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A comparison of the rheology of two polymeric and two micellar systems. Part II: Second normal stress difference

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With 8 figures and 2 tables

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Notation

$\dot{\gamma}$	shear rate
$\dot{\gamma}_R$	shear rate at edge of gap
σ_1	first normal stress difference
σ_2	second normal stress difference
σ_2^*	point value of σ_2
ρ	density
Ω	rotational speed
ψ_0	cone angle
C	centre gap between platens
d	edge separation
f	thrust per unit area of platens
f_1	thrust per unit area of platens due to σ_1
g	acceleration due to gravity
P_{22}	2-2 component of stress tensor
P'_{22}	P_{22} corrected for hole pressure
p_H	hole pressure
R	radius of platen
r_0	radius at which $P_{22} = 0$
h	rise height of fluid in manometer platen
$p(r)$	pressure on plate at distant r from axis of rotation
	$\bar{p} - p_a$
p_a	atmospheric pressure

1. Introduction

This work is a continuation of our previous paper where we compared the rheology of two polymeric and two micellar solutions (1). Here, we present measurements of the second normal stress difference, σ_2, for the same four systems.

Much published work has been based on the assumption that σ_2 can be neglected, (the *Weissenberg* hypothesis (2)) e.g. the quasi-molecular models used in part 1 do not take account of σ_2. Recently there has been a renewed interest in σ_2 not only for establishing a complete characterisation of elastic liquids but also to explain the striking differences in hydrodynamic stability between visco-elastic and *Newton*ian fluids. *McIntire & Schowalter* (3) analysed the stability of plane couette flow with a superimposed temperature gradient and showed that relative stabilisation or destabilisation (with respect to the *Newton*ian case) depended on the sign of σ_2. Similar effects have also been reported by *Denn &* co-workers (4) and *Hayes & Hutton* (5). A related phenomenon is the development of secondary flows driven by elasticity.

Various values of σ_2 have been derived from theoretical models of the behaviour of elastic liquids. The

Table 1. Theoretical values for σ_2.
Number of stars indicates ratio of σ_2/σ_1, **** ≡ ~1, arrows indicate behaviour with increasing shear rate

Author	Reference	Negative	Zero	Positive
Weissenberg	2		*	
Bird	6	**	* ←	**
Bogue	7	****	* ←	****
Williams	8	**	*	**
Ikeda	10		*	
Mooney	11		*	
Hayashi	12		*	
Lodge	13		*	
Walters	14	****	*	
Roscoe	15	**		
Walters/Waters	16	**		
Kaloni & de Silva	17	**		
Schowalter	18	**		
Allen, Kline et al.	19	***		

Table 2. Experimental values of σ_2

Author	Reference	Method	Negative	Zero	Positive	"Holes"
Denn and *Roisman*	4	5	**			
Hayes and *Hutton*	5	5	**			0
Kaye, *Lodge* and *Vale*	9	2	*			
Roberts	20	1		*		
Kotaka et al.	21	1		*		
Sakamoto and *Porter*	22	2		*		
Blyler	23	2		*		
Pollett	24	1		*		
West	25	2	**	*	***	
Hayes and *Tanner*	26	3			**	0
Huppler	27	3			**	0
Markowitz	28	1			***	0
Tanner	29	3			**	0
Han and *Charles*	30	4			***	0
Batchelor and *Berry*	31	2	**			
Marsh and *Pearson*	32	2	**			
Hayes and *Hutton*	33	6	***			
Ginn and *Metzner*	34	2	**			
Christiansen and *Miller*	35	1	**			
Jackson and *Kaye*	36	2	**			
Tanner	37	7	**			
Pritchard	40	1	**			0

1 – force distribution in cp, pp
2 – total thrust in cp, pp
3 – annular flow
4 – exit flow
5 – instabilities
6 – curved pipe
7 – channel flow
0 – holes used (see text)

most important findings are shown in table 1. As will be seen where the predicted value of σ_2 is nonzero, most theories predict σ_2 to be negative and small compared with σ_1. Some theories that predict σ_2 positive show that it goes negative with increasing shear rate (6–8).

Taken together, the theories considered for various mathematical and physical models of rheological systems seem to indicate a prediction of a negative σ_2 which is small compared with σ_1.

The experimental studies of σ_2 are summarised in table 2. It is evident that the picture is not as clear as the theoretical studies of σ_2. However, of the various methods used which yield σ_2 positive, nearly all have used holes as pressure tappings to measure the pressure distribution in various geometries. This has been shown to lead to gross errors in measurement due to a "hole pressure" generated in elastic liquids (9). Other methods, which involve for instance the measurement of total thrust in various geometries, or the onset of instabilities in couette flow or flow in curved pipes etc., do not suffer from this disadvantage and nearly all give σ_2 negative and small compared with σ_1.

