Rod climbing and normal stresses in heavy crude oils at low shears

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Synopsis

This paper gives the results of a study of the nonlinear viscoelastic behavior of three heavy crude oils from California and Venezuela. A linear combination of normal stress coefficients at zero shear is expressed in terms of the quantity (the climbing constant) used to measure the height rise on a rotating rod. Measurements of the climbing constants are given for the crude oils. Values of both the first and second normal stress coefficients at zero shear are determined by the climbing constant when another combination of the two coefficients is known. In principle, the required information can be obtained by back extrapolation of the first normal stress difference, by back extrapolation of the dynamic modulus or by back extrapolation of the ratio of the second to first normal stress difference. Back extrapolation of data can be achieved when measurements are available at shear rates low enough to enter onto the second-order plateau of the functions generated by different instruments. Examination of previously published data for well-characterized solutions suggests that second-order rheology is most readily obtained in rod climbing.

I. INTRODUCTION

This work describes the viscoelastic behavior of three very viscous crude oils using a rotating rod rheometer. A viscoelastic fluid will climb up a rotating rod; a Newtonian liquid will not. Hence, rod climbing is a purely viscoelastic phenomenon. A rotating rod rheometer is a simple and convenient device for measuring normal stresses at low rates of shear. A cup is filled with the sample and a thin rod is partially immersed in the fluid. The rod is rotated at a given angular speed Ω and the height h that the fluid rises is measured. The height of climb at a given angular velocity varies strongly among different viscoelastic fluids. The slope of the h vs Ω^2 curve at the origin determines the climbing constant

$$\hat{\beta} = \frac{\Psi_{10}}{2} + 2\Psi_{20}, \tag{1}$$

where Ψ_{10} and Ψ_{20} are the first and second normal stress coefficients at low rates of shear, respectively. In principle, the first normal stress coefficient can be obtained by back extrapolation of the first normal stress difference or the storage modulus under the rules

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given by Eqs. (9) below. If $\hat{\beta}$ and Ψ_{10} are known, then $\Psi_{20} = \hat{\beta}/2 - \Psi_{10}/4$. Conversely, if Ψ_{20}/Ψ_{10} and $\hat{\beta}$ are given, Ψ_{10} and Ψ_{20} can be computed. The constitutive equation for each and every viscoelastic fluid is determined asymptotically for sufficiently slow and slowly varying motion by the zero shear viscosity η_0, and by Ψ_{10}, and Ψ_{20}. In this paper we will apply this convenient method to characterize three heavy crude oils.

II. BACKGROUND

A number of good studies on rheological properties of heavy crude oils are available in the literature. Most of them deal with the viscosity of the oil in shear and are motivated by problems of transporting highly viscous crudes. Barry (1971) considered problems of pumping non-Newtonian waxy crude oils. Dealy (1979) measured standard rheological data for different Alberta bitumens and concluded that these oils were only mildly non-Newtonian at low rates of shear. A rather remarkable decrease in viscosity for intermediate shear rates led Dealy to some conclusions about the nature of the microstructure of the substance. Dealy also observed a strong temperature dependence of shear viscosity. He found only weak elastic effects, except for high-frequency oscillations. Christensen *et al.* (1984) studied the viscous characteristics of Utah tar-sand bitumens, verifying Dealy's results on the weak shear rate dependence of viscosity and strong temperature effects. Flow properties of Australian crudes were studied by Wardhaugh *et al.* (1986) and by Wardhaugh and Boger (1986). The authors last named, Schramm and Kwak (1988), and Van Hombeck (1988) discuss the strong dependence of rheology of waxy crudes on the temperature and thermal history that is associated with the melting and recrystallization of the waxes. At relatively high temperatures, these oils usually act like a Newtonian liquid, exhibiting at most weak shear thinning with low viscosity. Yet when the temperature is below a certain threshold value, crystallization of the waxes gives rise to complex microstructures that produce a sudden increase in viscosity and viscoelastic behavior. This phenomenon was also studied by Herh (1992) at Rheometrics Inc [see also Rheometrics (1990)]. In a recent paper, Wardhaugh and Boger (1991) describe and compare different ways to measure the yield stress and fracture stress for waxy crude oils. They found that the characteristics seen in the yielding behavior of these oils "do not conform to any (existing) rheological model, are entirely consistent with the mechanisms of the fracture of solids, showing a transition from ductile to brittle fracture behavior as the strain rate is increased or the temperature reduced."

III. ROTATING ROD RHEOMETER

The theory of rod climbing was given by Joseph and Fosdick (1973) and the applicability of the theory to measurements of the properties of normal stresses at low rates of shear was demonstrated by Joseph *et al.* (1973), Beavers and Joseph (1975), Joseph *et al.* (1984), Hu *et al.* (1990), and in other papers reviewed in the book by Joseph (1990). The theory emerges from a series solution for steady flow in a general (model-independent) viscoelastic fluid in powers of ω(rad/s) induced by the rotation of the rod. The first deviation of the free surface from flatness arises at second order $O(\omega^2)$. At this order, the constitutive equation of every viscoelastic (simple) fluid collapses into a universal form, called a second-order fluid, in which the stress $\mathbf{T}$ is given by

$$\mathbf{T} = -p\mathbf{I} + \eta_0 \mathbf{A}_1 - \frac{\Psi_{10}}{2} \mathbf{A}_2 + (\Psi_{10} + \Psi_{20}) \mathbf{A}_1^2, \tag{2}$$

where $\mathbf{A}_1$ is twice the symmetric part of the velocity gradient, $\mathbf{A}_2$ the second Rivlin–Ericksen tensor, and p the pressure. The only parameters entering into Eq. (2) are the zero shear viscosity η_0 and the two normal stress coefficients given by Eq. (4), which are also zero shear rheological parameters. The second-order fluid is the first nonlinear approximation of a general fluid under slow and slowly varying motions, which Coleman and Noll (1960) called retarded. At the risk of boring some readers, it is necessary to assert for others that the rheology of rod climbing does not depend on the rheological equation of state since every equation of state reduces asymptotically to a second-order fluid in motions that are nearly steady and sufficiently slow. Any such motion, including slow, steady extensional flow, is determined once the zero shear parameters in Eq. (2) have been measured.

When a rod of radius a is rotated slowly at an angular speed Ω (rev/s), the resulting velocity field can be considered to satisfy the aforementioned conditions in which the fluid response is described asymptotically by a second-order fluid. Theory shows that for slow rotation, the fluid level at the rod surface rises to a height

$$h(a,\Omega^2) \cong h_s(a)+\frac{4\pi^2 a}{2\sigma\sqrt{S}}\left(\frac{4\hat{\beta}}{4+\lambda}-\frac{\rho a^2}{2+\lambda}\right)\Omega^2+O(\Omega^4), \tag{3}$$

where $h_s(a)$ is the static climb on the rod due to capillarity, σ the surface tension, ρ the fluid density, $S = \rho g/\sigma$, $\lambda^2 = a^2 S$ and $\hat{\beta}$ is the climbing constant.

We compute $\hat{\beta}$ from measurements of the slope of the linear asymptote at low angular velocities of the curve $[h(a)-h_s(a)]$ vs Ω^2, as given by Eq. (3)—a procedure illustrated in Fig. 2. As one increases the angular velocity, the higher-order terms in Eq. (3) become predominant, giving the curve its nonlinear shape.

The climbing constant is a linear combination [see Eq. (1)] of the first and second normal stress coefficients

$$[\Psi_{10},\Psi_{20}] = \lim_{\dot{\gamma}\to 0}\left[\frac{N_1(\dot{\gamma})}{\dot{\gamma}^2}, \frac{N_2(\dot{\gamma})}{\dot{\gamma}^2}\right], \tag{4}$$

where $N_1(\dot{\gamma})$ and $N_2(\dot{\gamma})$ are the first and second normal stress differences and

$$[N_1,N_2] = [T_{11}-T_{22},T_{22}-T_{33}], \tag{5}$$

where T_{11} is the normal stress in the direction of shear, T_{22} the normal stress in the direction perpendicular to the direction of shear in the plane of shear, and T_{33} the normal stress in the third direction. $N_1(\dot{\gamma})$ and $N_2(\dot{\gamma})$ are even functions of $\dot{\gamma}$. Any fluid for which

$$\frac{\Psi_{20}}{\Psi_{10}} < -\frac{1}{4} \tag{6}$$

will not climb a rod when $\dot{\gamma}$ is small. Lodge *et al.* (1988) have shown that the Doi–Edwards model of a fluid will not climb a rod, and they have discussed some other consequences of rod climbing for critical evaluation of other models and even some contradictory rheological data.

