

Climbing Constants for Various Liquids

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Synopsis

In this article we present tables of values of the climbing constant $\hat{\beta} = 3\alpha_1 + 2\alpha_2$, where α_1 and α_2 are the parameters of the second-order approximation to the stress in a slow, slowly varying flow of any simple non-Newtonian fluid. The parameter $\hat{\beta}$ arises in the analysis of rod climbing, and it is proportional to the height of climb in slow steady flow. A method is presented for computing the first normal stress difference and the extensional viscosity at low rates of deformation, using $\hat{\beta}$ alone. This method is useful for all fluids whose unknown second normal stress is nonpositive at low rates of shearing.

INTRODUCTION

It is well known that many non-Newtonian fluids will climb a rotating rod whereas Newtonian fluids will not climb. The climb is associated with nonlinear effects, normal stresses, which cannot occur in fluids like Newtonian fluids, in which the stress is linearly related to the gradient of velocity. The climbing property of non-Newtonian fluids can be used to characterize important rheological parameters in those fluids. The most important of these is the climbing constant $\hat{\beta}$. This constant appears in some perturbation studies of Kaye,¹ Böhme,² and Joseph and Fosdick.³ Joseph, Beavers, and Fosdick⁴ showed that it is necessary to include surface tension effects if $\hat{\beta}$ is to be computed from measured values of the climb. Values of $\hat{\beta}$ for some liquids were given by Joseph, Beavers, and co-workers.⁵⁻¹⁰ In this article we describe an improved apparatus, tabulate all the previous values obtained for $\hat{\beta}$, give new tables of $\hat{\beta}$

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for a variety of polymer solutions, and show how to use the measurements to find the first normal stress difference at low rates of shear and the extensional viscosity at low rates of stretching.

RHEOLOGICAL PARAMETERS FOR SIMPLE NON-NEWTONIAN LIQUIDS IN SLOW, SLOWLY VARYING MOTIONS

The stress \mathbf{T} in an incompressible simple fluid can be expressed as

$$\mathbf{T} = p\mathbf{1} + \mathbf{S}, \quad (1)$$

where the extra stress is determined as a functional of the history of the relative Cauchy strain. The isotropic part of the stress has no constitutive equation; it is determined by dynamics as one of the unknown fields governed by the equations of motion. Most liquids which are isotropic in the rest state fit in this framework. Many models for the constitutive equation relating \mathbf{S} to deformation have been proposed. Whatever may be the choice for a constitutive equation it may be approximated by expressions of the form

$$\mathbf{S}_{(N)} \stackrel{\text{def}}{=} \mathbf{S}_1[\mathbf{U}] + \mathbf{S}_2[\mathbf{U}] + \cdots + \mathbf{S}_n[\mathbf{U}], \quad (2)$$

with an error of $O(\|\mathbf{U}\|^{n+1})$, where $\mathbf{U}(\mathbf{x}, t)$ is the velocity of a slow, slowly varying motion

$$\mathbf{U}(\mathbf{x}, t) = \epsilon \mathbf{v}(\mathbf{x}, \tau, \epsilon), \quad t = \epsilon \tau, \quad (3)$$

and ϵ is a small parameter measuring slowness usually associated with prescribed data,

$$\|\mathbf{v}(\mathbf{x}, \tau, 0)\| < \infty \quad (4)$$

and t is a slow time. Moreover,

$$\mathbf{S}_{(N)} = \epsilon \mathbf{S}_1[\mathbf{v}] + \epsilon^2 \mathbf{S}_2[\mathbf{v}] + \cdots + \epsilon^n \mathbf{S}_n[\mathbf{v}]. \quad (5)$$

For slow, steady motions, \mathbf{S}_n is homogeneous of degree n in \mathbf{U} . Slow, slowly varying motions are equivalent to those which Coleman and Noll¹¹ call retarded.

The expansions (2) were introduced by Coleman and Noll¹¹ and they were justified in the context of their theory of fading memory. These expansions are robust in the sense that they carry over to more general theories,¹² which contain most of the constitutive equations presently used by rheologists. The form which such expansions

must take is strongly suggested in the (1956) theory of Rivlin and Ericksen.¹³ We are interested in the stress $S_{(2)}$ of grade two where

$$\begin{aligned} S_1 &= \mu A_1[U], \\ S_2 &= \alpha_1 A_2[U] + \alpha_2 A_1^2[U], \end{aligned} \quad (6)$$

μ is the zero shear viscosity, α_1 and α_2 are constants, called parameters of $S_{(2)}$,

$$A_1[U] = \nabla U + \nabla U^T,$$

and

$$A_2[U] = \frac{\partial A_1}{\partial t} + (U \cdot \nabla)A_1 + A_1 \cdot \nabla U + \nabla U^T \cdot A_1.$$

The stress $S = f(A_1)$ in a nonlinear viscous fluid may be represented, without loss of generality, in the form

$$S = \phi_1(\text{II, III})A_1 + \phi_2(\text{II, III})A_1^2, \quad (7)$$

where ϕ_1 and ϕ_2 are functions of the second and third invariants of A_1 . The expression (7) is called a Reiner–Rivlin fluid. It is not presently used in rheology because it has a zero first normal stress in shear flow. On the other hand, every constitutive equation can be represented by Eq. (7) in motions which are purely extensional since the history of such motions can be expressed in terms of A_1 alone. $S_{(2)}$ is also of the form (7) because in pure extension $A_2 = A_1^2$.

