# An Attempt to Measure the First Normal-Stress Difference $N_1$ in Shear Flow for a Polyisobutylene/Decalin Solution "D2b" at Shear Rates up to $10^6\ s^{-1}$

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## Synopsis

For a polyisobutylene/decalin solution "D2b," agreement over a range of values of shear rate $\dot{\gamma}$ up to 29,000 $s^{-1}$ (where the stress ratio $N_1/\sigma = 5$; $\sigma$ = shear stress) is found between values of $N_1$ measured near 20°C using a Torsional Balance Rheometer ("TBR") and a "Stressmeter" ("SM", a slit-die rheometer using transverse slots to measure hole pressures); viscosity values also agree. Time-temperature superposition behavior exhibited by SM data taken in a temperature range 22–99°C suggest that the range of validity of the SM method for determining $N_1$ approximately extends up to $\dot{\gamma} = 1.3 \times 10^6\ s^{-1}$; here, $N_1/\sigma = 10$ and, in the SM die, the Reynolds number Re = 100. This $\dot{\gamma}$ value is four times higher than the greatest $\dot{\gamma}$ value used in previous similar tests of the SM method made with a similar but more concentrated solution "D2".

## INTRODUCTION

It is well known[1] that the state of stress for viscoelastic liquids in steady shear flow is determined by a shear stress $\sigma$ and by $N_1$ and $N_2$, the first and second normal stress differences, together with an isotropic contribution which is not of direct rheological significance. The need to measure $\sigma$ and $N_1$ at shear rates equal to or greater than $10^6\ s^{-1}$ has been increasingly recognized in recent years[2] in connection with paper coating and journal bearing lubrication,[3] for example. Recent results on commercial multigrade oils[3] suggest that $N_1$ can contribute as much as the viscosity $\eta$ contributes to the minimum oil film thickness in a front main journal bearing of a V-6 engine running at 3000 rpm; since $N_1$ is associated with conservative forces, these results favor the possibility of formulating low-friction oils if suitable stable polymeric additives can be found which increase $N_1$ enough to allow lower $\eta$ values to be used.

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Unfortunately, the measurement of $N_1$ near $10^6$ $s^{-1}$ is fraught with difficulty, especially for multigrade oils (which have rather low elasticity). Using a jet thrust method with one Newtonian oil and three polymer-thickened oils equivalent to 20W-50 motor oils, Oliver and Shahidullah[4] state that "The jet thrusts of the polymer-thickened oils are only 2–3% lower than those of the Newtonian oil, which makes accurate measurement difficult. . . ."

A more promising method is based on the measurement of the "hole pressure" $P^*$ generated by shear flow of test liquids over the mouth of a transverse slot located in one wall of a slit die.[2,5] The analysis of the data depends on the use of the so-called "HPBL equations" (5) and (6) whose derivation involves the use of a number of assumptions. Some of these are known to be invalid within the range of variables $(\dot{\gamma}, \sigma, N_1, b/h, \mathrm{Re})$ for which independent experimental tests (made with absolute instruments) have shown paradoxically that the HPBL equations are valid to a sufficient approximation to be of practical use. This paradox has yet to be resolved; recent computations[6] suggest that at least some cancellation of errors is involved. We can, however, use the method without waiting for the paradox to be resolved, provided that we make adequate experimental tests over the range of variables required. An extensive discussion of the assumptions involved in using the HPBL equations to determine $N_1$ has been given elsewhere;[5] it is, perhaps, helpful to emphasize here that one of the assumptions involved is that any changes of shape in the stream surfaces, which might occur on going from Newtonian to non-Newtonian liquids, have negligible effects on the results.

It is also assumed that $P^*$ is a sum of an elastic contribution $P_e^*$ (related to $N_1$ and $\sigma$ by the HPBL equations), a flush transducer contribution $P_f^*$, and an inertial contribution $P_N^*$. The latter two are here determined (by "Method C") from measurements made using two Newtonian liquids; the procedure is tested (over part of the Re range only) by data obtained using a third Newtonian liquid having a viscosity lying between those of the other two.

In a previous article,[7] we used samples drawn from a single batch of a polyisobutylene solution "D2" to compare data obtained near 25°C with a Torsional Balance Rheometer (TBR) and a Stressmeter (SM) over a $\dot{\gamma}$ range (up to 20,700 $s^{-1}$) available to both instruments; a time–temperature superposition assumption was then used with SM data obtained up to 111°C to extend the $\dot{\gamma}$ range to $2.9 \times 10^5$ $s^{-1}$. (Some such assumption has to be made at present in order to test the SM method, because no other instrument is available which will give reliable $N_1$ data at the high shear rates involved.)

The aim of the present report is to extend to still higher shear rates this method of testing SM measurements of $N_1$. For this purpose, we use a polyisobutylene/decalin solution D2b obtained from D2 by dilution. The SM shear stress range is restricted at the upper end to about 14 to 16 kPa; use of a less concentrated solution thus allows us to attain higher shear rates than before. We also present, for the first time, additional tests by comparing SM data obtained using two different (slot unit) + (flush transducer) combinations (unit E and unit S); because these have different characteristics, comparison of their results affords some test of the validity of the measurements. The apparatus and procedure have been described in detail elsewhere;[2,7] therefore our description will be brief.

## EXPERIMENTAL

### Materials

The only non-Newtonian liquid used in the measurements reported here is D2b: an 8.7 wt% solution in decalin of a polyisobutylene, Oppanol B50, from BASF, having a viscosity-average molecular weight of 400,000; the molecular weight distribution is not known; at 22°C, $\eta_0$, the limiting viscosity at low shear rates (near 0.2 $s^{-1}$, measured with a Weissenberg rheogoniometer) is 1.17 Pa.s. For D2 at 20°C, $\eta_0 = 2.14$ Pa.s. The intrinsic viscosities of D2 and D2b are not known. We recognize the importance of making high shear rate measurements with well-characterized polymer solutions in order to test molecular theories; we hope to do this in the future. The present work is, however, restricted to an investigation of the validity of the measurement techniques employed; for this, stability of the test liquid is important; polymer characterization is not.

