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Extrapolation procedures for zero shear viscosity with a falling sphere viscometer

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With 3 figures and 1 table

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Notation

D sphere diameter, cm
D_C container diameter, cm
$F = 1/6\pi D^3(\varrho_s - \varrho)g$ = drag force on sphere, dynes
$F_s = 6\pi\eta_0 R v_\infty$ = drag force from *Stokes* law, dynes
f_W wall correction factor for *Newton*ian flow past a sphere
f_B bottom correction factor for *Newton*ian flow past a sphere
f_I inertial correction factor for *Newton*ian flow past a sphere
g gravitational acceleration, cm/sec²
$Re = 2Rv_t\varrho/\eta_0$ = *Reynolds* number
v_t measured sphere velocity, cm/sec
v_∞ sphere velocity in an infinite medium, cm/sec
W correction factor by *Caswell* [eq. 4]

Greek letters

η_0 zero shear viscosity, poise
$\eta_0^{(N)}$ corrected viscosity [Eqn. 2], poise
η_s apparent *Stokes* viscosity, poise
ϱ fluid density, gm/cm³
ϱ_s sphere density, gm/cm³
$\tau_m^{(N)}$ maximum pseudo-*Newton*ian shear stress [eq. 2], dyne/cm²
λ_i combination of material parameters
$(i = 1, 2, 3)$ [eq. 4, 5, 6]

Introduction

Most non-*Newton*ian materials approach *Newton*ian behaviour at very low shear rates. The limiting value of this *Newton*ian viscosity is termed as the "zero shear viscosity" and denoted by η_0. The determination of η_0 is important for many applications, for instance η_0 is an important parameter in the constitutive equations which model the non-*Newton*ian flow. It also gives a test of the theoretical interpretation of the polymer melt viscosity. From an engineering viewpoint, it is important in the case of flow in porous media. Unfortunately there are very few instruments where shear rates could be obtained which are low enough to achieve the experimentally elusive zero shear limit. Thus, most typical rotational viscometers (e.g. *Couette* viscometer) give shear rates in the range of 10 to 10,000 sec^{-1}. In some cases (e.g. *Weissenberg* Rheogoniometer) it is possible to obtain very small shear rates but for liquids with reasonably small consistency, the torque readings are rather inaccurate. The falling sphere apparatus used in this work appears to be an attractive method for determining the value of η_0.

Usually it is possible to achieve sufficiently small shear rates by reducing the dimension of the sphere as well as the density difference between the sphere and the liquid to a sufficiently small value. However, extremely small values of terminal settling velocities cause large time delays in the determination of η_0. Hence, it is appropriate to work with sufficiently high velocities. This causes difficulties because one now enters the non-*Newton*ian regime. It is very important to ascertain the accurate methods of extrapolation to the value of η_0 by considering the values from the proper non-*Newton*ian regime. Several methods have been proposed to achieve this object, some of them are purely empirical whereas the rest are theoretical or semitheoretical. There are, however, no attempts to analyse these methods critically and test them experimentally. The present paper is an experimental investigation into the study of these aspects.

Theory

When an unbounded incompressible *Newton*ian fluid of viscosity η_0 flows past a sphere of radius R with an approach velocity v_∞, it exerts a drag force on the sphere given by the well known *Stokes* law

$$F_s = 6\pi\,\eta_0\,R\,v_\infty. \qquad [1]$$

This equation is valid only in the so-called creeping flow regime in which the *Reynolds* number, $Re = 2Rv_\infty \varrho/\eta_0$ is less than about 0.1. Extension of *Stokes'*, solution to higher *Re* has been proposed by *Oseen* (1), *Goldstein* (2) and by *Proudman* and *Pearson* (3). Corrections of Eq. [1] to account for the effect of the cylindrical wall of the fixed container have been presented by *Ladenburg* (4) and by *Faxen* (5). *Ladenburg* (4) has also presented a correction for the effect of the bottom of the cylinder. *Tanner* (6) has carried out a numerical calculation in which the effects of both the cylindrical wall and the bottom of the container were taken into account. Most of these corrections have been reviewed (7) and will not be repeated here. The various procedures of extrapolation to zero shear viscosity from the non-*Newton*ian regime will be reviewed and analysed in the section "Results and discussion".