The stress $S_{(2)}$ has been widely used in rheological studies because it is one of the simpler nonlinear constitutive equations and, in fact, is the form which is taken by every constitutive equation when the motion is slow and slowly varying. However, apart from the measurements which we have collected here, there are no other tables giving these physical constants.

FIRST AND SECOND NORMAL STRESS DIFFERENCES AND EXTENSIONAL VISCOSITY FOR SLOW, SLOWLY VARYING MOTIONS

We first evaluate the first and second normal stress differences in simple shear, using $S_{(2)}$. The velocity gradient is given as

$$[\nabla U] = \begin{bmatrix} 0 & \kappa & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (8)$$

in the basis ($\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$) where \mathbf{e}_1 defines the direction of motion and ($\mathbf{e}_1, \mathbf{e}_2$) define the plane of motion and κ is the rate of shear. We find

$$T_{12} = \kappa\mu, \quad (9)$$

$$T_{11} - T_{22} = N_1 = -2\alpha_1\kappa^2, \quad (10)$$

$$T_{22} - T_{33} = N_2 = (2\alpha_1 + \alpha_2)\kappa^2. \quad (11)$$

The motion known as simple extension in the direction \mathbf{e}_1 is given by

$$[\mathbf{A}_1] = \begin{bmatrix} 2\dot{s} & 0 & 0 \\ 0 & -\dot{s} & 0 \\ 0 & 0 & -\dot{s} \end{bmatrix},$$

$$[\mathbf{A}_1^2] = \begin{bmatrix} 4\dot{s}^2 & 0 & 0 \\ 0 & \dot{s}^2 & 0 \\ 0 & 0 & \dot{s}^2 \end{bmatrix},$$

$$\mathbf{A}_2 = \mathbf{A}_1^2, \quad (12)$$

where \dot{s} is the rate of stretching, $dU_1/dx_1 = 2\dot{s}$. The stress differences in extension

$$T_{11} - T_{22} = T_{11} - T_{33} = S_{11} - S_{22} = S_{11} - S_{33}$$

are evaluated on $\mathbf{S}_{(2)} = \mu\mathbf{A}_1 + (\alpha_1 + \alpha_2)\mathbf{A}_1^2$ as

$$T_{11} - T_{22} = 3[\dot{s}\mu + (\alpha_1 + \alpha_2)\dot{s}^2]. \quad (13)$$

For fluids which climb, α_2 is frequently positive and large. For these fluids the effects of nonlinearity on stretching can be very large. The "extensional viscosity" for $\mathbf{S}_{(2)}$ is $3\mu + 3(\alpha_1 + \alpha_2)\dot{s}$.

The rheometers used to measure $N_1(\kappa)$ are nearly useless when κ is very small (less than about 0.1 s^{-1})* and they do not give accurate values of $N_2(\kappa)$ for small or even large values of κ . The graphs of $N_1(\kappa)$ which are common in the rheological literature usually have blank places where κ is small. The values of $N_1(\kappa)$ for small κ are determined by Eq. (10) when α_1 is known. It is well known that $\alpha_1 < 0$ in polymeric liquids, and there are theoretical reasons for this (see refs. 12 and 14). It is generally believed that $N_2(\kappa) < 0$. The experimental method leading to measured values of $N_2 < 0$ in some fluids involves the measurement of the bulge of a free surface on the top of a liquid falling down a tilted trough.¹⁵⁻¹⁷

*For example, the normal stress data given in this article were obtained using a Rheometrics System Four rheometer, which did not give accurate data for shear rates below $0.1\text{--}10 \text{ s}^{-1}$, depending on the fluid.

Weissenberg conjectured that $N_2(\kappa) = 0$, a conjecture that is realized in some old molecular models. The climbing constant is

$$\hat{\beta} = 3\alpha_1 + 2\alpha_2 > 0. \quad (14)$$

Let

$$n_2 = \lim_{\kappa \rightarrow 0} \frac{N_2(\kappa)}{\kappa^2} = 2\alpha_1 + \alpha_2. \quad (15)$$

Since $\alpha_1 < 0$ we have $\alpha_2 > 0$, and if $n_2 < 0$, then $\alpha_2 < -2\alpha_1$. The parameters α_1 and α_2 of $\mathbf{S}_{(2)}$ are therefore determined by n_2 and $\hat{\beta}$ as

$$\begin{aligned} \alpha_1 &= 2n_2 - \hat{\beta}, \\ \alpha_2 &= 2\hat{\beta} - 3n_2. \end{aligned} \quad (16)$$

If we suppose that a fluid climbs up a rod ($\hat{\beta} > 0$) and bulges out when falling down a trough ($n_2 < 0$), we may conclude that there is a number k , $1 \leq k \leq 4/3$, such that

$$2\alpha_1 + k\alpha_2 = 0. \quad (17)$$

It is even more useful to put

$$\lim_{\kappa \rightarrow 0} (-N_2/N_1) = 1/m,$$

where m is a real number which is larger than one in liquids for which N_2 and N_1 are known. Then

$$k = \frac{m}{m-1}$$

and

$$n_2 = -\frac{2}{m-4}\hat{\beta}.$$

Thus, for $\hat{\beta} > 0$ and $n_2 < 0$, we have $m > 4$. Also,

$$\alpha_1 = -\left(\frac{m}{m-4}\right)\hat{\beta}$$

and

$$\alpha_2 = \frac{2(m-1)}{m-4}\hat{\beta}. \quad (18)$$

For many polymeric liquids, m is about 10. In this case

$$\alpha_1 = -(5/3)\hat{\beta}$$

and

$$\alpha_2 = 3\hat{\beta}.$$

The values of α_1 and α_2 computed in this way are probably more accurate than the ones which one might try to compute by extrapolation of the data using conventional rheometers (cf. Table VII). If it were possible to obtain an accurate limiting value for the first normal stress coefficient, then this and the climbing constant would suffice to determine α_1 and α_2 and the limiting value of the second normal stress coefficient. Unfortunately, existing rheometers seem not to give accurate limiting values for the first normal stress coefficient.