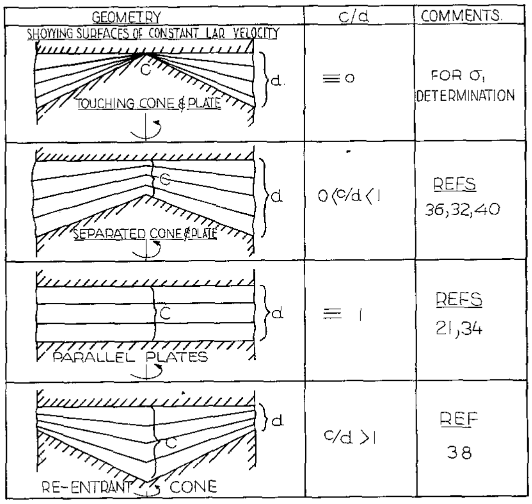


Fig. 1. Various geometries used in determining normal forces from total thrust measurements

2. Theory

Total thrust measurements in separated cone and plate geometries can be used to calculate the second normal stress differences (see fig. 1 for these geometries). Many workers have used this technique with various calculation procedures, all of which can be shown to be approximations to the general formula derived by *Marsh* and *Pearson* (32) (eq. (1)).

$$\sigma_2(\dot\gamma_R) = \frac{C + R\tan\psi_0}{C}\left\{\sigma_1(\dot\gamma_R) - f\left(2 - \frac{\partial \ln f}{\partial \ln C}\right)\right\}\Bigg|_{\Omega} \quad [1]$$

a) Cone and plate

Marsh and *Pearson* (32) ($\psi_0 > 0$), and *Cowsley* (38) ($\psi_0 < 0$), used expression [1] as it stands. *Cowsley* saw that for a re-entrant cone $(C + R \tan\psi_0)/C$ is smaller than for an ordinary cone. This means that the term $\sigma_1(\dot\gamma_R) - f\left(2 - \frac{\partial \ln f}{\partial \ln C}\right)$ must be larger and hence for the same $\dot\gamma_R$ the increase must be due to $f(2 - \partial \ln f/\partial \ln C)$. This gives larger differences between measured variables and hence accuracy should be increased.

Jackson and *Kaye* (36) considered variations of thrust as $C \to 0$ in which case [1] is not directly applicable. They assume that as $C \to 0$, the shear rate throughout the gap is constant and equal to the shear rate at the outer edge and that then $\psi_0 \equiv \psi_0$. By considering these approximations it can be shown that [1] transforms to their result. If [1] is rewritten in the form

$$\sigma_2(\dot\gamma_R) = \frac{R\psi_0}{\Delta C}(\sigma_1(\dot\gamma_R) - 2f) + R\psi_0\frac{\partial f}{\partial c} \quad [1a]$$

where C is very small, the increase in shear-rate at the edge by altering the gap by a small amount ΔC from $C = 0$ is

$$\partial\dot\gamma_R = -\frac{\dot\gamma_R \Delta C}{R\psi_0} \quad [2]$$

where $R\psi_0 \gg \Delta C$. As ΔC becomes smaller the shear-rate tends to become constant throughout the gap so that the change in thrust $(\sigma_1(\dot\gamma_R) - 2f)$ must be due to the change in σ_1, i.e.

$$\partial\sigma_1 = \sigma_1(\dot\gamma_R) - 2f. \quad [3]$$

Substituting [2] and [3] into [1a] we obtain the expression of *Jackson* and *Kaye*.

$$\sigma_2(\dot\gamma_R) = -\dot\gamma_R\frac{\partial\sigma_1}{\partial\dot\gamma_R} + R\psi_0\frac{\partial f}{\partial C}\bigg|_{C=0} \quad [4]$$

b) Parallel plates

This was the configuration used by *Kotaka* et al. (21), *Ginn* and *Metzner* (34). For this arrangement $\psi_0 = 0$ so that $(C + R \tan\psi_0)/C \equiv 1$ and the shear rate is given by:

$$\dot\gamma_R = \frac{R\Omega}{C}.$$

From this we obtain

$$\dot\gamma_R\frac{\partial}{\partial\dot\gamma_R} = \Omega\frac{\partial}{\partial\Omega}\bigg|_C - C\frac{\partial}{\partial c}\bigg|_\Omega,$$

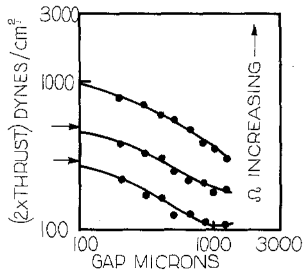
which for constant Ω reduces (1) to the form of *Kotaka* et al. (eq. (5)).

