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A Study of the “Spurt Effect” in Wormlike Micelles Using Nuclear Magnetic Resonance Microscopy

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Abstract. — The non-Newtonian flow properties of the wormlike surfactant system, cetyl pyridinium chloride/sodium salicylate in water, have been studied using dynamic and steady rheometry and nuclear magnetic resonance velocity imaging. The NMR measurements of velocity profiles across a 5.0 mm diameter glass tube reveal a discontinuity in the flow behaviour, once a critical shear strain rate of around 1 s⁻¹ is exceeded, a manifestation of the so-called “spurt effect”. Rheological measurements show that three characteristic regimes are observed. Below 0.2 s⁻¹ the system is near-Newtonian. Between 0.2 and 0.8 s⁻¹, shear-thinning behaviour is observed. Above this a multi-valued shear-rate regime is found at constant stress. This “spurt” regime exhibits shear rates up to values of around 50 to 100 s⁻¹, at which an upturn in the shear stress is found. The rheological flow curves are characteristic of those predicted by a Wagner model and in turn are found to be broadly consistent with the velocity profiles as measured by NMR.

1. Introduction

In 1958, Bagley et al. [1] reported a discontinuity in the flow behaviour of polyethylene, an effect subsequently investigated by Vinogradov [2,3] who coined the term “spurt” effect. From a rheological standpoint the effect is believed [4,5] to arise from a double valued-ness in the constitutive relation between shear stress and strain rate. However, both the unambiguous observation of this phenomenon, as well as a molecular basis for understanding its origins, have been the subject of intense speculation.

In the case of polymer melts and semi-dilute solutions, an explanation has been advanced by McLeish and Ball [6] based on the Doi-Edwardh [7,8] model of entanglement dynamics. In this picture the Rouse time and disengagement (reptation) times provide two characteristic inflexions in τ vs. ɣ as shown in Figure 1. Hence the shear rate in a tube will be multi-valued when the wall shear stress exceeds a critical value, τc. Because both the tube disengagement

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and Rouse times are strongly dependent on molar mass (as $M^3$ and $M^2$ respectively), any polydispersity will result in strong smoothing of the constitutive relation, thereby masking the underlying double valued-ness. This may help explain why an understanding of the spurt effect in high molecular weight polymers has proven somewhat elusive.

An alternative candidate for the study of this phenomenon is provided by “wormlike micelles”. These molecular assemblies arise from an association of surfactant molecules into long polymer-like chains in which the apparent chain length is concentration dependent. Wormlike micelles are known to exhibit strongly non-Newtonian rheological properties [9–12] and possess a narrow distribution of characteristic relaxation times. This quality suggests that the spurt effect might be more easily observed in these structures than in high molecular weight polymers where polydispersity broadening is unavoidable.

In this article we report on the use of Nuclear Magnetic Resonance Imaging methods to investigate the tube flow of one of the best known wormlike micelle systems, cetyl pyridinium chloride/sodium salicylate. The mean micelle length is not known precisely for this system but is thought to be of the order of 1 $\mu$m. Strong but indirect evidence for double-valued stress vs. shear data was found for this system in a study by Hoffman and Rehage [9,10]. The hypothesis of a non-monotonic curve explains both the shear and normal stress data in that system [12]. The existence of such a curve has also been predicted by microscopic theory [12].

In our method we pump the fluid through a tube and image the velocity across a planar cross-section, thus gaining access to the flow profile. In this sense we are able to directly view any abrupt features which could arise from any double valued-ness in the constitutive relation, by obtaining access to a range of shear rates in a single image.

In previous NMR studies the velocity profile has been used to characterise the fluid in terms of a simple power law model, for which the radial dependence of velocity is represented by

$$v(r) = v_{\text{max}}[1 - (r/R)^{(n+1)/n}]$$

(1)

where $n$ is the power law exponent, $R$ is the radius at the tube wall and $v_{\text{max}}$ is the fluid velocity at the centre. For a Newtonian fluid ($n = 1$) equation (1) returns the parabolic profile characteristic of Poiseuille flow. While this relation will not be particularly useful in

Fig. 1. — Schematic representation of shear stress vs. rate of strain (shear rate) for material exhibiting the spurt effect (after McLeish and Ball [6], and Doi and Edwards [8]. The characteristic inflexion points arise when the shear rate, $\gamma$, is comparable with some rate $\omega$, characteristic of the molecular dynamics. $\tau_c$ is the critical stress above which spurt occurs.
characterising a fluid exhibiting rheological discontinuities, it does represent a reference against which deviations can be ascertained.

The NMR method used has been described in detail elsewhere [15,16] and only a brief overview needs to be given here. We acquire information about both nuclear spin positions and nuclear spin velocities via the precession of nuclear spins in a magnetic field. Because the nuclear spin precession frequency is dependent on the strength of the magnetic field in which it is placed, it is possible to determine the location of these spins by employing spatially-dependent magnetic fields. Magnetic field gradients can also be used to reveal molecular translational motion, simply by carefully measuring precessional phase changes. Because the hydrogen nucleus provides the most sensitive spin for nuclear magnetic resonance, proton NMR is the favoured mode of magnetic resonance imaging. In the work reported here the predominant signal arises from water molecules which thereby provide a marker for the velocity of elements of the viscous fluid.