THE CLIMBING CONSTANT

Joseph and Fosdick³ studied rod climbing by a perturbation method in which the perturbation parameter is the speed of the rod. They found that the shape of the free surface can be expressed in the form

$$Z = h(r, \Omega) = h_0(r) + h_2(r)\Omega^2 + O(|\Omega^4|), \quad (19)$$

where Ω is the angular frequency of the rod and $h_0(r)$ is the static climb. They found that when surface tension is neglected

$$h_2(r) = \frac{1}{\rho g} \left(\frac{2a^4}{r^4} \hat{\beta} - \frac{\rho a^4}{2r^2} \right), \quad (20)$$

where a is the radius of the rotating rod, ρ is the density of the liquid, and g is gravity.

Equations (19) and (20) suggest that climbing is not possible when Ω is small and

$$r^2 > 4\hat{\beta}/\rho. \quad (21)$$

The fluid inside the critical radius $r = 2(\hat{\beta}/\rho)^{1/2}$ climbs, the fluid outside sinks as in a Newtonian fluid. This implies that it is not possible to get climbing on a rod whose radius is greater than the critical one.

Equation (20) could be used to compute $\hat{\beta}$ from measurements of $h(r, \Omega)$ for small Ω . Joseph, Beavers, and Fosdick⁴ showed that to get the shapes of $h(r, \Omega)$ to agree with measured ones, it is necessary to retain the effects of surface tension. In this case the height rise function $h_2(r)$ is governed by the following problem:

$$\frac{T}{r}(rh_2)' - \rho gh_2 = -\frac{2a^4}{r^4}\hat{\beta} + \frac{\rho a^4}{2r^2}, \quad (22)$$

$$h_2(a) = 0, \quad h_2(r) \rightarrow 0 \text{ as } r \rightarrow \infty,$$

where T is the surface tension. A very accurate approximate solution of Eq. (22) was derived by Joseph, Beavers, and Fosdick.⁴ When evaluated at the rod this solution gives

$$h_2(a) \sim \frac{a}{2T\sqrt{S}} \left(\frac{4\hat{\beta}}{4+\lambda} - \frac{\rho a^2}{2+\lambda} \right), \quad (23)$$

where $\lambda^2 = a^2 S$ and $S = \rho g/T$. Joseph, Beavers, and Fosdick⁴ and Beavers and Joseph⁵ showed that computations based on (22) and (23) were in very good agreement with experiments with polymeric oils.

Beavers and Joseph⁵ proposed (22) and (23) as a basis for a rotating rod viscometer. A possible defect of this kind of rheometer is that it requires values for the surface tension. Fortunately, the values of T which have been measured in the different liquids used in experiments reported here are nearly the same. The value computed for $\hat{\beta}$ from the graph of the measured height of climb at the rod is not strongly affected by small changes in surface tension as the following argument shows.

Under the conditions of most of the experimental observations reported here, the second term on the right of (23) is small compared with the first. Then

$$\hat{\beta} \sim \frac{2T\sqrt{S}h_2(a)}{a} \left(\frac{4+\lambda}{4} \right).$$

Thus, for fixed values of $h_2(a)$, a , and ρ , we have

$$\frac{d\hat{\beta}}{\hat{\beta}} \sim \left(\frac{2}{4+\lambda} \right) \frac{dT}{T}. \quad (24)$$

For the operating conditions of most of our experiments ($a \sim 0.3$ cm, $\rho \sim 1$ g/cm³, $T \sim 30$ dyn/cm), expression (24) gives

$$\frac{d\hat{\beta}}{\hat{\beta}} \sim 0.35 \frac{dT}{T}.$$

So an error in the value of T of 1% leads to an error in the computed value for $\hat{\beta}$ of about 0.35%.

EXPERIMENTS

Apparatus

The apparatus used to obtain all the new data reported here was an updated version of the rotating rod viscometer described in ref. 5. The new viscometer consists of a rod inserted vertically into a jar of the test fluid. The rod is driven from above by an Electrocraft dc servomotor with a feedback control system to maintain constant speed under varying torque conditions. The apparatus can accommodate rods of any diameter up to approximately 0.7 cm. This limitation is imposed by the diameter of the fluid container (6.52 cm) with the requirement that the ratio of the container diameter to the rod diameter be greater than about 10 for the infinite fluid approximation to be valid.

Each rod is made of steel with a hardened conical tip at the lower end. The conical tip rests lightly in a small conical indentation in the center of the container bottom, which thus serves as an alignment bearing for the rod. The fluid containers are glass jars (50-cm³ capacity), which also serve as storage vessels for the liquids.