$$\sigma_2(\dot\gamma_R) = \sigma_1(\dot\gamma_R) - 2f - R\frac{\partial f}{\partial\dot\gamma_R}\bigg|_\Omega. \quad [5]$$

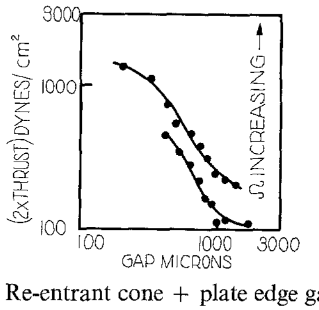
The general expressions for shear rate for all geometries can be written as

$\dot\gamma = \left(\frac{C + R\tan\psi_0}{C + r\tan\psi_0}\right)\left(\frac{r}{R}\right)\dot\gamma_R$, or in functional form, $\dot\gamma = \dot\gamma(r, \dot\gamma_R, C)$.

For the special case of the parallel plates, $\dot\gamma = \frac{r}{R}\dot\gamma_R$, i.e. $\dot\gamma = (r, \dot\gamma_R)$. This means that for parallel plates, the shear-rate profile is unaltered by changing the gap C at constant $\dot\gamma_R$. Thus, for this configuration, the thrust will be independent of how $\dot\gamma_R$ is altered, so that all the necessary information can be obtained at constant gap by varying Ω. This is therefore a convenient experimental method. Typical ex-



Separated cone + plate edge gap. Arrows denote zero gap thrust $\equiv \sigma_1$



Re-entrant cone + plate edge gap

Fig. 2. Typical log-log plots of thrust versus gap for cones with non-zero angle

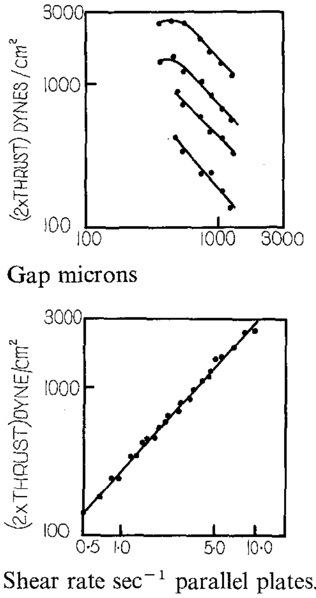


Fig. 3. Typical plots of thrust versus gap and thrust versus shear rate for parallel plates.
Because of the shear rate profile within the gap, the above curves are exactly equivalent

perimental curves for these geometries are shown in figs. 2 and 3.

Although it is possible to obtain σ_2 from any one of the three geometries, there is such a divergence of reported values that measurements using more than one geometry are preferable. In addition, σ_2 can be calculated from measurements of the radial pressure distribution from both

$$\sigma_2 = -\frac{1}{2}\left[\frac{\partial \bar{p}}{\partial \ln r} + \sigma_1\right] \qquad [6]$$

and

$$\sigma_2 = -\frac{\partial \bar{p}}{\partial \ln r}\ln\left(\frac{R}{r_0}\right). \qquad [7]$$

Eq. [6] is the same as eq. (2.10) of *Kaye* et al., and eq. [7] is obtained by applying their eq. (2.11) at $r = r_0$ where $\bar{p}(r_0) = 0$.

3. Experimental

a) Procedure

This work was carried out at the same time as the results reported in Part I (1) and the same solutions were used. Measurements were made with a *Weissenberg* R.18 Rheogoniometer. All plates used for total thrust measurements were 7.5 cm diameter and the cone angles for both ordinary and re-entrant cones were ca. 2°. Pressure profiles were measured using a 10 cm plate and reservoir cone of angle ca. 1°.

b) Results

System 1: Polyacrylamide system. Thrusts (f) were measured over the range 400–10 000 dynes/cm². A plot of the positive σ_2 versus shear-rate for the three geometries is shown in fig. 4. σ_2 has a value ca. 0.1 σ_1 over the rim shear-rate range $\dot{\gamma}_R = 8 \rightarrow 80\ \text{sec}^{-1}$.