Many models of a viscoelastic fluid satisfy Weissenberg's hypothesis that the second normal stress is zero in all motions. In this case, $\Psi_{20} = 0$ and $\hat{\beta} = \Psi_{10}/2$. Measurements do not support $\Psi_{20} = 0$, but they appear to show that Ψ_{20} is small and negative for many fluids. Ever since the pioneering works of Kuo and Tanner (1974) and Keentok *et al.* (1980) using the shape of a free surface on a fluid flowing down a tilted trough as a second normal stress difference stress meter, it has been widely assumed that the magnitude of the ratio of the second to the first normal stress is usually of the order or less than 0.1 [for example, see Barnes *et al.* (1989) and Bird *et al.* (1987), among others]. For $\Psi_{20} = -\frac{1}{10}\Psi_{10}$, $\hat{\beta} = 3\Psi_{10}/10$ and if the usual ratio is between 0 and $-1/10$, then

$$\frac{3}{10}\Psi_{10} \leqslant \hat{\beta} \leqslant \frac{\Psi_{10}}{2}, \tag{7}$$

where the measured values cluster more nearly around 3/10 value in the typical cases [see Keentok *et al.* (1980)]. For such typical polymeric liquids, $\Psi_{10} = 10\hat{\beta}/3$ is a good estimate of the first normal stress coefficient. The measurement of $\hat{\beta}$ is easy and accurate; it can be done in any laboratory because expensive rheometers with torque and force transducers are not required.

On the other hand, it is clear that the stress ratio is not always in the usual range [Eq. (7)]. Tanner (1985) cites a range of $0.05 < -N_2/N_1 < 0.2$ as typical, and he cites a measured value of 0.3 for National Bureau of Standards nonlinear fluid number 1 from Keentok *et al.* (1980). This fluid should not, but it does, climb a rod [see Lodge *et al.* (1988)]. The values of $\dot{\gamma}$ reported in the experiments by Keentok are evidently not in the region of low shear in which N_2 and N_1 are quadratic functions of $\dot{\gamma}$. To our knowledge, the tilted trough has not been used by any rheologist outside of Tanner's group, so that direct verification of their results has not been carried out.

Like the tilted trough, the rotating rod is a free-surface rheometer which, when combined with backward extrapolation of the first normal stress difference or the storage modulus, gives rise to the following expressions:

$$\Psi_{20} = \frac{\hat{\beta}}{2} - \lim_{\dot{\gamma}\to 0} \frac{N_1(\dot{\gamma})}{4\dot{\gamma}^2} = \frac{\hat{\beta}}{2} - \lim_{\omega\to 0} \frac{G'(\omega)}{2\omega^2} \tag{8}$$

for the second normal stress coefficient. The backward extrapolation of N_1 and G' to plateau values using data from standard rheometers is not accurate and the extrapolated values of N_1 and G' leading to Ψ_{10} do not appear to agree, with the limiting values of $2G'/\omega^2$ larger than the limiting values of $N_1/\dot{\gamma}^2$.

IV. WHAT IS A SMALL SHEAR RATE?

The answer to this question depends on the function being measured. Low shear rates on one instrument can be high on another.

In principle,

$$\Psi_{10} = \lim_{\dot{\gamma}\to 0} \frac{N_1(\dot{\gamma})}{\dot{\gamma}^2} \tag{9a}$$

$$= \lim_{\omega\to 0} \frac{2G'(\omega)}{\omega^2} \tag{9b}$$

The relation (9a) implies that for small $\dot{\gamma}$,

$$N_1(\dot{\gamma}) = \Psi_{10}\dot{\gamma}^2, \tag{10}$$

so that Ψ_{10} appears as a plateau at the origin in a plot of $N_1(\dot{\gamma})/\dot{\gamma}^2$ vs $\dot{\gamma}$. The values of $N_1(\dot{\gamma})$ can be obtained by thrust measurements and cone and plate devices. Relation (9b) implies that for small ω,

$$2G'(\omega) = \Psi_{10}\omega^2, \tag{11}$$

so that Ψ_{10} appears as a plateau at the origin in a plot of $2G'(\omega)/\omega^2$ vs ω which is a dynamic measurement using a torque transducer rather than a force transducer. The accurate measurements of Ψ_{10} using either Eq. (9a) or (9b) depends on whether or not measurements can be carried out at values of $\dot{\gamma}$ or ω that are small enough to enter the plateau, Eq. (10) in one case and Eq. (11) in the other.

It does not matter that good $G'(\omega)$ may be obtained at values of ω that are much less than the $\dot{\gamma}$ for which good values of $N_1(\dot{\gamma})$ can be obtained. It only matters that the apparatus on which measurements are taken is sensitive enough to record reliable data in the plateau region of the function they are supposed to measure. Comparing $\dot{\gamma}$ or ω can be like comparing apples and oranges. Our point here is brought out clearly in Fig. 12 of the paper by Binding *et al.* (1990) which is reproduced in Fig. 1. The back extrapolation of data for $N_1/2\dot{\gamma}^2$ and G'/ω^2 suggest a common value of Ψ_{10} of approximately 0.3 Pa s^2, but neither graph has definitely entered onto the plateau region. In fact, it appears that $N_1/2\dot{\gamma}^2$ is closer to a plateau value than G'/ω^2, even though the effective shears ω of $G'(\omega)$ are an order of magnitude smaller than $\dot{\gamma}$ of $N_1(\dot{\gamma})$. The conclusion is that the decision about how small the shear rate must be to enter on the plateau depends on the function being measured, on the fluid, and on the device being used.

The limiting relation (9b) is cited by Bird *et al.* (1987) and by Barnes *et al.* (1989) and in some other textbooks of rheology. The proof of (9b) is given in the book by Joseph (1990, Sec. 16.6) and is close to the original proof of Coleman and Markovitz (1964), which is actually quite deep and very important. The proof requires that one compare two different asymptotic expressions: one for small amplitude unsteady motions and the the other for slow steady motions leading to second-order fluids for which the normal stress coefficients arise naturally. After expanding for small frequencies of ω, one finds that

$$G'(\omega) = \int_0^{\infty} G(s)\omega \sin(\omega s)\, ds = \omega^2 \int_0^{\infty} sG(s)ds + O(\omega^4),$$

where

$$\Psi_{10} = 2\int_0^{\infty} sG(s)ds. \tag{12}$$

There is no way to come up with Eq. (12) without doing the mathematics of continuum mechanics, and Eq. (12) is not more fundamental than the second-order fluid or any other asymptotic relation on which it is based.

It appears to be quite generally true that plots of the type shown in Fig. 1 are such that $2G'(\omega)/\omega^2 < N_1(\dot{\gamma})/\dot{\gamma}^2$ for larger values of $\omega = \dot{\gamma}$ with the inequality reversed for smaller values. This reversal is clearly evident in Fig. 1 and is yet more evident in Fig. 4.15 of Barnes *et al.* (1989) and Fig. 9 of Hudson and Jones (1993). These two figures suggest that the zero shear value of $G'(\omega)/\omega^2$ as given by backward extrapolation of data from standard rheometers can be as much as ten times more than the backward extrapolation of $N_1(\dot{\gamma})/\dot{\gamma}^2$. For the case displayed in Fig. 1, the results of Laun and Hingmann (1990) suggest that the limiting value of $2G'(\omega)/\omega^2$ is over twice the backward extrapolation of $N_1/\dot{\gamma}^2$. We do not find agreement between dynamic and thrust measurements at low shears.