The angular speed of the rod is measured by means of a Kaman proximity pickup and a toothed wheel with 100 indentations mounted on the motor drive shaft. The output of the pickup is registered on a digital counter, allowing the angular speed to be measured to within 0.002 revolutions per second.

The height of climb of the fluid is measured at the contact line on the rod with a microscope mounted on a vertical vernier scale. Measurements are repeatable to within 0.005 cm.

The rod and fluid container are enclosed in a Plexiglas chamber with an adjoining storage area that houses fluids to be tested. The motor and all other auxiliary equipment are outside the chamber. The motor drive shaft couples with the rod through a small hole in the top of the chamber. The rod and the climbing fluid are viewed through a small slit in the front of the chamber.

A closed-loop forced air heating system is used to maintain a predetermined temperature in the chamber. The system consists of a heating element and a blower that are controlled by a Partlow Solid State Controller with the temperature-sensing probe set at 2 cm above the surface of the fluid being tested. This system can maintain the chamber temperature to within $\pm 0.2^{\circ}\text{C}$.

Calculation of $\hat{\beta}$

The value of $\hat{\beta}$ is determined from the measured values of the height of climb on the rod. The rod is rotated slowly, at a speed for which a measurable height of climb can just be distinguished. The climb is measured as a function of increasing rotational speed, and the slope of the plot of $h(r, \Omega)_{r=a}$ vs. Ω^2 is computed for $\Omega \rightarrow 0$. From (19)

$$h_2(a) = \left. \frac{dh(r, \Omega)}{d\Omega^2} \right|_{r=a} \Omega \rightarrow 0,$$

and the measured value of the slope is used with (23) to determine $\hat{\beta}$.

Results

The values of the climbing constants for all our test liquids are presented in Tables I(a)–VI(b) and in Figures 1–4. We also include in Figures 5–7 the shear rate dependence of the shear viscosity and the first normal stress difference for a selection of the test liquids. The data of Figures 5–7 were obtained using a Rheometrics System Four rheometer.

Table I(a) gives $\hat{\beta}$ for solutions of acryloid K-125 in Dowanol over a concentration range of 3.5–7.5% by weight. Acryloid K-125 is a terpolymer consisting of 82 mol % methyl methacrylate, 12 mol % ethyl acrylate, and 6 mol % butyl acrylate. Dowanol is the trade name for the solvent dipropylene glycol methyl ether. Measurements were made on these solutions immediately after they had been prepared, and after they had been held in storage for one year. For the latter measurements the same rod was used as in the former measurements, and then the experiments were repeated using a rod of smaller diameter. The values in Table I(a) are plotted in Figure 1(a). There seems to be little evidence of a change in $\hat{\beta}$ after one year in storage except at the higher concentrations where a decrease in $\hat{\beta}$ of about 35% is observed.

The shear viscosity and first normal stress difference for these solutions, measured one year after mixing, are presented in Figures 5(a) and 5(b) respectively. The shear rate dependence of these functions is typical of polymer solutions. There is some scatter in the first normal stress difference for shear rates below about 10 s^{-1} ,

TABLE I(a)
Acryloid K-125 (PMMA) in Dowanol (30°C)

Concentration (% by wt)	Surface Tension (dyn/cm)	$\hat{\beta}$ (g/cm)		
		New Solution $a = 0.304$ cm	After one year	
			$a = 0.304$ cm	$a = 0.156$ cm
3.5		0		
4.0	28.6	0.10		
4.5	28.6	0.13	0.24	0.23
5.0	28.9	0.76	0.66	0.69
5.5	28.5	1.71	1.66	1.60
6.0	28.5	6.17	4.29	4.82
6.5	29.5	14.7	14.3	13.5
7.0	30.0	36.2	20.9	23.5
7.5	29.9	135	80.0	108

TABLE I(b)
PMMA in DEM

Concentration (% by wt)	Surface Tension (dyn/cm)	$\hat{\beta}$ (g/cm)	
		$T = 21^\circ\text{C}$	$T = 30^\circ\text{C}$
0.5	~30.2	0.9	
1.0	~30.2	4.4	
1.5	~30.2	8.4	0.23
2.1	~30.2	50.2	4.09

TABLE I(c)

Solution	Surface Tension (dyn/cm)	Temperature (°C)	$\hat{\beta}$ (g/cm)
9.8% Elvacite in DEM	~30	21	8.32
5.2% Copolymer in DEM	~30	21	8.06

which was the lower limit of the shear rate range of the Rheometrics rheometer for this group of PMMA solutions. At a fixed shear rate the viscosity and the first normal stress differences increase monotonically with increasing concentration.

TABLE II(a)
PIBMA (Lot 28)* in Dowanol (30°C)

Concentration (% by wt)	Surface Tension (dyn/cm)	$\hat{\beta}$ (g/cm)
1.0	29.2	0.058
1.5	28.8	0.77
2.0	29.2	2.85
2.15	28.9	3.11
2.35	29.0	4.39
2.50	29.1	5.42
2.75	29.3	11.8
3.0	29.7	30.2
3.5	30.4	50.3
4.0	32.9	86.7

*Molecular weight $> 16.0 \times 10^6$, but exact value uncertain.

TABLE II(b)
PIBMA (Lot 23)* in Dowanol (30°C)

Concentration (% by wt)	Surface Tension (dyn/cm)	$\hat{\beta}$ (g/cm)
9.0	28.7	0.060
10.0	29.3	0.131
11.0	28.7	0.276
12.0	29.5	1.02
14.0	29.2	1.97

*Molecular weight = 1.66×10^6 .

