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THE HYDRODYNAMICS OF NON-NEWTONIAN FLUIDS
III. THE NORMAL STRESS EFFECT IN HIGH-POLYMER SOLUTIONS

By H. W. GREENSMITH and R. S. RIVLIN
Davy Faraday Laboratory of the Royal Institution

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CONTENTS

Normal stress effects arising in the torsional motion of a cylindrical mass of poly*iso*butylene solution are measured. The precautions which must be taken in making the measurements and the corrections which must be applied to them in order that the results may be compared with theory are discussed in some detail. The distribution of normal stresses over the plane ends of the cylindrical mass and the dependence of this on the experimental conditions is shown to be consistent with the phenomenological theory advanced by Rivlin (1948*a*).

From the normal stress measurements, the normal stress coefficient, defined in this theory, is evaluated and the manner in which it depends on velocity gradient is found.

Finally, the dependence of the normal stress coefficient on solution concentration and temperature is investigated.

1. Introduction

It has been remarked (Weissenberg 1946, 1947; see also Garner, Nissan & Wood 1950) that when certain colloidal suspensions or high-polymer solutions are in a steady state of laminar flow, certain anomalous effects arise. For example, if the liquid is contained between two coaxial cylindrical surfaces, as in a Couette viscometer, and one of these is rotated, the liquid

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level rises at the inner surface and falls at the outer one. Alternatively, if the liquid is contained between the flat bases of two coaxial cylindrical cups and is subjected to a steady torsional state of flow by uniform rotation of the outer cup, normal tractions are observed to act on the base of the inner cup. Effects of this type have been termed, variously 'Weissenberg effects', 'cross-elasticity' and 'normal stress effects'.

They appear to have first attracted critical scientific attention during the Second World War. As a result of restrictions on publication then in force, priority of discovery appears to be somewhat in doubt (see, however, Garner *et al.* 1950). It is possible, too, that such effects have been familiar in certain industries for a considerable time. In view of these facts it appears desirable to describe them by a title which is as non-controversial as possible. Accordingly, in this paper the term 'normal stress effects' will be used. This is equally applicable on the basis of all the theories for the description and origin of the effects which have so far been advanced, with the exception of that of Garner *et al.* (1950). It will, however, be seen that this latter theory is hardly likely to prove acceptable as an explanation of the effects observed. The term 'cross-elasticity' which has been used by Reiner (1948) presupposes a particular type of phenomenological theory for the effects and, in the present state of our knowledge, it seems scarcely justifiable to assume its correctness.

In the last few years the study of normal stress effects has attracted a considerable amount of attention both from the theoretical and experimental point of view. A number of theories of a phenomenological character have been advanced. However, in many cases these have not been brought to the point at which specific predictions of experimental results can be made from them. There appears to be fairly general agreement that normal stress effects arise, in practice, only in liquids which exhibit visco-elastic effects, and consequently most of the theories ascribe an elastic character to the liquids they consider.

Certain of the theories, notably those of Weissenberg (1946, 1947, 1948), Burgers (1948), Reiner (1948) and of Mooney (1951), use an analogy with the theory of finite strain of elastic solids. It is assumed that there are in the liquid elastic elements which, as a result of the velocity gradients existing in the liquid, are subjected to finite strains, and that normal stresses arise as a result of these finite strains and may be calculated from them by means of the stress-strain relations for an elastic solid. With the exception of that of Mooney (1951), none of these theories gives any indication of how the finite strain in the liquid is to be determined in terms of the state of flow. Mooney assumes that, in a liquid in steady-state laminar flow, the elastic elements are in a state of simple shear of amount proportional to the velocity gradient, and is thereby enabled to relate the normal stresses to measurable quantities describing the state of flow of the liquid.

Oldroyd (1950) has formulated stress-strain-velocity relations for a visco-elastic liquid and has shown, on the basis of these, that normal stress effects can arise in the steady-state laminar flow of such a liquid as a result of the presence in these relations of 'elastic terms'.

Garner & Nissan (1946) and Garner *et al.* (1947, 1950) have advanced a theory of quite a different character from those so far mentioned. They assume that a liquid which exhibits normal stress effects is a two-component system, one of the components of which suffers an increase of free energy as a result of the velocity gradient to which it is subjected. If the liquid is in an inhomogeneous state of steady laminar flow, there is a tendency for the free energy of the whole system to be reduced by the movement of this component from regions of high velocity gradient to regions of low velocity gradient. Differences of concentration are therefore set up in the liquid which in turn give rise to osmotic pressure differences. These are considered to be responsible for the normal stress effects observed. Amongst other objections to this theory, it would appear to predict that, in a Couette viscometer, the liquid should rise on the outer cylinder, in disagreement with experimental observation.

Rivlin (1948*a*) has formulated the most general stress-strain-velocity relations which can describe the flow properties of an incompressible visco-inelastic liquid and, on the basis of a physical argument, has concluded that these may be applied to describe steady-state laminar flow in a visco-elastic liquid. It appears that these stress-strain-velocity relations can be used to describe normal stress effects, at any rate superficially, similar to those observed. In this phenomenological theory, which is further described in §2, the flow properties of the fluid are characterized by two physical parameters, which may or may not depend on the state of flow. One of these is the viscosity coefficient Θ and the other has been called the normal stress coefficient Ψ (Rivlin 1948*b*). The non-vanishing of Ψ gives rise to normal stress effects in the liquid.

On the basis of a very simple molecular model for a concentrated high-polymer solution, it has been shown (Rivlin 1949) that $\Psi \neq 0$ for such a solution and, indeed, might be expected to be large enough to give rise to normal stress effects of appreciable magnitude. In this theory the non-vanishing of Ψ arises as a result of the orientation of the high-polymer molecules in a solution in which a velocity gradient exists. This orientation of the high-polymer molecules is also responsible for the elastic character of a high-polymer solution, and in this fact there may well be some point of contact between the phenomenological theory advanced by Rivlin (1948*a*) and the theories in which an elastic origin for the normal stress effects is introduced phenomenologically.

A number of experimental arrangements have been used to demonstrate normal stress effects in a variety of liquids. However, very few normal stress measurements of quantitative significance have been made. Russell (1946) has used a number of techniques for measuring the normal stresses associated with steady-state laminar flow of a variety of gels and solutions. In most of his measurements the working material was contained in a rotatable cylindrical cup above which was held a fixed disk. The resultant vertical force on the disk, produced by rotation of the cup, was measured. It will be seen in the light of the experiments discussed in the present paper that these forces may well have been determined as much by the departure from a torsional state of flow at the edge of the cup, as by the torsional motion of the fluid between the disk and the base of the cup. It does not therefore seem that these measurements are likely to lend themselves readily to theoretical interpretation. Both these measurements and the few measurements made by Russell with other techniques seem to involve considerable experimental error, and consequently their main interest lies in the variety of the methods of observing normal stress effects which they introduce and in the qualitative results.

Garner *et al.* (1950) have studied the distribution of the normal surface traction over the plane surface of a liquid in a torsional state of flow. The method of measurement used was similar in principle to that employed in the present paper. Their results are, however, apparently subject to large experimental error, and the manner in which they have been related to their theory appears to be open to question.

Both Russell (1946) and Garner *et al.* (1950) have examined the flow between coaxial cylindrical surfaces of liquids exhibiting normal stress effects. They found that the level of the liquid in a manometer tube communicating with the annular mass of liquid through a small hole in the inner surface did not change appreciably on rotation of the outer surface.

From the brief review given above of the principal theoretical and experimental studies of the normal stress effect which have so far been carried out, it will be readily appreciated that there is a considerable need for a systematic experimental study of them. It immediately appeared that an experimental arrangement, similar to that used by Garner *et al.* (1950) for studying the normal stresses associated with steady-state torsional flow of a cylindrical mass of liquid, was most likely to provide a flexible method of measuring normal stresses under conditions which would lend themselves to theoretical interpretation. Consequently, an apparatus of this type was used in the investigation.

Solutions of poly*iso*butylene were used as the working liquids, on account of their relative freedom from degradation and the greater understanding which exists of high polymeric solutions in comparison with other systems which show normal stress effects. Two commercial grades of poly*iso*butylene were used, and these will be referred to by their commercial designations of B 120 (viscosity average molecular weight $\approx 2\times 10^6$) and B 15 (viscosity average molecular weight $\approx 76\times 10^3$). It will, of course, be appreciated that two samples of the same grade of poly*iso*butylene are not necessarily identical in their physical properties, and consequently it is not to be expected that exact quantitative correlations will be obtained between experiments in which different samples have been used in preparing the solutions. Where it was desired to make quantitative comparisons between different solutions, they were, of course, prepared from a single high-polymer sample. *o*-Dichlorobenzene and tetralin were used as solvents, the former in the preliminary experiments and the latter in the final systematic measurements of normal stress effects. The change in solvent was made after the mention by Mooney (1951) of unpublished measurements by De Witt on the normal stress effect in solutions of Vistanex (poly*iso*butylene) in tetralin. It was felt that on account of the higher boiling-point of tetralin, it might possess advantages over *o*-dichlorobenzene as a solvent in an extensive series of measurements on a single solution. In practice the results obtained with both solvents were very similar (Greensmith & Rivlin 1951), but since the results obtained with tetralin solutions covered a wider range of operating conditions, only these are reported in the present paper.

Early in the investigation it was found that a number of secondary effects, which might confuse the interpretation of the experimental results, could arise if inadequate attention was paid to precision of construction of the apparatus, and that, even with an accurately constructed apparatus, certain corrections which are discussed in detail in §§ 6 to 8 had to be applied to the measurements.

In §§ 9 to 13 are described a series of measurements of the normal stresses associated with the torsional flow of two typical poly*iso*butylene solutions—one of high and the other of low molecular weight—contained between the disk-like bases of two cylindrical cups. In these experiments, the dependence of the normal stress distribution over the base of the inner cup on the speed of rotation of the outer cup and the distance between the cup bases was investigated. The results are discussed in terms of the phenomenological theory advanced by Rivlin (1948*a*), and it is shown how the magnitude of the normal stress coefficient and its dependence on velocity gradient can be determined from such experiments.

In §§14 and 15 experiments are described in which the dependence of the normal stress coefficient on solution concentration and temperature was studied. Finally, in §16, the relation of certain of the theories that have been advanced to the experimental results is discussed.

2. Theoretical considerations

It has been shown (Rivlin 1948*a*) that, for an incompressible visco-inelastic fluid, the stress components $t_{xx}, \ldots, t_{xy}$ and strain-velocity components $a, \ldots, \frac{1}{2}h$ in a rectangular Cartesian co-ordinate system (x, y, z) must be related by the six equations

$$\left.\begin{aligned} t_{xx} &= 2\Theta a + 2\Psi A' + p, \text{ etc.} \\ \text{and} \qquad t_{yz} &= \Theta f + \Psi F', \text{ etc.} \end{aligned}\right\} \tag{2·1}$$

The strain-velocity components $a, \ldots, \frac{1}{2}h$ are defined in the usual manner in terms of the velocity components (u, v, w) thus:

$$a = \partial u/\partial x, \text{ etc.} \quad \text{and} \quad f = \partial v/\partial z + \partial w/\partial y, \text{ etc.}, \tag{2·2}$$

while $A', \ldots, \frac{1}{2}H'$ are given by

$$A' = a^2 + \tfrac{1}{4}(g^2 + h^2), \text{ etc.} \quad \text{and} \quad F' = \tfrac{1}{2}gh + (b+c)f, \text{ etc.} \tag{2·3}$$

Θ and Ψ are physical parameters determining the flow properties of the fluid and may either be constants or dependent on the strain-velocity components through the two flow invariants K_2 and K_3, defined by

$$\left.\begin{aligned} K_2 &= ab + bc + ca - \tfrac{1}{4}f^2 - \tfrac{1}{4}g^2 - \tfrac{1}{4}h^2 \\ \text{and} \qquad K_3 &= abc + \tfrac{1}{4}fgh - \tfrac{1}{4}af^2 - \tfrac{1}{4}bg^2 - \tfrac{1}{4}ch^2. \end{aligned}\right\} \tag{2·4}$$

$-p$ is a hydrostatic pressure.

These assumptions may be expressed in mathematical form by the relations

$$t_1 = F(U_1, U_2, U_3) + p, \quad t_2 = F(U_2, U_3, U_1) + p \quad \text{and} \quad t_3 = F(U_3, U_1, U_2) + p, \tag{2·5}$$

between the principal components of stress t_1, t_2 and t_3 and the principal strain-velocity components U_1, U_2 and U_3, F being an arbitrary function. The relations (2·1) may then be obtained by a mathematical transformation to fixed rectangular Cartesian co-ordinate axes.

In view of the incompressibility of the fluid, a, b and c are related by the equation

$$a + b + c = 0. \tag{2·6}$$

In equations (2·1), Θ is the viscosity of the fluid as normally defined and Ψ is a new parameter which has been called the normal stress coefficient (Rivlin 1948*b*). Equations (2·1) are derived by a purely mathematical argument from the following physical assumptions regarding the fluid: (i) the fluid is isotropic in its state of rest; (ii) the stress at a point of the fluid depends uniquely on the state of flow in an infinitesimal element at that point, at the instant considered, and not on the state of flow in neighbouring elements or on that in the element considered at earlier instants of time; (iii) the material is incompressible.