The problem of determining Ψ_{10} by thrust measurements [Eq. (9a)] has been considered by Quinzani *et al.* (1990) in an interesting study of weakly concentrated solution of polyisobutelene in a viscous solvent (Boger fluids). They find that $\Psi_1(\dot{\gamma})$ is a decreasing function of $\dot{\gamma}$, as expected, and they find easily detected plateaus for $\Psi_1(\dot{\gamma})$ when $\dot{\gamma}$ lies between 1 and 30 s^{-1}, depending on the fluid. This plateau is not the zero shear plateau

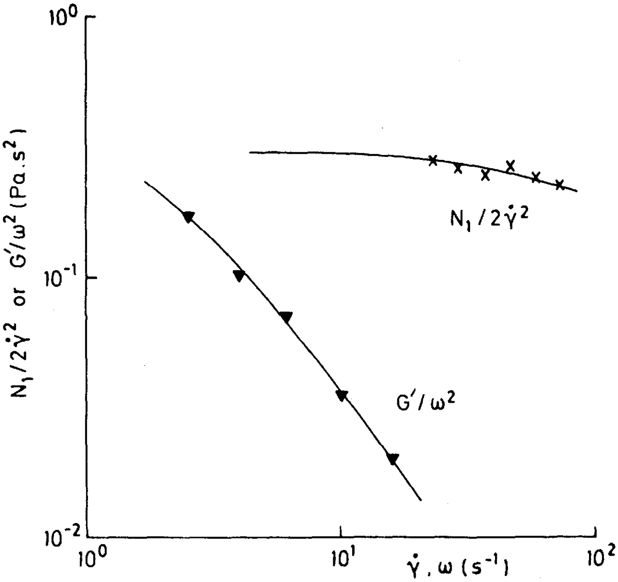


FIG. 1. Comparison of $N_1/2\dot{\gamma}^2$ and G'/ω^2 for fluid M1 at 20 °C. [Reproduction with permission of Fig. 12 from Binding *et al.* (1990).]

on which $\Psi_1(\dot{\gamma}) \approx \Psi_{10}(\dot{\gamma}^2)$ because $\Psi_1(\dot{\gamma})$ again begins to increase for lower $\dot{\gamma}$ values. In some cases, the data suggest a low shear plateau which can be reasonably assumed to be near to zero shear plateau. They note that the high shear plateau can easily be mistaken for a zero shear plateau, giving rise to too small of a value for Ψ_{10}. The data of Quinzani *et al.* (1990) at the lowest shears may be uncertain because the lowest shear rates probed in the experiments are already in regimes of low thrust in which the normal stress transducers are unreliable. We think that it is also necessary to remark that "false" plateaus may be found in some kinds of polymeric solutions and not in others.

Quinzani *et al.* (1990) also compare thrust and dynamic measurements on the same graph, and their data are consistent with the crossover that we have observed in all data from all sources; namely, there is a crossover frequency $\tilde{\omega}$ such that

$$\frac{2G'(\omega)}{\omega^2} < \frac{N_1(\dot{\gamma})}{\dot{\gamma}^2}, \quad \omega > \tilde{\omega}, \quad \dot{\gamma} > \tilde{\omega},$$

$$\frac{2G'(\tilde{\omega})}{\tilde{\omega}^2} = \frac{N_1(\tilde{\omega})}{\tilde{\omega}^2}, \quad \omega = \tilde{\omega}, \quad \dot{\gamma} = \tilde{\omega},$$

$$\frac{2G'(\omega)}{\omega^2} > \frac{N_1(\dot{\gamma})}{\dot{\gamma}^2}, \quad \omega < \tilde{\omega}, \quad \dot{\gamma} < \tilde{\omega}.$$

Of course, the values at the lowest shears are in much better agreement than when the shear rates are on the high shear plateaus of $\Psi_1(\dot{\gamma})$.

Zero shear plateaus can be reached easily with rotating rod rheometers because in many fluids, $(h-h_s)$ is linear in ω^2 even for not so small ω's of the order of 1–10 rad/s or even higher. It follows that a plot of $(h-h_s)/\omega^2$ give rise to a plateau region for normal stresses which can be easily accessed. This is not true for all fluids; for some fluids like the polyacrilamide solutions studied by Beavers *et al.* (1980) and Al [see Liao *et al.* (1994)], no second-order range can be observed and higher-order effects are observed immediately. As a rule of thumb, we may expect a measurable second-order climb in fluids that climb well for rates of shear below those for which marked shear thinning first becomes evident.

V. PREVIOUS RESULTS

Rod climbing results have been compared with standard rheological data in some previous papers. Joseph *et al.* (1973) did an independent determination of $\hat{\beta}$ for STP motor oil additive from normal stress data obtained by W. M. Davis and C. W. Macosko, who used a Rheometrics Mechanical Spectrometer in both the cone and plate and parallel-plate modes. They obtained

$$\Psi_{10} = \lim_{\dot{\gamma} \to 0} \frac{N_1(\dot{\gamma})}{\dot{\gamma}^2} = 2.95 \pm 0.1 \ \text{g/cm} \tag{13}$$

and

$$\Psi_{10} - \Psi_{20} = \lim_{\dot{\gamma} \to 0} \frac{N_1 - N_2}{\dot{\gamma}} = 3.2 \pm 0.2 \ \text{g/cm}. \tag{14}$$

Hence

$$\hat{\beta} = \frac{\Psi_{10}}{2} + 2\Psi_{20} = 0.98 \pm 0.5 \ \text{g/cm}, \tag{15}$$

which compares with values

$$0.63 \leqslant \hat{\beta} \leqslant 0.94$$

directly measured by Joseph *et al.* (1973).

A second independent determination of the value of $\hat{\beta}$ was obtained by assuming that

$$-0.1 > \frac{N_1}{N_2} \geqslant -0.15.$$

When combined with Eqs. (13) and (14), this gives

$$0.6 \leqslant \hat{\beta} \leqslant 0.9,$$

which is in excellent agreement with the values obtained by direct measurement. Joseph *et al.* (1984) reported that the scatter of data for $N_1(\dot{\gamma})$ for small $\dot{\gamma}$ of $O(1 \ \text{s}^{-1})$ taken on the Rheometrics System Four cone and plate rheometer was too great to permit the backward extrapolation to zero shear rate.

Hu *et al.* (1990) have given very extensive reliable values for climbing constants in M1 as a function of temperature. M1 has a large second-order range so that $\hat{\beta}$ was accurately measured with reproducible results. They find that

$$\hat{\beta} = 1.68 \ \text{g/cm at } 20\ ^\circ\text{C},$$

$$\hat{\beta} = 0.54 \ \text{g/cm at } 27.2\ ^\circ\text{C}.$$

Measured values for $N_1/2\dot{\gamma}^2$ and G'/ω^2 taken from Binding *et al.* (1990) are shown in Fig. 1. These curves may be imagined to back extrapolate to a value of $\Psi_{10} = 6$ g/cm, which when combined with $\hat{\beta} = \Psi_{10}/2+2\Psi_{20} = 1.68$ g/cm gives $\Psi_{20}/\Psi_{10} = -0.11$. Back extrapolation of $N_1/2\dot{\gamma}^2$ data at 27.2 °C of Prud'homme given on page 524 of Joseph (1990) leads to $\Psi_{20}/\Psi_{10} = -0.12$.

The back extrapolation of $2G'/\omega^2$ given by Binding *et al.* (1990) does not agree with the back extrapolation of apparently accurate data at 20 °C for very low values of ω offered by Laun and Hingmann (1990). The data are presented in their Fig. 9, and $2G'/\omega^2$ extrapolates to a value of 1.24 Pa s^2 = 12.4 g/cm. When combined with $\hat{\beta} = 1.68$ g/cm, this leads to

$$\frac{\Psi_{20}}{\Psi_{10}} = -\frac{2.26}{12.4} = -0.18$$

instead of -0.11. This kind of discrepancy in published values of the stress ratio is not uncommon. As a matter of fact, the special issue of the *Journal of Non-Newtonian Fluid Mechanics* (Vol. 35, Nos. 2 and 3, July 1990) dedicated to M1 fluid contains at least a dozen papers in which authors measure the first normal stress coefficient at low shear rates. Some authors get Ψ_{10} by thrust measurements, some through dynamic measurements and others use both techniques. At 20 °C, the values reported for Ψ_{10} range from 0.55 to 1.24 Pa s^2. Te Nijenhius (1990) summarizes results of the round-robin tests of M1, as "presented by various authors at the Combloux Conference," concludes that "the agreement between the storage modulus and the first normal stress difference is good" and point to a value of $\Psi_{10} = 0.81$ Pa s^2. Together with the climbing constant, this result yields $\Psi_{20}/\Psi_{10} = -0.15$.