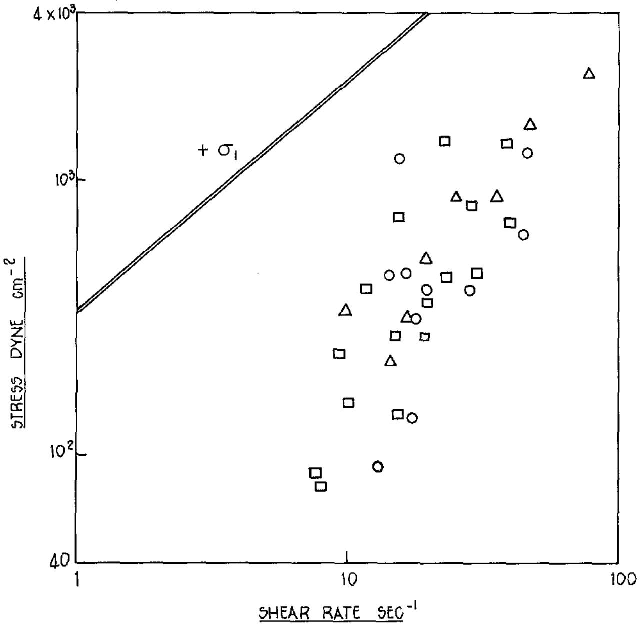


Fig. 4. System 1 – Polyacrylamide system. Normal stress differences.

σ_2 from cone and plate ○
from parallel plates □
from re-entrant cone △.

Double lines associated with σ_1 indicate confidence limits

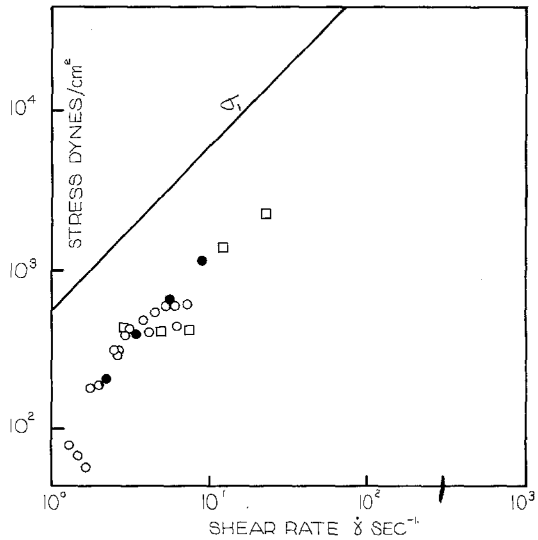


Fig. 5. System 2 – Paratac. Normal stress differences $-\sigma_2$ from cone and plate. ○ ●; from parallel plates □. For cone and plate: ○ *Marsh* and *Pearson* equation, ● *Jackson* and *Kaye* equation

System 2: Paratac. The measured thrusts were about the same as those for the polyacrylamide solution at comparative shear-rates. The range of $\dot{\gamma}_R$ was 1–400 $\sec^{-1}$. Results for cone-and-plate and parallel plate geometries are shown in fig. 5. σ_2 data for the cone-and-plate system was calculated using both the general *Marsh* and *Pearson* (32) expression and the analysis of *Jackson* and *Kaye* (36) which is based on the gradient $\partial f/\partial c|_{c\to 0}$. Unfortunately, the sample had aged before re-entrant cone measurements were taken, and σ_1 had decreased. However, the ratio σ_2/σ_1 remained the same at ca. ≈ -0.2. The data for both σ_1 and σ_2 for the aged sample are shown in fig. 6.

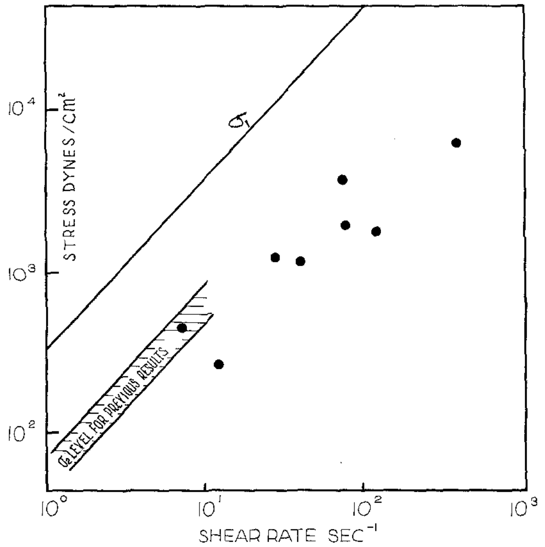


Fig. 6. System 2 – Paratac (after ageing). Normal stress differences.
– σ_2 re-entrant cone only

System 3: CTAB/TSA. Because of the skin effect noted with this system extreme care was taken in trimming the edge after each change in gap. Consistent data was obtained for the three geometries with Batch 1 over a rim shear-rate range $0.2 < \dot{\gamma}_R < 4\,\sec^{-1}$ and is shown in fig. 7. Again, some of the cone-and-plate data was analysed using the *Jackson* and *Kaye* method. Also included in fig. 7 is data from the pressure distribution calculated from eqs. [6] and [7]. The thrusts measured for this system were about one quarter of the thrusts measured for the polyacrylamide system, even so no more scatter of the σ_2 results was found. For this system $\sigma_2 \approx -0.25\,\sigma_1$. Parallel plate data for batch 2 gave a consistent σ_1/σ_2 ratio.