TABLE III
Vistanex (PIB) in Decalin (30°C)

Concentration (% by wt)	L100 Mol. Wt. = $(1.04-1.44) \times 10^6$		L140 Mol. Wt. = $(1.88-2.3) \times 10^6$	
	Surface Tension (dyn/cm)	$\hat{\beta}$ (g/cm)	Surface Tension (dyn/cm)	$\hat{\beta}$ (g/cm)
5.5	31.2	11.4		
6.0	31.5	16.3	32.4	105
6.5	32.4	19.5	33.4	203
7.0	33.4	36.3	35.3	436
7.5	34.4	39.9	36.2	830
8.0	34.4	52.2	39.2	1773
8.5	34.4	81.2		

TABLE IV
 Separan AP30 (PAA) in Distilled Water (30°C)

Concentration (% by wt)	Surface Tension (dyn/cm)	$\hat{\beta}$ (g/cm)
0.5	48.0	9.55
0.8	46.4	15.6

TABLE V
 Silicone Oils (21°C)

Shear Viscosity (poise)	$\hat{\beta}$ (g/cm)
120	0
950	2.85

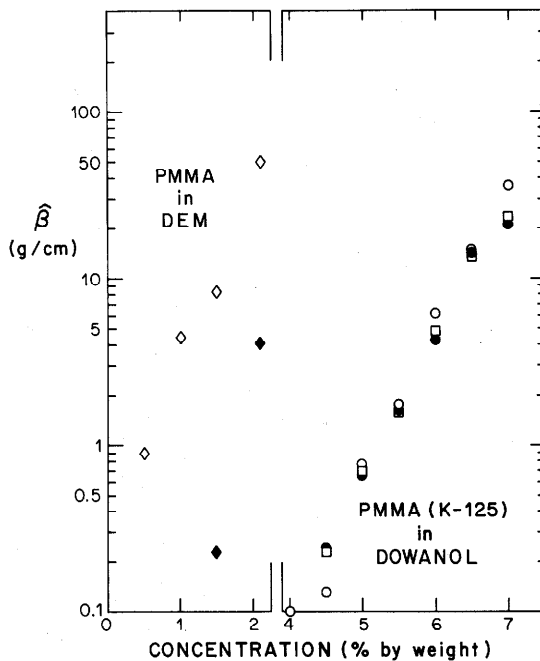


Fig. 1. The climbing constant for PMMA in (a) DEM and (b) Dowanol as a function of concentration. (a) (\diamond) 21°C, (\blacklozenge) 30°C, $a = 0.304$ cm; (b) (\circ) new solution, $a = 0.304$ cm; (\bullet) same solution one year after mixing, $a = 0.304$ cm; (\square) same solution one year after mixing, $a = 0.156$ cm; all measurements at 30°C.

TABLE VI(a)

Temperature (°C)	$\hat{\beta}$ (g/cm) ^b
<i>STP (sample 1)^a</i>	
25.0	1.23
25.3	1.06
25.6	1.07
25.6	1.11
25.6	1.01
25.6	1.04
25.6	1.04
25.8	1.00
25.9	0.96
26.0	1.02
26.0	0.95
26.4	0.93
26.8	0.97
27.9	0.86
28.9	0.75
28.9	0.66
29.2	0.65
31.3	0.55
32.8	0.46
33.1	0.42
36.1	0.33
36.1	0.23
36.3	0.34
39.3	0.20
41.8	0.24
47.2	0.093
23.0	1.42 ^c
<i>STP (sample 2)^d</i>	
23.5	1.07 ^e
27.8	0.78 ^e
27.8	0.83 ^e
28.2	0.65 ^e
<i>STP (sample 3)^f</i>	
21.9	0.89 ^g
21.0	0.9 ^h
26.0	0.5 ^h

^aSurface tension = 30.9 dyn/cm.

^bReference 5 unless indicated otherwise.

^cReference 7.

^dSurface tension = 31 dyn/cm.

^eReference 6.

^fSurface tension = 30.7 dyn/cm.

^gReference 7.

^hReference 8.

TABLE VI(b)

Fluid	Temperature (°C)	$\hat{\beta}$ (g/cm)
TLA-227	22.2	23.5 ^a
TLA-227	23.0	29.0 ^b
TLA-227	26.7	18.0 ^c
TLA-227	26.7	17.9 ^d
Paratone	26.7	15.1 ^c

^aReference 7.

^bReference 8.

^cReference 9.

^dReference 10.