VI. COMPARISON OF DIFFERENT METHODS FOR MEASURING THE FIRST AND SECOND NORMAL STRESS COEFFICIENTS

There are a few conventional methods for measuring normal stresses. Whorlow (1992) recommends either pressure gradient distributions [as in Christiansen and Leppard (1974)] and total force measurements for flow between a cone and plate or the Wineman–Tanner–Kuo tilted trough. This latter method, like rod climbing, is a free-surface method in which the deflection of the free surface is proportional to the normal stress coefficients at second order in slowness. The trough is interesting because at lowest order, the deflection is proportional only to the second normal stress coefficient. The deflections of the free surface in the trough are very small even in fluids with modest values of the first normal stress coefficient, so that reliable data can be expected only in fluids with relatively large values of the second normal stress coefficient [see Joseph (1990), pages 525–526, and Sturges and Joseph (1975) for discussion of the accuracy of the trough]. In contrast, the rise in the height of the free surface next to a rotating rod is appreciable even in fluids with normal stresses so low that deflections could not be read in the trough. The rotating rod is a more convenient instrument whose configuration closely adheres to the model that guides the rheological measurements.

We have compared the rotating rod to state-of-the-art mechanical rheometers (Rheometrics RFS-II) equipped with the best transducer available for normal stress measurement, the Force Rebalanced Transducer (FRT). These transducers are said to be capable of measuring normal forces "as low as 0.2 g." At 24 °C, however, we could not sense normal stresses on Zuata crude oil even at shear rates as low as 0.5 s^{-1}. By contrast, we had no trouble detecting a climb for shear rates as of about 0.2 s^{-1} when the Zuata was at 25 °C, and we also had no trouble in getting G' and G'' data.

Another way to get the second normal stress is to compare total force measurements for flow between a cone and plate and flow between parallel plates [Ginn and Metzner (1969)]. Despite recent advances in transducer technology, these methods are either very costly (a new RFS-II rheometer with a FRT transducer can cost upwards of $150,000) or provide data with a high uncertainty at low shear rates.

The high scatter in the data is inherent for these measurements. Consider, for example, comparing cone-plate (which measures N_1) and parallel-plate (which measures N_1-N_2) force measurements. As stated previously in this paper, N_2 is usually an order or magnitude smaller than N_1 and is negative. This means that at low shear rates, N_1-N_2 measured on the parallel-plate rheometer is slightly larger than the N_1 measured on the cone and plate. Thus, when the difference is computed, the resulting number is of the same size as the uncertainty of the instrument. And many things can influence the results of cone and plate/parallel plate rheometry, e.g., thermal gradients or background vibrations.

In contrast, the rod climbing technique is relatively low in cost (a good instrument can be quickly built for under $10,000). Also, rod climbing uses very sensitive hydrostatic and surface-tension forces. There is no need for transducers and signal conditioners.

VII. MODEL-INDEPENDENT RHEOMETRY FOR RETARDED MOTIONS

We wish to draw the reader's attention to the fact that we are using second-order fluids not as models in their own right, but as asymptotic forms that all the models assume when they are evaluated on the slow and slowly varying motions which Coleman and Noll (1960) called retarded. The first approximation for slowness gives rise to a Newtonian fluid in which the relevant stress parameter is the zero shear viscosity η_0. At the second order of slowness, we find zero shear values of the two normal stress coefficients Ψ_{10} and Ψ_{20}. Then, up to order three, all the retarded motions are completely described by a second-order fluid with three rheometrical parameters η_0, Ψ_{10}, and Ψ_{20}, which may be determined by direct measurements that are apparently sound, widely applicable, and do not involve any direct measurement of normal stresses.

All motions in the second-order range are determined by these three constants. Of particular interest is the Roscoe (1965) formula for the extensional viscosity

$$T_{11}-T_{22} = 3\dot{\epsilon}\left[\eta_0+\left(\frac{\Psi_{10}}{2}+\Psi_{20}\right)\dot{\epsilon}\right]+O(\dot{\epsilon}^3), \tag{16}$$

where $\dot{\epsilon}$ is the rate of extension. The Roscoe formula (16) is the only model-independent formula for the extensional viscosity $\eta_E(\dot{\epsilon})\dot{\epsilon}$, where

$$\eta_E(\dot{\epsilon}) = \frac{T_{11}-T_{22}}{\dot{\epsilon}} = 3\left[\eta_0+\left(\frac{\Psi_{10}}{2}+\Psi_{20}\right)\dot{\epsilon}\right]+O(\dot{\epsilon}^2). \tag{17}$$

The second-order correction $\Psi_{10}/2+\Psi_{20}$ of Trouton's viscosity is slightly larger than the climbing constant $\Psi_{10}/2+2\Psi_{20}$. If $\Psi_{20} = -\Psi_{10}/10$, then

$$T_{11}-T_{22} = 3\dot{\epsilon}(\eta_0+\tfrac{4}{3}\hat{\beta}\dot{\epsilon}) \tag{18}$$

is determined by the zero shear viscosity and the climbing constant. It is, of course, better to measure Ψ_{10} and Ψ_{20} by the procedure outlined in Eq. (4).

We have been asked, "How can the extensional viscosity be measured in shear?" The answer is that the parameters of the constitutive equation that arise asymptotically in slowness at second order are measured in shear, and these and only these parameters enter into each and every motion, including extensional motions, which is evaluated up to

TABLE I. Gross composition of the crude oils.

Crude oil	Asphaltenes (wt %)	Paraffines and naphtenes (wt %)	Resins and aromatics (wt %)
CND	13	15	72
Zuata	< 4	...[a]	...[a]
Lakeview	24	20	56

[a]No information provided.

the second order in slowness. There is not much to this; it is equivalent to saying that at first order of slowness, there is only one rheological parameter to consider, the viscosity η_0, which is measured in shear and determines the Trouton viscosity $3\eta_0$, which arises in extension without shear.

VIII. SAMPLE DESCRIPTION

Three samples of heavy crude oil were used in this study. Two of them are from the Zuata and Cerro Negro fields of the Venezuelan Orinoco Belt. Oil was extracted from the Zuata fields by conventional mechanical pumping, whereas oil from the Cerro Negro field was recovered by a downhole emulsification procedure. This emulsion is formed by the controlled injection of a water and surfactant solution into the well bottom. This solution is mixed with the oil and reservoir water, thus becoming an emulsion with a viscosity considerably smaller than that of the oil at the same temperature. Once the emulsion is formed, it is removed from the well and the oil is obtained by breaking and separating the emulsion components by mechanical means. The final water content of the oil after the referred dehydration procedure is typically 2%. Hereinafter, this report will refer to these hydrocarbons simply as Zuata and CND. These samples were provided by INTEVEP S.A.-PDVSA. The other sample examined originated from the Californian Lakeview field, and was provided by Shell Research Co. It is a very viscous crude with high asphaltene and wax content, thoroughly dried. In this paper, it will be simply called Lakeview. Table I presents the original composition of each of these oils.

In Table II we display the relevant physical properties of these oils. The viscosity versus shear rate was measured using the cone-and-plate fixture in the Rheometrics System Four Rheometer (Lakeview) and the parallel plate apparatus in the Rheometrics

TABLE II. Physical properties of the crude oils.

	Lakeview	CND	Zuata
Zero shear viscosity (Pa s)	2.78×10^3 (25 °C) 646 (36 °C) 18.5 (56 °C)	1.29×10^3 (25 °C) 56.9 (50 °C)	806 (10 °C) 115.2 (25 °C)
Density (kg/m^3)	1001 (25 °C) 998 (36 °C) 995 (56 °C)	1009 (25 °C) 992 (50 °C)	1003 (10 °C) 996 (25 °C)
Surface tension (mN/m)	21 (25 °C) 20 (36 °C) 19 (56 °C)	35 (25 °C) 33 (50 °C)	36 (10 °C) 35 (25 °C)
Pour point (°C)	27	21	< 20

TABLE III. Measured climbing constants.

Sample	Temperature (°C)	Climbing constant (kg/m)
Lakeview	25	565
	36	81
	56	0.32
CND	25	170
	50	0.27
Zuata	10	18
	25	5.4

RFS-II rheometer (Zuata and CND). Our results were consistent with those presented by Dealy (1979). From our measurements we estimated the zero shear viscosity η_0, shown in Table II. Density was measured by using a picnometer, and surface tension by a ring tensiometer, capillary rise and/or drop weight method. Pour point was measured according to ASTM D-97-66.