Experimental

The solutions used were glycerol, aqueous solutions of carboxy methyl cellulose (CMC, ICI), aqueous solutions of polyacrylamide (PAA, Separan AP30, Dow Chemicals). Also used were polydimethylsiloxanes (MS 200 silicone fluids, Midland Silicones Ltd.). The concentrations used were from about 0.5% to 2% by wt for CMC in water and 1% to 2% by wt for PAA solutions.

The range of the solutions so chosen enabled us to study fluids with different flow behaviours. Thus glycerol solutions were *Newton*ian. Aqueous CMC solutions showed negligible elastic effects up to a concentration of approximately 1.1% and hence could be classified as inelastic. They showed, however, pronounced elastic effects at higher concentrations. These were tested qualitatively by a rotating sphere elasticoviscometer and quantitatively by a *Weissenberg* Rheogoniometer. PAA solutions were viscoelastic in character, whereas polydimethyl siloxanes did not show any shear thinning viscosity but showed some elastic effects.

The falling sphere apparatus consisted of a glass cylinder of 7.5 cm i.d. with an overall length of about 150 cm. Thus unlike the other apparatus mentioned in the literature, the infinite cylinder approximation was closely achieved. Precision ball bearings of stainless steel ($\varrho_s = 7.8$ gm/cm^3) and lead ($\varrho_s = 11.8$ gm/cm^3) were used. The diameters of the balls ranged from 0.15 cm to 0.635 cm and 16 different diameters in this range were used. Some acrylic resin spheres

$$(\varrho_s = 1.17 \text{ gm/cm}^3)$$

with diameters ranging from 0.225 cm to 0.25 cm were also used. All the spheres were rigorously tested for sphericity and uniformity of density.

The fall experiments were conducted in a constant temperature room. Most of the experiments reported here have been conducted at a temperature of approximately 21 °C. The fall distances were measured with a travelling cathetometer and the fall times by an electric watch. The fall velocities were measured at two different sections of the cylinder thereby ensuring that the spheres fell at their terminal settling velocities. The estimated accuracy of the fall velocities was within 2% in most of the cases.

In many cases, rheograms were obtained at the same temperature in a cone and plate or a *Couette* viscometer. This helped us to check the accuracy of the experiments, particularly in the case of *Newton*ian liquids. Preliminary experiments indicated that the experiments on the *Newton*ian solutions were accurate enough to predict the zero shear viscosity within 0.2%.

Results and discussion

Several empirical and theoretical procedures for extrapolation were experimentally tested.

Williams (8) proposed an empirical extrapolation procedure where a corrected viscosity term was plotted against a pseudo-*Newton*ian shear stress. He assumed that the *Newton*ian correction factors could be assumed valid even in the case of non-*Newton*ian liquids. Thus he defined

$$\eta_0^{(N)} = \eta_s f_W f_B f_I = \left(\frac{2R^2(\varrho_s - \varrho)g}{9v_t}\right) f_W f_B f_I \quad [2]$$

$$T_m^{(N)} = \frac{D(\varrho_s - \varrho)g}{6} \quad [3]$$

$T_m^{(N)}$ is the value of the maximum shear stress which could exist at the sphere surface, if the fluid were *Newton*ian and f_W, f_B, f_I are the correction factors for wall, bottom and inertial effects. The relevant *Reynolds* number was obtained as $Re = \frac{Dv_t \varrho}{\eta_s}$ and an extrapolation to $T_m^{(N)}$ equal to zero gave the value of η_0. Sometimes it was necessary to plot the values of $\eta_0^{(N)}$ vs. $(T_m^{(N)})^x$ where the exponent x was so adjusted that the data fall on a straight line.

