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# Wormlike micellar solutions: III. VCM model predictions in steady and transient shearing flows

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ABSTRACT

The two species, scission/reforming Vasquez–Cook–McKinley (VCM) model was formulated to describe the coupling between the viscoelastic fluid rheology and the kinetics of wormlike micellar assembly and deformation-induced rupture. The model self-consistently captures the nonlocal effects of stress-induced diffusion and has been studied in various limits for a number of canonical flow fields including Large Amplitude Oscillatory Shear (LAOS), steady and transient extensional flow as well as steady pressure-driven channel flow. However, a complete study of the spatiotemporal model predictions in shearing flow, both with (and without) inertia, and with (or without) the stress-concentration diffusive coupling, has not yet been reported. In this paper we present a comprehensive investigation of the full VCM model in steady and transient shearing flow including inertial and diffusive (non-local) effects. The consequences of varying the model parameters, the effect of the start-up ramp rate, and the role of geometry on the steady state flow curve are each investigated. As a result of the onset of shear-banding and nonlocal effects in the velocity, stress and concentration profiles, we show that the measured rheological properties in a wormlike micellar solution described by the VCM model can depend on the initial ramp rate as well as specific details of the geometry such as the length scale of the rheometric fixture chosen and its curvature. The complete time evolution of the rheological response at high Deborah numbers is examined, from the initial formation of inertial waves through nonlinear overshoots in the viscoelastic stresses, shear band formation (and elastic recoil in the local velocity), to the long time diffusion-mediated approach to a final steady state.



## 1. Introduction

Wormlike micellar mixtures exhibit properties making them valuable for commercial uses, for example in detergents, shampoos and as oil recovery enhancers. These mixtures show high and constant viscosities at low shear rates with strong shear thinning occurring at larger shear rates. Wormlike micelles are composed of amphiphilic surfactant molecules which, in an aqueous solvent, self assemble into long flexible cylindrical (wormy) structures protecting their hydrophobic tails in the interior of the worm. The length of the worms can be on the order of microns with radii on the order of ten nanometers. These long flexible worms entangle in solution at moderate surfactant concentrations and, as a result of these entanglements, wormlike surfactant mixtures exhibit viscoelastic properties similar to those exhibited by concentrated polymer solutions. By contrast with covalently-connected flexible polymer chains, the wormlike micelles continuously break and reform thus earning the name 'living polymers'. The rheology of these mixtures is dominated by two distinct relaxation processes; firstly a disentanglement process in which the worms dissociate from the network, similar to reptation of entangled polymers, the second due to the breakage and reformation of the worms.

Wormlike micellar solutions of various chemistries (CPyCl, CTAB, EHAC) in a range of solvents have been the subject of many experimental investigations, for example [1–7]. A good overview of experimental findings and the different surfactants used in each fluid is given in [8]. These experiments show a commonality in the rheological response of these mixtures in that they can exhibit kinematic inhomogeneities even in simple shearing flow, developing shear-bands and strong shear-thinning. In a narrow gap Taylor-Couette device, with inner cylinder rotating at a fixed velocity and outer cylinder fixed, the steady state velocity profile across the gap is nearly linear at low shear rates. When the velocity of the inner cylinder is increased such that the velocity gradient across the

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gap exceeds a critical shear rate, $\dot{\gamma}_1$, the velocity profile splits into (at least) two regions; with a high shear rate (i.e. large velocity gradient) near the inner wall and a slower moving region with low shear rate closer to the outer wall. The transition region between the two shear bands shifts outwards toward the stationary outer cylinder as the shear rate is increased until, at a certain shear rate, $\dot{\gamma}_2$, the high shear rate band spans the gap. At shear rates larger than $\dot{\gamma}_2$, the velocity profile is again close to linear. The steady state flow curve of shear stress as a function of shear rate rises monotonically (and almost linearly) for small shear rates, then begins to level off until, at the shear rate of $\dot{\gamma}_1$ the flow curve plateaus. The plateau continues until the shear rate reaches $\dot{\gamma}_2$, thereafter the flow curve is again a monotonic increasing function of shear rate. Experiments also show [7] that under shear rate control the first normal stress difference initially increases quadratically with shear rate until $\dot{\gamma}_1$, at which point the increase becomes linear, up to a shear rate of $\dot{\gamma}_2$, at which point the rate of increase in $N_1$ becomes approximately quadratic again. Small Amplitude Oscillatory Shear (SAOS) experiments show two highly separated time scales suggesting a superposition of two Maxwell modes [7]. The shear-banding and the correlated flow curve plateau are generally attributed to a multi-valued underlying rheological constitutive relation between shear stress and shear rate if one assumes viscometric (homogeneous) kinematics [8–10]. Flows along the locally decreasing portion of this rheological constitutive curve have been shown to be unstable [11] so that, under shear-rate controlled conditions (with velocity imposed at the walls) the flow bifurcates into two branches with one flow domain located on the stable low shear rate branch of the rheological flow curve and the other on the stable high shear rate branch. The portion of the gap which each shear rate occupies is determined by a lever rule in order that the appropriate total velocity change across the gap is obtained. A number of comprehensive review papers describing the flow structure and dynamics have appeared [8–10].