Although many authors stress the dependence of rheological properties of heavy crudes on their thermal history, we did not investigate these effects. Therefore, all measurements reported here correspond to oil without any prescribed thermal treatment.

IX. MEASUREMENTS OF CLIMBING CONSTANTS FOR THE OIL SAMPLES

In these experiments, a tungsten rod of 3.01 mm radius was used. The fluid sample was placed in a glass container of 30 mm radius. The shear rate may be computed from $\dot{\gamma} = 4\pi\Omega$ where Ω is in rev/s. The sample temperature was controlled by covering the container and immersing it in a constant-temperature water bath. When measuring the climbing constant at temperatures different from ambient, one could speculate that thermal conduction through the rod would adversely affect its temperature and create unwanted thermal gradients in the fluid. We found that typically, even under severe conditions, this should not be a problem. We modeled the rod as a long, thin cylindrical fin and applied the classical theory of heat transfer to show, for example, that for a fluid temperature of 50 °C with air at 22 °C immediately above, the temperature of the rod 1 mm above the fluid would be 49.5 °C as a worst case.

The measurements of the height of climb were done with the help of a microscope system and are repeatable within 0.02 mm. Uncertainty in the measured values of surface tension is a source of error. An error of 1% in the measurement of the surface tension leads to an error of about 0.35% in the value of the climbing constant.

Table III displays the measured values for climbing constants. For Lakeview, rod climbing measurements were done at 25, 36, and 56 °C. The high climbing constants at lower temperatures, indicate strong normal stress effects. At 56 °C, smaller climbs were observed; this is probably explained by the melting and dissolution of the heavy components (e.g., asphaltenes and/or paraffins). For the CND sample, the test temperatures were 25 and 50 °C; for the Zuata sample, 10 and 25 °C.

Figure 2 shows the height rise at the rod versus the square of the angular velocity Ω (rev/s) plots, obtained at the test temperatures for Lakeview. In all cases, we can identify a second-order region where $h - h_s$ is proportional to Ω^2 [see Fig. 2(b)]. In Fig. 3, we exhibit photographs of rod climbing in Lakeview crude, at 25 °C, for two angular speeds.

The climbing constants for CND are smaller than the corresponding constants for Lakeview crude. The Zuata sample climbed a rod, but with only a small climb at ambient temperatures, where it behaves almost as a very viscous Newtonian fluid. This behavior

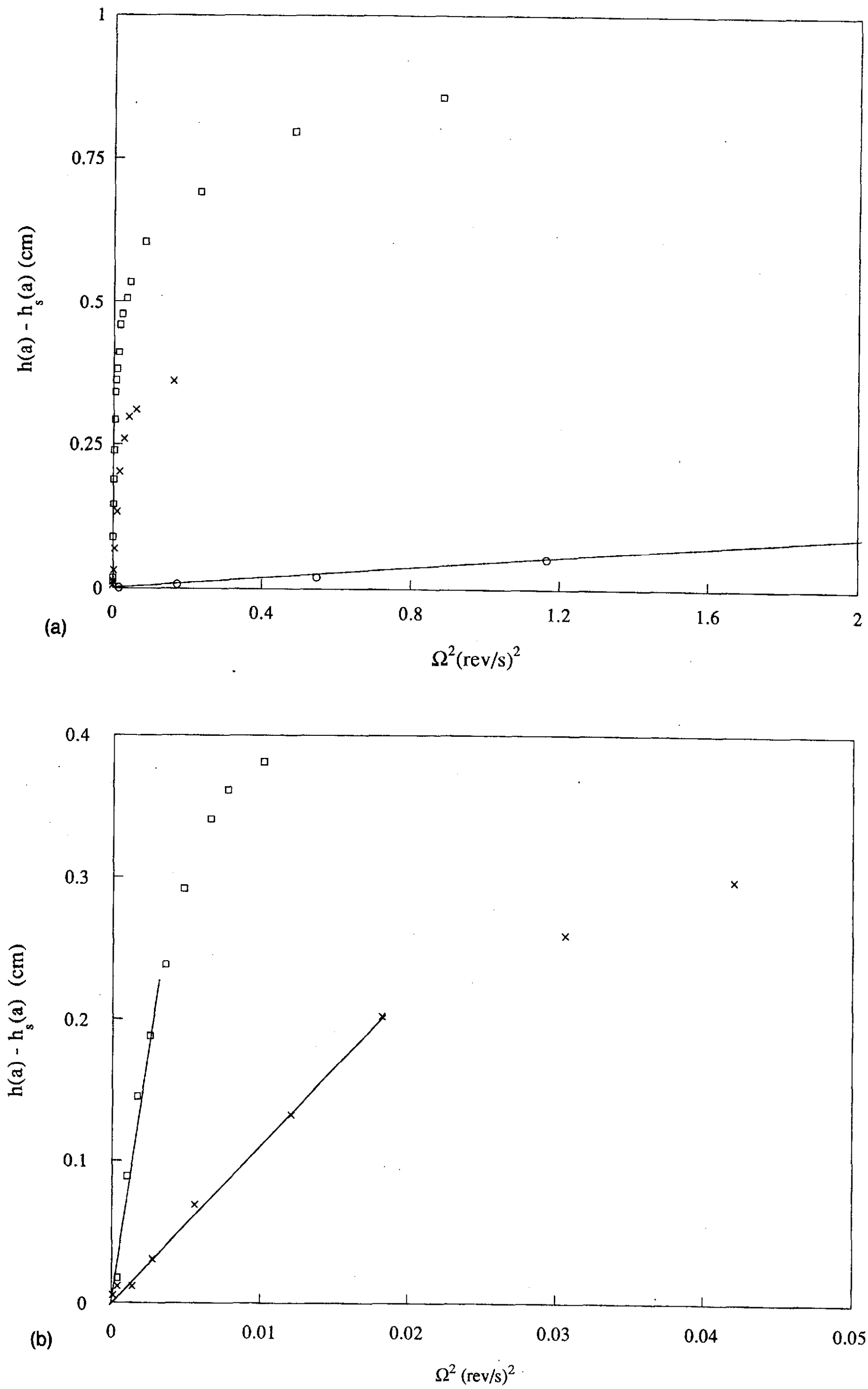
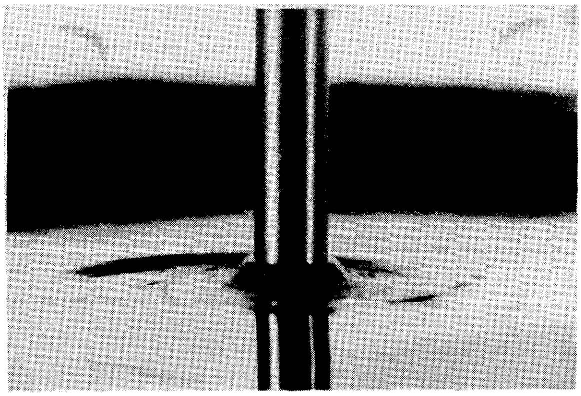


FIG. 2. (a) Height climb vs the square of angular velocity of Lakeview for all temperatures and (b) with axes expanded for the lower temperatures. There is a huge drop of the climbing constant for 56 °C. The least-squares fits are: □—25 °C—$h(a)-h_s(a) = 76.6\ \Omega^2$; ×—36 °C—$h(a)-h_s(a) = 11.2\ \Omega^2$; ○—56 °C—$h(a)-h_s(a) = 4.58\times10^{-2}\ \Omega^2$.


(a)

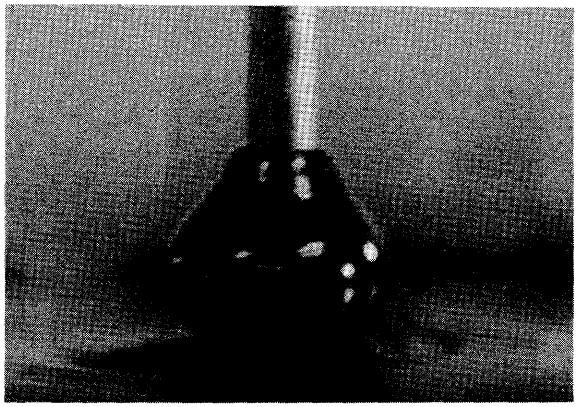

(b)

FIG. 3. (a) Rod climbing in Lakeview crude oil at 25 °C, 0.033 rev/s and (b) rod climbing in Lakeview crude oil at 25 °C, 0.72 rev/s. The climb in (b) is obviously nonlinear, so it was not used to compute the climbing constant.

was also observed by Dealy (1979) in Alberta tar sands. For the Zuata sample attempts were made to measure the climbing constant at 50 °C, but no noticeable climb was observed at this temperature. Figures 4 and 5 show, respectively, the height rise versus the square of the angular velocity for one experiment with CND (at 25 °C) and for the experiment with Zuata at 10 °C.