This procedure could be criticized on several grounds. *Tanner* (9) has shown that the effects of top and bottom corrections are negligible for non-*Newton*ian solutions. Thus the bottom correction used here is unnecessary. The correction for the wall effects used here is the one which is proposed by *Faxen* for *Newton*ian solutions. *Sato* et al. (10) have determined the wall corrections for *Newton*ian solutions and shown that the wall correction factor for non-*Newton*ian solutions is lower than that given by the *Faxen* equation. *Caswell* (11) derived the non-*Newton*ian equivalent of the *Faxen* wall correction formula from theoretical considerations and he has shown that for shear thinning liquids, *Faxen* formula overcorrects for the effect of walls. The data obtained by *Turian* (12) in various sizes of containers is also indicative of the same effect. Thus the wall correction used in this procedure may be taken to overcorrect the data. In any case, the correction used by *Williams* was unjustified because the data obtained from only one single diameter container were available to him. Further, for some of the solutions which were used by *Williams*, he found it necessary to plot $\eta_0^{(N)}$ vs. $(\tau_m^{(N)})^x$ where the exponent x was so adjusted that the plots fell on straight lines on a semi-log scale. Obviously such a procedure is highly arbitrary.

Turian (12) proposed an extrapolation procedure, where he plotted the value of η_s vs $\frac{\eta_s v_\infty}{D}$ on a semi-log plot. In fact the value of the abcissa used by *Turian* is one third of the value used by *Williams*. This procedure although entirely empirical at least avoids the uncertain corrections used by *Williams* and was consequently tested in this work. Fig. 1 shows a typical plot obtained by using this approach.

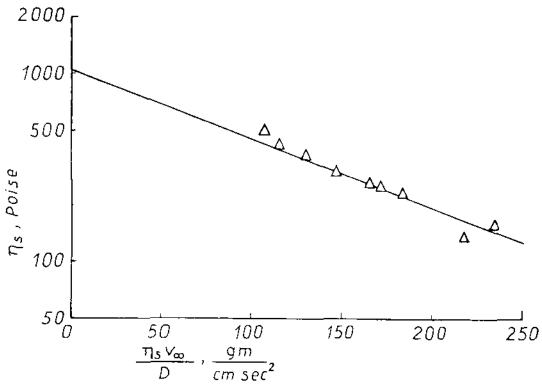

Fig. 1. Determination of zero shear viscosity for 2% PAA by *Turians* extrapolation procedure

Turian also proposed a further extrapolation procedure based on the plot of η_s vs D/D_C (the ratio of sphere to container diameter) and an extrapolation to $D/D_C = 0$. Although these plots are useful for ascertaining the wall effects, data will have to be obtained in several containers. Usually this will be impracticable under most conditions because data on only one container are normally available. *Turian* has also suggested extrapolation procedures based on the *Faxen* wall correction but as has been pointed out earlier the unrestricted use of this correction with non-*Newton*ian liquids is inappropriate and it could work only in the cases where the correction itself is very small or when the non-*Newton*ian effects are small.

All the extrapolation procedures mentioned above are empirical but there have been some procedures having some theoretical grounds. *Caswell* (13) obtained an expression for the drag force for the creeping flow past a sphere of a *Rivlin-Ericksen* fluid of third order. This expression was written in the form

$$\frac{\eta_s}{W} = \eta_0 + \frac{\lambda_1\left(\frac{v_\infty}{R}\right)^2}{W} \qquad [4]$$

