An activation energy approach to analysing non-Newtonian slurry viscosities with application to a suspension of starch in a carboxymethylcellulose solution

H.D. Chandler

School of Mechanical, Industrial and Aeronautical Engineering, University of the Witwatersrand, Johannesburg, Private Bag 3, P.O. 2050 WITS Gauteng, South Africa

ARTICLE INFO

ABSTRACT

Many suspensions of practical importance exhibit non-Newtonian fluid behaviour. For a given particle concentration and temperature, these often have relative viscosities that vary with shear rate and this necessitates modifications to the frequently applied Krieger–Dougherty equation. A simple way to analyse viscosity data is by consideration of the activation energy. It is demonstrated as an example of the approach that the properties of a non-Newtonian suspension of starch in a carboxymethylcellulose solution may be described simply in terms of the activation entropy which can be interpreted as a semi-empirical measure of the degree to which structural re-arrangement occurs during flow.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Fluid viscosity is most frequently expressed in terms of how the shear stress or viscosity varies as a function of an imposed shear strain rate. Although many such relationships have been proposed, one of the simplest and most popular, which is obeyed at least approximately by many fluids, is the Ostwald–de Waele or power law (PL) relationship in which τ, the shear stress is written in terms of the shear rate $\dot{\gamma}$, as:

$$\tau = k\dot{\gamma}^{n'} \tag{1}$$

where the constant k is referred to as the consistency index and n' is the power law exponent. For $n' = 1$, the behaviour is Newtonian, for $n' < 1$, behaviour is shear thinning and for $n' > 1$, shear thickening. In terms of viscosity η_L Eq. (1) is expressed by dividing by the shear rate, as:

$$\eta_L = K\dot{\gamma}^{n'-1} \tag{2}$$

where K is a constant

When solid particles are suspended in the fluid, the viscosity is increased and the viscosity of the suspension η_S may be expressed as:

$$\eta_S = K\dot{\gamma}^{n'-1}f(\phi) \tag{3}$$

E-mail address: david.chandler@wits.ac.za.

where ϕ is the volume fraction of the suspended solids. Rather than expressing the effect of solids addition in terms of the viscosity, it is written as the relative viscosity η_r obtained by dividing the viscosity of the suspension by the viscosity of the suspending fluid, η_L i.e.:

$$\eta_r = \eta_S/\eta_L = f(\phi) \tag{4}$$

This has the advantage that the result should be independent of whether the fluid is Newtonian or non-Newtonian. For very dilute suspensions of rigid spherical particles, the relative viscosity often obeys the Einstein equation [1] :

$$\eta_r = 1 + 2.5\phi \tag{5}$$

Most suspensions of practical interest, however, are too concentrated to obey this relationship and other factors such as, among others, particle crowding, interaction and particle shape become important. Many empirical or semi-empirical modifications to the Einstein equation have been proposed and a review in 1962 by Rutgers [2] classifies and lists over 96. Of these, the most frequently used is the Krieger–Dougherty equation [3] which is often expressed in the form:

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-n} \tag{6}$$

where ϕ_m is the maximum solids fraction. The exponent n has values typically around 2–3.

A modification that is frequently applied is to express the maximum solids fraction, which is often difficult to measure, in terms of an effective maximum volume fraction, ϕ_{meff} which is generally more accessible experimentally. Since it is often found that the relative viscosity for a given solids concentration is dependent on the shear rate, modifications to this relationship are frequently necessitated [4]. Such modifications are generally of the form:

$$\eta_r = f(\dot{\gamma}, \phi) \left(1 - \frac{\phi}{\phi_{meff}}\right)^{-n} \tag{7}$$

Some of these have been applied to materials such as suspensions of fly ash in water [5–7].

One possible mechanism to explain a decrease in viscosity for a given particle concentration as shear rate is increased is that the effective maximum volume fraction increases due to the structure tending to change from random close packing ($\phi_{meff} \sim 0.6$) to hexagonal close packing ($\phi_{meff} \sim 0.7$) [4]. This has been observed for fairly large (70 μm) monodisperse spherical particles [8]. However, other mechanisms may be envisaged as elaborated further below and the exact mechanism and its effect on viscosity may well depend on the nature of each individual suspension.