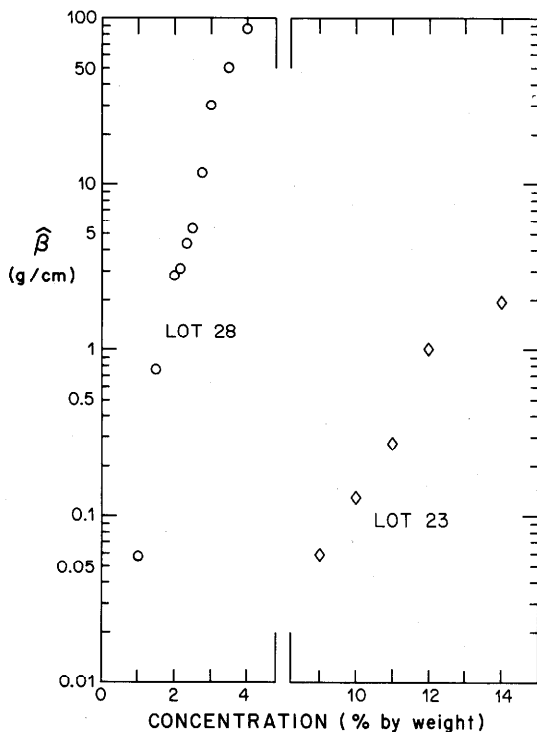


Fig. 2. The climbing constant for two samples of PIBMA in Dowanol as a function of concentration at 30°C: (a) lot 28, mol. wt. $> 16.0 \times 10^6$, (b) lot 23, mol. wt. = 1.66×10^6 .

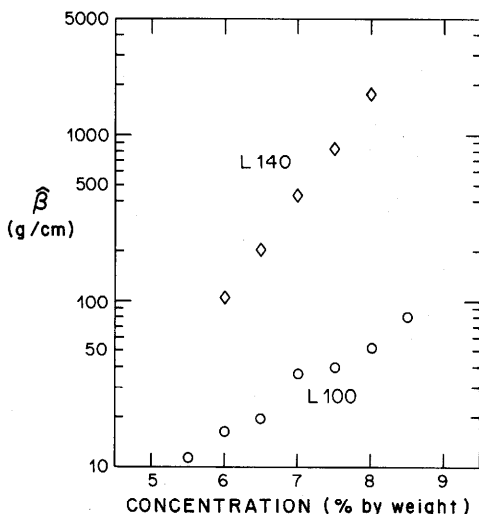


Fig. 3. The climbing constant for two samples of Vistanex (PIB) in Decalin at 30°C: (a) Vistanex L-140, mol. wt. = $(1.88-2.3) \times 10^6$, (b) Vistanex L-100, mol. wt. = $(1.04-1.44) \times 10^6$.

Table I(b) presents $\hat{\beta}$ values for four concentrations of PMMA in DEM. These data are also plotted on Figure 1.

Acryloid K-125 is also soluble in chloroform, and we attempted to measure values for $\hat{\beta}$ and N_1 for various concentrations. Unfortunately, the evaporation rate was very high, even when the rotating rod and the cone and plate were enclosed in a chloroform-saturated environment, so that we were unable to generate reliable data.

Tables II(a) and II(b) and Figure 2 give results for several concentrations of two different molecular weight samples of PIMBA in Dowanol. There is a large increase in the climbing constant with increase in molecular weight. This is also apparent from Table III and Figure 3 which give results for two different molecular weight samples of Vistanex (PIB) in decalin.

The shear rate dependence of the viscosity and the first normal stress difference for both samples of Vistanex are given in Figures 6(a), 6(b), 7(a), and 7(b). As in Figures 5(a) and 5(b), there is a monotonically increasing dependence upon concentration at a fixed shear rate.

Tables IV and V give $\hat{\beta}$ values for two concentrations of Separan AP30 in distilled water and for two high-viscosity silicone oils.

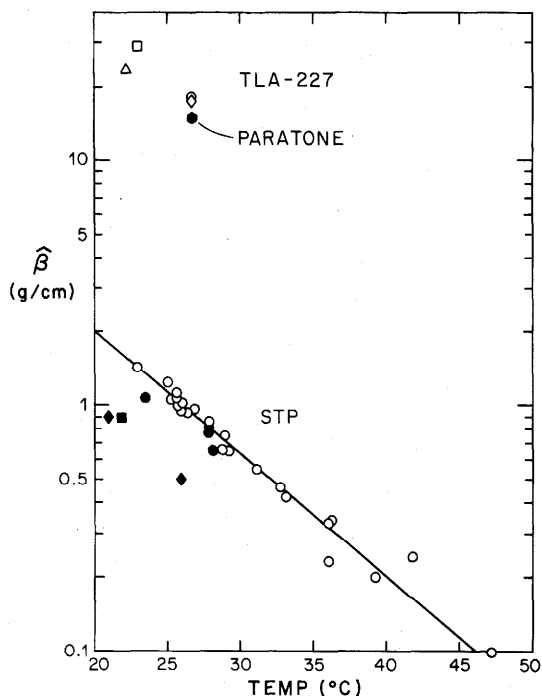
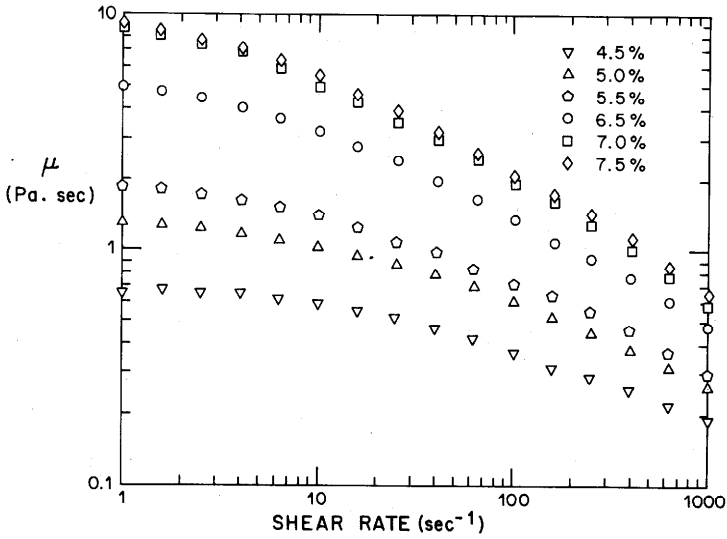