X. SECOND NORMAL STRESS COEFFICIENTS AND THE SECOND-ORDER CORRECTION OF TROUTON'S VISCOSITY

In Table IV we present the values for the first normal stress coefficient Ψ_{10}, and for the second-order correction of Trouton's viscosity calculated from the climbing constant $\hat{\beta}$, assuming $\Psi_{20} = -\Psi_{10}/10$.

For the Lakeview sample, at 25 °C, we attempted to compare the values of Ψ_{10} obtained by rod climbing with direct measurements made in a Rheometrics System Four rheometer using the cone and plate fixtures. Because of the limitations of the normal force transducer, we could not measure Ψ_{10} for shear rates below 0.5 s^{-1}. At this shear rate, we measure $\Psi_1 = 943$ Pa s^2. By comparison, the rod climbing measurements along

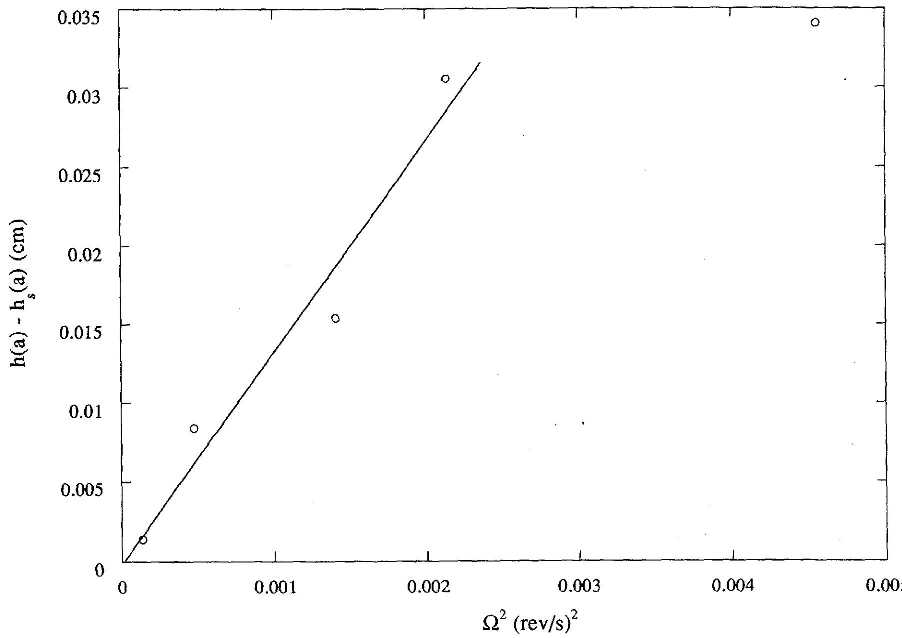


FIG. 4. Height climb vs the square of angular velocity for CND at 25 °C. $h(a)-h_s(a) = 18.0\ \Omega^2$.

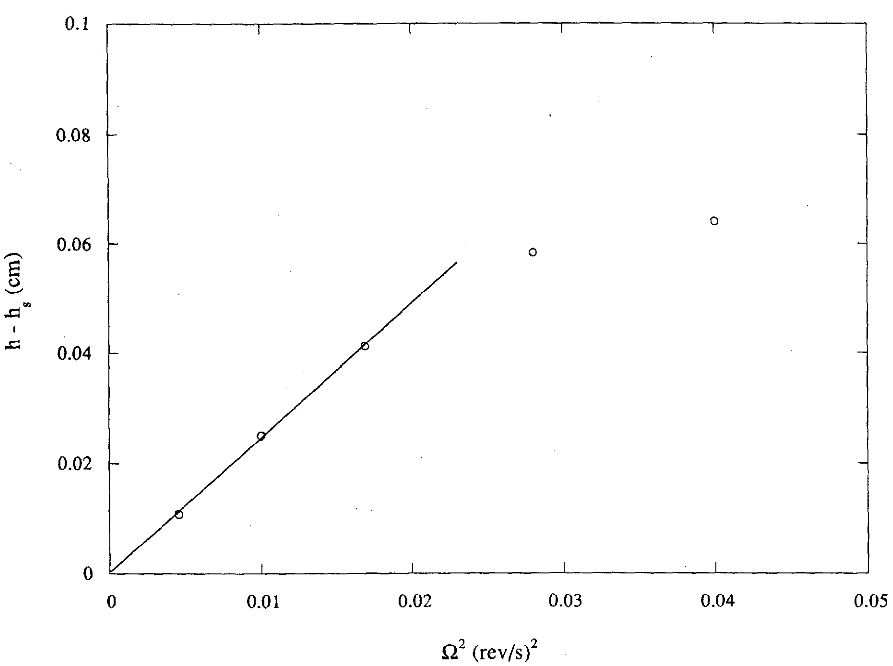


FIG. 5. Height climb vs the square of angular velocity for Zuata at 10 °C. $h(a)-h_s(a) = 2.46\ \Omega^2$.

TABLE IV. First normal stress coefficient and second-order correction of Trouton's viscosity calculated from the climbing constant by assuming that $\Psi_{20} = -\Psi_{10}/10$.

Sample	Temperature (°C)	Ψ_0 (Pa s^2)	Ψ_{20} (Pa s^2)	Extensional viscosity η_E, (Pa s)—from Eq. (18)
Lakeview	25	1.88×10^3	-188	$8340+2300\dot{\epsilon}$
	36	270	-27	$1940+320\dot{\epsilon}$
	56	1.1	-0.11	$55.5+1.3\dot{\epsilon}$
CND	25	550	-55	$3870+660\dot{\epsilon}$
	50	0.90	-0.09	$171+1.1\dot{\epsilon}$
Zuata	10	58	-5.8	$2420+70\dot{\epsilon}$
	25	18	-1.8	$346+22\dot{\epsilon}$

with $\Psi_{20} = -\Psi_{10}/10$ yield $\Psi_{10} = 1.88\times10^3$ Pa s^2, and dynamic measurements $\Psi_{10} = 2.99\times10^3$ Pa s^2 (at 30 °C). We also tried to obtain parallel-plate normal stress measurements for Zuata and CND using a Rheometrics RFS-II rheometer, but the transducer was not sensitive enough to give consistent data at low rates of shear. Since the viscosity of the oils is very high, high shear rate measurements could not be done without damaging the torque transducer. Joseph *et al.* (1984) also report difficulties of the same kind in their attempt to obtain reliable normal stress measurements at rates of shear low enough to compare with rod climbing measurements.