It has been argued by Rivlin (1948*a*) that, although equations (2·1) are derived on the assumption that the fluid is visco-inelastic they should be applicable to the description of states of steady laminar flow in an incompressible visco-elastic fluid, since in such flow states each element of the fluid is subjected throughout its flow to identical conditions of stress, so that time derivatives of the stress or strain-velocity will not enter into the equations determining the stress components in terms of the strain-velocity components. Oldroyd (1950) has questioned this argument on grounds which appear to have the following physical content. If we consider the motion of any element of the fluid to be resolved into its rotational and irrotational parts, then, although at all points along a stream-line the principal components of the irrotational part of the motion are the same in magnitude, their directions will, in general, rotate relative to the element of the fluid, due to the rotational part of the motion of the latter. This relative rotation will, it seems, give rise to strain-acceleration and strain derivatives of still higher order within the element of fluid and, in this manner, the elastic effects in a visco-elastic fluid can make themselves felt, even in steady-state laminar flow.

However, for such a state of flow, the strain-acceleration, etc., will be constant along a stream-line and will be determined by the principal components U_1, U_2 and U_3 of the irrotational velocity. They will, therefore, contribute to the expressions for the principal components of stress t_1, t_2 and t_3 terms in U_1, U_2 and U_3. Since the fluid is isotropic when in a state of rest, t_1, t_2 and t_3 must be expressed in terms of U_1, U_2 and U_3 by means of relations of the form (2·5), so that equations (2·1) should be valid for the steady-state laminar flow of a visco-elastic fluid. Θ and Ψ will then involve, in general, physical constants which characterize the visco-elastic behaviour of the fluid. It will not, however, be possible to distinguish these from experiments on steady-state laminar flow alone.

If equations (2·1) describe the flow properties of the fluid, then the forces necessary to maintain a state of torsional motion about its axis, in a cylindrical mass of it, can be calculated (Rivlin 1948*a*). We find that, neglecting centrifugal forces and assuming that the curved surface of the fluid mass is force-free, azimuthal and normal surface tractions, Θ' and Z' per unit area respectively, must be applied to the plane ends of the cylindrical mass. These are given by

$$\Theta' = r\psi\Theta \quad \text{and} \quad Z' = \tfrac{1}{2}\psi^2 r^2 \Psi + \tfrac{1}{2}\psi^2 \int_a^r r\Psi \,\mathrm{d}r, \tag{2·7}$$

at a radial distance r from the axis of the cylinder, where ψ is the relative angular velocity of two planes normal to the cylinder axis and unit distance apart and a is the radius of the cylindrical mass. In (2·7), Θ and Ψ are, in general, functions of K_2 and K_3, which, for the type of motion considered, are given by

$$K_2 = -\tfrac{1}{4}\psi^2 r^2 \quad \text{and} \quad K_3 = 0. \tag{2·8}$$

EXPERIMENTAL ARRANGEMENT AND METHOD OF MEASUREMENT

3. Method of measurement

In order to achieve experimentally a state of torsional motion in a liquid approximating closely to that envisaged in §2 and to investigate the distribution of the normal surface tractions on the plane surfaces of the fluid mass and their dependence on ψ, an apparatus was constructed similar in principal to one employed by Weissenberg (1947, 1948) and by Garner *et al.* (1950).

The liquid under investigation was subjected to a torsional motion between the parallel bases of two coaxial cylindrical cups, the inner cup being stationary and the outer one rotating at a constant speed. The surface traction normal to the base of the stationary cup was measured manometrically by allowing the liquid between the cup bases to flow into manometer tubes through small holes in the base of the stationary cup. At equilibrium, the hydrostatic pressure head of liquid in each manometer tube is equal to the normal surface traction exerted on the base of the stationary cup at the point of entry of the manometer tube. The change in this pressure head due to rotation of the outer cup gives a measure of the surface traction due to the normal stress effect.

4. Description of the apparatus

The apparatus is shown in vertical projection in figure 1. An outer cup A, machined from an aluminium alloy casting to an internal diameter of 19·4 cm and an internal height of

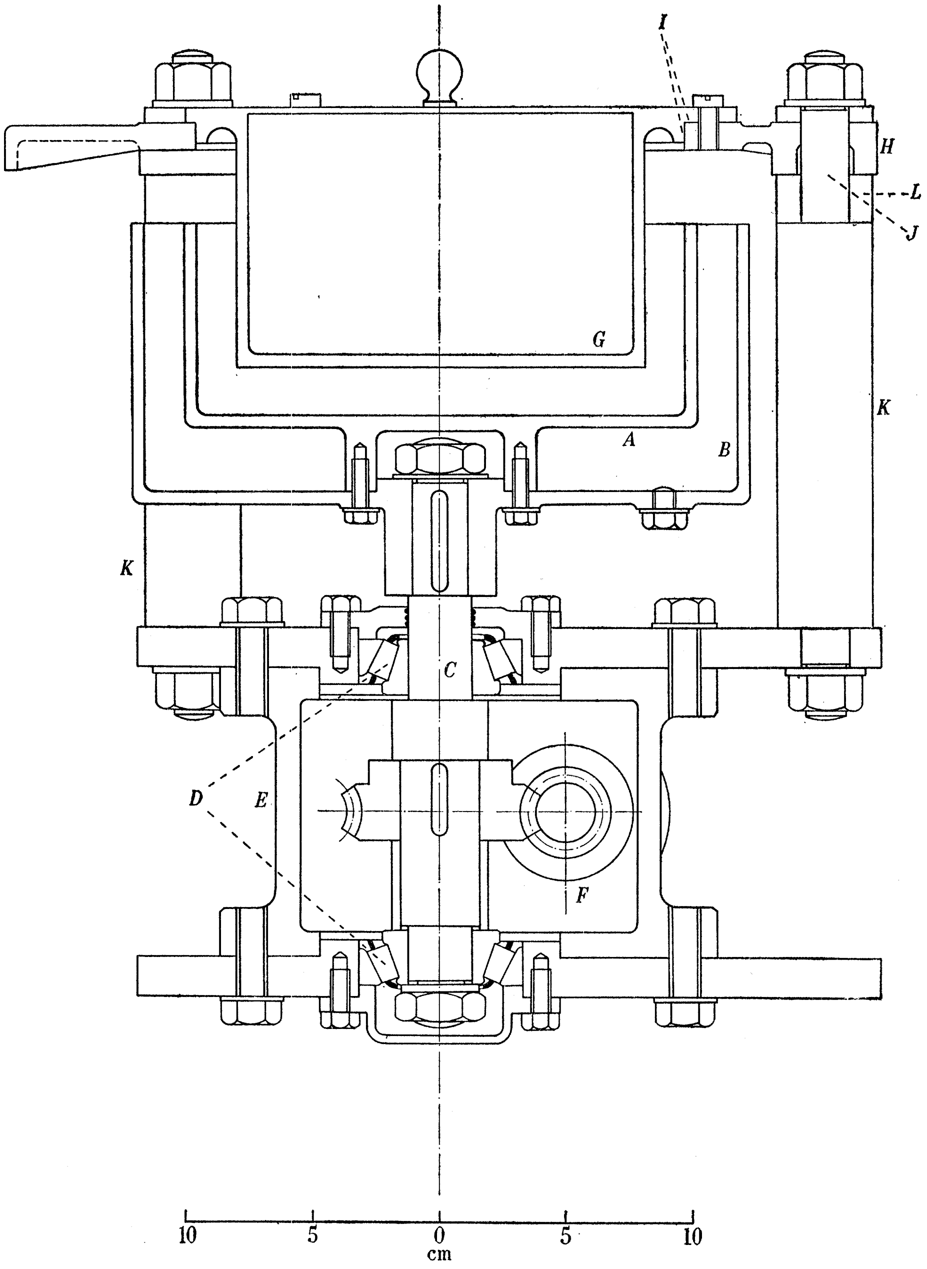

FIGURE 1. Diagram of apparatus (vertical projection).

7·5 cm, was mounted coaxially inside a phosphor-bronze water jacket *B*. This assemblage was mounted on a vertical (rotating) shaft *C*. Inclined roller bearings *D*, by which the vertical shaft was mounted in a cast-iron gear casing *E*, ensured free rotation with a minimum of longitudinal and lateral movement. The construction was such that the base of the outer cup was perpendicular to the axis of rotation to within $\frac{1}{2}$ min.

Rotational motion was transmitted to the vertical shaft from a horizontal input shaft through a 12 : 1 reduction gear *F*, the input shaft being flexibly coupled to a 1 h.p. variable-speed d.c. motor through a gear-box. In this way a continuous range of rotational speeds of the outer cup from 8 to 100 rev/min could be obtained for both directions of rotation. The base of the apparatus was mounted on three levelling screws (not shown in the figure).

Three inner cups were used in the experiments. Each of them was machined from aluminium alloy castings to an external diameter of 16·2 cm and an external height of about 10 cm, and had eight holes drilled in its base at various radial distances r from the centre. In each case the holes were arranged on a spiral in order to separate them, one of the holes being central. Details of their radial distances r and azimuthal positions θ in relation to a radius joining the centres of holes 1 and 2 are given in table 1. The diameters of the holes in cups nos. 1 and 3 were 1·7 and 2·3 mm respectively, while in cup no. 2 the holes were 1·7 mm in diameter except for holes nos. 3 and 7 which had diameters of 1 mm.

Table 1

hole no.	1	2	3	4	5	6	7	8
cup no. 1, r cm	0·00	2·52	3·62	4·43	5·10	5·76	6·28	6·77
cup no. 2, r cm	0·10	1·38	2·31	3·24	4·10	4·99	5·87	6·66
cup no. 3, r cm	0·00	1·34	2·31	3·24	4·09	5·02	5·91	6·73
cup no. 1, θ rad.	—	0	$2\pi/7$	$4\pi/7$	$6\pi/7$	$8\pi/7$	$10\pi/7$	$12\pi/7$
cups 2 and 3, θ rad.	—	0	$\pi/3$	$2\pi/3$	π	$4\pi/3$	$5\pi/3$	0

Aluminium tubes (not shown in the figure) of about 5 mm internal diameter were screwed into sockets over the position of each hole, thin cork washers being used as seals. The aluminium tubes were surmounted by glass tubes of similar bore, which constituted the manometers, the junctions being of the simple cone and socket type to facilitate cleaning. A thin film of the liquid under test was used to seal the junction.

The mounting of the inner cup *G* was so designed that (i) a set of interchangeable cups could be used, (ii) a cup could be replaced with correct alinement after removal for cleaning or introduction of the liquid into the apparatus and (iii) the vertical separation of the cups could be altered while maintaining them coaxial. This was achieved by mounting the inner cup in a phosphor-bronze annular ring *H*, the horizontal and vertical locating surfaces *I* ensuring correct alinement. Guide pins *J*, surmounting the three pillars *K*, located the annular ring in a position concentric with the axis of rotation, while the distance of this ring from the base of the outer cup could be varied, by interposing spacers *L* between the ring and the shoulders of the pillars, from practically zero to 3 cm. Parallelism between the cup bases was maintained to 0·003 cm, and the centre of the inner cup base coincided with the axis of rotation to 0·003 cm.

An annular cover was used to minimize evaporation of the solvent when solutions were used as test liquids.

The temperature of the liquid under test was controlled by pumping water from an external thermostat through the inside of the inner cup and the water-jacket by means of small centrifugal pumps. In the range 5 to 45° C the temperature of the circulating water was maintained constant to within $\pm 0{\cdot}05°$ C.

5. Experimental procedure

Test liquids were introduced into the outer cup after removal of the inner cup. Time was allowed for air bubbles to disappear from the liquid before the inner cup was replaced and clamped in position, care being taken in doing this not to trap air bubbles under its base. The quantity of liquid introduced was always sufficient to ensure that the height of liquid in the annular gap was at least 2 cm above the base of the inner cup.

After levelling the apparatus the liquid menisci in the manometer tubes were adjusted to zero levels convenient for observation by connecting the manometer tubes to a common air reservoir maintained at a suitable pressure below that of the atmosphere. This pressure difference was maintained to a constancy of $\pm 0{\cdot}2$ mm of oil, by means of a simple Servo mechanism, operated from a reference manometer in conjunction with a water pump and air leak. The equilibrium level of the meniscus in each tube was then measured by means of a cathetometer.

The outer cup was rotated at the desired speed and the equilibrium levels of the menisci were again measured. The accuracy of measurement was such that the increase h in the height of each meniscus was determined to within $\pm 0{\cdot}05$ mm.

The average speed of rotation Ω (in rev/min) of the outer cup was measured by counting the number of revolutions during a period of about 5 min in which measurements of h were being made. The driving motor was sufficiently lightly loaded for the speed of rotation to be constant to 1 %.

The direction of rotation of the motor was then reversed and similar measurements of menisci levels and speed were again made. It was found possible to adjust the rotational speed in the reverse direction to within 2 % of that in the forward direction.

Actual temperatures attained by the test liquids with the outer cup rotating were measured with a sensitive thermometer introduced into the liquid. In all the experiments presented in this paper, they were less than $0{\cdot}1°$ C above that of the thermostating water.

The poly*iso*butylene solutions used in the experiments were prepared by shaking together weighed amounts of high polymer and solvent until substantially complete solution had occurred. Any small amount of gel which had proven insoluble was removed by filtration through a sintered glass mat. This may have introduced small errors in the solution concentrations, but it will be seen that such errors would in no way invalidate the conclusions drawn from the experiments.