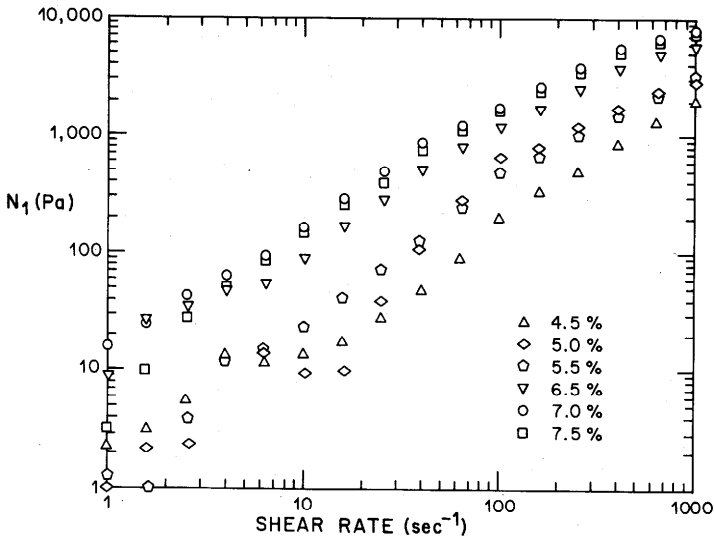
Fig. 4. The climbing constants of some commercial polymeric oils. (a) TLA-227 (methacrylate copolymer in oil); all observations from the same batch: (Δ) ref. 7; (\square) ref. 8; (\circ) ref. 9; (\diamond) ref. 10. (b) Paratone (olefin polymer in oil) ref. 9. (c) STP (PIB in petroleum oil); three different production batches: (\circ) sample 1 (ref. 5); (\bullet) sample 2 (ref. 6); (\blacksquare) sample 3 (ref. 7); (\blacklozenge) sample 3 (ref. 7). The straight line is the empirical result $\hat{\beta} = 20 \exp(-0.115/T)$ g/cm (ref. 5).

Tables VI(a) and VI(b) and Figure 4 bring together the results we have obtained in several earlier projects using various commercially available polymeric oil additives. More details about these liquids are given in the references listed in Tables VI(a), VI(b), and Figure 4. The data of Figures 1 and 4 emphasize the strong dependence of the climbing constant on temperature. Also, the considerable variation in $\hat{\beta}$ for STP from one batch to another is worth noting.

Finally, in Table VII we have attempted to compare values computed for $\lim_{\kappa \rightarrow 0} (N_1/\kappa^2)$ using measured values of $\hat{\beta}$ and various assumed values for the ratio m of the normal stress differences with measured values of N_1/κ^2 obtained from the Rheometrics rheometer.

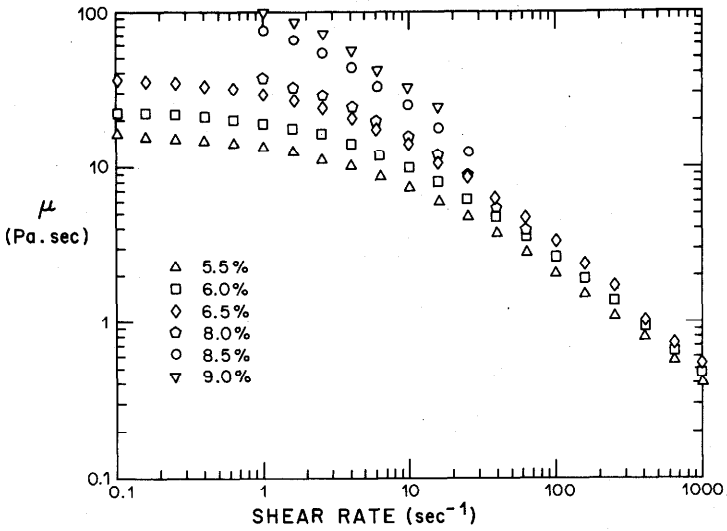


(a)

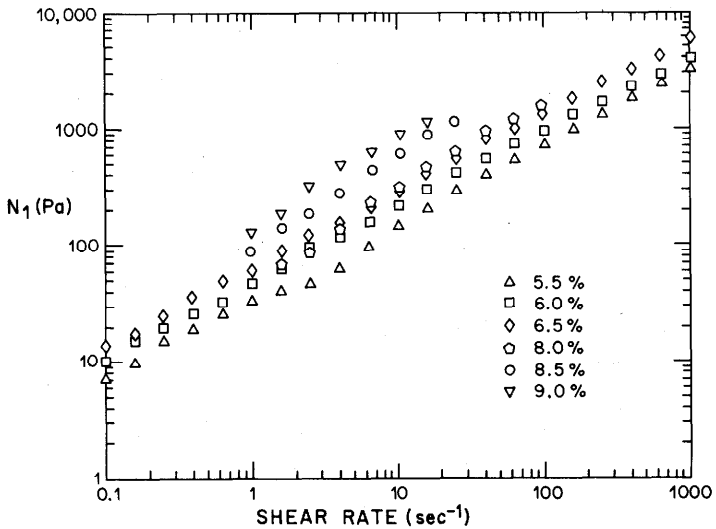


(b)

Fig. 5. (a) Viscosity versus shear rate for Acryloid K-125 (PMMA) in Dowanol. (b) First normal stress difference versus shear rate for Acryloid K-125 (PMMA) in Dowanol.