The use of NMR to investigate velocity distributions has recently become well-established in rheology [17–21]. Each of these utilizes a different approach to velocity-encoding. Our own method [20–22] trades speed of data acquisition in favour of high spatial and velocity resolution. In particular we are able to resolve pixels on the order of ten microns while our velocity resolution is around ten microns per second, depending on the self-diffusion coefficient of the molecule being tracked. The method is best suited to steady-state flow measurement and to the study of model systems where only limited sample volumes may be available. As an additional advantage, the ability to work with narrow flow regions means that relatively high shear rates are accessible. The method has been previously used [20] in a study of polymer flow in a narrow (700 μm) diameter capillary at shear rates up to 100 s⁻¹. In the wormlike surfactant study reported here, the characteristic shear rates at which flow discontinuity is expected are much smaller, on the order of 10⁻¹ s⁻¹. Hence it is imperative that we will be able to work with velocities well below 1 mm s⁻¹ if we are to investigate transitions between nearly Newtonian and strongly non-Newtonian behaviour in a tube of a few millimeters diameter.

A suggested model for flow discontinuity in wormlike micelles concerns the characteristic “breakage” process described by Cates and co-workers [12–14]. Other mechanisms have been suggested for the observation of spurt-like effects including elastic flow instabilities [23,24] and secondary flow [25,26]. It is not the purpose of this article to distinguish between these different pictures in any definitive way. Rather, we seek to relate discontinuities in the stress/shear-rate data to possible discontinuity in velocity profiles as measured by NMR. At the same time we will use the micellar breakage picture as a model in aspects of our interpretation.

It should be recognised that the existence of double-valuedness in the stress vs. rate of strain relationship raises delicate issues concerning measurement. For example a steady uniform flow is impossible under conditions in which the decreasing part of the curve would be measured. Double-valuedness can only be inferred by its effect on the observed behaviour, which will either be unsteady or non-uniform. In the latter case, which corresponds to shear-banding, the effect of non-uniformity is to transform the decreasing part of the stress/shear-rate curve into a flat plateau. Such a plateau might be expected to lead to the existence of a velocity profile exhibiting a sudden transition in shear rate. This is the phenomenon which we seek to investigate here.

2. Theory

2.1. Rheology of Wormlike Micelles. — As shown in a recent paper by Mackley et al. [27], the rheological characterisation of many polymeric and some colloidal systems can be carried out successfully by using a generalised Maxwell model and a strain-dependent damping
function. In this scheme, the material’s linear viscoelastic behaviour is modelled by a number of Maxwell elements in parallel.

A Maxwell element consists of a spring and a dashpot in series, characterised by any two of the three quantities: dashpot viscosity $\eta$, spring modulus $g$ and relaxation time $\lambda$. The generalised Maxwell model of a fluid introduces a spectrum of relaxation times $(g_i, \lambda_i)$. With this modification the memory function has the form

$$M(t) = \sum_i (g_t/\lambda_t) \exp(-(t-t')/\lambda_t).$$  \hfill (2)

The storage and loss moduli $G'$ and $G''$ which result from the generalised Maxwell model are as follows:

$$G'(\omega) = \sum_i \frac{g_t \lambda_t^2 \omega^2}{(1 + \lambda_t^2 \omega^2)}$$  \hfill (3)

and

$$G''(\omega) = \sum_i \frac{g_t \lambda_t \omega}{(1 + \lambda_t^2 \omega^2)}$$  \hfill (4)

The memory function can be determined by carrying out linear viscoelastic measurements which yield the frequency dependence of $G'$ and $G''$. By fitting the observed behaviour to equations (3) and (4), one may obtain the appropriate spectrum of relaxation times. First, however, the extent of the linear region has to be determined by a dynamic strain sweep at a fixed frequency.

The non-linear behaviour of the fluid is quantified by a damping function, $\exp(-k|\gamma|)$, introduced by Wagner [28] where $k$ is the damping coefficient and $\gamma$ is the shear strain. The constitutive equation used in the present scheme contains the usual memory function as well as the damping function:

$$\tau(t) = -\int_{-\infty}^{t} \sum_i \frac{g_t}{\lambda_t} \exp(-(t-t')/\lambda_t) \gamma(t, t') \exp(-k|\gamma(t, t')|) \, dt'$$  \hfill (5)

with $\tau(t)$ being the shear stress at time $t$.

This method for rheological characterisation relies on an assumption that the time and strain dependent parts of the constitutive equation are separable. The damping coefficient $k$ can be determined by carrying out step-strain experiments involving a series of step-wise deformations (with strains varying from linear to non-linear values) after which the stress relaxation is measured. The manner in which the relaxation modulus, $G(t)$, decreases in time is, for linear strains, determined only by the spectrum of relaxation times, thus leading to an exponential decay. Non-linear strains lower the overall value of $G(t)$ for a strain-softening material. Provided that the strain-dependence of the material does not contain any time-dependence, it follows that the shapes of the $G(t)$ curves do not depend on strain. By comparing the relaxation modulus,

$$G(t) = e^{-k\gamma} \sum_i \frac{g_t}{\lambda_t} e^{-t/\lambda_t}$$  \hfill (6)

with the relaxation modulus at linear strains,

$$G_0(t) = \sum_i \frac{g_t}{\lambda_t} e^{-t/\lambda_t}$$  \hfill (7)
one may calculate the damping coefficient $k$ from the relation,

$$e^{-k\gamma} = \frac{G(t)}{G_0(t)}$$

Clearly, a plot of $\ln(G(t))$ versus $\gamma$ should yield a straight line with slope $-k$.