6. Investigation of secondary effects

Before accurate and significant measurements of the normal stress effect could be made, it was found necessary to study a number of secondary effects which might be expected to occur in the apparatus. These were (i) the effect of non-parallelism of the bases of the cups, (ii) centrifugal effects, (iii) effects arising from the finite size of the holes in the bases of the inner cup, and (iv) the effect of tilting the apparatus as a whole, so that the axis of rotation was not vertical.

These investigations enabled us to determine the manner in which corrections for these effects could be applied to the measured normal stresses, in those cases where they could not be avoided.

It was found that non-parallelism of the cup bases gave rise to effects for which corrections had to be made in order to obtain accurate determinations of the normal stress effect. The manner in which these effects arise and that in which corrections may be made for them are discussed in § 7.

It was also found that for the solutions used in carrying out the normal stress measurements it was necessary to make corrections for centrifugal effects and the manner in which this may be done is discussed in § 8.

It might be expected that the presence of a hole in the base of the inner cup would disturb the motion of the liquid in its neighbourhood from that envisaged in the theoretical analysis, particularly if the diameter of the hole was comparable with the cup separation. In order to investigate this, measurements of the normal stresses were made using 4·9 and 2 % solutions of grade B 120 poly*iso*butylene in *o*-dichlorobenzene. Cup no. 2 was used and the distance l between the bases of the inner and outer cups was 1·9 mm. All the holes except 3 and 7 had diameters of 1·7 mm, while holes 3 and 7 had diameters of 1 mm. The latter were then enlarged to 2·6 mm and the measurements repeated. It was found that no appreciable change in the measured normal stresses occurred.

Again, we might anticipate that the presence of a hole at one point of the base of the inner cup would give rise to a wake which would, in turn, contribute to the surface traction at another point of the base and hence introduce an error into the measurement of the normal stress at that point. In order to test whether this did, in fact, occur, measurements were made of the heights of rise in the manometers resulting from rotation of the outer cup with various combinations of holes sealed to leave a smooth plane surface. Again, no changes were observed in the measured normal stresses.

It was therefore considered that the presence of holes of finite size in the base of the inner cup did not influence the normal stresses significantly.

The effect of tilting the apparatus as a whole was also examined, and it was found that although appreciable changes of the normal stress distribution could occur for sufficiently high degrees of tilt, careful levelling of the apparatus was adequate to reduce such errors to negligible magnitude.

7. NON-PARALLELISM OF THE CUP BASES

Unless extreme care was taken in adjusting the bases of the inner and outer cups to parallelism, it was found that reversal of the direction of rotation of the outer cup gave rise to a change in the distribution over the inner cup of the measured heights h of the liquid in the manometers. This is illustrated in figure 2, in which are plotted corresponding values of h and r for a 6 % solution of B 120 poly*iso*butylene in *o*-dichlorobenzene, with $l = 1·3$ mm and $\Omega = 40·9$ rev/min. Curve I refers to clockwise and curve II to counter-clockwise rotation of the outer cup, as viewed from above.

It was considered that this dependence of h on the direction of rotation was an effect resulting from non-parallelism of the cup bases, the effect being similar in character to that described by Reynolds (1886) in his theory of lubrication. The dependence of the h against r curves on the degree of non-parallelism was accordingly investigated using a viscous lubricating oil which does not show the normal stress effect.

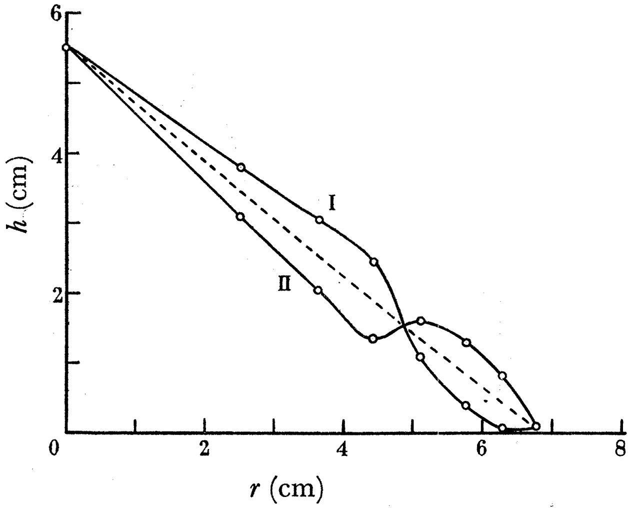

FIGURE 2. h against r relation for a 6 % B120 poly*iso*butylene solution. I, clockwise rotation; II, counter-clockwise rotation.

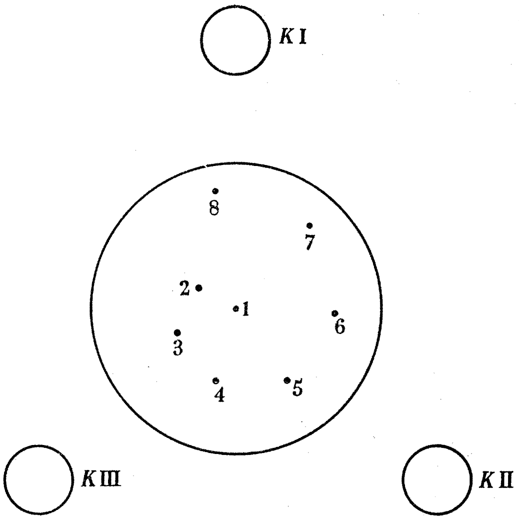

FIGURE 3. Plan of base of inner cup no. 1 and supporting pillars.

Cup no. 1 was used and the disposition of holes in its base, as viewed from above, is shown in figure 3, together with the positions of the supporting pillars (K in figure 1). With $l = 1{\cdot}3$ mm and $\Omega = 60$ rev/min, thin shims were introduced under the supports for the inner cup until only a negligible change of h was observed on reversal of the direction of rotation of the outer cup. Then, a shim of thickness 0·5 mm was introduced under the supporting ring at each of the pillars K in turn and h was measured for both clockwise and counter-clockwise directions of rotation of the outer cup. The values of h so obtained with the shim on KI are shown in figure 4. In each case the mean values $\bar{h}$ of h for the two directions of rotation were calculated, a smooth $\bar{h}$ against r curve being obtained. This is shown by the broken line in figure 4. It is considered that the non-vanishing of $\bar{h}$ is due to centrifugal effects (see §8 below). The values of $(h-\bar{h})$ for the clockwise direction of rotation were then calculated for each of the three positions of the shim and the corresponding values of $(h-\bar{h})$ and r so obtained are shown in figure 5. Curves I, II and III apply to the introduction of the shim above the supporting columns KI, KII and KIII respectively.

Assuming that before the introduction of this shim the cup bases were parallel, we can explain the observed results qualitatively in the following manner. Consider the case when the shim is introduced over the column KI. Then at holes 2, 3, 4 and 8 the liquid is moving in a divergent channel, so that negative values of $(h-\bar{h})$ are to be expected, while at holes 5, 6 and 7 it is moving in a convergent channel so that positive values of $(h-\bar{h})$ are to be expected. Similar qualitative arguments can be employed to explain the forms of curves II and III.

It was found that the amplitudes of the wave-like curves in figure 5 increased with the angular velocity of the rotation of the outer cup and with the viscosity of the liquid used.

Furthermore, it was found quite generally that the means $\bar{h}$ of the values of h measured for the two directions of rotation always lay on a smooth non-wavy curve, when plotted against r, whether or not the liquid used showed a normal stress effect. This is illustrated, for the case of a poly*iso*butylene solution showing an appreciable normal stress effect, in figure 2, in which the broken line represents the $\bar{h}$ against r relation.

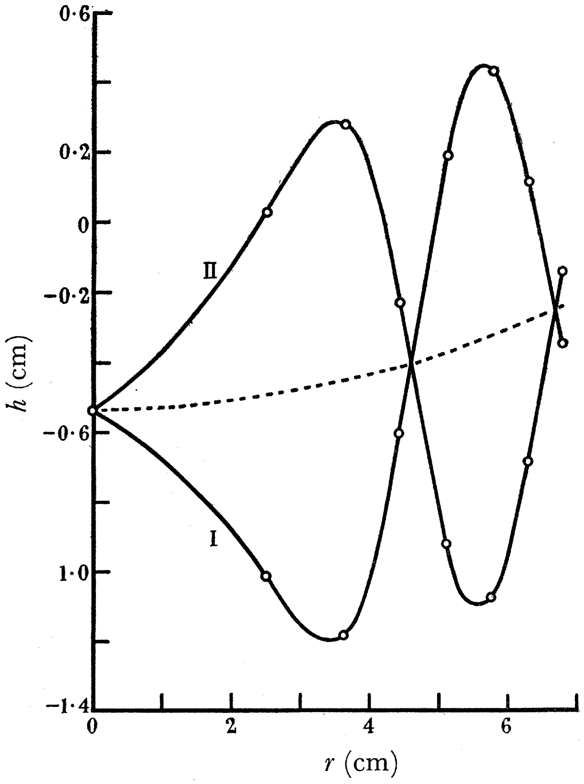

FIGURE 4. Effect of non-parallelism of cup bases on h against r relations for lubricating oil. I, clockwise rotation; II, counter-clockwise rotation. Broken line gives $\bar{h}$ against r relation.

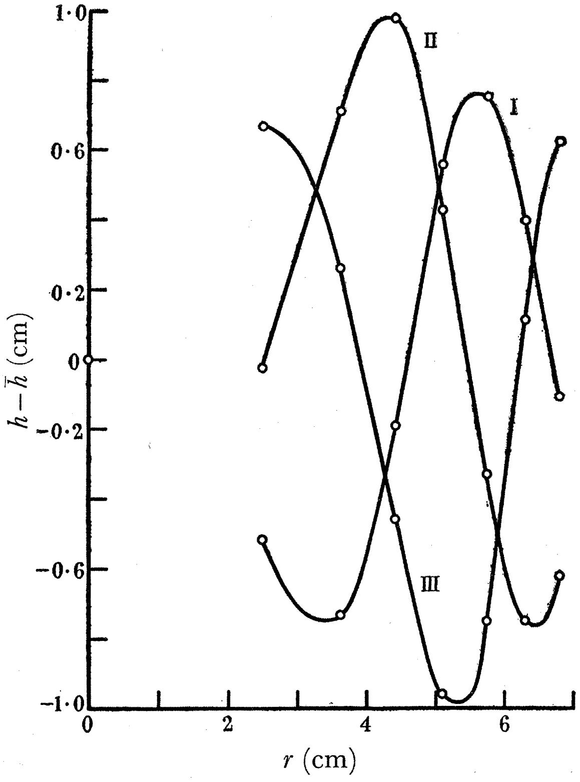

FIGURE 5. $(h-\bar{h})$ against r relations for lubricating oil, for three directions of mutual inclination of cup bases and clockwise rotation.

Moreover, it appears that the $\bar{h}$ against r relation obtained experimentally is determined, in the case of a small degree of non-parallelism of the cup bases, by the mean separation of these bases. Experiments illustrating this fact are described in §12.

In making normal stress measurements on liquids of high viscosity, it was not found possible to adjust the cup bases to a sufficiently high degree of parallelism to eliminate completely the effects described above. This may be readily appreciated from the magnitude of the effects shown in figure 5. Accordingly, in carrying out normal stress measurements, these effects were minimized as far as possible by adjusting the parallelism of the cup bases and were then further corrected by measuring the values of h for clockwise and counter-clockwise directions of rotation and finding their means.

8. Centrifugal effects

In deriving equation (2·7) for the normal surface traction on the plane ends of the liquid mass, the centrifugal forces associated with the assumed state of flow were neglected. In practice it may not be permissible to do this.

It is shown in Appendix 1 (§17) that the centrifugal forces will result in the superposition, on the torsional motion of the liquid, of a circulatory flow in vertical planes through the axis of rotation.* Such a circulatory flow has been noted by Batchelor (1951) in an analysis of viscous fluid flow between parallel infinite disks rotating at different angular velocities. It appears, however, that this circulatory flow should have a negligible effect on the normal stress measurements, provided that the viscosity of the liquid is sufficiently high and the distance l between the cup bases is sufficiently small.

In addition, it appears that the centrifugal forces make a contribution to the measured surface traction on the plane ends of the liquid mass, and this is calculated approximately in §17, on the assumption that the effects of the circulatory motion are negligible. Under these conditions, it is found that the formula (2·7) for the normal surface traction is changed by the addition of a term which is independent of the viscosity or normal stress coefficients for the liquid. The equation may therefore be verified experimentally using liquids which do not exhibit a normal stress effect (i.e. for which $\Psi = 0$).

Measurements were therefore made of the heights of rise of liquid in the manometer tubes, resulting from rotation of the outer cup, using lubricating oil, *o*-dichlorobenzene and xylene. The orders of magnitude of the viscosities of these liquids at the working temperature (15 to 20° C) are 3, 10^{-2} and 10^{-2} poises respectively. The measurements were made over the range of values of Ω of about 40 to 70 rev/min, and a range of values of l of 1·3 to 10·8 mm. For each value of Ω and of l, measurements were made for both clockwise and counter-clockwise directions of rotation of the outer cup in the manner described in §5 and the mean heights of rise $\bar{h}$ were obtained. Typical results are shown in figure 6 in which $\bar{h}$ is plotted against r^2 for *o*-dichlorobenzene. The values of Ω employed here (the mean of the values for the two directions of rotation) were 71·0 and 41·2 rev/min and the value of l was 1·3 mm.