System 4: DMH/SDS. Again thrusts were about one quarter of those measured for the polyacrylamide system. Six sets of results were taken using the three cone angles and the two batches, five of these gave consistent results showing σ_2 changing sign at a shear-rate of about 10 $\sec^{-1}$. (The exception was the parallel plate data with Batch 1).

$$\sigma_2 \approx 0.25\,\sigma_1(\dot{\gamma}_R \sim 6) \to 0\ (\dot{\gamma}_R \sim 10) \to -0.3\,\sigma_1(\dot{\gamma}_R > 15)$$

This data is plotted in fig. 8.

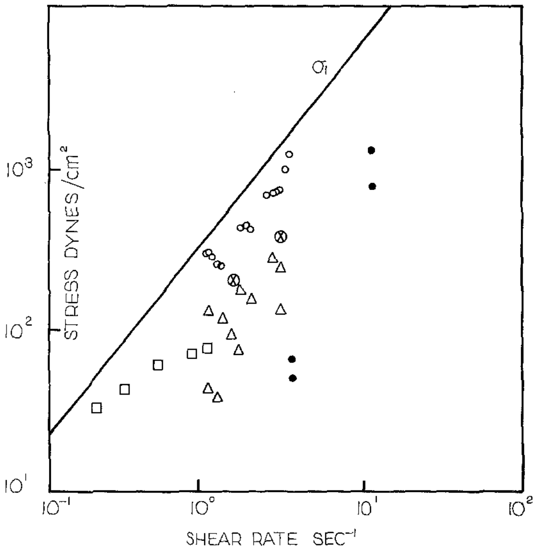


Fig. 7. System 3 – CTAB/TSA (Batch 1). Normal stress differences
– σ_2 from cone and plate ○ ● ⊕; from parallel plates □; from re-entrant cone △
For cone and plate.
○ *Marsh* and *Pearson* equation
● Pressure distribution measurements
○ *Jackson* and *Kaye* equation

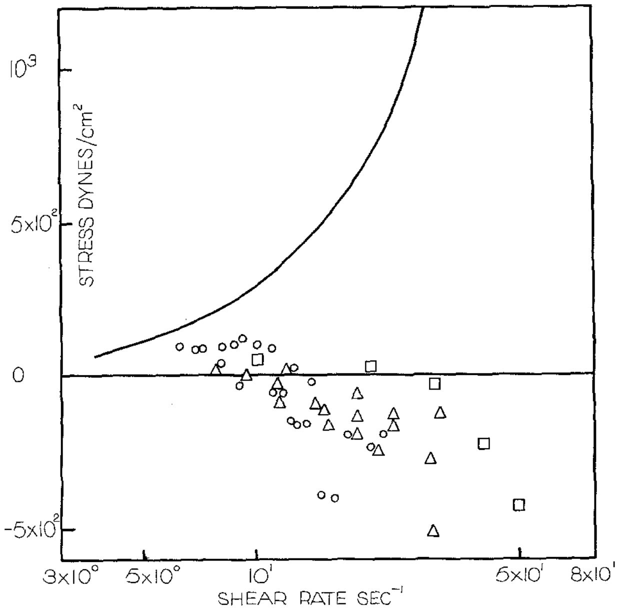


Fig. 8. System 4 – DMH/SDS (Batch 2). Normal stress differences
σ_2 from cone and plate ○; from parallel plates □; from re-entrant cone

4. Errors in σ_2 determination

There is still much controversy in the literature about the magnitude and even the sign of

σ_2 (37). It is well worth considering the sources of error in any experimental study of σ_2, particularly as the results showed quite large random scatter. For most of the work, we used methods based on total thrust measurements where σ_2 is calculated from eq. [1]. There are two main sources of error in σ_2, these being (a) caused by deviations from the flow pattern assumed in deriving (1); and (b) those due to inaccuracies in estimating the terms in the square brackets. These are discussed separately below.

a) Flow pattern, i.e. "edge effects"

In deriving (1) a viscometric flow is assumed to hold right up to the edge and a pressure equilibrium at the edge is used as a mathematical boundary condition. (See ref. (32).) In practice, two different boundary conditions are used i.e.

(i) The sample is held between the plates by surface tension. This has been discussed in detail by *Lodge* (13) and there is some doubt as to the exact boundary shape. This condition was used in the bulk of our work.

(ii) The edge is drowned in a "sea" of liquid – this is the case when a reservoir is used.

The major difference between these two conditions should arise from the surface-tension contribution to the pressure at the free surface (condition (i)). However, this should be constant for all rotation speeds. *Kaye* et al. (9) suggest that this effect can be neglected and the good agreement between σ_1 for CTAB/TSA for both boundary conditions (1) tend to confirm their conclusion.