Newtonian liquids, used to determine the die height and the flush transducer and slot unit characteristics, $P_f^*$ and $P_N^*$, were Cannon standard viscosity liquids S60 and S200 and a base oil S100N-LP; Table I gives viscosity data and Reynolds number ranges. Cannon standard liquid viscosity values at temperatures intermediate between those listed by the manufacturer were obtained by interpolation, using the equations

$$\log\log(\eta/\rho - 0.7) = C_0 + C_1 \log T + C_2(\log T)^2,$$

$$\rho = D_0 + D_1(T - 273) + D_2(T - 273)^2,$$

where $\eta$ denotes the viscosity in cP, $\rho$ denotes the density in g/ml, and $T$ denotes the absolute temperature. The coefficients

TABLE I
Liquids Used

| Day | Unit | Method C use | Liquid | Degrees (°C) | Viscosity cP | Maximum Re | Figure(s) |
|---|---|---|---|---|---|---|---|
| 1 | E |  | S200 | 60 | 53 | 4.4 | 5 |
| 1 | E | x | S200 | 99 | 13 | 70 | 1, 2, 5 |
| 1 | E | x | S200 | 50 | 86 | 1.6 | 1, 2, 5 |
| 4 | E |  | D2b | 79 | 12–197 | 70 | 4, 5, 7 |
| 5 | E |  | D2b | 23 | 35–452 | 7.6 | 3, 4, 5 |
| 5 | E |  | D2b | 59 | 16–199 | 37 | 4, 5, 7 |
| 6 | E |  | D2b | 99 | 9–108 | 130 | 4, 5, 7 |
| 7 | E |  | D2b | 89 | 13–70 | 56 | 4, 5 |
| 18 | S | x | S60 | 60 | 19 | 46 | 1, 2, 6 |
| 19 | S |  | S60 | 80 | 10 | 125 | 6 |
| 19 | S | x | S60 | 99 | 6.2 | 178 | 1, 2, 6 |
| 20 | S |  | D2b | 60 | 17–79 | 34 | 6, 7, 8 |
| 20 | S |  | D2b | 80 | 12–60 | 65 | 6, 7, 8 |
| 20 | S |  | D2b | 99 | 6–114 | 98 | 4, 6, 7, 8 |
| 24 | E |  | S100N-LP | 23 | 34 | 10 | 5 |

$C_i$ and $D_i$ were determined for each liquid by second-order linear regression analyses using the manufacturer's data as input. The equations are obtained from ASTM D-341 by omitting exponential terms which make negligible contributions for kinematic viscosities above 2 cS. The values of $\eta$ obtained in this way are believed to be accurate to 1% or better; this is adequate for our purposes.

## Torsional Balance Rheometer

This absolute instrument is a parallel-plate rotational rheometer[8,9] which can be operated with an unusually small gap between the plates to obtain reliable data at shear rates up to 30,000 $s^{-1}$. It is difficult to make useful measurements at much higher shear rates because of the smallness of the gaps involved; at $10^5$ $s^{-1}$, for example, the gap is about 30 $\mu$m. It appears that smaller gaps (and higher shear rates) are attainable with the floating upper plate (used in the "TBR") than with the nonfloating upper plate used in other parallel-plate rotational rheometers. Because no temperature control system is installed, measurements can be made at ambient temperatures only. Total thrust, torque, gap, and angular speed are measured, from which $\sigma$ and $N_1 - N_2$ are calculated as functions of $\dot{\gamma}$. In order to obtain the values of $N_1$ from these data, we use a value $N_2/N_1 = -0.1$, an average[7] of values obtained from other kinds of measurement on a different polyisobutylene/decalin solution D1 used in a "Round Robin" investigation[10,11] of methods of measuring $N_1$ and $N_2$: over a range 10–50 Pa in shear stress at 25°C, Tanner's "Tilted Trough" data for $N_2$ gave a range of values $-0.12$ to $-0.10$ for $N_2/N_1$; Christiansen's cone-plate flush-transducer rim pressure-data for $N_2$ gave a range $-0.09$ to $-0.08$ for $N_2/N_1$. In each case, values of $N_1$ from Christiansen's cone-plate apparatus were used. It should be emphasized that a large extrapolation in shear stress range is involved in our assumption that $N_2/N_1 = -0.1$ for our data in general and for Figure 3 in particular; however, a change in value of $-N_2/N_1$ from 0.1 to 0.05 would correspond to a change of only 5% in the value assigned to $N_1$, and this would not be noticeable in relation to the scatter of the present measurements.

## Stressmeter

This is a pressure-driven slit-die rheometer having, in one die wall, two small transverse slots connected to transducers which give pressure readings $P_2$, $P_3$ from which one calculates the wall shear stress $\sigma = h(P_2 - P_3)/(2z)$, where $h$ is the die height and $z$ is the slot separation. The flow rate $Q$ is measured from the rate of change of pressure recorded by a transducer connected to the base of an output cylinder into which the liquid discharges; as the liquid level rises, the pressure on the cylinder base and on the transducer increases; the time derivative of this pressure gives the flow rate. The wall shear rate $\dot{\gamma}$ is calculated from $Q$ and $\sigma$ by means of Eq. (8), the well-known slit-die analog[12] of the Weissenberg-Rabinowitsch equation. The other die wall contains a flush-mounted transducer which gives a pressure reading $P_1$ at a point located as closely as possible to the centerline of the $P_2$ slot (produced). A detailed description of the apparatus, including the flow path, temperature control system, and transducer system, has been given elsewhere.[2,5] The HPBL Eqs. (5) and (6) are used to calculate $N_1$ from the "hole pressure" $P^* := P_1 - P_2$ and $\sigma$.