The consistency of this scheme can finally be checked using steady shear measurements. It can be shown that the steady shear behaviour may be calculated from a knowledge of $(g, \lambda_i)$, $k$ and the rate of shear strain (i.e. shear rate) $\dot{\gamma}$, namely

$$\tau(\dot{\gamma}) = \sum_i \frac{\eta_i \dot{\gamma}}{1 + k \lambda_i \dot{\gamma}^2}$$

This theoretical prediction may be compared to the measured flow curve, $\tau$ vs. $\dot{\gamma}$. In the present article the Wagner model is not central to our analysis but it will be shown that it can be used to parameterize the rheological data in terms of a spectrum of relaxation times, $\lambda_i$, and a damping coefficient, $k$.

2.2. MICROSCOPIC THEORY. — The modelling framework outlined above (Eqs. (2-9)) is not specific to micelles and provides a general but empirical tool for inter-relating different viscoelastic measurements. In the case of micelles, a microphysical model has been formulated [12–14] which predicts a near-Maxwell behaviour (a single dominant relaxation time) at low frequencies. The Maxwell time, $\lambda_M$, is determined by an interplay of breakage and disengagement processes for the self-assembled micellar “polymers”. At sufficiently higher frequencies, a spectrum of relaxation times corresponding to the local (Rouse) motion of the micelles is expected. The model also gives a direct prediction for $\tau(\dot{\gamma})$, at least for modest shear rates ($\gamma \lambda_M$ not too large) which shows a non-monotonic behaviour. In fact, the resulting curve is quite similar to that predicted empirically from equation (9) (see Fig. 3a) and resembles Figure 1.

Crudely speaking, the molecular origin of the non-monotonicity in $\tau(\dot{\gamma})$, leading to the spurt effect, is that chains which are strongly aligned along the flow direction do not exert much shear stress (although they provide large normal stresses). The largest $\tau$ arises when the orientation distribution of chain segments is peaked at an angle roughly midway between the flow and shear gradient directions, which occurs at $\dot{\gamma} \lambda_M \approx 1$.

An important issue in the interpretation of wormlike-micelle rheology concerns the role of elastic effects. It should be noted that the flow instability in wormlike micelles is visco-elastic in origin and not purely viscous. The role of normal stress in the shear-banding scenario is discussed in reference [11].

2.3. RELATIONSHIP OF FLOW CURVE TO VELOCITY PROFILE. — In the NMR imaging experiment we measure the velocity profile, $v(r)$. In a cylindrical tube, this profile has a simple and direct relationship to the flow curve, $\tau$ vs. $\dot{\gamma}$. Provided that the velocities are sufficiently small that inertial effects may be neglected (certainly the case here where Re $< 1$ for all data) then pressure will be constant across any given circular cross section. Consider a cylinder of fluid of radius $r$ and length $l$ sited in the fully-developed flow such that the pressure drop along the length of the cylinder is $\Delta P$. The shear stress exerted on the cylinder surface is $(\Delta P/2l)r$ and may be directly related to the rate of strain, $\dot{\gamma}$, by the constitutive relation $\tau = f(\dot{\gamma})$. Hence we may write

$$\frac{\partial v}{\partial r} = f^{-1}[\Delta P/2lr]$$

The linear dependence of stress, $\tau$, on radial displacement, $r$, is a particularly useful result since it enables one to derive the flow curve directly from the tube velocity profile by calculating the derivative, $\partial \tau / \partial r$. If the parameter $(\Delta P/2l)$ has been measured in the experiment, then this curve will be absolute in both $\tau$ and $\gamma$. If the pressure gradient is unknown then the $\tau$ axis will be arbitrarily scaled. Such scaling is used in the subsequent analysis.

Equation (10) may be easily integrated to yield $\nu(r)$ given $f(\gamma)$. In particular

$$v(r) = (\Delta P/2l)^{-1} \left( \int_0^{(\Delta P/2l)R} f^{-1}[\tau] d\tau - \int_0^{(\Delta P/2l)r} f^{-1}[\tau] d\tau \right)$$

(11)

This implies that a knowledge of the constitutive relation, $\tau = f(\gamma)$, permits one to directly calculate the velocity profile.

3. Experimental

Samples of wormlike surfactant were made by mixing the required amounts of cetyl pyridinium chloride (CPyCl) and sodium salicylate (NaSal) with distilled water and leaving for a few days to allow air bubbles to disappear. As in reference [10] the respective molar concentrations were 100 mM and 60 mM. CPyCl/NaSal solutions undergo a phase transition below 19 °C in which the sample is inhomogeneous and scatters light strongly. NMR work reported here was performed above this phase transition at 25 °C. All NMR measurements were carried out at Massey University using a Bruker AMX300 spectrometer with specialised micro imaging capability.

The solutions were contained in a closed loop and driven by a Gilson Minipuls 3 peristaltic pump. This pump has intrinsically low pulsatility due to the large number of rollers in the drive head. However we were able to strongly damp any remaining pulsation by driving the fluid through a closed reservoir containing a large air volume. This air space acted as a pressurising buffer in which smaller volume fluctuations were absorbed due to the compressibility of the gas. Because of the nature of the peristaltic roller action, this pump did not sweep fluid at a fixed volume flow rate but allowed some “slippage” when driving a viscous fluid. Consequently the rate was determined by the pressure head which the pump was able to develop in the reservoir. Thus the flow is, in effect, pressure controlled rather than flow rate controlled. The reservoir fluid then entered a glass tube of 1.0 m length. The reservoir consisted of a cylinder of 40 mm diameter and the entrance to the glass tube was flush with the bottom of this cylinder.