It will be seen that $\bar{h}$ is a linear function of r^2, in accordance with the prediction of equation (17·8) in appendix 1. Similar linear relations between $\bar{h}$ and r^2 were obtained for all the liquids studied and for all the values of Ω and l employed. So, in each case, the experimental results can be expressed by an equation of the form

$$\bar{h} = A + Br^2, \tag{8·1}$$

in which, from equation (17·8), B should be given by

$$B = \pi^2\Omega^2/5400g, \tag{8·2}$$

where g is the gravitational acceleration. The problem of determining A theoretically would be a difficult one, if, indeed, it were soluble.

Corresponding values of B and Ω^2 obtained for the various liquids used and the various values of l are shown in figure 7. The line represents the theoretical relation between B and

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* It is of interest that Garner *et al.* (1950) have observed circulatory flow of a similar character in a mass of liquid showing the normal stress effect. They have, however, interpreted this as being associated with the redistribution of solute in the solvent.

Ω^2 given by equation (8·2). It is seen that the agreement between the experimental and theoretical values of B is fairly good for lubricating oil, while departures are obtained with the liquids of lower viscosity—*o*-dichlorobenzene and xylene. These departures increase with increase of Ω or of l and with decrease of the viscosity, and are no doubt due to the effects of circulatory flow.

From the experimentally determined $\bar{h}$ against r^2 relations, the values of A were found for each of the values of Ω and l and for each of the liquids used. It was found that, within the limits of experimental error, A was proportional to Ω^2 and was independent of l and of the liquid used, being given by

$$A = -1{\cdot}6\times10^{-4}\Omega^2\,\text{cm}, \tag{8·3}$$

where Ω is expressed in rev/min.

Since the high-polymer solutions on which normal stress measurements were made were of very high viscosity, it was considered permissible, in the light of the experiments described above, to make corrections for centrifugal effects by means of the formula (8·1) in which A and B are given by (8·2) and (8·3) respectively.

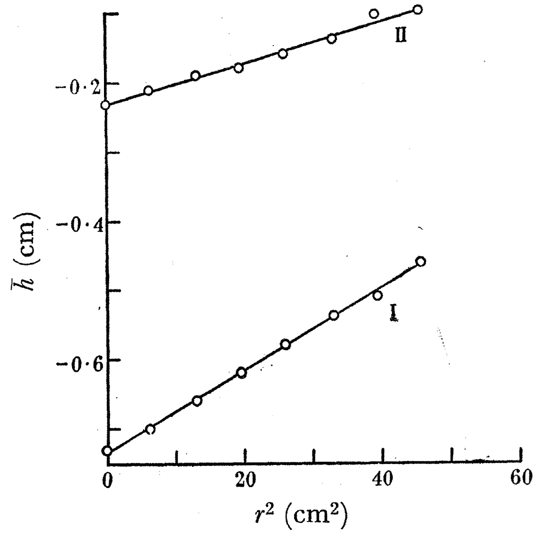

FIGURE 6. $\bar{h}$ against r^2 relations for *o*-dichlorobenzene. I, $\Omega = 71{\cdot}0$ rev/min; II, $\Omega = 41{\cdot}2$ rev/min.

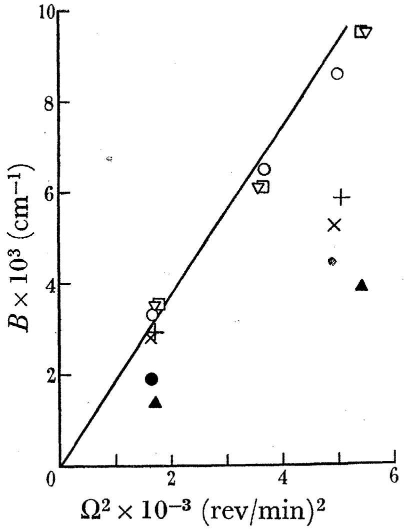

FIGURE 7. B against Ω^2 relation for various liquids.

l (mm) ○ 1·3, □ 4·4, ∇ 10·8 } lubricating oil,
\+ 1·3, ▲ 4·4 } *o*-dichlorobenzene,
× 1·3, ● 4·4 } xylene.

MEASUREMENTS OF THE NORMAL STRESS EFFECT IN SOLUTIONS OF POLY*ISO*BUTYLENE

9. RELATION BETWEEN EXPERIMENTAL AND THEORETICAL FLOW CONDITIONS

The measurements of the normal stress effect described in §§ 10 and 11 below were carried out with a view to determining whether the second of equations (2·7) can be used to describe the distribution of the normal surface tractions acting on the plane ends of a cylindrical mass of liquid, which exhibits the normal stress effect, in a steady state of torsional flow, for various values of Ω and l.

It will be appreciated that in an apparatus of the type described in §§3 and 4 and used in these experiments, the state of flow is not precisely that envisaged in the theory. Apart from the presence of centrifugal effects and effects due to inevitable accidental departures from the ideal in the mechanical construction, which have been discussed in §§6 to 8 and for which corrections can be made in the manner there described, the mass of fluid does not have a cylindrical force-free surface as envisaged in the derivation of equations (2·7).

Provided that the distance between the disk-like bases of the cups is small compared with the radius of the inner cup, the state of flow between them conforms (neglecting centrifugal effects) to that envisaged in the theory, at any rate up to a distance from the axis of rotation comparable with the radius a_1 of the inner cup. We can imagine a cylindrical surface of such a radius $a'(<a_1)$ and coaxial with the rotation to be drawn in the fluid. The fluid lying outside it will exert on it a uniform normal surface traction Z'_0 (say), and consequently the measured surface traction over the plane ends of the mass of fluid should be given by

$$Z'-Z'_0=\tfrac{1}{2}\psi^2r^2\Upsilon+\tfrac{1}{2}\psi^2\int_{a'}^{r}r\Upsilon\,\mathrm{d}r. \tag{9·1}$$

The measured mean heights of rise $\bar{h}$ of the liquid in the manometer tubes, after correction for centrifugal effects, should therefore be given by

$$\rho g(\bar{h}-\bar{h}_0)=-\tfrac{1}{2}\psi^2r^2\Upsilon-\tfrac{1}{2}\psi^2\int_{0}^{r}r\Upsilon\,\mathrm{d}r, \tag{9·2}$$

where ρ is the density of the liquid, g is the gravitational acceleration and $\bar{h}_0$ is defined by

$$\rho g\bar{h}_0=-Z'_0+\tfrac{1}{2}\psi^2\int_{0}^{a'}r\Upsilon\,\mathrm{d}r, \tag{9·3}$$

so that $-\rho g\bar{h}_0$ is the normal surface traction at $r=0$. Writing $\psi=\pi\Omega/30l$, equation (9·2) may be rewritten

$$\rho g(\bar{h}-\bar{h}_0)=-\frac{\pi^2}{1800}\left(\frac{\Omega}{l}\right)^2\left[r^2\Upsilon+\int_{0}^{r}r\Upsilon\,\mathrm{d}r\right], \tag{9·4}$$

in which Υ is a function of $K(=-K_2)$. From (2·8), K is given by

$$K=\frac{\pi^2}{3600}\left(\frac{\Omega r}{l}\right)^2. \tag{9·5}$$

Since the state of flow outside the cylindrical mass bounded by $r=a'$ is complicated in character, we cannot make an accurate theoretical determination of the magnitude of Z'_0, and hence of $\bar{h}_0$, in terms of Ω, l, Υ and the geometry of the apparatus.

10. VERIFICATION OF THE NORMAL STRESS EQUATION

It is seen from equation (9·4) that $(\bar{h}-\bar{h}_0)$ is determined by $r\Omega/l$. In this section the results are given of experiments designed to verify this conclusion, using a 6 % solution of B120 poly*iso*butylene (viscosity average molecular weight $\approx 2\times10^6$) in tetralin and a 34·8 % solution of B15 poly*iso*butylene (viscosity average molecular weight $\approx 76\times10^3$) in tetralin. The experiments were carried out at 25·0° C.

With the B120 poly*iso*butylene solution, measurements were made of $\bar{h}$ for the various values of r using cup no. 3 with a value of l of 1·85 mm and various values of Ω from 7 to 50 rev/min. The values of $\bar{h}$ obtained are plotted against r in figure 8, after correction for centrifugal effects in the manner described in § 8. In this figure, curves for successive values of Ω are shifted parallel to the ordinate by $\frac{1}{2}$ cm for clarity of display. From these curves the values of $(\bar{h}_0-\bar{h})$ are obtained and are plotted against Ωr in figure 9. It is seen that they lie on a single smooth curve in accord with the prediction of equation (9·4). Further measurements of $\bar{h}$ were made with various values of l as well as of Ω. The results obtained are shown, after correction for centrifugal effects, in figure 10. Again for clarity of display successive curves are shifted parallel to the ordinate by 0·2 cm. The values of $(\bar{h}_0-\bar{h})$ obtained from these curves are plotted against $\Omega r/l$ in figure 11. Again, it is seen that all the experimental points lie on a single curve in accordance with the prediction of equation (9·4).

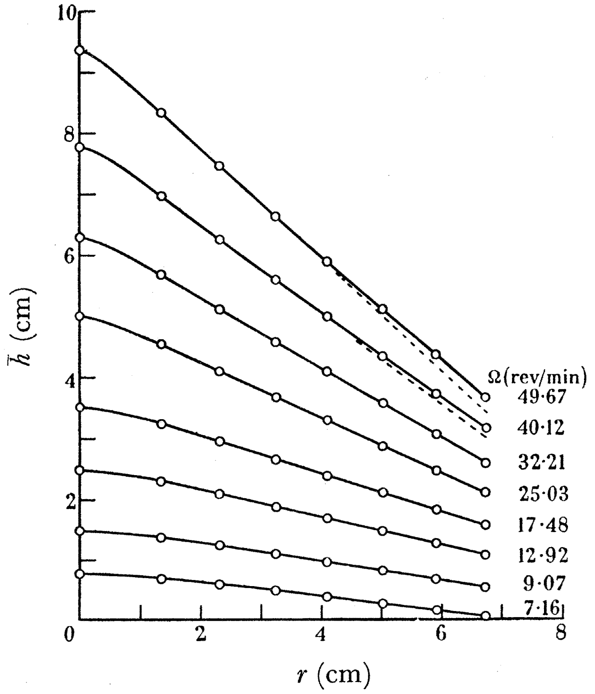

FIGURE 8. $\bar{h}$ against r relations, for various values of Ω, for 6 % B120 poly*iso*butylene solution. $l = 1·85$ mm.

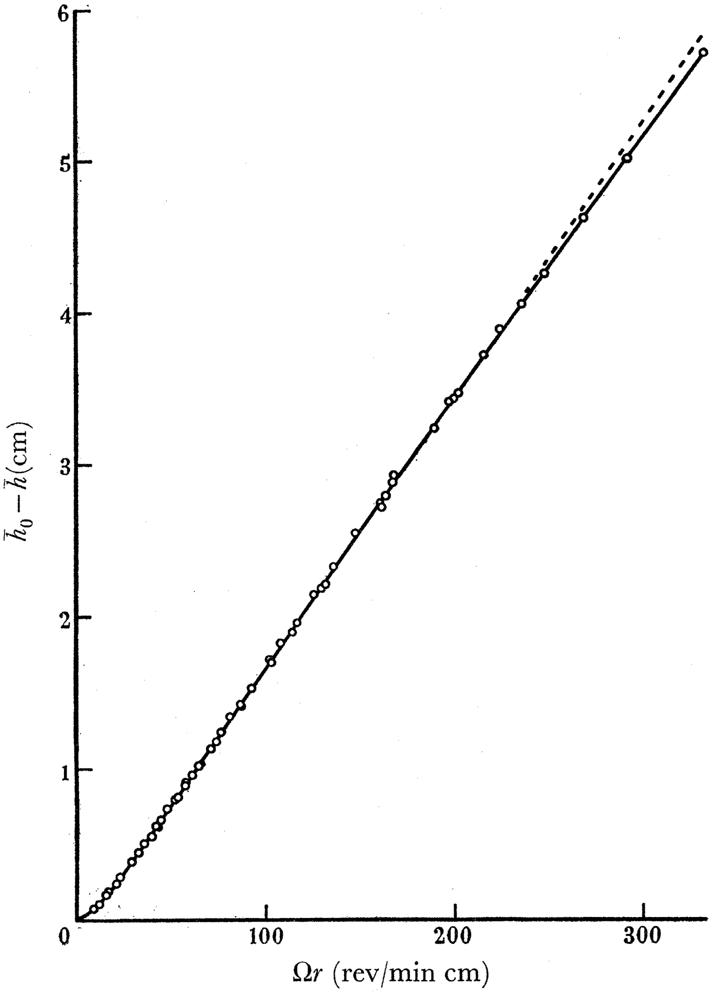

FIGURE 9. Relation between $(\bar{h}_0-\bar{h})$ and Ωr obtained from curves of figure 8.