In this series of experiments, we did not observe the large effects caused by variable surface wetting and change in contact angle reported by *Hutton* (39).

A more subtle error arises if "edge effects" disturb the flow within a region near the edge so that the flow is no longer viscometric, and the assumed equation of motion will not apply to some "corner-layer". Although the details of this "edge penetration" will be different for the two boundary conditions, the general principle will be the same. *Tanner* (37) has recently analysed the "corner-layer" in cone-and-plate geometry for a drowned edge boundary and showed that the flow is over-determined in a region extending inwards a distance of order d (d = the edge separation). He also showed that this flow must be of a different form to the main flow and as a result the thrust will be altered from its expected value by an amount dependent on the thrust due to σ_2 within this "corner-layer". We cannot apply this analysis directly to our free-surface results but the main trends in the data can be interpreted in the light of *Tanner*'s work.

If we consider the shear profile in the gap ($\dot{\gamma} = \dot{\gamma}(r)$), we would expect most pronounced effects with the re-entrant cone at small gaps where most of the thrust is due to σ_2 and is developed close to the end of the gap. We have found that at small gaps the re-entrant cone thrust data decreased as the gap was decreased (see fig. 2) which seems to indicate some edge effects. However, in the parallel-plate configuration we can alter the region over which edge effects are expected by altering the gap h but keeping the same shear-rate by compensatory adjustment of the rotational speed. In this way, we can vary any "edge effect" by an order of magnitude. From our data no systematic error can be found with variations in gap (see fig. 3) and so it would appear that the edge effects are not very important in our experiments provided we work within certain limits on gap size.

b) Errors in estimating σ_1, f and m

In the present work, we can summarise the inaccuracies as follows:

(i) σ_1

There was quite an amount of scatter in the σ_1 data for systems 1, 3 and 4 (see figs. 1, 3–5 of Part 1), particularly at low shear-rates. We averaged the data and used the mean values $\sigma_1 = \sigma_1(\dot{\gamma}_R)$ in [1] for the majority of calculations. These mean lines are shown in figs. 4–8. If a current measurement of $\sigma_1 = \sigma_1(\dot{\gamma}_R)$ which was consistently different from the spread was available we used this value in preference to the mean, e.g. for the σ_1 data for the aged sample of Paratac (fig. 6).

(ii) *f and m*

We used edge-gaps between 2 mm and 100 μ for the parallel-plate and re-entrant cone geometries and the same range as the centre-gap in the cone-and-plate configuration. Typical data are shown in figs. 2 and 3. At gaps > 1.4 mm and values < 300 μ the thrust curves flatten off but good estimates of the slope m can be obtained from data over the range 300–1200 μ.

From these considerations, we would expect to be able to obtain consistent values of σ_2 provided we restrict our measurements to the range of gaps 400–1200 μ. However, as described above, there is still scatter in point values of σ_2, denoted by σ_2^* (see figs. 4–8). This has always been found when σ_2^* is calculated from [1] (38). *Cowsley* (38) has considered this problem and suggested an analysis that seeks admissible forms for σ_1 and σ_2 which are compatible (within experimental error) with all the observed thrusts for many gaps (and several geometries). The method in essence, consist of finding polynomial forms $\sigma_1 = \sigma_1(\dot{\gamma}_R)$, $\sigma_2 = \sigma_2(\dot{\gamma}_R)$ which provide reasonable predictions for the thrust data $f = f(c, \text{geometry})$.

We have investigated this error analysis of *Cowsley* for System 3 (Batch 1) and 4 (both batches). The computer program was arranged so that three types of calculation could be performed – i.e.

a) σ_1 and σ_2 are found as polynomials from the $f = f(c, \Omega)$ data ($c \neq 0$).

b) The contribution to the thrust from $\sigma_1 (f_1)$ is found using the $\sigma_1 = \sigma_1(\dot{\gamma}_R)$ data measured separately in touching cone-and-plate experiments ($c = 0$). f_1 is then subtracted from the observed thrust f to find the contribution from $\sigma_2 (f_2 = f - f_1)$ and σ_2 is found from f_2 using the inversion procedure described by *Cowsley*.

c) Both σ_1 and σ_2 are stipulated and the thrust calculated.

In all these calculations the difference between the predicted and observed thrusts was compared with a subjective error estimate which we assumed to be $(10 + .05f)$ dynes/cm^2 (see *Cowsley* (38)).