In the first set of experiments the tube inner diameter was 5 mm with pixel size 55 µm, whilst in a second set a 2.8 mm ID tube was used and the pixel size was 31 µm. Velocity profile measurements were made at a distance of between 0.8 and 0.9 m from the entrance. Volume flow rates in all experiments were determined from our knowledge of the cross sectional velocity map obtained directly by NMR measurement.

Velocity maps were obtained from a succession of NMR images of the tube in which the magnetic field gradient used to encode for velocity is successively stepped in magnitude, the entire data set being acquired over a period of several hours. This period was required for the acquisition of each velocity image. The set is subsequently Fourier analysed to provide a “propagator” for the motion in each pixel of the image. From these spectra the velocity value for each pixel is calculated and a velocity image obtained. While our method is slower than most single-step-encoding methods, it is ideally suited to steady state flow measurement and is particularly robust, being capable of yielding accurate and precise velocity maps.

Our confidence that the data acquired using the peristaltic pump drive were not influenced by flow pulsation effects is confirmed by our comparison of the flow profile data with that
obtained on the same system but using a constant flow rate drive. For these experiments a Pharmacia 500 twin syringe pump was used. This system provided a satisfactory fluid drive at low flow rates but was not able to cover the complete range of flow rates accessible to the peristaltic pump. However, these experiments were particularly useful in that they provided means of checking the profiles obtained at the same flow rates but with differing pump systems. In each case the agreement was good. Furthermore, because the syringe pump delivers very accurate flow rates we are able to use this system to confirm the validity of the NMR technique used to measure $Q$. These flow rates agreed within a few percent.

It should be noted that the NMR signal is obtained from the protons in the water solvent. Because these protons experience long spin lattice relaxation times, it is necessary to allow a significant recovery period between each signal acquisition to obtain the full signal-to-noise ratio. At finite repetition times some loss in signal amplitude is experienced. However, we are able to enhance the signal-to-noise ratio in the final velocity images by utilizing the symmetry available in tube flow. Since we are concerned to obtain diametral profiles of velocity, we employ azimuthal averaging of the pixels. This of course requires that we take great care in ensuring circular cross sections before the averaging of the data, a correction which is handled by our image processing software.

Rheological measurements were carried out at 25 °C using both a Rheometrics RDSII strain-controlled and a Rheometrics DSR stress-controlled rheometer which are located at the University of Cambridge. These rheometers utilized a 25 mm diameter cone and plate geometry. In the case of the strain-controlled device, a 0.01 Nm force rebalance transducer was fitted.

4. Results

4.1. STRAIN-CONTROLLED RHEOLOGICAL EXPERIMENTS. — Dynamic strain sweep experiments were carried out at a frequency of 1 rad/s on 100 mM/60 mM CPyCl/NaSal wormlike micelle solution at 25 °C. The results are shown in Figure 2a where it is clear that the linear region of strain extends to around 30%. The values of $G'$ and $G''$ versus frequency (at a strain of 20%) show a typical Maxwell-like pattern with dominantly viscous behaviour at low frequencies and dominantly elastic behaviour at high frequencies. As the frequency is increased the data, shown in Figure 2b, exhibit a $G' - G''$ crossover and a high frequency region of approximately constant $G'$. These data can be fitted using the series of relaxation times shown in Figure 2c. The linear viscoelastic behaviour is strongly dominated by a relaxation time at 2 s while at time scales longer than this, no relaxation times are found. (Note that the Maxwell time is shorter than the 8 s reported in Ref. [10] because of the higher temperature used here.) At time scales on the order of 1-10 ms, a second region of significant relaxation times seems to be present. This is also apparent in Figure 2 where an upturn of $G''$ is exhibited at around 100 rad/s.

The non-linear behaviour was investigated by carrying out step-strain experiments. In Figure 2d we show the results of the stress-relaxation measurements for strains between 20 and 500%. At 20% strain the behaviour is clearly linear, exhibiting a simple exponential decay. As strains increase, the curves shift progressively downwards. In order to determine the value of $k$ from the slope of a plot of $\ln(G(t))$ vs. $\gamma$, the $G$ values at a fixed time of 2 s are chosen. This leads to the expected exponential dependence and a strain-independent value for $k$ of 0.32 ± 0.01. This simple dependence of $G$ on $\gamma$ is assumed in Wagner's model, but, as reported by Mackley et al., cannot be relied upon to describe the behaviour of all fluids. In the present instance it should be noted that below $t = 0.5$ s the curves do not retain their shape, indicating that separability is not entirely obeyed at these short times.
The steady shear behaviour of the wormlike surfactant solution is remarkable (Fig. 3a). At shear rates below $\dot{\gamma} \approx 0.2 \, \text{s}^{-1}$ the material behaves as a near-Newtonian fluid. (The material is in fact characterised by a power law exponent of around 0.85 at these low shear rates but for the purpose of the present analysis we shall refer to this as the Newtonian region). Above this critical shear rate, the shear stress passes through a narrow transition region to become roughly independent of $\dot{\gamma}$. This region of constant shear stress is very reproducible. Note however that perfect constancy is not achieved; within experimental precision we measure a single valued (though sharply varying) shear rate rather than the discontinuity predicted by theory. At high shear rates the experiment becomes increasingly difficult to perform as the material is expelled from the rheometer gap. (We have ascertained this expulsion had not yet
Fig. 3. — a) Steady shear, shear stress vs. rate of strain behaviour of the wormlike surfactant solution. The solid curve shows the experimental strain-controlled rheometry data. Below \( \dot{\gamma} \approx 0.2 \text{ s}^{-1} \) the material behaves as a near-Newtonian fluid and above this the shear stress passes through a narrow transition region to become roughly independent of \( \dot{\gamma} \). The dotted curves are theoretical predictions based on the Wagner model. \( k = 0 \) gives the limiting behaviour in the low shear rate regime while the curve labelled 0.32 is calculated using the measured Wagner damping coefficient. b) Superposition of strain-controlled (solid line) and stress controlled (dots) rheometric data. Note the upturn observed at high shear rates in the strain-controlled data. This inflexion is expected to result in a shear band in capillary flow in the region near the walls.