The above relationships are all temperature independent. Viscosity, however, is usually fairly sensitively temperature dependent and Eq. (2) can usually account for this by inclusion of an Arrhenius term:

$$\eta = K' \dot{\gamma}^{n'-1} \exp\left(\frac{\Delta G}{RT}\right) \tag{8}$$

where ΔG is the activation energy for flow, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T the absolute temperature. In turn, the activation energy may be written in terms of the activation enthalpy ΔH and the activation entropy ΔS as:

$$\Delta G = \Delta H - T\Delta S \tag{9}$$

So that Eq. (8) becomes:

$$\eta = K' \dot{\gamma}^{n'-1} \exp\left(\frac{\Delta H - T\Delta S}{RT}\right) \tag{10}$$

Comparing Eq. (3) with Eq. (10), it appears that $f(\phi)$ from Eq. (3) can be written in terms of the change in activation energy due to the presence of the suspended solids, i.e. that the relative viscosity in Eq. (4) can be written in terms of activation parameters $\Delta H'$ and $\Delta S'$ associated with the solids additions. These are given by $\Delta H' = \Delta H_S - \Delta H_L$ and, $\Delta S' = \Delta S_S - \Delta S_L$ where the subscripts S and L refer to the suspension and to the suspending fluid respectively. In terms of these, and separating temperature dependent and independent quantities, the relative viscosity at a given shear strain rate may be written as:

$$\eta_r = \exp\left(\frac{\Delta H'}{RT}\right) \exp\left(\frac{-\Delta S'}{R}\right) \tag{11}$$

By plotting the natural logarithm of the relative viscosity against reciprocal temperature, it should be relatively simple to separate the activation enthalpy and activation entropy, the slopes and intercepts of such curves representing, respectively, the thermally activated and the temperature independent contributions. These could be further analysed to quantify the behaviour of each as functions of input variables such as solids concentration, shear rate, pH etc. Consideration of Eqs. (7) and (11) suggests that the effect of the suspended solids is to alter the flow activation energy. It has, in fact, been demonstrated that an entropy argument can be used to obtain an expression similar to the Krieger–Dougherty equation [9] based on the probability that there is a suitable space into which a particle can move rather than the usual crowding argument, the two approaches being equivalent.

It is well known that non-Newtonian behaviour is often due to flow induced changes in the material structure. Structures in fluids may often be quite complex [10] and occur through a variety of mechanisms on both the molecular and larger scales and some of which may have antagonistic effects when it comes to determining whether or not the overall viscosity would increase or decrease. Such mechanisms may result in structural ordering as in the case of flow induced molecular alignment in polymeric materials or could lead to disruption of one structure and the formation of another as in the break-up of aggregates in suspensions [11] or where shear could lead to compaction of the structure as noted above or alternatively to shear induced structures such as banding. An example of antagonistic effects is that of flow in surfactant solutions where structural alignment tends to cause shear thinning but also tends to inhibit flow perpendicular to the shear plane which inhibits the formation of kinks necessary for the reptation flow mechanism to operate. This can lead to viscosity tending to increase rather than decrease with temperature at increasing shear rates [12]. When, as is frequently the case, multiple structural change mechanisms may occur and it is not known what the precise nature and contribution of each is, then a convenient way is to quantify behaviour in terms of activation entropy. The overall effect of multiple mechanisms may be determined from Eq. (11) by the sign of the entropy term, a negative sign indicating structural ordering tending to add a thickening component and a positive activation entropy indicating disordering and a thinning component.

The purpose of the present work was to carry out an experimental investigation into the effect of solids concentration and temperature on the viscosity of a suspension of solid particles in a non-Newtonian fluid and analyse the results in terms of the activation energy for flow as outlined above. The materials tested comprised corn starch at different concentrations suspended in an aqueous solution of carboxymethylcellulose (CMC), a commonly used viscosity modifying agent that finds applications in a number of industries including the food industry and which shows shear thinning characteristics at the concentration investigated.

2. Experimental

Material used was a low viscosity sodium salt of carboxymethylcellulose supplied by Sigma-Aldrich Co. (product code C5678). This was made into a 5% by weight solution by dissolving it in distilled water. The corn-starch used was a proprietary brand "Maizena" manufactured by Bokomo Foods, Atlantis, Western Cape. Several starch concentrations were prepared by weight and results presented in terms of volume fractions using a density for starch of 1.5 Mg/m^3. No settling of the suspensions was observed during the time frame of each experiment.

Tests were performed using a rheometer (TA instruments AR 2000ex) fitted with a cup of 30 mm diameter, which included Peltier temperature control, together with a cylindrical rotor of 28 mm diameter. Testing was carried out under shear strain rate control mode using stepped testing at constant temperature. For each strain rate step, the rotor rotation rate was held constant for a time of 20 s and the torque averaged over the last 5 s was recorded. Strain rate steps of 5 /s from 0/s to 900/s were used. The relatively long time (~1 hour) for each test was to minimise any effects due to thixotropy. Although most tests were for increasing strain rates some tests were carried out with an increasing followed by a decreasing rate which indicated very little hysteresis. Data was output as shear stress, shear strain rate, viscosity and temperature at each step. Testing temperatures were between 4 °C and 28 °C at 4 °C intervals and starch concentrations ranged from 0 to 0.33 by volume. Viscosities are expressed below as apparent relative viscosities by dividing the apparent viscosity of the suspension by that of the carboxymethylcellulose at the corresponding shear strain rate.