The instrument used here was a commercially available[13] Lodge Stressmeter for High Shear Rates (Serial No. H301) supplied to Exxon Chemical Co. Nominal die dimensions in mm were: $h = 0.083$; $z = 0.5$; width $w = 5.6$; no. 2 slot width $b = 0.05$; length $L = 6$. For the first time, data were obtained on the same liquid using two different (slot unit)/(flush transducer) combinations: unit E (slot unit HSU501; transducer H103) and unit S (HSU503, H102). These units had nominally the same dimensions but different characteristics (Figs. 1 and 2). Cannon standard viscosity liquids were used to measure the die height at several temperatures.

### Determination of SM Characteristics

It is assumed[2,5] that the hole pressure can be expressed in the form

$$P^* = P_f^* + P_N^* + P_e^*, \tag{1}$$

where

$$P_f^* = \sigma(B_1 + B_2\sigma^p + \cdots + B_{M+1}\sigma^{pM}); \tag{2}$$

$$-P_N^* = \sigma(A_1 \,\mathrm{Re}^q + A_2 \,\mathrm{Re}^{2q} + \cdots + A_N \,\mathrm{Re}^{Nq}); \tag{3}$$

$$\mathrm{Re} = \rho b h \dot{\gamma}/(4\eta); \tag{4}$$

$$N_1 = 2nP_e^*; \tag{5}$$

$$n = d(\log P_e^*)/d(\log \sigma). \tag{6}$$

$A_i$, $B_i$, $p$, and $q$ are constants at a given temperature for a given slot unit and flush transducer. $P_f^*$ is a "flush transducer contribution" arising in part from slight, unavoidable misalignment of the flush transducer effective center and the $P_2$ slot centerline and in part from the migration of this center[14] with changing pressure gradient. $P_N^*$ is an inertial contribution. $P_e^*$ is the "elastic contribution" from which (it is hoped) $N_1$ may be calculated[5] by means of the transverse slot form (5), (6), of the "HPBL equations." The polynomials (2), (3) are merely convenient forms for describing the assumed functional relations between $P_f^*$ and $\sigma$, and between $P_N^*/\sigma$ and Reynolds number Re. The constants $p$, $q$ and the coefficients $A_i$ and $B_i$ can be chosen[2,5] to fit values of $P^*$ measured for two Newtonian liquids (for which $N_1 = 0$) of different viscosities; in some cases, use of values of $p$ and $q$ different from unity enables one to fit data with a regression polynomial of order lower than that required when $p = q = 1$; the scatter of the data is usually such that it appears to us to be unwise to use regressions of order higher than 3. The assumed forms (1)–(3) are not unreasonable[5] provided that the flush transducer diaphragm deflection is sufficiently small, that the common mode errors are negligible, and that Re is not too large; the full Re range is not known. The aim of the present article is to conduct tests of the validity of the system (1)–(6) in addition to those tests already conducted.[2,5,7] Values for $P_N^*$ have been computed for the flow of Newtonian liquids past symmetric slots.[15]

For completeness, we add the following well-known equations used to determine values of $\sigma$ and $\dot{\gamma}$ at the wall (unperturbed by slot effects):

$$\sigma = h(P_2 - P_3)/(2z); \tag{7}$$

$$\dot{\gamma} = 2(2 + m)Q/(wh^2); \tag{8}$$

$$m = d(\log Q)/d(\log \sigma); \tag{9}$$

$$\eta = \sigma/\dot{\gamma}. \tag{10}$$

Figures 1 and 2 show the values of $P_f^*$ and $P_N^*$ obtained for the two SM units used here. It is noteworthy (i) that the units differ significantly, notably in the flush transducer characteristics, and (ii) that unit S gives a $P_f^*(\sigma)$ (for a Newtonian liquid) which is qualitatively similar to the function $P_e^*(\sigma)$ expected for elastic liquids. The explanation for the differences found between data for units E and S in Figure 1 is not known. Figure 2 also includes a cubic spline fitted to the points obtained for a symmetric slot by numerical simulation;[15] the difference between this curve and the measured curves for units E, S may be due to slight imperfections in the slot edges, and the difference in measured values for units E, S may reflect slight differences in slot edge shapes for these slot units; the slots are so small that their edges cannot be reproduced very accurately or even with known accuracy. Discussions with numerical analysts suggest that it

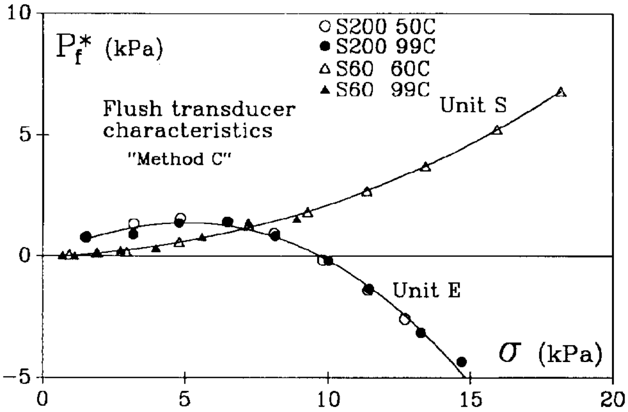

Fig. 1. Flush transducer characteristics for Stressmeter units E, S determined from values of hole pressure $P^*$ measured for Newtonian liquids (Table I) of different viscosity. $\sigma$ = wall shear stress. The smooth lines represent regression curves.