happened in the case of the data presented here.) The point of fluid expulsion shifts to higher shear rates as temperatures increase.

Using the constitutive equation based on a generalised Maxwell model and Wagner-type damping function, one may predict the steady shear behaviour of Figure 3a. In the low shear rate regime the behaviour is Newtonian and the correspondence between experiment and prediction is good, the dotted curve labelled \( k = 0 \) giving the limiting behaviour in the low shear rate regime. Using our measured Wagner damping coefficient of 0.32, the overall flow curve can be calculated. As can be seen in Figure 3a, the dotted curve labelled \( k = 0.32 \) predicts a maximum in shear stress. This agrees qualitatively with our observations in that such a maximum in shear stress would lead to unstable flow, and result in a shear rate discontinuity.

4.2. STRESS-CONTROLLED RHEOLOGICAL EXPERIMENTS. — Because the shear rate is multi-valued at a certain shear stress, some experiments were carried out on CPyCl/NaSal solutions
using a stress-controlled rheometer to investigate the behaviour of the shear rate upon gradual increase of the stress. Six stress sweeps were performed, with data concentrated on the region of rapidly increasing shear rates. The results of these experiments are shown in Figure 3b together with those from the strain-controlled study. At low stresses a Newtonian region is seen with a zero-shear viscosity of 70 ± 5 Pa s, followed by a short region of shear thinning. Then a critical stress is exceeded and the shear rate increases quickly to values higher by 1 to 2 orders of magnitude. At stresses in excess of the critical stress of 26 ± 1 Pa, the shear rate becomes multi-valued. The lowest shear rate at this stress is of order 1 s⁻¹ (0.8 ± 0.2 s⁻¹) and the reproducibility in this region of rapidly increasing shear rates, between 1 and 10 s⁻¹, is very good. As the stress is further increased, the shear rate typically increases more slowly, and is even observed to decrease slightly over a region which is identified by the clustering of data points between 40 and 100 s⁻¹. This upturn in the stress-strain rate curve is also found by Rehage and Hoffmann [10] and has been predicted in a recent paper by Spenley et al. [12]. Although this high shear region can be indicated with confidence, it is situated close to shear rates at which the material is expelled from the rheometer gap so that data above stresses of order 35 Pa are unavailable. Clearly, the shear rates are extremely sensitive to applied stresses of around 26 Pa and the region in which the shear rate is multi-valued can be given only with a degree of approximation. Our data suggest that this region extends from (0.8 ± 0.2 s⁻¹) to (40 ± 20 s⁻¹).

4.3. NMR VELOCITY PROFILE EXPERIMENTS. — A set of seven diametral velocity profiles, \( v(r) \), for the same CPyCl/NaSal wormlike surfactant system is shown in Figure 4a, corresponding respectively to flow rates in the 5.0 mm diameter tube of 0.22, 0.30, 0.38, 0.99, 1.2, 1.5 and 2.1 ml min⁻¹. At the lowest flow rate used, the data follows a nearly parabolic profile, characteristic of the Poiseuille tube flow of a Newtonian fluid. In the vicinity of 0.4 ml min⁻¹ the velocity profile deviates from its parabolic shape near the tube wall where an enhanced shear rate is apparent.

In order to clearly demonstrate the transition from the Newtonian to the spurt region which occurs with increasing flow rate, we show in Figure 4b four normalised velocity profiles at a range of flow rates. These have been obtained from the raw data by the azimuthal averaging process referred to above. Note that the velocities have been normalised to the maximum value exhibited at the capillary centre. Also shown is the theoretical profile for a power law exponent of 0.85. The agreement with the low \( Q \) data is very good. The maximum shear rate at the walls for this velocity map is 0.2 s⁻¹ As \( Q \) is slightly increased a delicate transition is apparent in the velocity profiles. This transition occurs so suddenly, between \( Q = 0.36 \) and 0.40 ml min⁻¹, that unstable flow is apparent at an intermediate value. In the unstable flow regime, the profile fluctuates over the data acquisition. This can be seen by examining the individual pixel velocity distributions which, instead of exhibiting a single peak, exhibit doublet or highly smeared velocity distributions, characteristic of flow rate changes over the 2 hr period during which the velocity image is acquired.