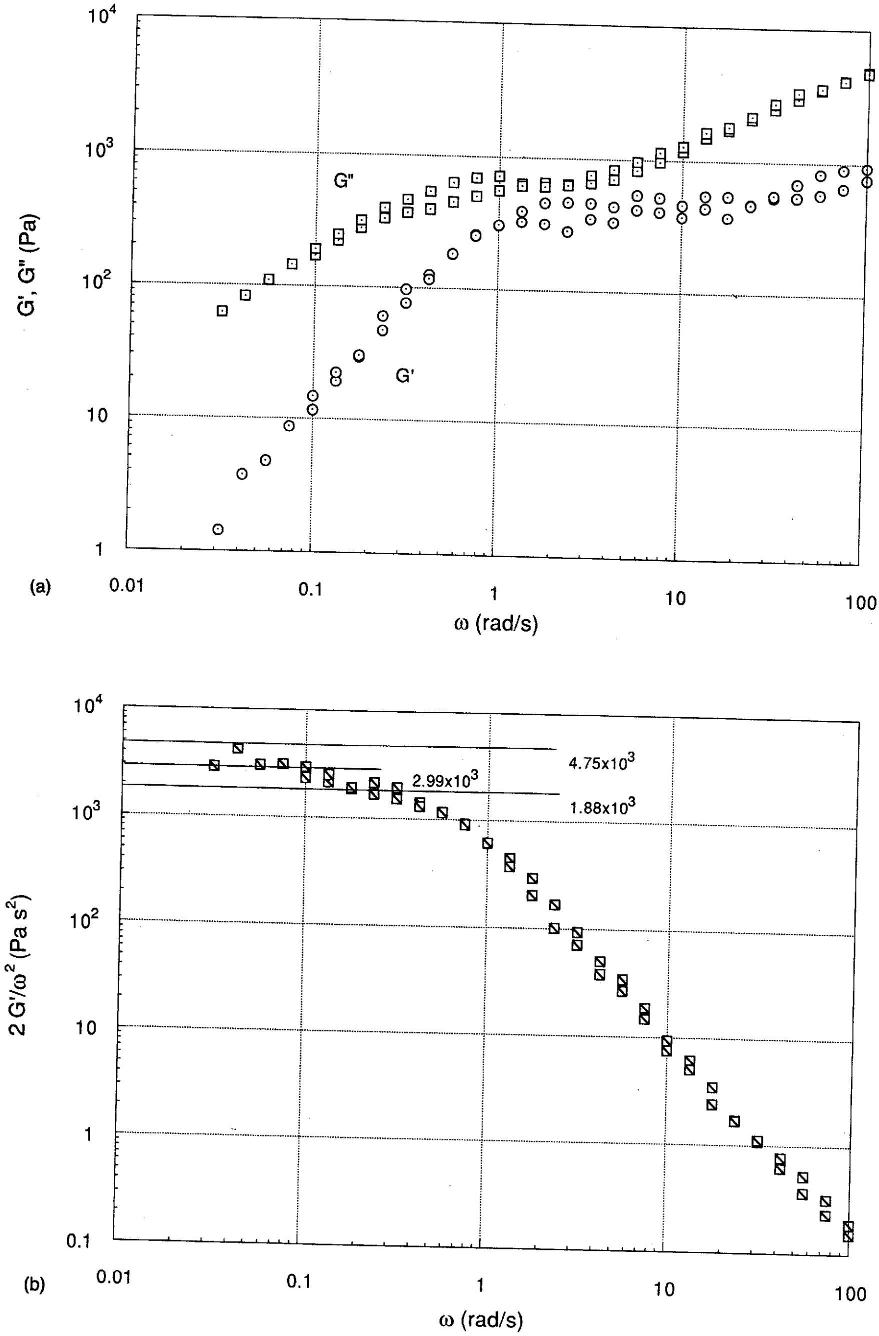
Figures 6, 7, and 8 show the results of dynamic measurements for Lakeview at 30 °C, which we obtained with a Rheometrics System Four with a cone-and-plate device and for Zuata and CND at 25 °C, which we obtained on the Rheometrics RMS-800 and the Rheometrics Fluid Spectrometer with cone-and-plate or parallel-plate fixtures. The data in Fig. 6, 7, and 8 along with the climbing constant (interpolated to the proper temperature), allow us to calculate values for the second normal stress coefficient by using Eq. (8) and the second-order correction to Trouton's viscosity by using Eq. (17). These values are shown in Table V.

Table V can be compared with Table IV. Both tables use the measured values of the climbing constant but in Table V, Ψ_{10} is a measured value from dynamic measurements rather than an assumed value from $\Psi_{20}/\Psi_{10} = -\frac{1}{10}$. The limiting or plateau values used in Table V are taken from Figs. 6(b), 7(b), and 8(b). These are guessed values which may be low. There is only a rather limited form of agreement between Tables IV and V.

XI. DISCUSSION AND SUMMARY

The constitutive equation of all simple fluids in slow, and slowly varying flows are fixed once and for all by the values of three constants: the zero shear viscosity η_0, the first normal stress coefficient Ψ_{10}, and the second normal stress coefficient Ψ_{20}. This second-order rheology applies on the zero shear plateau of the first and second normal stress coefficient and on the zero ω plateau of $2G'(\omega)/\omega^2$. The extent of the plateau depends on the function plotted and not on the shear rate. The measurement of Ψ_{10} is difficult and Ψ_{20} is more difficult. Many different methods of measurement have been proposed, and we have considered the ones based on backward extrapolation, $N_1/\dot{\gamma}^2 \rightarrow \Psi_{10}$, $2G'(\omega)/\omega^2 \rightarrow \Psi_{10}$, and $N_2/N_1 \rightarrow \Psi_{20}/\Psi_{10}$, and the climbing constant $\hat{\beta} = \Psi_{10}/2+2\Psi_{20}$. It appears that the measurement of $\hat{\beta}$ is most sensitive in the sense that for many fluids (but not all) the existence of a second-order plateau in which the height rise is linear in ω^2 is evident. Given $\hat{\beta}$, we can get Ψ_{10} and Ψ_{20} from any one of the three other measurements. It is believed that $|\Psi_{20}/\Psi_{10}| \leqslant 0.1$ in most fluids. We

(a)



(b)

FIG. 6. Dynamic tests results for Lakeview at 30 °C experiments done in the Rheometrics System Four. We estimate that $1.88\times10^3 < 2G'/\omega^2 < 4.75\times10^3$ [indicated in (b) by long lines] and a logarithmic median value of 2.99×10^3 [indicated in (b) by short lines]. (a) G'(⊙) and G''(⊡) as function of frequency. (b) Limiting value for $2G'/\omega^2$ (⧅).