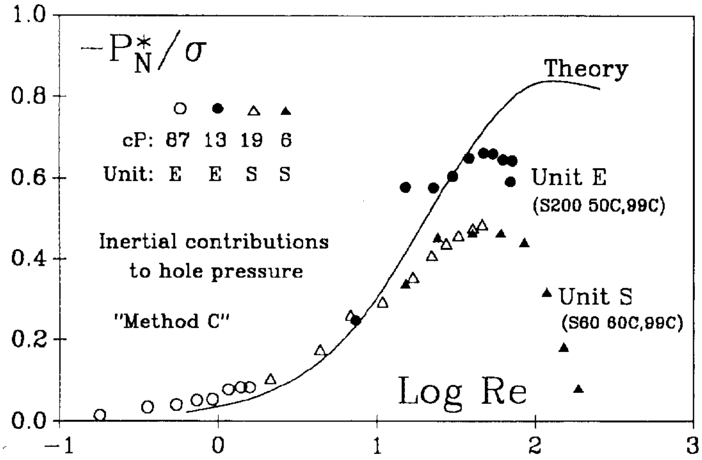

Fig. 2. Slot characteristics for Stressmeter units E, S, determined from values of hole pressure $P^*$ measured for Newtonian liquids (Table I) of different viscosity, differ from each other and from the values for a symmetric slot computed by Jackson and Finlayson (Ref. 15). Small differences in the shape of slot edges might account for the differences. $\sigma$ = wall shear stress; Re = Reynolds number.

would be feasible to extend the computations to investigate the effects of changing the slot edge shapes. However, the accuracy of measurement of $P_f^*$ and $P_N^*$ might need to be increased if one is to assess the significance of the difference between the measured and computed curves in Figure 2. We plan to make a more reliable investigation using a larger slot unit so that the slot edges can be more accurately machined. A comparison of data obtained with two different units (E and S) is here given for the first time.

## SM data: Sources of Error

The following possible sources of systematic error in SM measurements of $N_1$ and $\eta$ have been considered:

1. Wall slip
2. Turbulence
3. Failure to attain fully developed flow
4. Microbubbles, possibly induced by flow through the apparatus[2]
5. Common mode errors in the pressure-difference-measuring system

6. Nonuniform temperature, possibly caused by viscous heating
7. Inapplicability of the HPBL equations
8. Dependence of viscosity on pressure
9. Deflection of the flush transducer diaphragm and case
10. Nonparallelism of the die walls
11. Deposition of material on the die walls
12. Use of the polynomials (2), (3) outside the ranges of $\sigma$, Re used in their determination
13. Polymer degradation caused by passage through the filters and die
14. Changes in $P_f^*$ with time and temperature changes
15. Nonzero $N_1$ values in liquids used for "Method C"
16. Change of the flush transducer zero with change of temperature

Evidence that, for D2b under the ranges of variables investigated here, these errors are negligible in relation to the scatter of the data is furnished by the agreement shown in Figure 3 between SM and TBR data. Further evidence is given by the smallness of the values of $P_{er}^*$ obtained for S20 at 80°C (Fig. 6): these should be zero for this Newtonian liquid; since this liquid was used at two other temperatures (60°C, 99°C) in the determination of $P_f^*$ and $P_N^*$ for unit S by Method C, the near-zero values found for $P_e^*$ at 80°C support the validity of the procedure, and suggest, in particular, that errors 14 and 15 are unimportant in this case.

Of course, agreement between data obtained with different instruments of the kind shown in Figure 3 does not prove that the errors listed above were negligible; there may have been a fortuitous cancellation of individually significant errors over the limited range of variables common to both instruments. Further tests (e.g., with different die heights and entrance lengths) are called for. Estimates of errors, coupled with the results of some additional tests at present being made with the flush transducer replaced by a solid metal unit, suggest that errors 6, 8, 9, and 10 are in fact individually small (i.e., of the order of 1–3%). The die height and length have been chosen to make the residence time as short as possible (<1 ms at $10^6$ s$^{-1}$) to reduce errors due to viscous heating.

In regard to 4, viscosity data subsequently obtained with decalin,[2] before and after degassing, suggested that a systematic error in the measurement of $\sigma$, possibly due to microbubble agglomeration during passage through the instrument, can arise, especially when $\eta < 10$ mPa. s, $\dot{\gamma} > 5 \times 10^5$ s$^{-1}$, and $h = 25$ $\mu$m.

Liquids used in the experiments reported here were not, in fact, degassed prior to use, but the larger die heights used (about 83 $\mu$m) probably mean that microbubble errors were negligible, because more recent results (to be published elsewhere) have shown that, for a die height of 51 $\mu$m, degassing has no detectable effect on the measurement of viscosity for a 9 cP liquid (Cannon S6 at 20°C).

In regard to 12, in order to avoid errors which can arise in extrapolating regression polynomials, we now belatedly recognize that it is advisable to ensure that, when $P^*$ is measured for the two Newtonian liquids (as in Method C),[2] the $\sigma$ range for the higher $\eta$ liquid should equal or, preferably, exceed the $\sigma$ range used in the elastic liquid measurements; for the lower $\eta$ liquid, a similar requirement on the Re range should be imposed. These requirements were, in fact, met for unit S but not for unit E (Table I): there was in consequence some uncertainty in the D2b data obtained with unit E at the highest temperature and shear rates.

In regard to 5, any pressure-difference-measuring system in practice will have a nonzero "common mode response" $P_{CM}$, the output of the difference measurement arising from the application of the same pressure $P$ to each side of the pressure-difference-measuring system; ideally, the common mode ratio $P_{CM}/P$ would be zero. At the outset of the series of experiments, a special compensating technique was used to reduce the magnitude of the common mode ratios, for the $P^*$ and the $\sigma$ measuring systems, to about $10^{-4}$. Experience has since shown that it is advisable to check this compensation after each set of about two or three runs of measurements. This was not done in the experiments reported here, and so it is possible that the common mode ratio may have increased in magnitude during the course of the experiments; because $P_1$ depends on the die exit pressure (and so is not a function of $\sigma$ alone), it is likely that the common mode contribution $P^*_{CM}$ to the $P^*$ measurement is not taken care of by Method C and hence could give nonzero values for $P^*_e$ for any third Newtonian liquid having a viscosity different from the two used in Method C. This possibility is being investigated more thoroughly now than in the series of experiments reported here. The reduction of the common mode response is particularly important for the $P^*$ measurement, because the pressure difference $P^*$ is a small fraction of the local pressure $P_1$: for D2b at 99°C and $\dot{\gamma} = 1.2 \times 10^6$ s$^{-1}$, $P^*/P_1$ is about 0.02. Although the corresponding ratio for the $\sigma$ measurement is larger, common mode suppression is still important here because the slots are placed close together so that entrance and exit flow disturbances should be negligible.