CTAB/TSA (Batch 1) showed the largest scatter for σ_2 of all the systems. Thus, we chose to use this system to test the value of *Cowsley*'s analysis. Third order polynomials for both σ_1 and σ_2 gave the smallest RMS error but still 16% of the points exceeded the error estimate. Most of these points were for gaps near the limits discussed above, and if these were omitted a restricted set of data gave all points less than the error estimate. For all these calculations for CTAB/TSA the σ_1 values predicted from the polynomial analysis were larger than those found from touching cone-and-plate experiments. The predicted σ_2 values tended to lie below the calculated values reported above. The same general trend was observed with the DMH/SDS data. For both these systems, the re-entrant cone was only slightly more accurate than the separated cone-and-plate.

Although parallel plate data can be treated in the same general manner, all the inversion routines failed because of a nearly singular matrix. As the main point of *Cowsley*'s analysis is to locate "dubious" points it is somewhat superfluous for parallel plate data where consistency can be more easily established from the master plot of f vs. $\dot{\gamma}_R$ (see fig. 3).

The comparison with stipulated forms of σ_1 and σ_2 is not too successful as the polynomial coefficients are very dependent on the shear-rate range. However, as soon as a non-zero value of σ_2 was assumed, the predictions were improved. The last calculation, where σ_1 is fixed from $c = 0$ data, gave similar predicted stresses to those with both σ_1 and σ_2 stipulated. The ratio predicted/observed stress varied from 60–120% for CTAB/TSA, and 60–140% for DHM/SDS.

In summary, this analysis is useful in detecting "dubious" points using the error-trapping routine and the second and third calculations show that a non-zero σ_2 is essential to explain the observed thrusts $f = f(c, \Omega)$. The polynomial forms for σ_2 predict values of the same sign as those found from the calculations based on the $\ln f$ vs. $\ln c$ gradient, (see above). We could have carried this analysis further by fitting polynomials to reduced data sets (i.e. with the trapped points removed) and examined how close these predictions lay to the mean σ_2 lines shown in figs. 4–8. At present, we have restricted our attention to the use of *Cowsley*'s procedure in assessing errors from a large set of raw data.

Pressure measurements

Recently, the effect of a systematic error (p_H) in pressure measurements in elastic liquids has been described (Ref. (9)). This is of the form:

$$P'_{22} = P_{22} + p_H \qquad [8]$$

where P'_{22} is the measured value subject to this systematic error and P_{22} is the value which would exist if the holes contributed no perturbation to the stress pattern.

If it is assumed that p_H is determined solely by τ_{21} (the unperturbed value of the shear stress) and is independent of the gap between the walls, then the equation for the pressure gradient in cone-and-plate geometry is unchanged (eq. [6]). However, eq. [7] depends upon the extrapolated value of $P_{22}(R)$ so that the correction [8] must be applied. The resultant expression is:

$$\sigma_2 = -\rho g \frac{\partial h}{\partial \ln r} \ln \frac{R}{r_0} + p_H . \qquad [9]$$

Thus, we can estimate the "hole pressure" p_H from [9] using estimates of σ_2 found either from the pressure-gradient (eq. [6]) or total-thrust (eq. [1]).

We carried out pressure measurements on systems 1 and 3 at shear-rates of 11 and 35 $\sec^{-1}$ for polyacrylamide system and 3.5 and 11 $\sec^{-1}$ for CTAB/TSA. The plots of h vs. $\ln r$ were good straight lines and of the same general form as those described by *Kaye* et al. (9). From these limited results, σ_2 values which lay within the spread of values from total thrust measurements could be calculated from [9], assuming $p_H = 0$. There was some discrepancy between the data from the same experiment calculated via [1] and [9] which could be reconciled by introducing a negative p_H but this effect was smaller than that described by *Kaye* et al. and is less than the scatter of σ_2 data shown in fig. 7.

(In this context, it is worth pointing out that *Kaye* et al. estimated p_H from the discrepancy between σ_2 from [1] and [9]. They also presented σ_2 data calculated using the *Jackson* and *Kaye* method from separated cone-and-plate experiments and found that the values were higher than those from the pressure-profiles. They could not explain this discrepancy).

In general, the main trends reported by *Kaye* et al. were found in this work but we did not measure enough pressure-profile data to obtain reliable estimates of p_H. Recently, *Pritchard* (40) has presented a more detailed consideration of hole effects and the difficulties this causes in measuring σ_2 and concludes that σ_2 is opposite in sign and smaller than σ_1.

5. Conclusions

The measurement of σ_2 from total thrust is by no means an easy technique and is very dependent on sources of errors as discussed in the text. However, from our results from several geometries it was possible to establish the following values:

System	Polyacrylamide	Paratac	CTAB/TSA	DMH/SDS		
σ_2/σ_1	+0.1	−0.2	−0.25	+0.25	0	−0.3
$\dot{\gamma}_R(\sec^{-1})$	8–80	1–40 (cp. pp) 1–400 (rc)	0.2–10	~6	10	15–50

The values for Paratac and CTAB/TSA are quite similar to reported values in the literature (see table 2). DMH/SDS changes sign as the shear-rate changes which is predicted by some theories (e.g. *Bogue* (7), *Williams* (8)).