With the B15 poly*iso*butylene solution, similar measurements were made of $\bar{h}$ for the various values of r using cup no. 3 with a value of l of 1·85 mm and various values of Ω from 8 to 20 rev/min. The $\bar{h}$ against r^2 relations obtained are shown in figure 12*a*, successive curves

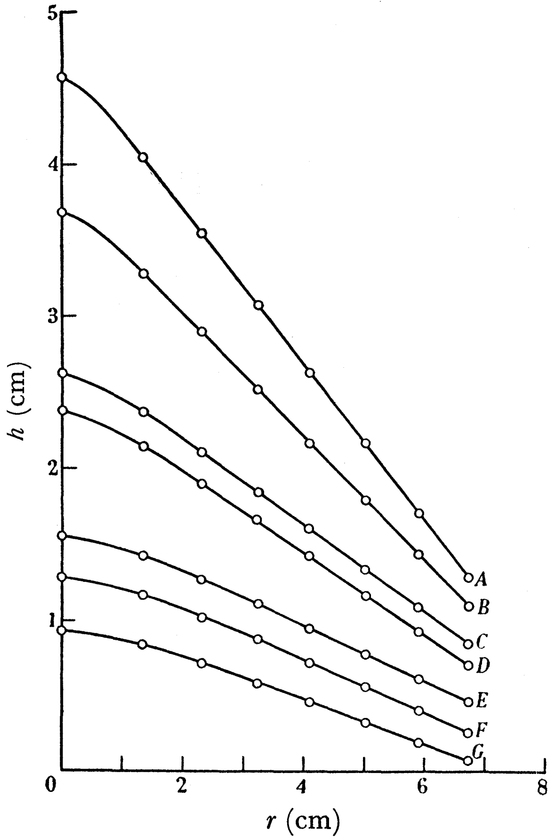

FIGURE 10. $\bar{h}$ against r relations, for various values of Ω and l, for 6 % B120 poly*iso*butylene solution.

	Ω (rev/min)	l (cm)
A	28·54	0·185
B	41·24	0·343
C	15·92	0·185
D	39·81	0·503
E	27·28	0·503
F	41·22	0·805
G	35·49	0·805

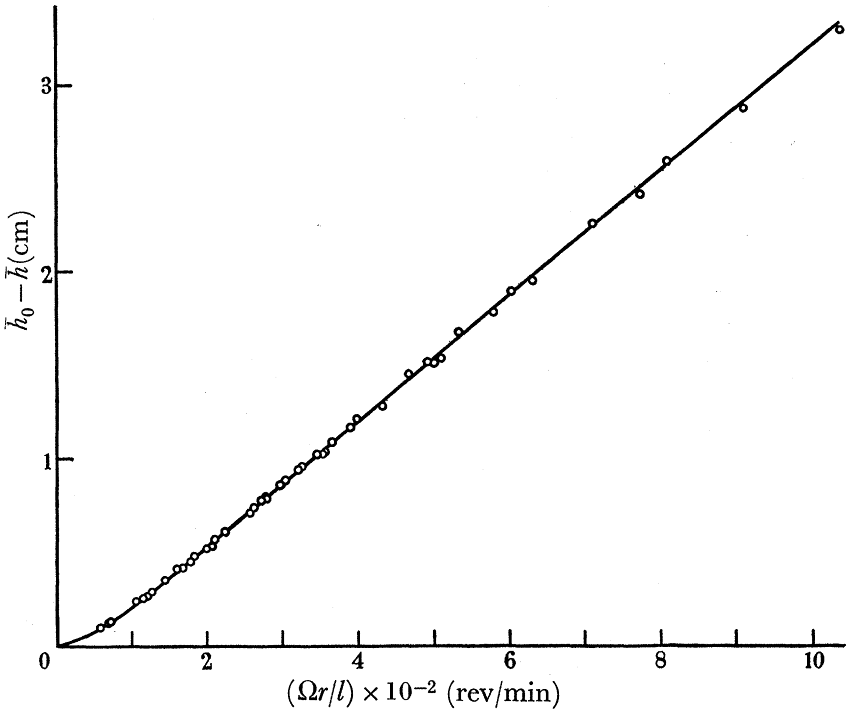

FIGURE 11. Relation between $(\bar{h}_0-\bar{h})$ and $\Omega r/l$ obtained from curves of figure 10.

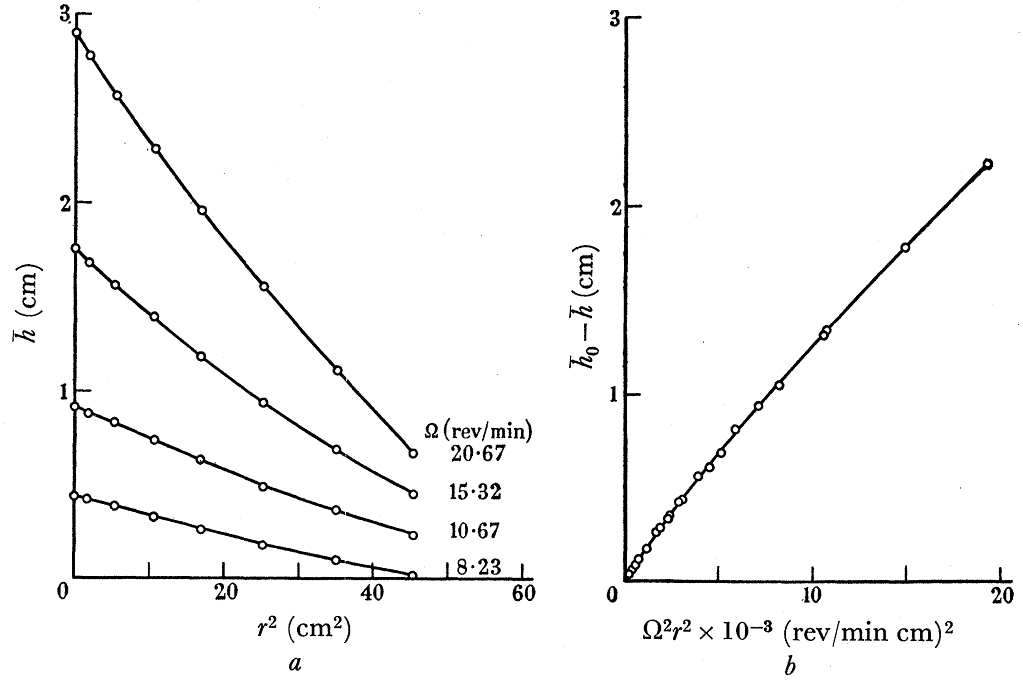

FIGURE 12. Experimental results for 34·8 % B15 poly*iso*butylene solution. (*a*) $\bar{h}$ against r^2 curves for various values of Ω and $l = 1{\cdot}85$ mm. (*b*) Relation between $(\bar{h}_0-\bar{h})$ and Ω^2r^2 obtained from (*a*).

being displaced by 0·2 cm parallel to the ordinate. From these values of $\bar{h}$, $(\bar{h}_0-\bar{h})$ is plotted against Ω^2r^2 in figure 12*b*. It is again seen that the experimental points lie on a single curve in accordance with the prediction of equation (9·4).

11. Determination of the normal stress coefficient

From the experimentally determined dependence of $(\bar{h}-\bar{h}_0)$ on $\Omega r/l$, we can, in principle, determine how the normal stress coefficient Ψ depends on $\Omega r/l$ or on K. Introducing (9·5) into (9·4) and differentiating with respect to K we obtain

$$\rho g\frac{\mathrm{d}(\bar{h}_0-\bar{h})}{\mathrm{d}K}=3\Psi+2K\frac{\mathrm{d}\Psi}{\mathrm{d}K}, \tag{11·1}$$

which yields

$$\Psi=\tfrac{1}{2}\rho g\left\{K^{-1}(\bar{h}_0-\bar{h})-\tfrac{1}{2}K^{-\frac{3}{2}}\int_0^K K^{-\frac{1}{2}}(\bar{h}_0-\bar{h})\,\mathrm{d}K\right\}. \tag{11·2}$$

Figures 8 and 10 show that, for the 6 % solution of B 120 poly*iso*butylene in tetralin, the relation between $\bar{h}$ and r is linear over most of the range of values of r, for each value of Ω and l employed, the slope of the linear relation increasing with increase of Ω and with decrease of l. This is reflected in the linearity of the relations between $(\bar{h}_0-\bar{h})$ and $\Omega r/l$ shown by the curves of figures 9 and 11, over nearly the whole range of values of $\Omega r/l$.

It will be observed, however, that in the neighbourhood of $r=0$ the $\bar{h}$ against r curves are slightly concave to the r axis. This departure from linearity is seen to be proportionately greater at the lower values of Ω and the higher values of l employed and is reflected in the slight departure from linearity of the $(\bar{h}_0-\bar{h})$ against $\Omega r/l$ curves in the neighbourhoods of the origins.

Again, it will be noticed in figure 8 that the $\bar{h}$ against r curves become slightly convex to the r axis at the higher values of Ω. This departure from linearity is reflected in a corresponding departure from linearity of the curve of figure 9 at the higher values of Ωr.

Over the range of values of $\Omega r/l$ for which the relation between $(\bar{h}_0-\bar{h})$ and $\Omega r/l$ is linear, we can write

$$\bar{h}_0-\bar{h}=\alpha+\beta K^{\frac{1}{2}}, \tag{11·3}$$

where α and β are constants. Introducing this relation into (11·2), we find that

$$\Psi=\Psi' K^{-\frac{1}{2}}, \tag{11·4}$$

where

$$\Psi'=\tfrac{1}{4}\rho g\beta=15\ \text{dyne sec cm}^{-2}.$$

In order to investigate more fully the variation of Ψ with $\Omega r/l$ for small values of $\Omega r/l$, for which a departure from linearity is observed in figures 8 and 10, measurements of $\bar{h}$ were made with the 6 % B 120 poly*iso*butylene solution for values of Ω in the range 7 to 14 rev/min and a value of l of 1·138 cm. Cup no. 3 was used and the temperature of the solution was 25·0° C. The values of $\bar{h}$ obtained, after correction for centrifugal effects, are plotted against r^2 in figure 13*a*. Curves for successive values of Ω are displaced 0·05 cm parallel to the ordinate. It is seen that the curve obtained for the lowest value of Ω employed is very nearly linear, and that the curves become increasingly convex to the r^2 axis as Ω increases. From these results $(\bar{h}_0-\bar{h})$ is plotted against Ω^2r^2 in figure 13*b*. Again we see that all the points lie on a single curve, as is predicted by equation (9·4), and at the lower values of Ω^2r^2 they lie on a straight line passing through the origin. This is in accord with the expectation that, since Ψ' must be expressible as a function of K, for sufficiently low values of K it will be substantially constant. This limiting value of Ψ', Ψ'_0, at $K = 0$, is given, from figure 13*b*, as 6 dyne sec^2 cm^{-2}.

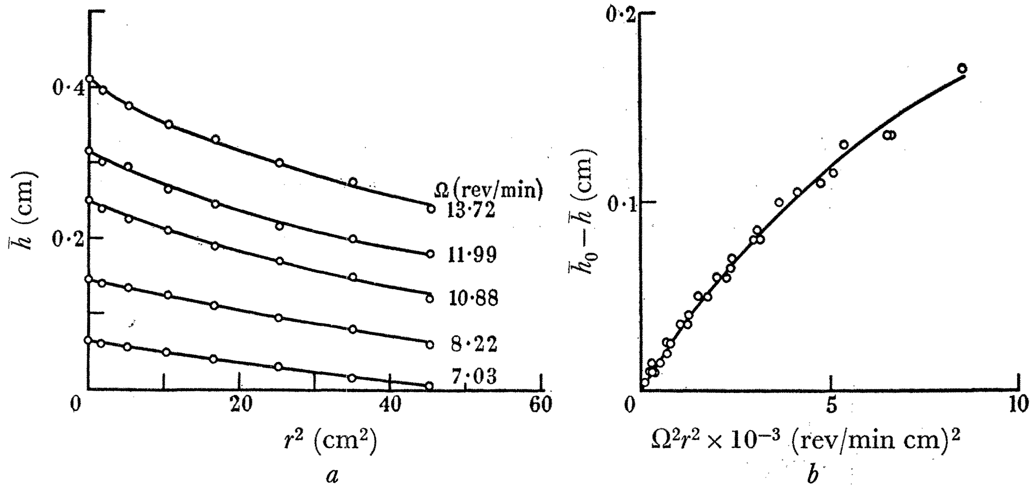

FIGURE 13. Experimental results for low velocity gradients in 6 % B120 poly*iso*butylene solution. (*a*) $\bar{h}$ against r^2 curves for various values of Ω and $l = 1{\cdot}138$ cm. (*b*) Relation between $(\bar{h}_0 - \bar{h})$ and $\Omega^2 r^2$ obtained from (*a*).