## "D2b" RESULTS

### TBR and SM Data Near 20°C

The values of log $N_1$ and log $\sigma$ obtained with two instruments are plotted against log $\dot{\gamma}$ in Figure 3. The fact that SM data were obtained at 22°C and 23°C whereas TBR data were obtained at 20°C is not significant for the present purposes because the temperature coefficient of viscosity for this solution is less than 2% per degree Centrigrade. It is clear from Figure 3 that, except for the highest TBR $N_1$ data point (which is far enough off the line through the other points to suggest that some error was involved), the two instruments agree over the common range of $\dot{\gamma}$. The agreement between $\sigma(\dot{\gamma})$ values is consistent (in particular) with the view that in both instruments wall slip was absent or, if present, had negligible effect. The agreement between $N_1(\dot{\gamma})$ values supports the approximate validity (within the scatter of the data) of the HPBL equations (5), (6), together with the Eqs. (1)–(3) used to determine $P_f^*$ and $P_N^*$. It should, perhaps, be emphasized that Re < 8 (in the Stressmeter die) for the data of Figure 3; it

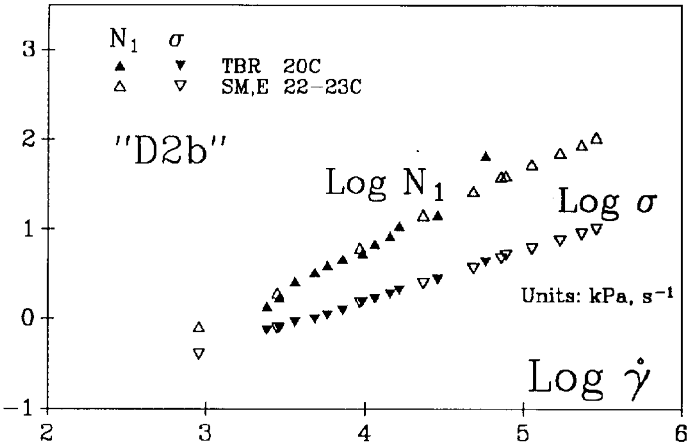

Fig. 3. Agreement is found between Torsional Balance Rheometer data and Stressmeter (unit E) data for both the functions $N_1(\dot{\gamma})$ and $\sigma(\dot{\gamma})$ over most of the common range of $\dot{\gamma}$. At the upper end of the agreement range, $\sigma$ = 2.8 kPa, $\dot{\gamma}$ = 29,000 $s^{-1}$, and $N_1/\sigma$ = 5.2. A value of 0.1 is used for $-N_2/N_1$. The SM slot width b = 0.6 × the die height h.

was necessary to go to 99°C to get Re = 100; here, TBR data were not available.

## Time-Temperature Superposition

TBR data were obtained only at 20°C. SM data were obtained in the range 22–99°C. We shall use a well-known "time-temperature superposition" assumption, which may be expressed as follows. In this context, partial derivatives are used with the following choice of variables:

$$\textit{dependent:}\quad \sigma,\ \sigma_p,\ \sigma_r,\ \sigma_{pr},\ N_1,\ N_{1r},\ P_e^*,\ P_{er}^*;$$

$$\textit{independent:}\quad T,\ \dot{\gamma}_r. \tag{11}$$

Here, $\sigma_p := \sigma - \eta_s\dot{\gamma}$ (the polymer contribution to shear stress); $\eta_s$ denotes the solvent viscosity; $\dot{\gamma}_r := \dot{\gamma}a(T)$, where $a(T)$ is a function of the absolute temperature $T$ alone, chosen to give superposition; and $X_r := \rho_o T_o X/(\rho T)$ where $X$ denotes any stress or pressure variable and $\rho_o$ denotes the value of density $\rho$ at $T = T_o$. In this article, we take $T_o = 372$ (99°C).

Liquids are said to satisfy a *time-temperature superposition principle* in ranges $T_1 < T < T_2$, $\dot{\gamma}_{r1} < \dot{\gamma}_r < \dot{\gamma}_{r2}$ if a function $a(T)$ can be found such that

$$\partial\sigma_{pr}/\partial T = 0. \tag{12}$$

*We shall assume that the validity of* (12) *implies the validity of the equation*

$$\partial N_{1r}/\partial T = 0 \tag{13}$$

over the same range of $T$ and $\dot{\gamma}_r$. $a(T)$ is usually written $a_T$. For D2b in the ranges of variables used here, the solvent contribution to shear stress was small so that the difference between $\sigma$ and $\sigma_p$ was at most a few percent, which was hardly significant in comparison with the scatter of the data.

SM data given below are consistent with (12) and with the equation

$$\partial P_{er}^*/\partial T = 0. \tag{14}$$

It follows from (13) that

$$\partial(N_{1r} - 2nP_{er}^*)/\partial T = 0, \tag{15}$$

where

$$n := \frac{\partial \log P_{er}^*}{\partial \log \dot{\gamma}_r} \bigg/ \frac{\partial \log \sigma_r}{\partial \log \dot{\gamma}_r}, \qquad (16)$$

in agreement with (6).