To our knowledge, this is the first data showing such behaviour although several workers, e.g. *Miller* and *Christiansen* (41) have found the ratio $-\sigma_2/\sigma_1$ to decrease with increasing shear-rate. The polyacrylamide is the only system to give a positive value for σ_2. Although positive σ_2 have been reported before, (table 2) the bulk of acceptable σ_2 data (no hole effects) suggests σ_2 is generally negative. The absolute magnitude of σ_2 was smallest for this system and so is the most subject to errors. However, results from a subsequent study on a different batch gave this small positive value for two geometries. Recently, *Miller* and *Christiansen* (41) have presented data for a polyacrylamide in a 50:50 glycerine/water system and found $-\sigma_2/\sigma_1$ in the range 0.4 to 0.01. At this stage, we do not know if the apparent contradiction in sign of σ_2 can be explained by the differences in the composition of the glycerine/water solvent system used in the two studies.

The great advantages of the re-entrant cone claimed by *Cowsley* do not seem to be borne out by our results. The most useful aspect is that higher rim shear-rates and hence larger thrusts can be obtained before the sample is ejected from the gap. The polynomial analysis of *Cowsley* is quite useful as a formal method of screening for "dubious" experimental points. In any measurement of σ_2 from total thrust, we would recommend that at least two geometries be used. If only one geometry is used, the parallel-plate configuration is the most useful, as the consistency of the data can be checked by collapsing the $f = f(\Omega, C)$ data to one master plot of $f = f(\dot{\gamma}_N)$ as shown in fig. 2.

Summary

In this paper, several methods of measuring σ_2 have been compared for the four systems reported in Part 1 (1). These are a 1% solution of polyacrylamide in a water/glycerol mixture, a solution of polyisobutylene in oil (Paratac), 0.05 M/0.05 M solution of cetyltrimethyl ammonium bromide (CTAB) and toluene sulphonic acid (TSA), and a 16% tetradecyldimethyl ammonio propane sulphonate (DMH)/4% sodium dodecyl sulphate (SDS).

Total thrusts were measured in three geometries for all four systems and pressure profiles in a cone-and-plate configuration were measured for the polyacrylamide and CTAB/TSA solutions. The sources of errors arising from edge effects or experimental spread in the determination of thrusts at various gaps were examined comprehensively and a working range for obtaining reliable estimates of σ_2 was established. Both the Paratac and CTAB/TSA gave negative values which compared well with the generally accepted values in the literature (refs 4, 5, 9, 32–40). The polyacrylamide system gave a small positive σ_2 while for DMH/SDS, σ_2 was positive at low shear-rates, and became negative as the shear-rate increased. These latter results appear to be a true manifestation of the systems and cannot be explained by errors in the techniques.

Zusammenfassung

Es wurden in dieser Mitteilung einige Methoden für die Messung von σ_2 für die vier in Teil 1 angegebenen Systeme verglichen. Dies sind eine 1%-Lösung von Polyacrylamid in einem Wasser-Glyzerin-Gemisch, eine Lösung von Polyisobutylen in Öl (Paratac), eine 0.05 M/0.05 M-Lösung von Cetyltrimethylammoniumbromid (CTAB) resp. Toluolsulfonsäure (TSS), sowie eine 16%-Lösung von Tetradecyldimethylammoniopropansulfonat (DMH)/4% Natriumdodecylsulfat (NaDS).

Es wurden die Gesamtschubwerte in drei Geometrien für alle vier Systeme und Druckprofile in einer Konus-und-Platte-Konfiguration für die Polyacrylamid- und CTAB/TSS-Lösungen gemessen. Die Fehlerquellen, die von Randeffekten oder von versuchsbedingten Streuungen bei der Bestimmung von Schubwerten an verschiedenen Spalten stammen, wurden umfassend untersucht, sowie ein Arbeitsbereich, um verläßliche Schätzungen von σ_2 zu bekommen, festgestellt. Die Paratac- sowie auch die CTAB/TSS-Lösungen zeigten negative Werte, die in guter Übereinstimmung mit den allgemein angenommenen Literaturwerten waren (4, 5, 9, 32–40). Das Polyacrylamidsystem zeigte einen kleinen positiven σ_2-Wert, während bei DMH/NaDS σ_2 positiv wurde bei niedrigen Schubgeschwindigkeiten, er wurde negativ mit steigenden Schubgeschwindigkeiten. Diese Resultate geben anscheinend eine wahre Eigenschaft der Systeme wieder und sind durch Fehler in der Arbeitsweise zu erklären.

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