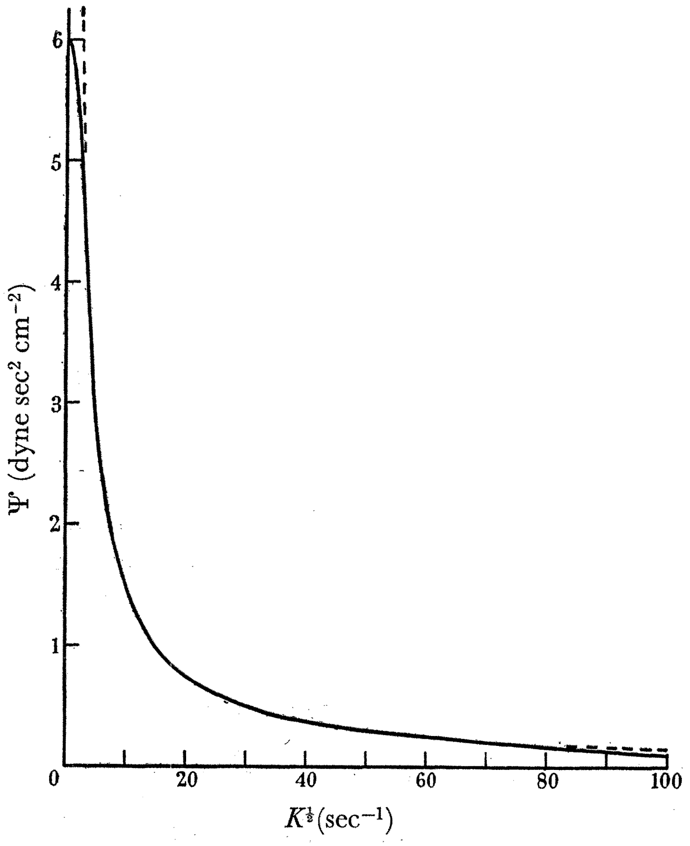

FIGURE 14. Schematic diagram of relation between Ψ' and $K^{\frac{1}{2}}$ for 6 % B120 poly*iso*butylene solution.

We note that the range of values of K covered by the results of figure 13 is about 0·3 to 17 sec^{-2}, while that covered by the results of figure 8 to 11 is about 8 to $9\times10^3\,\mathrm{sec}^{-2}$. From these results we can see qualitatively how Ψ must vary with $K^{\frac{1}{2}}$ for the 6 % B120 poly*iso*butylene solution over the whole range of values of K up to 9×10^3. This is shown in figure 14, in which the broken line represents the relation (11·4). It will be noted that the general character of the dependence of Ψ on $K^{\frac{1}{2}}$ and hence on the velocity gradient is qualitatively similar to that of the viscosity of a similar high-polymer solution.

With the 34·8 % B15 poly*iso*butylene solution, it was not possible to carry out experiments with the present apparatus at sufficiently high values of K to obtain a linear relation between Ψ and $K^{-\frac{1}{2}}$, if, indeed, there exists a range of values of K for which such a relation can be used to describe the normal stress effect for this solution.

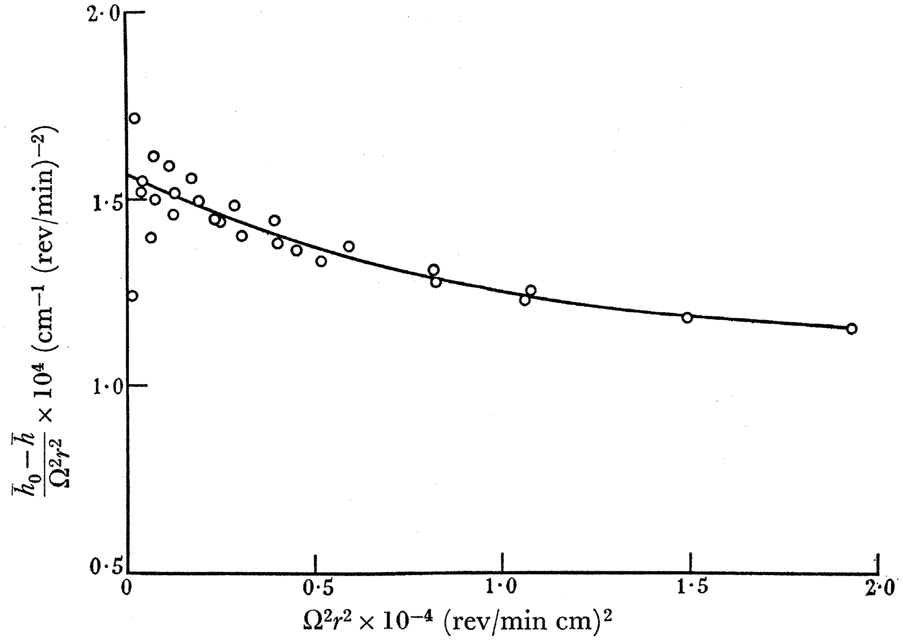

FIGURE 15. Relation between $(\bar{h}_0-\bar{h})/\Omega^2r^2$ and Ω^2r^2 for 34·8 % B15 poly*iso*butylene solution (from figure 12*b*)

However, we may express the dependence of Ψ on K by means of a polynomial in K and, for sufficiently low values of K, Ψ may be written as

$$\Psi=\Psi_0+\Psi_1K, \tag{11·5}$$

where Ψ_0 and Ψ_1 are constants. The values of Ψ_0 and Ψ_1 may be determined for the solution in the following manner. In figure 15 $(\bar{h}_0-\bar{h})/\Omega^2r^2$ is plotted against Ω^2r^2. Approximating to the curve at low values of Ω^2r^2 (i.e. at low values of K), by the tangent to it at $\Omega^2r^2=0$, we can write

$$\bar{h}_0-\bar{h}=(\alpha'-\beta'K)\,K, \tag{11·6}$$

where $\alpha'=1\cdot96\times10^{-3}\,\mathrm{cm\,sec^2}$ and $\beta'=7\times10^{-7}\,\mathrm{cm\,sec^4}$.

Introducing the relation (11·6) into equation (11·2), we obtain an expression for Ψ of the form (11·5), in which

$$\Psi_0=\tfrac{1}{3}\rho g\alpha'=0\cdot61\ \mathrm{dyne\,sec^2\,cm^{-2}}$$

and

$$\Psi_1=-\tfrac{2}{5}\rho g\beta'=-3\times10^{-4}\,\mathrm{dyne\,sec^4\,cm^{-2}}.$$

12. A FURTHER EXPERIMENT ON THE EFFECT OF NON-PARALLELISM OF THE CUP BASES

In carrying out normal stress measurements, correction was made for the effect of non-parallelism of the cup bases by measuring the h against r relations for clockwise and counter-clockwise directions of rotation of the outer cup and obtaining the mean relation, i.e. the $\bar{h}$ against r relation. Experiments have been carried out which show that, after correction for centrifugal effects, the $\bar{h}$ against r relation so obtained represents the normal stress distribution which would have been obtained with parallel cup bases separated by a distance equal to the mean separation which actually occurred in the experiments.

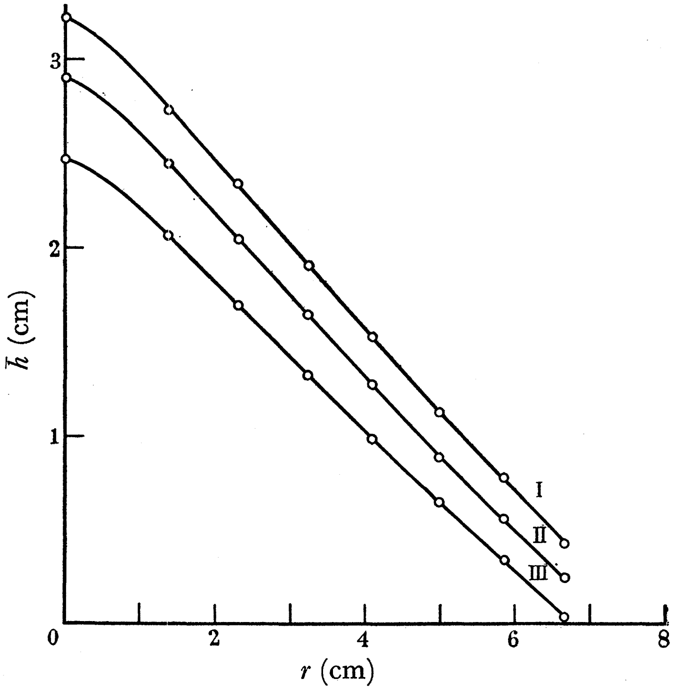

FIGURE 16. Effect of non-parallelism on $\bar{h}$ against r curves (for details see text).

For example, in figure 16 are plotted $\bar{h}$ against r relations, corrected for centrifugal effects, obtained with a 4·9 % solution of B 120 poly*iso*butylene in *o*-dichlorobenzene at 25·0° C using a speed of rotation of about 42 rev/min. Curve I represents measurements obtained with a normal degree of parallelism between the cup bases, and a mean distance between them of 1·90 mm. Curve II represents measurements obtained under similar conditions, but with a shim 0·3 mm thick introduced, at one of the pillars, under the ring supporting the inner cup. Curve III represents measurements obtained with shims 0·3 mm thick introduced under the supporting ring at all three pillars. In figure 16, curves II and I are displaced 0·2 and 0·4 cm respectively parallel to the ordinate for clarity of display. It is seen that the curves are slightly different in slope. The mean separations l between the cup bases obtaining in the experiments yielding curves I, II and III were 1·90, 2·00 and 2·20 mm respectively. Employing these values of l we can calculate the values of Ψ'' for the solution from the slopes of the linear portions of each curve, obtaining values of 12·6 dyne sec cm^{-2} in each case. It is seen that these values agree within experimental error.

13. THE ABSOLUTE VALUE OF THE NORMAL STRESS

So far, in discussing the results of normal stress measurements, we have restricted ourselves to the consideration of the dependence of $(\bar{h}_0-\bar{h})$ on Ω, l and r. It has already been remarked in §9 that on account of the complicated state of flow in the neighbourhood of the periphery of the inner cup, $\bar{h}_0$ cannot be accurately evaluated theoretically. However, in Appendix 2 (§18) an attempt is made to evaluate it approximately, by making certain simplifying assumptions regarding the state of flow in the neighbourhood of the periphery of the inner cup.

The liquid in the apparatus is considered to consist of a cylindrical mass, of radius equal to that of the outer cup and having a force-free cylindrical surface, above which is a further region in the annular space between the cylindrical walls of the cups. The flow of the liquid in this latter region is considered to approximate to steady-state laminar flow in which each point moves in a circular path about the axis of rotation with a velocity depending only on its distance from this axis. It is shown in appendix 2 that the effect of this flow in the annular region is to exert on the plane surface of the cylindrical mass, in the neighbourhood of its periphery, a downward vertical thrust $-t_{zz}$ per unit area given by equation (18·8). This should result in a displacement of the $\bar{h}$ against r curves parallel to the $\bar{h}$ axis of an amount $-t_{zz}/\rho g$.

It is unfortunately not possible to calculate the term C' in equation (18·8) theoretically on account of a lack of detailed knowledge of the flow conditions prevailing at the free surface of the mass of liquid in the annular gap.

It is seen in Appendix 2, however, that, neglecting centrifugal effects, C' is equal to the radial surface traction on the curved surfaces of the annular mass of liquid. It was therefore determined by measuring this radial surface traction on the inner curved surface. This was done by arranging a manometer tube communicating with the annular mass of liquid through a small hole in the cylindrical surface of the inner cup. The value of C' was then given by the change in height of the liquid in the manometer tube resulting from rotation of the outer cup. It was found that, under the experimental conditions given below, only small changes of height were measured, which were precisely accounted for by centrifugal effects. It is worth noting that this result is in accord with observations made by Russell (1946) and Garner *et al.* (1950) (see §1). It was therefore concluded that $C'=0$.

Measurements were made of the $\bar{h}$ against r distribution over the base of the inner cup, i.e. over a plane end of the mass of liquid which is considered to be in a state of torsional flow, for two radii a_2 (= 9·68 and 8·73 cm) of the outer cup, using a 4·9 % solution of B120 poly*iso*butylene in *o*-dichlorobenzene at 25·0° C. In each case the $\bar{h}$ against r distributions were measured for values of $\Omega = 40$ rev/min approximately and $l = 2{\cdot}9$, 4·4 and 10·8 mm. The reduction of the effective internal radius of the outer cup was achieved by introducing into it a hollow aluminium cylinder of outer diameter equal to the inner diameter of the outer cup and wall thickness 0·955 cm.

Each of the $\bar{h}$ against r curves obtained was linear over its whole extent, except for a slight departure in the neighbourhood of $r=0$. It is therefore permissible, since the velocity gradients obtaining in the annular region were in the range of those covered by the linear regions of the $\bar{h}$ against r curves, to treat the liquid as though Ψ were given by a formula of the form $\Psi = \Psi'' K^{-\frac{1}{2}}$. Ψ'' was evaluated for the liquid from the $\bar{h}$ against r curves in the manner described in §11, and from this value $-t_{zz}/\rho g$ was found from equation (18·8) for each value of l and a_2 employed, taking $C' = 0$. These values are compared in table 2 with the values of $\Delta\bar{h}$ by which the measured $\bar{h}$ against r curves are displaced parallel to the $\bar{h}$ axis from the positions in which they intersect the r axis at $r = \frac{1}{2}a_2$, and which they would have been expected to occupy had the cylindrical surface at $r = a_2$ been force-free (see §18).

It is seen that although the agreement between the values of $-t_{zz}/\rho g$ and $\Delta\bar{h}$ is not very good, the order of magnitude of $\Delta\bar{h}$ is predicted by the calculation and, in view of the approximate nature of the latter, this is all that can be expected.

