radius of the inner cylinder, r_2 the radius of the outer cylinder, η the viscosity, ρ the density, and η/ρ the kinematic viscosity.

When $h \ll r_1$, the shear rate, $\dot{\gamma}$ sec^{-1}, is given by $\dot{\gamma} \simeq U/h$. Consequently, the Reynolds number can alternatively be calculated as

$$Re = \dot{\gamma} h^2 \rho/\eta. \tag{2}$$

In the course of high-shear-rate viscometric studies on macromolecular solutions, numerous observations on instability related to Taylor vortices were made.

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The Couette viscometer used* is shown schematically in figure 2. Of relevance to this discussion are the following features. The liquid was fed continuously from a syringe *6* through a port *5* so as to issue into the annular gap, defined by the inner rotating cylinder *1* and the outer stationary cylinder *3*, halfway between the open top *7* and bottom *8*. The liquid under shear between cylinders *1* and *3* moved vertically towards the top and bottom of the annulus at varying rates depending

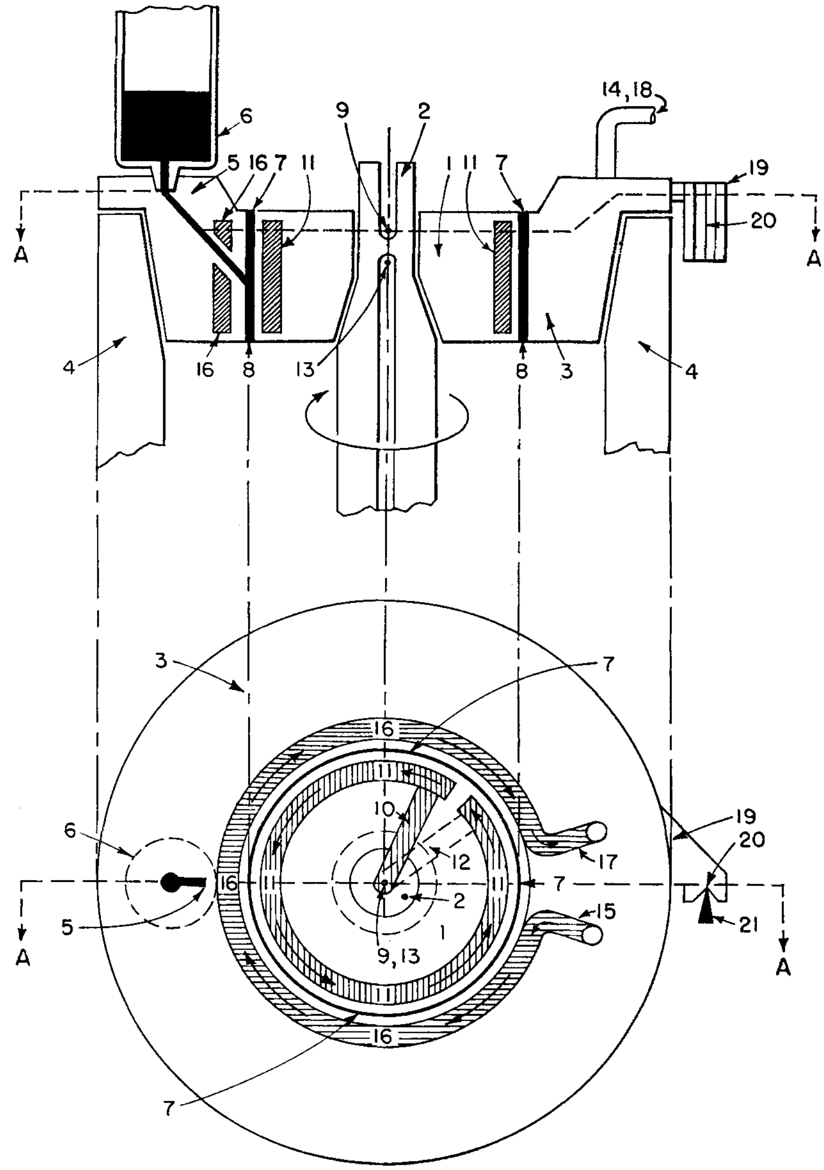

FIGURE 2. Side elevation and top elevation of coaxial cylinder viscometer for high-shear-rate studies.

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* Full details are given in the *Proceeding of the A.S.T.M. Symposium on Non-Newtonian Viscometry*, Washington, D.C. (1960).

on its viscosity and whether it was forced by a piston in the syringe *6* or whether it was allowed to drain under gravity. The radius of the inner cylinder, r_1, was 2·785 cm, that of the outer cylinder, r_2, was 2·800 cm and the annular width h was thus 0·01524 cm. Application of these values to the Taylor equation gave $Re_i = 535$.

In our experimental determinations of shear stress as a function of shear rate in the viscometer described, the onset of instability in both simple liquids and polymer solutions was quite reproducibly observed as a rather abrupt increase of slope. While we could not achieve sufficient resolution to show the discontinuity in the magnitude of effective viscosity as well as in the slope found in the precise measurements by Donnelly (1958) on micromolecular liquids, the general features of the abrupt change in our curves appear, from Donnelly's work, to be indicative of the onset of Taylor vortices.