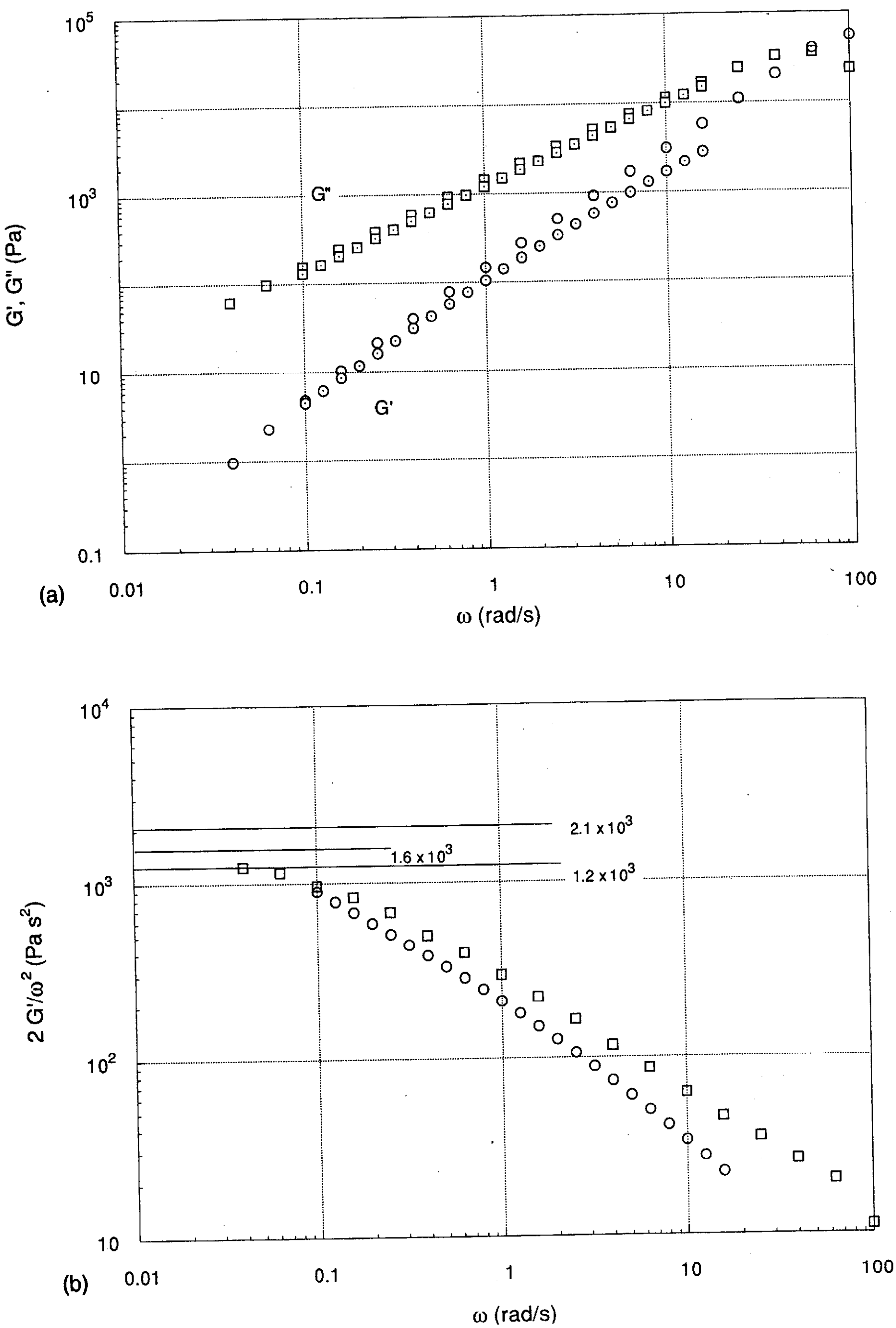


FIG. 7. Dynamic tests results for CND at 25 °C experiments done on the Rheometric RMS-800 (June, 1993) and Rheometric RFS-II (March, 1994). We estimate that $1.2\times10^3 < 2G'/\omega^2 < 2.1\times10^3$ [indicated in (b) by long lines] and a logarithmic median value of 1.6×10^3 [indicated in (b) by short lines]. (a) G' and G'' as function of frequency. ○ and □—RMS-800; ⊙ and ⊡—RFS-II. (b) Limiting value for $2G'/\omega^2$. ○—RMS-800; □—RFS-II.

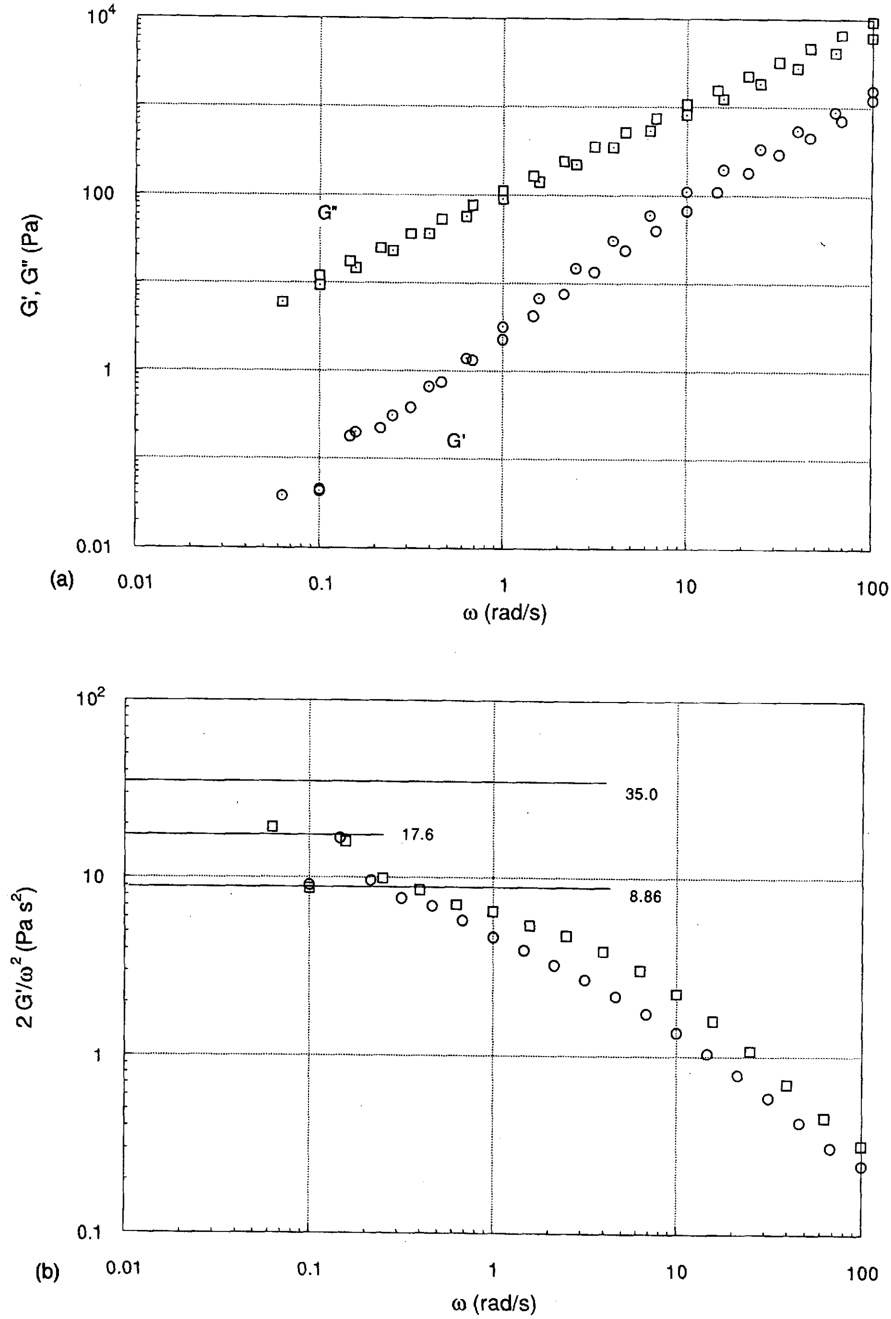


FIG. 8. Dynamic tests results for Zuata at 25 °C experiments done on the Rheometrics RFS-II. We estimate that $8.86 < 2G'/\omega^2 < 35.0$ [indicated in (b) by long lines] and a logarithmic median value of 17.6 [indicated in (b) by short lines]. (a) G' and G'' as function of frequency. ○ and □—06/93 data; ⊙ and ⊡—03/94 data. (b) Limiting value for $2G'/\omega^2$. ○—06/93 data; □—03/94 data.

TABLE V. Second normal stress coefficient and second-order correction of Trouton's viscosity calculated from the climbing constant and dynamic measurements.

Sample	$\hat{\beta}$ (kg/m)[a]	$\Psi_{10} = \lim_{\infty \to 0} \frac{2G'(\omega)}{\omega^2}$ (Pa s^2)[a]	Ψ_{20}(Pa s^2)	Ψ_{20}/Ψ_{10}	Extensional viscosity η_E, (Pa s)—from Eq. (17)
Lakeview	220	3.0×10^3	-640	-0.21	$4300+2600\dot{\epsilon}$
(30 °C)	(0.2–1.75 s^{-1})	(0.03–0.07 s^{-1})			
CND	170	1.6×10^3	-317.5	-0.20	$3900+1500\dot{\epsilon}$
(25 °C)	(0.1–0.09 s^{-1})	(0.1–0.4 s^{-1})			
Zuata	5.4	18	-1.7	-0.10	$350+21\dot{\epsilon}$
(25 °C)	(0.2–1.4 s^{-1})	(0.1–0.4 s^{-1})			

[a]Also displayed is the corresponding shear rate range in which the normal stress parameters were measured.

examined the literature and found that in every case, the backward extrapolation of $2G'(\omega)/\omega^2$ was larger than the backward extrapolation of $N_1/\dot{\gamma}^2$, perhaps ten times larger in some cases. The cause of this discrepancy is not known. The values of Ψ_{10} and Ψ_{20} obtained from the climbing constant and backward extrapolation of $N_1/\dot{\gamma}^2$ give rise to the expected values of $|\Psi_{20}/\Psi_{10}|$ while the climbing constant and backward extrapolation of $2G'(\omega)/\omega^2$ may give rise to larger values closer to 0.2 than to 0.1.

We have characterized the normal and extensional stresses of three heavy crude oils at low rates of shear using the rotating rod rheometer and dynamic measurement. All these crudes exhibit normal stress effects, with small but measurable effects for CND and Zuata crude oils and much larger effects for the Lakeview crude. Normal stresses could not be reliably measured at any rate of shear in CND and Zuata with the Rheometrics RFS-II rheometer or at low rates of shear in the Lakeview crude with the Rheometrics System Four rheometer. We obtained estimates of the values of the first and second normal stress coefficients for our three oils using rod climbing and dynamic measurements (Table V). These values may not be compatible with the backward extrapolation of thrust data, even if we could find transducers sensitive enough to carry out thrust measurements in the regions of low thrust that we encountered in the experiments reported here.

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