TABLE 2

l cm	0·29	0·29	0·44	0·44	1·08	1·08
a_2 cm	9·68	8·73	9·68	8·73	9·68	8·73
$-t_{zz}/\rho g$ cm (from (18·8))	0·20	0·52	0·20	0·52	0·20	0·52
$\Delta\bar{h}$ cm (experimental)	0·62	0·74	0·42	0·55	0·19	0·32

14. THE DEPENDENCE OF THE NORMAL STRESS COEFFICIENT ON SOLUTION CONCENTRATION

In this section, experiments are described in which the dependence of the normal stress coefficient on solution concentration was investigated for solutions in tetralin of B120 poly*iso*butylene and of B15 poly*iso*butylene. In both cases, measurements of $\bar{h}$ were made over the base of the inner cup (no. 3) at a temperature of 25·0° C with suitable speeds of rotation Ω and distances between the cup bases l. In the case of the B120 poly*iso*butylene solutions, concentrations of 3 to 10 % were used and, in the case of the B15 poly*iso*butylene solutions, concentrations of 25 to 40 % were used. In each case the solutions of various concentrations were prepared by dilution of a stock solution of higher concentration, which was itself prepared in the manner described in §5. Thus, any error arising in the concentration of the stock solution due to the filtration will be reflected in proportional errors in all the solutions of the series, and should therefore not introduce any error in the law of dependence of the normal stress coefficient on concentration.

(a) *B*120 *Poly*iso*butylene*

It was seen in §11 that for a 6 % solution of B120 poly*iso*butylene in tetralin at 25·0° C, the normal stress coefficient is substantially constant at sufficiently low values of K and decreases as K increases, becoming proportional to $K^{-\frac{1}{2}}$ over a substantial range of values of K. Over this latter range, Ψ may be expressed by the relation $\Psi = \Psi'' K^{-\frac{1}{2}}$, in which Ψ'' is a constant. A similar type of behaviour was found to obtain with the whole range of concentrations, 3 to 10 %. Accordingly, the experiments on the B120 poly*iso*butylene solutions were carried out for values of Ω and l which enabled us to determine in each case the substantially constant value Ψ_0 of Ψ at very small values of K and the coefficient Ψ'' in the relation $\Psi = \Psi'' K^{-\frac{1}{2}}$.

The values of Ψ_0 were obtained by plotting the experimentally determined values of $(\bar{h}_0 - \bar{h})/\Omega^2 r^2$ against $\Omega^2 r^2$, in a manner similar to that adopted in figure 15, and extrapolating the curves so obtained to the $(\bar{h}_0 - \bar{h})/\Omega^2 r^2$ axis. The values of Ψ_0 were readily obtained from the intercepts on this axis.

The values of Ψ' were determined directly from the slopes of the linear $\bar{h}$ against r relations obtained at higher values of K.

The values of $\log_{10} \Psi_0$ and $\log_{10} \Psi'$ so obtained are plotted against $\log_{10} c$ in figure 17, where c is the solution concentration, measured in per cent by weight, and Ψ_0 and Ψ' are measured in dyne sec^2 cm^{-2} and dyne sec cm^{-2} respectively.

It is seen that Ψ_0 is approximately proportional to c^n, where $n \approx 8$ and Ψ' may be taken as proportional to c^n, where n varies from 3 to 5 over the range of concentrations 3 to 10 %. It must be stressed that the experimental results from which the values of Ψ_0 for the solutions are calculated are subject to considerable inaccuracy as a result of the low values of the normal stresses which have to be measured.

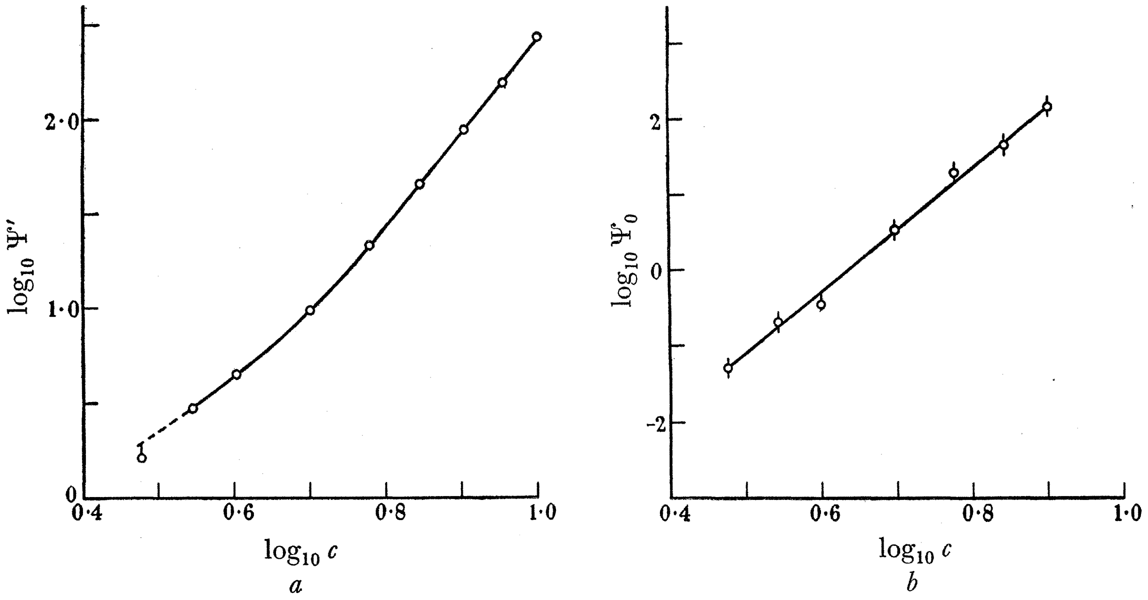

FIGURE 17. Dependence of Ψ' and Ψ_0 on concentration c for B120 poly*iso*butylene solutions. In (*b*), bars represent estimated experimental error.

Measurements of the viscosity were also made on similar solutions at 25·0° C. For each concentration studied it was found that the inverse of the viscosity varied linearly with shearing stress over the range of stresses used, in accordance with the results obtained by Ferry (1942) and by Bestul & Belcher (1950) with solutions of other high polymers. The value of the viscosity for zero shearing stress was determined by extrapolation in each case and was found to vary with concentration in the same manner as Ψ'. This is in accord with the unpublished results of De Witt, as quoted by Mooney (1951).

It was noted in §11 for the 6 % solution of B120 poly*iso*butylene in tetralin that, at the highest values of K employed, there were indications of a departure of the Ψ against $K^{-\frac{1}{2}}$ relation from linearity. In the experiments discussed in this section, it was observed that this departure from linearity occurred at lower values of K as the concentration of the solution increased.

It was further found that the value of K at which the departure from linearity in the Ψ against $K^{-\frac{1}{2}}$ relation, occurring at low values of K, became evident was decreased by increasing the concentration.

(*b*) *B*15 *Poly*iso*butylene*

For the B15 poly*iso*butylene solutions, Ψ_0 and Ψ_1 were determined in the manner described in §11 in connexion with the 34·8 % B15 poly*iso*butylene solution. The values of $\log_{10}\Psi_0$ and $\log_{10}\Psi_1$ thus obtained are plotted against $\log_{10}c$ in figure 18. Again c is the concentration in per cent by weight and Ψ_0 and Ψ_1 are measured in dyne $\mathrm{sec}^2\,\mathrm{cm}^{-2}$ and dyne $\mathrm{sec}^4\,\mathrm{cm}^{-2}$ respectively. It is seen that, except at the lowest values of c employed, Ψ_0 is proportional to c^n, where $n \approx 11$, and Ψ_1 is proportional to c^n, where $n \approx 21$.

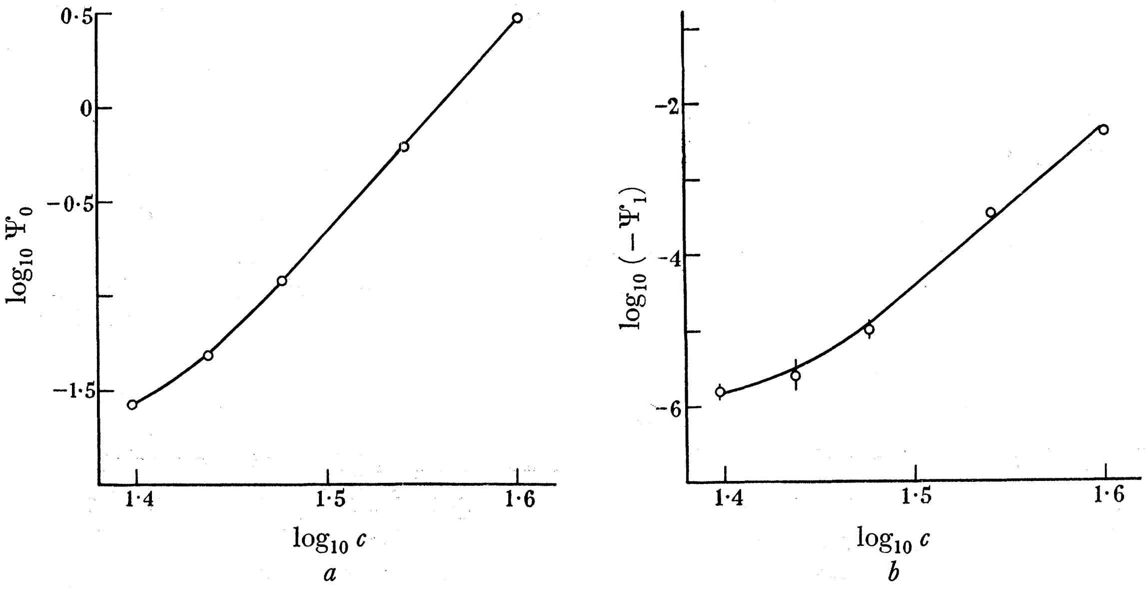

FIGURE 18. Dependence of Ψ_0 and Ψ_1 on concentration c for B15 poly*iso*butylene solutions. In (*b*), bars represent estimated experimental error.

15. THE DEPENDENCE OF THE NORMAL STRESS COEFFICIENT ON TEMPERATURE

In order to obtain some indication of the manner in which the normal stress coefficient depends on temperature, determinations were made of Ψ' and Ψ_0 for a 6 % solution of B120 poly*iso*butylene in tetralin over a temperature range from 20·8 to 45·5° C. The values obtained are plotted against temperature in figure 19. The bars indicate the estimated uncertainty in the values of Ψ_0. It is seen that both Ψ' and Ψ_0 decrease with increase of temperature in about the same proportions.

Furthermore, determinations were made of Ψ_0 and Ψ_1 for a 30 % solution of B15 poly*iso*butylene in tetralin over a temperature range from 17·5 to 30·1° C. The values of Ψ_0 obtained are plotted against temperature in figure 20. Again, the bars indicate the estimated uncertainty in the values of Ψ_0. The values of Ψ_1 were too inaccurately determined to merit their being plotted in this manner. However, it appeared that Ψ_1 fell from a value of about 3×10^{-5} dyne $\mathrm{sec}^4\,\mathrm{cm}^{-2}$ at 17·5° C to about $1{\cdot}5\times10^{-5}$ dyne $\mathrm{sec}^4\,\mathrm{cm}^{-2}$ at 30·1° C.

It appears from these results that the dependence of Ψ_0 on temperature is similar for the two solutions used, in spite of the great difference in the molecular weights of the poly*iso*butylene.

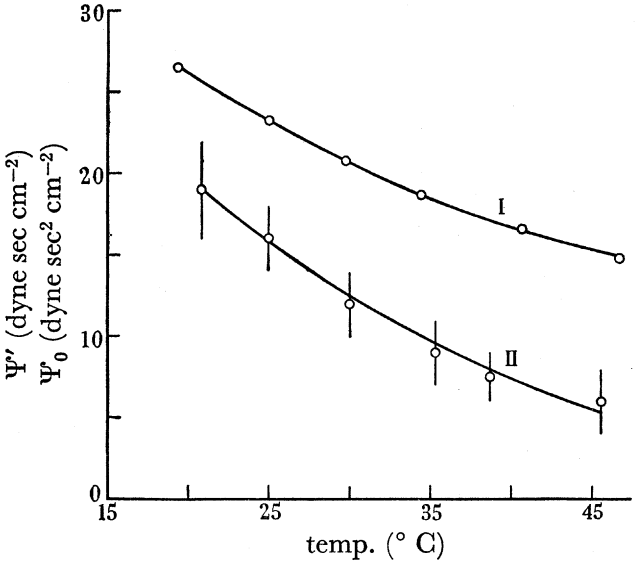

FIGURE 19. Dependence of Ψ'' (curve I) and Ψ'_0 (curve II) on temperature for B120 poly*iso*butylene solution.

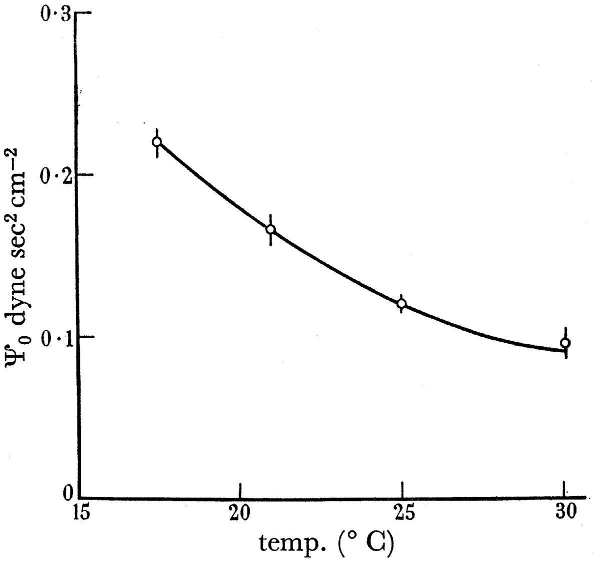

FIGURE 20. Dependence of Ψ'_0 on temperature for B15 poly*iso*butylene solution.