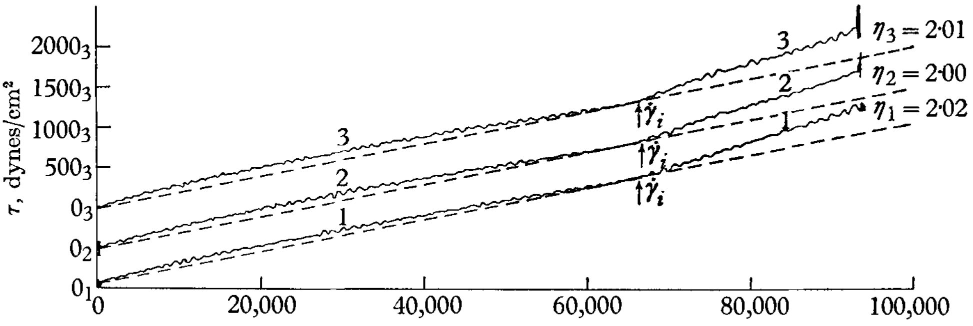

FIGURE 3. Original shear stress τ *vs* shear rate $\dot{\gamma}$ recorder plots for polystyrene ($\bar{M}_v = 1{\cdot}1 \times 10^6$, $c = 1{\cdot}055$ g/dl) in toluene at 25 °C. Three successive runs 1, 2, 3 were plotted, with zero shear stress for each shown as 0_1, 0_2, 0_3; $\dot{\gamma}_i$ is value of $\dot{\gamma}$ at which instability appears. Absolute value of $\eta/\dot{\gamma}$ at $\dot{\gamma} = \dot{\gamma}_i$ is shown as η_1, η_2, η_3 (numerical value in centipoise).

The problem of predicting the onset of turbulence in non-Newtonian macromolecular solutions in *various geometrical situations* has received limited experimental attention (Schnurmann 1949; Davies 1949; Ostwald & Auerbach 1926; Reiner 1926, 1960; Bestul & Bryant 1958), the concensus of opinion being that (for various geometries) turbulence in macromolecular solutions should occur at a lower value of Reynolds numbers than in micromolecular liquids. Graebel (1961) alone appears to have considered turbulence in the special geometry of Couette flow of non-Newtonian liquids, and this from an analytical rather than experimental viewpoint.

Our experiments shown that, except for solutions of macromolecules of *exceptionally* high molecular weight, there is no significant change in Re_i compared to micromolecular liquids. In general, it was found that for most of the macromolecular solutions the mean value of Re_i was 660 as compared to a mean value of 650 for all simple micromolecular liquids.

The method of determination will be understood with reference to figure 3, which shows the experimental recorder plots of shear stress τ *vs* shear rate $\dot{\gamma}$ for three successive runs on the same solution, viz. a 1·055 g/dl solution in toluene at 25 °C of polystyrene of molecular weight $1{\cdot}1 \times 10^6$. Above the values of $\dot{\gamma}_i$ shown, it is seen that there is an abrupt increase in the slope. In fact a more or less linear relation ensues which extrapolates to a large negative shear stress at zero shear rate. The critical shear rate $\dot{\gamma}_i$ was in all cases evaluated from the recorder plots in the manner illustrated in figure 3. Among runs on the same solution, or on pure solvents, the variation of $\dot{\gamma}_i$ was of the order of magnitude of ± 1 %. The viscosity at the critical shear rate was evaluated as the absolute (tangent) ratio $\tau/\dot{\gamma}$ at $\dot{\gamma} = \dot{\gamma}_i$, and is shown in figure 3 for each of the three runs. (With pure solvents since the τ *vs* $\dot{\gamma}$ relation was linear from 0 up to $\dot{\gamma}_i$, the value of η was constant up to $\dot{\gamma}$.) The Reynolds number Re_i was then evaluated as $\rho\dot{\gamma}_i h^2/\eta$. For example, with respect to the polystyrene solution for which run 1 of figure 3 is relevant, the density ρ was 0·866 g/cm^3; the tangent viscosity η_i and the critical shear rate $\dot{\gamma}_i$ as read from the figure were respectively 2·02 centipoise and 66,500 sec^{-1}. Consequently,

	Molecular weight	Solvent
Polystyrene	126,000	tol
	152,000	tol
	190,000	tol, dec, mek
	210,000	tol
	250,000	tol, dec, mek
	380,000	tol
	1,100,000	tol
	2,830,000	tol
	4,250,000	tol
Polyisobutylene	50,000	cyc, dec, tol, bz
	885,000	cyc, dec, tol, bz
	1,030,000	cyc, dec, tol, bz
	1,320,000	cyc, dec, tol, bz
	1,740,000	cyc, dec, tol, bz
	1,950,000	cyc, dec, tol, bz
Polymethyl-methacrylate	1,400,000,	bz, ed, mek
	5,200,000	bz, ed, mek

Abbreviations. tol = toluene, dec = decahydronaphthalene, mek = methyl-ethyl-ketone, bz = benzene, cyc = cyclohexane, ed = ethylene dichloride.

TABLE 1

$$Re_i = \rho\dot{\gamma}_i h^2/\eta = 659.$$

It is of interest to note that the low-shear-rate viscosity of this polystyrene solution, determined as the tangent at $\dot{\gamma} = 0$, was about 3·3 centipoise. Had this value been used instead of 2·02, the value of the Reynolds number would have been 398.

The range of the data on which these findings are based is indicated in table 1. The solvent power ranged from excellent (e.g. polyisobutylene in cyclohexane, polystyrene in toluene) to very poor, near the Flory theta-temperature (e.g. polyisobutylene in benzene, polystyrene in decalin).

In contrast, two ultra high-molecular-weight species of polyisobutylene (6×10^6 and 11×10^6) in solutions of decalin, cyclohexane, toluene, and benzene gave values of Re_i as low as 400 with a mean near 500. Other solution properties of these two species of polyisobutylene were anomalous: notably, the second viscosity number $(\eta_2 - \eta_s)/\eta_s c$ based on the second Newtonian (high shear) viscosity η_2, *decreased* markedly with increase of concentration c. The macromolecular physics underlying these anomalous solutions are not known.

This study was supported by a generous grant from the Film Division of E. I. duPont de Nemours, Inc., which is hereby gratefully acknowledged.

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