Above the transition flow rate the data all exhibit a consistent and steady behaviour in which a very high gradient in \( v(r) \), on the order of 10 s⁻¹, is apparent near the tube walls. For example, at \( Q = 0.99 \) ml min⁻¹ a sudden step in velocity is apparent in a single pixel adjacent to the wall, which in this experiment is indistinguishable from slip. At higher flow rates the high shear region near the wall appears to occupy a finite pixel range, for example at \( Q = 2.1 \) ml min⁻¹, the "jump" appears to occur over two pixels and is consistent with a wall shear rate of around 20 s⁻¹. We attribute this jump to the discontinuity in the shear stress vs. shear strain data once the critical shear rate is exceeded.
Fig. 4. — a) Seven raw velocity profiles obtained across a diametral slice in the 5.0 mm diameter tube using the CPyCl/NaSal wormlike surfactant system at flow rates of 0.22, 0.30, 0.38, 0.99, 1.2, 1.5 and 2.1 ml min\(^{-1}\). At the lowest flow rate used, the data follows a nearly parabolic profile, characteristic of the Poiseuille tube flow of a Newtonian fluid. A strong deviation from Newtonian flow along with enhanced shear rate at the wall is apparent around 0.4 ml min\(^{-1}\), above which a spurt in the flow occurs with a very high shear rate next to the walls. b) Azimuthally averaged, normalised velocity profiles in the 5.0 mm diameter tube for a representative range of flow rates of \(Q = 2.1\) (solid squares), 0.99 (solid circles), 0.38 (open squares) and 0.22 (open circles) ml min\(^{-1}\) in the 5.0 mm diameter tube. Normalisation has been carried out in each case by dividing each velocity value by the maximum value at the centre of the capillary. The theoretical profile behind the 0.22 ml min\(^{-1}\) data corresponds to a power law calculation with \(n = 0.85\).

It should be noted that the flow rate of 2.1 ml min\(^{-1}\) was the maximum which we were able to achieve using the peristaltic pump. If the shear stress vs. shear rate rheometry data does indeed indicate an upturn at high rates of strain, then we might expect a finite shear band once the wall shear rate approaches 40 s\(^{-1}\). Observation of such a band therefore requires higher shear rates than were achievable in the experiment using the 5 mm tube.

We have therefore repeated these measurements using a tube with the narrower diameter of 2.8 mm and at flow rates sufficiently high to exceed the wall shear rates found in the 5 mm diameter data. It is significant that in all these higher shear rate experiments, the velocity images were not perfectly symmetric, i.e. while the flow rates were steady, the profiles did not exhibit the azimuthal symmetry apparent in all the 5 mm diameter data. Without such symmetry the azimuthal averaging process was not justified and, in consequence, we display
Fig. 5. — a) Velocity profiles obtained across a diametral slice in the 2.8 mm diameter tube using the CPyCl/NaSal wormlike surfactant system at flow rates of 1.04 (open diamonds), 0.92 (vertical crosses), 0.77 (solid diamonds) and 0.55 (diagonal crosses) ml min\(^{-1}\), along with a set of absolute velocity data from the 5.0 mm capillary with flow rates \(Q = 2.1\) (solid squares), 0.99 (solid circles), 0.38 (open squares) and 0.22 (open circles). b) As for a) but with the 2.8 mm diameter velocity data scaled by \((5.0/2.8)\) along both the velocity and displacement axes, so as to preserve local shear rate. Only the raw velocity profiles for the 2.8 mm ID data, superposed on the (azimuthally averaged) data for the 5 mm tube. These data are plotted in Figure 5a. Figure 5b shows the data plotted in a manner which facilitates direct comparison. Here the radial dimension of the narrower tube data is scaled up to correspond with the distance scale for the 5 mm ID data. Because we wish to compare rheological behaviour in terms of shear rate, we also scale the velocity dimension by the same factor, thus retaining the same values of \(\partial v/\partial r\). In other words, we plot this higher shear rate data as velocity profiles which we would expect if all the experiments had been performed in the 5 mm ID tube.

At these higher shear rates we are unable to discern any clear band at the wall. At the maximum flow rates the jump in velocity associated with the spurt effect, occurs over two pixels, and corresponds to a shear rate of around 70 s\(^{-1}\). Given the present constraint of pumping rate we cannot provide definitive evidence of a shear band at the wall. At the same time we observe that our data is not inconsistent with a shear stress vs. shear rate upturn in the region 50 s\(^{-1}\) to 100 s\(^{-1}\).

As a further check on the transition behaviour, we have carried out a measurement of the velocity profile of 100 mM/60 mM CPyCl/NaSal solutions in a glass Couette cell. Here the
5. Discussion

Our rheological measurements using controlled stress are consistent with some predictions by Spenley et al. [12]. These authors suggest that the region of constant stress, $\tau_c$, will be characterised by a stress of $0.67G'(\infty)$ where $G'(\infty)$ is the plateau modulus of $G'$ at high frequencies. The value of $G'(\infty)$ that we found ($37 \pm 1$ Pa) implies $\tau_c \approx 25 \pm 1$ Pa, in excellent agreement with our measured value of $26 \pm 1$ Pa. Furthermore, it is predicted that the constant stress region sets in at shear rates of $2.6/\lambda_M$, where $\lambda_M$ is the Maxwell time introduced previously. This shear rate would correspond to $1.3$ s$^{-1}$ if we only take the most important relaxation time of $2$ s into account. This is quite close to the value $(0.4 - 0.9$ s$^{-1}$) we read from Figure 3b and is also of the same order of magnitude as the MRI observations, which suggest a critical shear rate of around $1$ s$^{-1}$. The implementation of the empirical scheme based

Fig. 6. — The velocity profile of 100mM/60mM CPyCl/NaSal solutions in a glass Couette cell where the fluid is contained in the 2.0 mm gap between a rotating inner cylinder of outer diameter 5.0 mm and an outer cylinder of inner diameter 9.0 mm. The radial distance is measured form the centre of rotation. Notice that the inner cylinder is filled with the fluid as well so that the velocity of the outer surface of the inner cylinder can be obtained by extrapolation. Next to this moving surface a high shear band is apparent in the fluid in the annulus.
on a Maxwell model and a Wagner-type damping function is also successful in that it predicts unstable flow behaviour at shear rates above order 1 s$^{-1}$.