where λ_1 was a combination of material parameters of the third order *Rivlin-Ericksen* fluid and W was a correction factor incorporating both end and wall effects. The factor W was obtained on the basis of the *Newton*ian corrections and is certainly inappropriate. Further, the expression obtained for the drag force is in error and this has been pointed out by *Caswell* (11) in a later publication. Attempts to plot this equation on a straight line on the basis of the data obtained in this work failed and there was a tendency for curvature. Although *Caswell* (13) has plotted his data on a straight line, a close examination of his data also indicated a considerable scatter and a tendency towards curvature at both very low and very high values of $(v_\infty/R)^2$. It is important to note that eq. [4] is valid only for a third order *Rivlin-Ericksen* fluid and at higher magnitudes of $(v_\infty/R)^2$ (which also correspond to higher values of rate of deformation tensor) this assumption may be no more valid. Thus the combination of material parameters λ_1 which is assumed constant for a given fluid may be also a function of the flow conditions or, in other words, the rate of deformation tensor.

It is interesting to observe that the data obtained by polyethylene spheres ($\varrho_s = 1.16$) used by *Caswell* (13) deviated considerably from the data obtained by s.s. spheres for solutions of polyisobutylene in decalin. A similar tendency was observed for the polyacrylic resin spheres used in this work. This effect was negligible in the case of pure glycerol or glycerol solutions but was considerable in the case of polymeric solutions. It is very difficult to explain these phenomena. *Caswell* (13) has attributed this effect to a combination of end effects and stress relaxation. In view of the fact that the ratio of cylinder length to diameter was approximately 20 and that the fall velocities were measured over the middle portion of the cylinder, the end effects are unlikely to be important. Further due to the reduced density difference between the sphere and the liquid the fall velocities and consequently the rates of deformation were very small. This implies that the assumption of slow relaxation mechanism was even more closely achieved in this case. It is very difficult to guess the proper reasons for this effect, but it is not unlikely that some surface effects are responsible for such phenomena. Fig. 2 shows a typical plot based on *Caswells* extrapolation procedure and the tendency for curvature could be clearly observed.

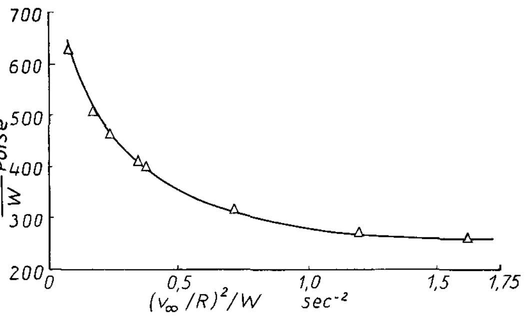

Fig. 2. Determination of zero shear viscosity for 2% PAA by *Caswells* extrapolation procedure [eq. 4]

Turian (12) simply rearranged *Caswells* analytical solution for the drag force as follows,

$$\left(\eta_s - \frac{3}{16}\varrho D v_\infty\right) = \eta_0 + \lambda_2 \left(\frac{v_\infty}{D}\right)^2. \qquad [5]$$

A linear plot of $\left(\eta_s - \frac{3}{16}\varrho D v_\infty\right)$ vs. $(v_\infty/D)^2$ will give the value of η_0 as intercept. Since this approach is essentially the same as used by *Caswell*, it suffers from the same drawbacks. Basically, in view of the doubts about the validity of the analytical expression for the drag on the sphere obtained by *Caswell*, it is incorrect to use plots based on this expression.

Caswell (11) considered the effect of finite boundaries on the motion of particles in non-*Newton*ian fluids and making use of the results of *Giesekus* (14) for the drag force on a sphere moving through a third order *Rivlin-Ericksen* fluid, derived the following expression

$$\frac{6\pi R v_\infty}{F} = \frac{1}{\eta_0} - \frac{\lambda_3}{\eta_0^3}\left(\frac{F}{6\pi R^2}\right)^2 + 0\left(\frac{F}{6\pi R^2}\right)^4. \qquad [6]$$

Here again, λ_3 is a combination of the material parameters in the *Rivlin-Ericksen* equation. A plot of $\frac{6\pi R v_\infty}{F}$ vs. $\frac{F}{6\pi R^2}$ could be made on the basis of this equation. Fig. 3 shows a typical plot. It is observed that the plot is