An extension of this treatment for a case in which the solvent makes a significant contribution to the solution shear stress has been given elsewhere.[2]

## SM data, 23°C to 99°C

Figure 4 gives SM data which establish the approximate validity of (12) over the range 23–99°C. At the higher shear rates at 99°C, the $\sigma_{pr}$ values appear to be slightly but systematically greater than the corresponding values at lower temperatures. The fact that both SM units E, S give the same anomaly here (i.e., at 99°C) suggests that a liquid property (rather than a slot unit artifact) is responsible; it is possible that errors in the shear stress measurement caused by microbubble agglomeration[2] are responsible, but further investigation is needed. The test liquid was not degassed prior to use. The same values of $a_T$ are seen to give superposition of the $P_e^*$ data also (Fig. 5), except for the

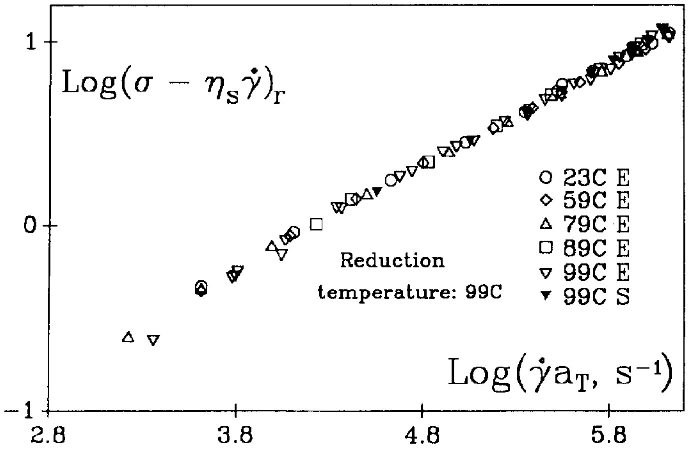

Fig. 4. Shift factors $a_T$ can be chosen to superpose the SM data for the reduced polymer contribution to shear stress over the range 23°C to 99°C. The small deviation at 99°C at the highest shear rates is unexplained, but may perhaps be due to errors in the shear stress measurement caused by microbubble agglomeration in the undegassed test liquid.

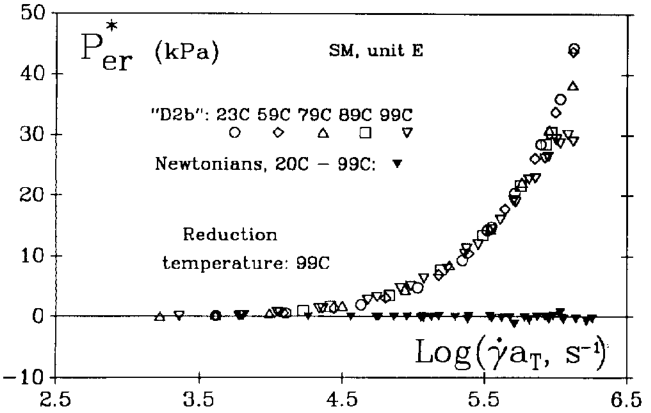

**Fig. 5.** The shift factors $a_T$ used in Fig. 4 for shear stress are seen here to give superposition for the elastic contribution to the hole pressure (obtained with the Stressmeter unit E), except for a few 99°C points at the highest shear rates. These are believed to be subject to some uncertainty arising from the determination of $P_N^*$. Corresponding data obtained with another (slot unit)/(flush transducer) combination ("unit S") did not give a similar anomaly (Fig. 6). Control data obtained with several Newtonian liquids are seen to be scattered close to and about zero, as expected, with the greatest deviation from zero occurring near the highest values of Re.

highest shear rate data obtained with SM unit E at 99°C, which appear to be anomalous; this anomaly is believed to be due to the fact that the Re values involved were above the range of values used in the determination of $P_N^*$. No such anomaly is seen in the corresponding data obtained using unit S (Fig. 6); it is seen that the superposition of data is better than that obtained using unit E (Fig. 5), and that the scatter about zero of the Newtonian control liquid data is smaller than for unit E, a fact which is consistent with the belief that $P_N^*$ was determined more accurately for unit S than for unit E. The 99°C point for D2b at the highest shear rate in Figure 6 lies slightly above a curve which could be drawn through the other points; this deviation, however, is not significant in comparison with the uncertainty involved in the determination of $P_f^*$ and $P_N^*$, as judged from a comparison of values obtained when different choices are made for the two Newtonian liquids used in Method C.

Figure 7 compares the hole pressure data for units E, S directly; it is seen that, for most of the data, the two units agree, and that, at the highest shear rates at 99°C, unit E gives $P_e^*$

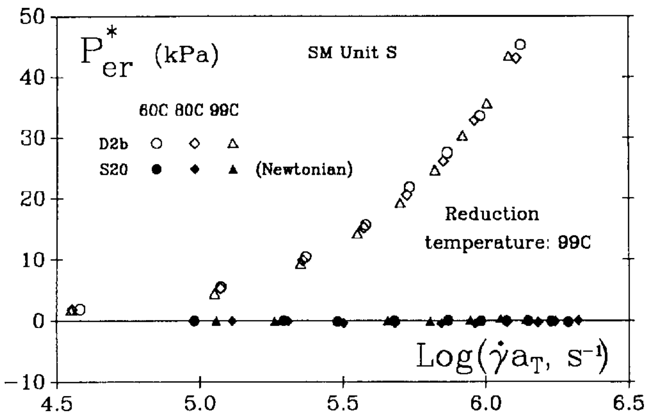

Fig. 6. The shift factors $a_T$ used in Fig. 4 for $\sigma$ also serve to superpose $P_e^*$ data obtained with unit S at 60, 80, 99°C. Control data obtained with a Newtonian liquid (Cannon S20) are seen to be scattered about zero, as expected.