The presence of unstable flow behaviour is further indicated by the difference between the constitutive relation obtained by the stress-controlled rheometer as compared with that yielded by the strain-controlled rheometer. This effect becomes even more prominent when the experiments are carried out at 20 °C as seen in Figure 7, where the strain-controlled measurements at first show correspondence with the stress-controlled data, but deviations occur near the critical point. The strain-controlled data show a pronounced maximum of the shear stress, whereas in a stress-controlled experiment, the material shows only a region of very fast increase of strain rate during a very narrow region of applied stress (three experiments shown). The calculation presented in Figure 7 used a value of $k = 0.32$.

In summary, the agreement between stress controlled and strain controlled measurements of the flow curves is good at small stresses. From the flow curves measured with both strain and stress controlled rheometers, it can be expected that with increasing shear stress, a gradual transition to non-Newtonian behaviour will occur at 0.2 s$^{-1}$ while at a shear rate of 0.8 s$^{-1}$ a discontinuous transition to the spurt region will occur. Both transitions can be clearly identified in the NMR imaging experiments carried out using the 5 mm ID tube.

Figure 8 shows the calculated local shear rate obtained the absolute velocity profiles for $Q = 2.1, 0.99, 0.38$ and 0.22 ml min$^{-1}$, in which the 0.2 s$^{-1}$ and 0.8 s$^{-1}$ transitions are indicated. For these data, Newtonian behaviour corresponds to a linear-dependence of shear rate on radius. (Note that the negative shear rate region simply corresponds to the left hand half of the capillary and that shear rates values above 1.4 s$^{-1}$ are not plotted). As expected, all flow rates exhibit a linear region for those radii sufficiently small that $\dot{\gamma}$ does not exceed 0.2 s$^{-1}$. For the lowest flow rate shown this region extends right across the tube diameter. At 0.38 ml min$^{-1}$, the maximum shear rate is just approaching the spurt region expected when $\dot{\gamma}$ exceeds 0.8 s$^{-1}$. The flow rates for which the maximum value of $\dot{\gamma}$ exceeds 0.2 s$^{-1}$ but is still less than 0.8 s$^{-1}$ exhibit a gradual transition from Newtonian to strongly non-Newtonian profiles but without any evidence of shear banding or wall slip. For the flow rates of 0.99 and 2.2 ml min$^{-1}$, maximum $\dot{\gamma}$ values close to the walls exceed 0.8 s$^{-1}$ and a region of apparent wall slip (but of finite width in the second case) occurs for which the rate of strain is
around 10 to 20 s\(^{-1}\). For these higher flow rates, a gradual transition from Newtonian to non-Newtonian flow is also apparent in the velocity profiles between \(\dot{\gamma} = 0.2\) s\(^{-1}\) and \(\dot{\gamma} = 0.8\) s\(^{-1}\).

In order to compare the velocity data with the predictions of the rheological measurements, we superpose, in Figure 9, experimental velocity graphs obtained by NMR imaging in the 5 mm ID tube with corresponding curves (i.e., at identical flow rate, \(Q\)) calculated using equation (11) and incorporating the measured constitutive relation data shown in the flow curves of Figure 3a. In other words, equation (11) is used to calculate \(v(r)\) using the stress vs. rate of strain data of Figure 3 so as to define \(f(\dot{\gamma})\) and hence, its inverse \(f^{-1}(\tau)\). Because the total flow rates correspond in the experimental and theoretical profiles, the absolute velocities are very similar and it is the shape of the profiles which we seek to examine. For that reason we choose to employ normalised profiles in order to illustrate the comparisons. With the exception of the data at 0.38 ml min\(^{-1}\), the agreement is fairly good.

Figure 10 shows the inverse comparison in which we plot the \(\tau vs. \dot{\gamma}\) data of Figure 3 along with those obtained from the NMR velocity profiles by arbitrarily scaling the radius values for each flow rate, in accordance with equation (10). This scaling was performed (on the log scale) by arbitrary vertical displacement so that the plateau regions of constant stress were roughly superposed. The solid line represents the experimental rheology data of Figure 3.

Again, with the exception of the \(Q = 0.38\) ml min\(^{-1}\) data the general shape of this NMR data is broadly consistent with the rheological measurements. This latter data shows evidence of a transition in shear stress dependence on radius at an intermediate region in the tube. We cannot explain this anomalous behaviour but we note that it occurs close to the onset of the spurt effect and attribute the deviation to instability in the flow conditions associated with this onset. The effect could be explained by invoking a pressure variation across the diametral slice for this intermediate flow rate. Such a variation might be associated with changes in the normal stress difference. We believe that these anomalies may arise because of the instability associated with the difference between stress-controlled and strain-controlled conditions. In the peristaltic drive system employed here, it is not clear that the fluid is consistently in one or other condition.
Fig. 9. — The normalised velocity data of Figure 8a along with corresponding theoretical predictions calculated from equation (11) and using the constitutive data from the rheological measurements shown in Figure 3. a) through d) are for $Q = 2.1$, 0.99, 0.38 and 0.22 ml min$^{-1}$ respectively. ([ ] exp. rad. ave., (—) theor. rheol.).