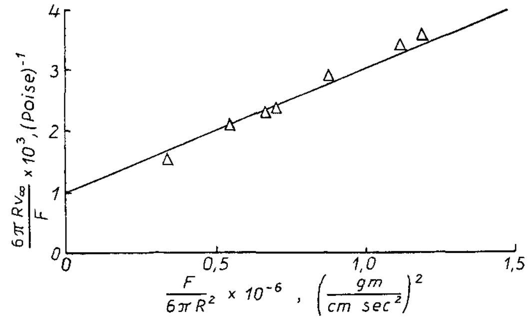

Fig. 3. Determination of zero shear viscosity for 2% PAA by *Caswells* extrapolation procedure [eq. 6]

linear and this indicates that the terms of the order of $\left(\frac{F}{6\pi R^2}\right)^4$ are negligible. Further λ_3 appears to be constant and this indicates that the third order approximation was really valid under the experimental conditions. Table 1 presents a comparison of the extra-

Table 1. Zero-shear viscosities obtained by extrapolation

Solution	zero shear viscosity, η_0, poise *Turians* procedure	*Caswells* procedure
2 % PAA	1040	1000
1 % PAA	130	125
0.5% PAA	39	37
2 % CMC	1100	1080
1.4% CMC	182	180
Polydimethyl siloxane	122	122

polated values of η_0 obtained by the procedures proposed by *Turian* (12) $\left(\eta_s \text{vs.} \frac{\eta_s v_\infty}{D}\right)$ and *Caswell* [eq. 6]. In view of the fact that *Turians* approach is entirely empirical, the agreement between the two values could be considered very sound. However, in view of the fact that *Caswells* extrapolation procedure is based on a sound theoretical reasoning, it is recommended for use. An analysis of some of the data given by *Williams* (15) and *Turian* (16) was made on the basis of the above two procedures and this also substantiated the conclusion of this work.

It was thought that it would be desirable to test the validity of the conclusions drawn in this work by doing some additional sets of experiments in some other non-viscometric and viscometric arrangements.

We have examined the possibility of using a rotating sphere apparatus for the purpose of determination of η_0 elsewhere (17, 18) and shown that this apparatus could be satisfactorily used for this purpose. The extrapolation procedures proposed for this non-viscometric arrangement are very similar to those used in this work. The value of η_0 obtained by this method for some of the PAA solutions was found to agree very well with that obtained in this work.

For some of the CMC solutions used in this work rheograms were determined on a *Weissenberg* Rheogoniometer. The data were obtained in the range of shear rates between 0.1 to 10 sec^{-1}. These viscometric data were fitted by an *Ellis* model and the value of η_0 was determined by a least square plot. The value of η_0 obtained in this work was found to differ by only 2.5% from this value.

An interesting result evident from the plot based on eq. [6] is the possibility of obtaining the combination of material parameters λ_3 from the slope of the curve. Another combination of material parameters could be obtained by doing experiments in another non-viscometric arrangement (e.g. a rotating sphere) or a viscometric arrangement (e.g. a *Couette* flow). It is thus possible to evaluate the individual material parameters for a *Rivlin-Ericksen* fluid of third order by the combination of these experiments (17, 18).

Summary

Several theoretical and empirical extrapolation procedures for the determination of zero shear viscosity in a falling sphere viscometer are critically analysed. They are experimentally tested and it is concluded that the extrapolation procedure based on *Caswells* work appears to be the most appropriate.

Zusammenfassung

Es werden einige theoretische und empirische Extrapolationsmethoden zur Bestimmung der Anfangs-Scherviskosität in einem Kugelfallviskosimeter kritisch analysiert. Diese werden experimentell überprüft, und es wird hieraus geschlossen, daß die Extrapolationsmethode, die auf der Arbeit von *Caswell* beruht, die geeignetste zu sein scheint.

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