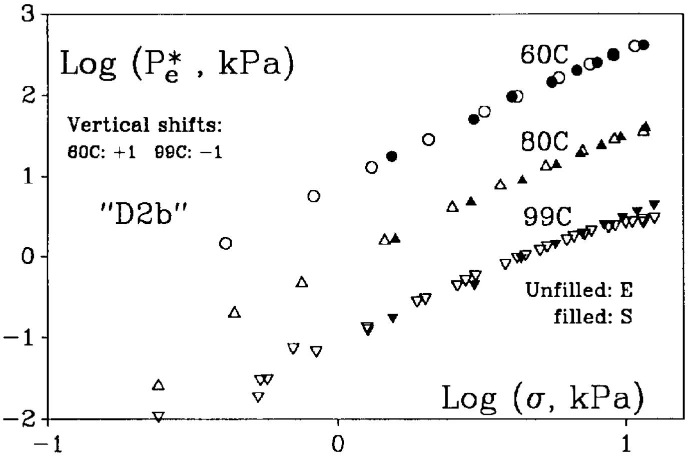

Fig. 7. Stressmeter data obtained for $P_e^*(\sigma)$ using two different (slot unit)/(flush transducer) combinations ("units E, S") are seen to agree, except for the highest shear rate data at 99°C. The discrepancy here is attributed to errors in the determination of $P_N^*$ for unit E at the highest Re values.

data lower than the unit S data. It is believed that this may reflect an error in the determination of $P_N^*$ for unit E: a more viscous standard liquid (Cannon S200) was used for unit E, with the result that the initial application of Method C did not extend to values of Re (Table I) as high as those which occurred in the D2b measurements at 99°C.

### Highest Shear Rate Data, SM Unit S

The temperature ranges for the different measurements made here were as follows (see Table I): TBR: 20°C; SM unit E: 22–99°C; SM unit S: 60–99°C. SM units E and S gave consistent data at 60°C and 80°C (Fig. 7). At 99°C, SM unit S data are believed to be more reliable than the corresponding unit E data. TBR and SM unit E data agreed at 20–23°C (Fig. 3). It seems reasonable to attribute the small deviations from time-temperature superposition to the failure to use adequately degassed test liquid on the one hand, and to a failure to determine $P_N^*$ for unit E over the full range of Re used in the D2b measurements. We proceed on the reasonable assumption that these deviations can be safely ignored for the present purposes. Further measurements should be made which avoid these difficulties and which allow one to compare data obtained with different die heights.

We may now use the time-temperature superposition results, taking $T_1 = 293\text{K}$ and $T_2 = 372\text{K}$ (20°C and 99°C, respectively). The data of Figure 3 support the result

$$N_1 - 2nP_e^* = 0 \qquad (T = T_1 = 293\text{K},\ 3.6 < \log \dot{\gamma} < 4.46),$$

which implies that

$$N_{1r} - 2nP_{er}^* = 0 \qquad (T = T_1 = 293\text{K},\ 4.06 < \log \dot{\gamma}_r < 5.14).$$

It then follows from (15) that

$$N_{1r} - 2nP_{er}^* = 0 \qquad (T_1 < T < T_2,\ 4.06 < \log \dot{\gamma}_r < 5.14),$$

which implies that

$$N_1 - 2nP_e^* = 0 \qquad (T = T_2 = 372\text{K},\ 4.06 < \log \dot{\gamma} < 5.14).$$

Thus the range of approximate validity of this HPBL equation has been extended to $\log \dot{\gamma} = 5.14$, that is, to $\dot{\gamma} = 138{,}000\ \text{s}^{-1}$. The reduced plots for $\log N_1$ and $\log \sigma_p$ are given in Figure 8.

Furthermore, the fact that the data of Figure 8 superpose and lie close to straight lines (on the log-log plots) strongly suggests (but does not prove) that the upper limit for $\log \dot{\gamma}$ in the above argument can be extended from 5.14 to 6.14, and hence that the range of approximate validity of the HPBL equation extends (for this liquid and slot unit dimensions) to $\log \dot{\gamma} = 6.14$, that is, to

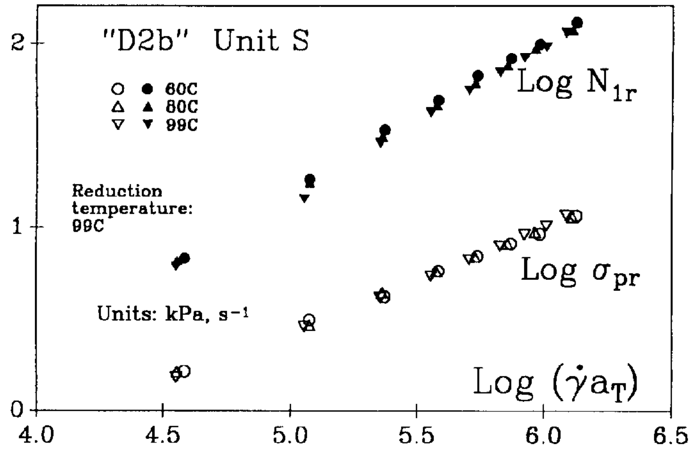

Fig. 8. The shift factors $a_T$ chosen to give superposition of SM unit E shear stress data (Fig. 4) are here seen to give reasonable superposition for $N_1$ data and for $\sigma$ data, obtained with unit S at 60, 80, and 99°C. The small deviations at 99°C are believed to lie within the uncertainty associated with microbubble errors (for $\sigma$, lower set of data) and with errors in the determination of $P_N^*$ (for $N_1$, upper set of data). The results give grounds for confidence in the approximate validity of the present method of measuring $N_1$ up to shear rates of $1.2 \times 10^6$ s$^{-1}$.

$\dot{\gamma} = 1{,}380{,}000$ s$^{-1}$. At this shear rate and temperature, inspection of the data gives the results $\sigma = 13$ kPa, $N_1/\sigma = 10$, $\eta = 10$ mPa. s. The greatest values of Re were 99 (unit S) and 107 (unit E).