Fig. 10. — $\tau$ vs. $\dot{\gamma}$ data of Figure 3 (solid line) along with the equivalent shear rate data obtained from the NMR velocity profiles for $Q = 2.1$ (solid squares), 0.99 (solid circles), 0.38 (open squares) and 0.22 (open circles) ml min$^{-1}$. The shear stress is obtained from the NMR data by arbitrarily scaling the radius values for each flow rate, in accordance with equation (10). With the exception of the $Q = 0.38$ ml min$^{-1}$ data the agreement is good.
The problem of non-steady behaviour in the region of the transition to high shear at the walls should be considered in the light of the expected origin of the discontinuity associated with spurt. In the paper by McLeish and Ball [6] the explanation of the spurt effect is that the flow rate, \( Q \), is discontinuous in the pressure drop \( P \) across the pipe. This is more complicated than in the case for Couette flow since once shear bands form at the edges of the pipe it is expected that they will be unstable and migrate towards the centre. This effect is shown in the two dashed horizontal lines in Figure 1 where the lower plateau corresponds to a higher total throughput for a given \( P \). If indeed this model is correct and the pump used is not at fixed stress \( P \) (i.e. it is either at fixed \( Q \) or some intermediate condition) then one would certainly expect a non-steady flow at flow rates which lie on the discontinuity of the \( Q(P) \) curve.

A problem of instability is also particularly apparent in the 2.8 mm tube data where higher shear rates were employed. A lack of circular symmetry was observed in the velocity images at the highest flow rates (data not shown) the velocity propagators were highly distorted, indicating flow rate inconsistency during the measurement. Because we were unable to perform (reliably) the azimuthal averaging process necessary for signal-to-noise enhancement in the velocity profiles, we have not carried out the shear rate analysis applied to the 5 mm ID data, since the process of taking derivatives of the velocity is highly sensitive to noise. We note however that the narrow tube data exhibits some curious features not predicted by the rheological measurements. In particular, as the flow rate increases the central region of the velocity profile becomes flat (characteristic of plug flow) rather than retaining the parabolic profile expected for the Newtonian region below \( 0.2 \) s\(^{-1} \). Furthermore, it would appear that the high shear jump at the wall is joined with the central plug by a transitional region in which the shear rate is approximately constant at \( 1.5 \) s\(^{-1} \). We are unable to explain this observation in terms of the rheometric data. This anomalous behaviour may be a result of flow development associated with high wall shear and will be the subject of future investigation.

It is clear that the velocity data observed with NMR velocity imaging in the 5 mm ID tube broadly agree with those predicted by the rheological measurements and that the associated shear rate profiles are consistent with the shear stress \( \tau \) shear rate data obtained by cone-and-plate rheometry. However it should be noted that the fitted curves are based on the smooth rheological data of Figure 3a and therefore do not show sharp slope discontinuities between shear bands. Clear evidence has been found for the spurt effect in this wormlike surfactant system. This effect differs from conventional slip in that the onset of the behaviour shows a characteristic critical stress (which accords with that predicted from bulk rheology), while the data suggests that region of very high shear rate may exist over a finite region. For example, in Figure 9d, it appears that the high-shear band extends over more than one pixel, a similar spread being apparent in Figure 6 where the worm-like micelles are subjected to shear in a Couette cell. Over a finite distance into the fluid, shear stresses exceed the critical stress, leading to the high shear band. Further into the fluid where stresses fall below the critical stress, the low shear band is obtained which is consistent with the near-Newtonian region of apparent viscosity, \( 70 \pm 5 \) Pa s, obtained in the rheometric measurements.

6. Conclusion

The data exhibited here represent the first observation of the spurt effect using NMR imaging methods and clearly demonstrate the power of this technique in rheological investigations. A key philosophy behind our work has been to provide a clear link between conventional rheometry and the new methodology based on velocity profiling. We have made this connection in two directions: by calculating velocity profiles from rheological flow curves and by converting the NMR velocity maps to plots of shear stress \( \tau \) shear rate which can then be superposed on
the rheometric data. We are as yet unable to make the link between absolute values of shear stress in both experiments because of the lack of pressure data in the NMR measurements. However, we note the convenience of the capillary geometry in velocity profiling experiments because of the simple linear dependence of shear stress on radius at all points within the tube inner diameter.

Because of the method of pumping used in the NMR experiments it is not clear whether the flow is stress-controlled or strain-controlled. This factor may explain some of inconsistencies which have been observed. Furthermore, at very high shear rates there is a suggestion that some changes in the fluid rheology may occur during flow development down the tube. This could be investigated by using a moveable tube in which the velocity map could be obtained as different distances from the entrance point. We also note that some very interesting questions concerning the molecular basis of complex rheology can be addressed using NMR methods. For example it is possible, in principle, to image NMR properties sensitive to molecular organisation and dynamics, and to superpose these upon the known shear rate profile. Both these areas of investigation will be pursued by us in the future.

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Note Added

Subsequent to submission of this article, a report has appeared (Deeruppe P., Cressely R., Makhoufi R. and Cappelaere E., Colloid. Polymer. Sci. 273 (1995) 346-351) reporting shear band observation in another wormlike surfactant by means of optical birefringence methods.

References