16. DISCUSSION

It has been seen from the experimental results given in §10 that the variation of the normal surface traction over the base of the inner cup and its dependence on the speed of rotation of the outer cup and distance between the cup bases is in accord with the predictions of the phenomenological theory advanced by Rivlin (1948*a*). The absolute values of the normal stresses developed cannot be calculated exactly on the basis of this theory owing to our lack of knowledge of the conditions prevailing in the neighbourhood of the periphery of the fluid mass. However, an approximate calculation made on the basis of simplifying assumptions regarding the behaviour of the fluid in this region gives roughly the correct absolute magnitude for these normal stresses.

It may well be that another phenomenological theory than that considered will explain the observed results equally well. However, none of those so far advanced and developed in sufficient detail to make possible a comparison with experiments of the type under discussion seems adequate.

It may be of interest to compare the dependence of the normal stress coefficient on solution concentration, which has been found experimentally, with that predicted from the molecular considerations of Rivlin (1949).

In this theory, it is assumed that the dissolved high-polymer molecules in a concentrated high-polymer solution interact with each other, but that their behaviour is such that they may be replaced, for the purposes of calculation, by a smaller number of non-interacting groups of molecules, each of these groups behaving as a larger high-polymer molecule. The effective number (N' per unit volume) of these non-interacting groups of molecules may be roughly related to the viscosity of the solution. Θ and Ψ are given by the formulae

$$\Theta = \frac{\gamma c^2}{N'} \quad \text{and} \quad \Psi = \frac{4}{5}\frac{\Theta^2}{\boldsymbol{k}TN'}, \tag{16·1}$$

where γ is a constant depending on the nature of the high polymer and solvent, c is the solution concentration, T is the absolute temperature and $\boldsymbol{k}$ is Boltzmann's constant.

In deriving equations (16·1), an assumption is made, for mathematical convenience, which restricts the calculations to low-velocity gradients for which Θ and Ψ are substantially independent of velocity gradient. Therefore, the comparison of equations (16·1) with experimental results is restricted to those obtained for limitingly low velocity gradients, i.e. the viscosity Θ is taken as that at zero velocity gradient and Ψ is taken as Ψ_0.

For the B120 poly*iso*butylene solutions, $\Theta \sim c^3$ to c^5 over the concentration range covered, from which equations (16·1) predict that Ψ_0 should vary as c^n, where n varies from 7 to 13. The experimental results shown in figure 17*b* indicate that, in practice, n was about 8.

It will be appreciated that the theory under discussion involves a large number of assumptions and, in view of this, even this very rough agreement with experiment may be fortuitous.

17. Appendix 1. Analysis of the effect of centrifugal forces

Let us consider the torsional flow of a cylindrical mass of incompressible liquid, such that each point of the liquid moves in a circular path about the axis of the cylindrical mass and in a plane perpendicular to it, with a velocity V given by

$$V = \psi rz, \tag{17·1}$$

where r is the radial distance of the point from the axis of rotation, z its distance from one end of the liquid mass and ψ is a constant. We further assume that the stress components at a point of the liquid are given in terms of the strain-velocity components by equations (2·1). Then, the surface tractions and body forces necessary to maintain this state of flow can be determined. It has been shown that, if centrifugal forces are neglected, the state of flow may be maintained by azimuthal and normal surface tractions applied to the plane ends of the liquid mass only. The azimuthal surface tractions involve the viscosity Θ and the normal surface tractions involve the normal stress coefficient Ψ.

If, however, centrifugal effects are not neglected, it is necessary to apply also body forces in order to maintain the postulated state of flow. These are obtained from the equations of motion for the liquid mass, which yield in a cylindrical polar co-ordinate system (r, θ, z) the equations

$$\left.\begin{aligned} \rho R + \frac{\partial p}{\partial r} - \tfrac{1}{2}\psi^2 r \Psi &= -\rho\psi^2 rz^2 \\ \text{and} \qquad \frac{\partial p}{\partial z} &= 0, \end{aligned}\right\} \tag{17·2}$$

in which ρ is the density of the liquid and R is the body force per unit mass, acting radially outwards, which must be applied in order to maintain the assumed state of flow. These equations are compatible only if

$$R = -\psi^2 rz^2, \tag{17·3}$$

and then the surface tractions which must be applied are given by the same formulae as are obtained by the neglect of the centrifugal force $\rho\psi^2 rz^2$ in the first of equations (17·2).

With the apparatus described in §§3 to 5, it is, of course, not possible to apply the body forces R, and consequently the centrifugal forces will give rise to a circulatory motion of the liquid in the region between the cup bases. This will be in a radially inward direction on the base of the inner cup, vertically downwards near the axis of rotation and in a radially outward direction on the base of the outer cup (cf. Batchelor 1951). Since the centrifugal forces do not depend on the viscosity of the liquid used, we should expect the velocity of the circulatory motion to be reduced by an increase in viscosity.

Furthermore, if the angular velocity of the outer cup is Ω rev/min and the distance between the cup bases is l, we have $\psi = \pi\Omega/30l$, so that equation (17·3) becomes

$$R = -\frac{\pi^2 r z^2 \Omega^2}{900 l^2}. \tag{17·4}$$

At the base of the outer cup, $z = l$, so that the centrifugal force there is independent of l and, therefore, a reduction of l will decrease the velocity of the circulatory motion as a result of the increased viscous resistance of the region between the cup bases.

If we assume that the velocity gradients resulting from the induced circulatory motion are sufficiently small so that their effect on the measured surface traction is negligible, then we can calculate approximately the contribution of the centrifugal force to the measured normal surface traction in the following manner.

We replace the centrifugal force $\rho\psi^2 r z^2$, at the radial distance r from the axis of rotation, by a uniform centrifugal force equal to its mean value $(\frac{1}{3}\rho\psi^2 r l^2)$ over the range of values of z from 0 to l, i.e. over the height of the cylindrical mass of liquid. The equations of motion then become

$$\left.\begin{aligned} &\frac{\partial p}{\partial r} - \tfrac{1}{2}\psi^2 r \Psi = -\tfrac{1}{3}\rho\psi^2 r l^2 \\ \text{and} \qquad &\frac{\partial p}{\partial z} = 0. \end{aligned}\right\} \tag{17·5}$$

From these equations, we obtain

$$p = \tfrac{1}{2}\psi^2 \int r\Psi \,\mathrm{d}r - \tfrac{1}{6}\rho\psi^2 r^2 l^2. \tag{17·6}$$

The surface tractions may now be calculated in a manner similar to that adopted (Rivlin 1948*a*) in arriving at equation (2·7). Assuming that the surface traction acting on the curved surface $r = a$ of the cylindrical mass of liquid is zero, we obtain, for the normal surface traction Z' exerted on the plane ends,

$$Z' = \tfrac{1}{2}\psi^2 r^2 \Psi + \tfrac{1}{2}\psi^2 \int_a^r r\Psi \,\mathrm{d}r - \tfrac{1}{6}\rho\psi^2 l^2 (r^2 - a^2). \tag{17·7}$$

For a liquid which does not exhibit the normal stress effect $\Psi = 0$, so that

$$Z' = -\tfrac{1}{6}\rho\psi^2 l^2 (r^2 - a^2). \tag{17·8}$$

In practice, with the apparatus employed in the experiments described in this paper, the surface traction on the cylindrical boundary of the liquid mass cannot be given a specific value, so that Z' should depart from the expressions (17·7) or (17·8) to the extent of an added constant.

18. APPENDIX 2. APPROXIMATE CALCULATION OF EDGE EFFECTS

If Ψ varies with $K(=-K_2)$ in accordance with the relation

$$\Psi = \Psi' K^{-\frac{1}{2}}, \tag{18·1}$$

in which Ψ' is a constant, then for a cylindrical mass of liquid of radius a, with a force-free curved surface, in a state of torsional flow, the normal stress Z' over the plane ends is given, from equations (2·7) and (2·8), by

$$Z' = \Psi' \psi (2r-a). \tag{18·2}$$

We see that $Z'=0$ when $r=\frac{1}{2}a$, a conclusion which is in disagreement with the experimental results for the solutions, for which the form of Ψ given by (18·1) has been found to apply. For example, for a 6% solution of B120 poly*iso*butylene in tetralin, at 25·0° C, it is seen from figures 8 and 10 that $Z'=0$ at approximately $r=0{\cdot}85a_1$, if a is taken as the external radius a_1 of the inner cup, and when $r=0{\cdot}71a_2$, if it is taken as the internal radius a_2 of the outer cup. This disagreement is quite comprehensible in view of the fact that under the experimental conditions the cylindrical mass of liquid does not have a force-free curved surface (see §9).

It was seen in §9 that this would result in a displacement of the $\bar{h}$ against r curves parallel to the $\bar{h}$ axis. An estimate may be made of the expected amount of this displacement from the following considerations.

We consider the liquid in the apparatus to consist of a cylindrical mass of length l and radius a_2 in torsional flow and an annular mass above it in the region between the cylindrical walls of the two cups.

We idealize the state of flow in the annular region between the cylindrical walls of the two cups as a uniform steady state of laminar flow in which each point of the liquid moves in a circular path about the axis of rotation of the outer cup with a velocity dependent only on its distance from this axis. Then, it can be shown (Rivlin 1948*a*) that the stress components t_{rr} and t_{zz} in a cylindrical polar co-ordinate system coaxial with the rotation are given by

$$\left.\begin{aligned} t_{rr} &= -\int \rho r \omega^2 \,\mathrm{d}r + C' \\ \text{and} \qquad t_{zz} &= -\int \rho r \omega^2 \,\mathrm{d}r - \tfrac{1}{2}\Psi r^2 \left(\frac{\partial \omega}{\partial r}\right)^2 + C', \end{aligned}\right\} \tag{18·3}$$

where ω is the angular velocity of a point of the liquid at a radial distance r from the axis of rotation and C' is a constant determined by the boundary conditions at the horizontal free surface of the annular mass of liquid. The terms $-\int \rho r \omega^2 \,\mathrm{d}r$ represent the contributions of the centrifugal forces to these two stress components. Ψ is, in general, a function of K_2 which is given by

$$K_2 = -\tfrac{1}{4} r^2 \left(\frac{\partial \omega}{\partial r}\right)^2. \tag{18·4}$$

Assuming for simplicity that the viscosity of the liquid is independent of velocity gradient, as we may do without significant error, in view of the small variation of velocity gradient in this region, we can obtain

$$\omega = \tfrac{1}{2} C \frac{r^2 - a_1^2}{a_1^2 r^2}, \tag{18·5}$$

where

$$C = \frac{\pi \Omega}{15} \frac{a_1^2 a_2^2}{a_2^2 - a_1^2}. \tag{18·6}$$

If Ψ is given in terms of K_2 by (18·1), then, neglecting the centrifugal force, we obtain from (18·3) and (18·5)

$$t_{zz} = -\Psi' C r^{-2} + C'. \tag{18·7}$$

Since $a_1 \approx a_2$ we can write approximately

$$t_{zz} = -\Psi' \frac{\pi\Omega}{30} \frac{a_1}{a_2 - a_1} + C'. \tag{18·8}$$

It is seen from equations (18·3) that, neglecting centrifugal effects, C' is the radial surface traction on the cylindrical walls of the cups.

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REFERENCES

Batchelor, G. K. 1951 *Quart. J. Mech.* **4**, 29.
Bestul, A. B. & Belcher, H. V. 1950 *J. Colloid Sci.* **5**, 303.
Burgers, J. M. 1948 *Proc. Acad. Sci. Amst.* **51**, 787.
Ferry, J. D. 1942 *J. Amer. Chem. Soc.* **64**, 1330.
Garner, F. H. & Nissan, A. H. 1946 *Nature, Lond.*, **158**, 634.
Garner, F. H., Nissan, A. H. & Wood, G. F. 1947 *J. Inst. Petrol.* **33**, 71.
Garner, F. H., Nissan, A. H. & Wood, G. F. 1950 *Phil. Trans.* A, **243**, 37.
Greensmith, H. W. & Rivlin, R. S. 1951 *Nature, Lond.*, **168**, 664.
Mooney, M. 1951 *J. Colloid Sci.* **6**, 96.
Oldroyd, J. G. 1950 *Proc. Roy. Soc.* A, **200**, 523.
Reiner, M. 1948 *Amer. J. Math.* **70**, 433.
Reynolds, O. 1886 *Phil. Trans.* A, **177**, 157.
Rivlin, R. S. 1948*a* *Proc. Roy. Soc.* A, **193**, 260 (part I).
Rivlin, R. S. 1948*b* *Nature, Lond.*, **161**, 567.
Rivlin, R. S. 1949 *Trans. Faraday Soc.* **45**, 739.
Russell, R. J. 1946 Ph.D. Thesis, London University.
Weissenberg, K. 1946 *Conf. British Rheologists' Club, London.*
Weissenberg, K. 1947 *Nature, Lond.*, **159**, 310.
Weissenberg, K. 1948 *Proc. Int. Rheological Congr., Holland*, **1**, 29.