The results obtained may be summarized as follows. Values 0.66, 0.295, 0.128, 0.06, and 0 for log $a_T$ at 22, 59, 79, 89, and 99°C were chosen to give the superposition of data shown. Densities in kg/m$^3$ at these temperatures were 892, 861, 849, 846, and 833, respectively. Second-order regression polynomials for the reduced data (unit S, 60°C, 80°C, 99°C; Fig. 8) were:

$$\log \sigma_{pr} = -1.647 + 0.2955 \log \dot{\gamma}_r + 0.02416(\log \dot{\gamma}_r)^2; \tag{17}$$

$$\log N_{1r} = -3.748 + 1.125 \log \dot{\gamma}_r - 0.02788(\log \dot{\gamma}_r)^2. \tag{18}$$

Units: kPa. s$^{-1}$. The reduction temperature is 99°C. The regressions were evaluated over the range $4.55 < \log \dot{\gamma}_r < 6.12$. The values of $R^2$ for the regressions were 0.9985 for (17) and 0.9968 for (18) (25 data pairs in each case).

## DISCUSSION

Experimental data obtained with a high shear rate stressmeter have successfully passed four tests: (a) comparison with TBR data (Fig. 3); (b) comparison of data obtained using two units E, S (Figs. 4, 7); (c) data obtained for a third Newtonian liquid (Figs. 5, 6); and (d) time-temperature superposition (Figs. 4–6, 8). The most compelling test (a) covers Re values only up to 8; it is the other tests which extend the Re range up to about 100. To extend the range of test (a) to higher Re, it would be desirable either to extend the $\sigma$ range of the TBR measurements for D2b or to use a solution of still lower viscosity.

It should be noted that D2b is much more elastic than typical multigrade oils (for example) and that the values of $P_e^*$ are significantly greater than the values of $P_f^*$ and $P_N^*$; the agreement between SM and TBR data shown in Figure 3 is not, therefore, a strong test of the reliability of our determination of $P_f^*$ and $P_N^*$, and more careful measurements may be required if the method is to be applied successfully to determine $N_1$ for multigrade oils.

On the other hand, the general consistency of the present data goes some way towards establishing the usefulness of the hitherto relatively unused measurement techniques employed in the present Stressmeter, namely, the use of hole pressure data to get approximate values for $N_1$ at shear rates higher than any successfully used in other apparatus, and the use of small, transverse slots (coupled with a special pressure-difference-measuring system) in a small slit die for measuring viscosity without any need to make corrections for entrance and exit effects.

A referee commented that "it is surprising to me that we don't see an upper Newtonian region at high shear rates since we're near a million with this material." In a somewhat limited literature search, we have failed to find compelling evidence of the existence of such a region. Data in Figures 1, 3, 4, and 5 of Brodnyan et al.[16] were claimed to show that such a region exists, but would, in our opinion, need to be replotted on a magnified scale to show whether the viscosity variation with shear rate was indeed insignificant in comparison with the scatter of the data; the authors state that such regions had also been found by Brodnyan et al.[17] and by Merrill.[18] The former give smooth curves but omit the data points; the latter gives neither curves nor data points. Merrill also refers to high shear rate data obtained by Bestul and Belcher[19] and Goodman;[20] neither of these reports presents data showing the existence of an upper Newtonian region. It appears possible to us that, in drawing their published curves of log $\dot{\gamma}$ *v.*

log $\sigma$, Brodnyan and co-workers may have been influenced by the then fashionable belief that, as the shear rate is increased to sufficiently high values, the viscosity of a polymer solution must remain above that of the solvent. Recent measurements of dynamic viscosity[21] have, however, shown that, for certain polymer/solvent combinations, the solution dynamic viscosity can fall significantly below the viscosity of the solvent; although dynamic viscosity and viscosity are different properties, these results suggest (but do not prove) that polymer solution viscosities may in some cases be less than their solvent viscosities. Capillary viscometer data for several multigrade oils at shear rates up to $10^6$ s$^{-1}$ obtained by Graham et al.[22] show no sign of any upper Newtonian region. Similar data obtained and analyzed more extensively by Duda et al.[23] may approach an upper Newtonian limit but may be influenced by limitations of the data analysis procedure if a certain iteration step is not utilized. Concentric cylinder viscosity data of Wright and Mather[24] show that, of the three multigrade oils tested up to $10^6$ s$^{-1}$, only one (Oil B, Fig. 11) shows a possible approach to an upper Newtonian region. According to the evidence cited, the referee's surprise appears to us to be somewhat astonishing.

## NOMENCLATURE

| | |
|---|---|
| $\dot{\gamma}$, $\sigma$ | Wall shear rate and shear stress |
| $N_1$, $N_2$ | 1st and 2nd normal stress differences in unidirectional shear flow |
| $P_1$, $P_2$, $P_3$ | Pressures measured using one flush- and two slot-mounted transducers |
| $P^*$ | $P_1 - P_2$ ("hole pressure") |
| $P_f^*$ | Flush transducer finite-width contribution to $P^*$ |
| $P_e^*$, $P_N^*$ | Elastic and inertial contributions to $P^*$ |
| $P_{CM}$ | Common mode response of pressure-difference-measuring system |
| $n$ | $d(\log P_e^*)/d(\log \sigma)$ |
| $h$, $w$ | Height, width of slit die cross-section |
| $z$, $L$ | Slot separation and die length |
| $b$ | Slot width |
| $T$ | Absolute temperature |
| $a(T)$ | Time-temperature shift function ($= a_T$) |
| $\eta$, $\eta_s$ | Solution and solvent viscosities |
| Re | $\rho b h \dot{\gamma}/(4\eta)$ (Reynolds Number at the SM die wall) |
| $\sigma_p$ | $\sigma - \eta_s \dot{\gamma}$ |

| | |
|---|---|
| $\dot{\gamma}_r$ | $\dot{\gamma}a(T)$ ("reduced shear rate") |
| $X_r$ | $\rho_o T_o X/(\rho T)$ for $X = \sigma, \sigma_p, N_1, P_e^*$ ("reduced stress variables") |
| $A_i, B_i$ | Coefficients in polynomials for $P_N^*$ and $P_f^*$ |
| $Q, m$ | Flow rate, $d(\log Q)/d(\log \sigma)$ |
| $A := B$ | A is *defined* by the equation $A = B$ |

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