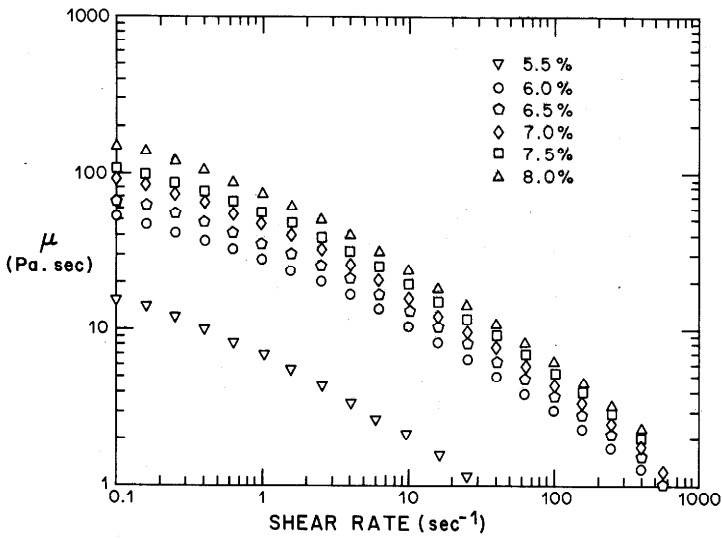


(a)

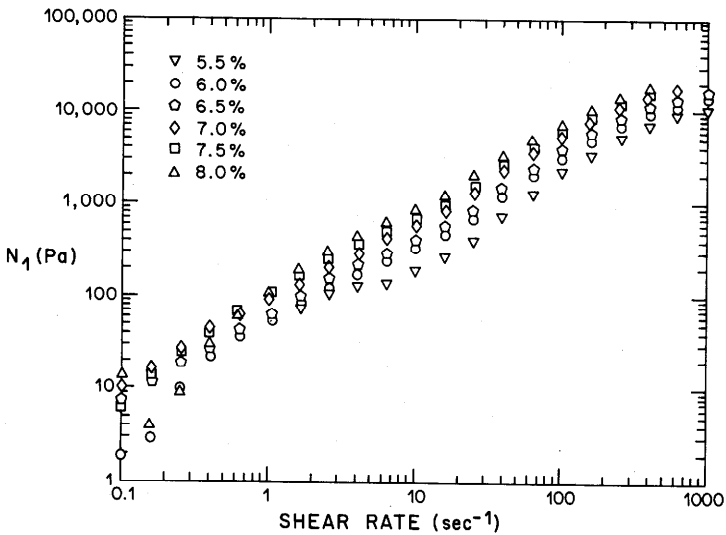


(b)

Fig. 6. (a) Viscosity versus shear rate for Vistanex L-100 in Decalin. (b) First normal stress difference versus shear rate for Vistanex L-100 in Decalin.



(a)



(b)

Fig. 7. (a) Viscosity versus shear rate for Vistanex L-140 in Decalin. (b) First normal stress difference versus shear rate for Vistanex L-140 in Decalin.

TABLE VII

Comparison of Measured Values of N_1/k^2 and Values Computed from Measured $\hat{\beta}$ Values
Using Various Values for m [Eqs. (10) and (18)]

	m	10^5				Measured Value of N_1/k^2 at $k(s^{-1})$	
		10^5	$3.33\hat{\beta}$	$2.5\hat{\beta}$	$2.17\hat{\beta}$		
K-125 (PMMA) in Dowanol	4.5	2.4	0.8	0.6	0.5	2.3	1
	5.0	6.6	2.2	1.7	1.4	1.0	1
	5.5	16.6	5.5	4.2	3.6	1.3	1
	6.5	42.9	14.3	10.7	9.3	9.2	1
	7.0	209	69.7	52.3	45.4	15	1
	7.5	800	267	200	174	3.3	1
	5.5	114	38.0	28.5	24.8	34	1
PIB (L-100) in Decalin	6.0	163	54.3	40.8	35.4	49	1
	6.5	195	65.0	48.8	42.4	74	1
	7.0	363	121	90.8	78.9		
	7.5	399	133	99.8	86.7		
	8.0	522	174	131	113		
	8.5	812	271	203	177	90	1
	6.0	1050	350	263	228	190	0.1
PIB (L-140) in Decalin	6.5	2030	677	508	441	680	0.1
	7.0	4360	1453	1090	948	990	0.1
	7.5	8300	2767	2075	1804	660	0.1
	8.0	17,730	5910	4433	3854	1380	0.1

We have used the rheometer data at the lowest shear rates we have available ($\kappa \approx 1 \text{ s}^{-1}$), with the result that there is considerable scatter in the data. The primary objective of Table VII is to show that the limiting value of N_1/κ^2 computed from measurements of the climbing constant are not inconsistent with corresponding values measured using a conventional rheometer. The scatter in all the N_1 data at the lowest shearing rates shown in Figures 5(b), 6(b), and 7(b) makes it impossible to extrapolate to zero shear rate.

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