Several single species (plus solvent) models which exhibit non-monotone rheological constitutive curves have been examined in the literature as a basis for understanding flows of wormlike micellar solutions; for example, the Johnson–Segalman model [12–15], the reptation–reaction model [10,16], a "Toy" model based on reptation theory [17], a more complete reptation model (known as the "Rolie-Poly" model) [18], the Giesekus model [19–21] and the PEC (Partially Extended Convected) model [22]. These models can, under appropriate parameter conditions, all exhibit a non-monotone rheological constitutive curve and thus can each capture some key aspects of the linear and nonlinear rheology observed experimentally. Some of these single-species models are phenomenological in basis (e.g. the Johnson–Segalman and Giesekus model) and may respond unphysically in step-strain and/or extensional flow response (e.g. the Johnson–Segalman model [23]), or may be difficult to manipulate and fit to actual experimental data (the reptation–reaction model). These single species models generally coarse-grain the solvent and low molecular weight species into a single Newtonian mode and thus do not exhibit fluid elasticity at high frequencies or shear rates.

One model that takes into account (in an approximate way) the breakage and reforming of the worms is the Vasquez–Cook–McKinley (VCM) model [24]. This model is a two species (plus solvent) model in which worms of length $L$ can break into two worms of length $L/2$, and two worms of length $L/2$ can reform to a single worm of length $L$. The VCM model thus incorporates a physical breakage-reforming processes and is appropriately frame-invariant. The model allows for a realistic (aqueous) solvent viscosity and also captures the presence of a second, short species which gives rise to a weak viscoelastic contribution at high shear rates. The VCM model reduces to a single species PEC model (with additional diffusive terms) [23] in a Newtonian solvent, in the limit that the relaxation time of the second species goes to zero and that the number densities of each wormy species are constant. The PEC model was extensively examined in [22]. The Rolie-Poly model, in the limit that the convective constraint parameter $\beta$ is zero and chain stretching is ignored, can be reduced to the reptation–reaction model [25]. In this limit, in shearing flow, the Rolie-Poly model is similar to the PEC model but without the free nonlinear parameter. More recently, a thermodynamically consistent two-species model has been derived from non-equilibrium thermodynamics considerations and its predictions have been compared with those of the two-species VCM model [26].

Analysis of the rheological predictions of the VCM model has been carried out in several geometries and for a range of boundary conditions including steady shearing flow in a Taylor-Couette geometry under Large Amplitude Oscillatory Shear (LAOS) [27]; fast and slow stepped-ramps up to steady state shearing in a Taylor-Couette geometry (during which localized shear waves may develop) [28]; steady pressure-driven channel flows [29], and extensional flows [30]. Predictions of those studies compare well with many of the principal features of wormlike micellar rheology observed in experiments. In these previous studies, theoretical predictions are contrasted with those of simpler single species models and shown to be an improvement in several cases, for example the capability of predicting the highly localized rupture event in an elongating filament of a wormlike micellar solution in extensional flow [30]. The predictions of a non-interacting version of the two species VCM model, namely the PEC+M model (as well as the PEC model plus solvent) have been analyzed extensively for the case of step strains and ramps up to steady state shearing flows [22].

While the VCM model has been demonstrated to successfully model wormlike micellar mixtures in various shearing and elongational deformations, it does have its own limitations including: (i) the second normal stress difference $N_2$ is identically zero; (ii) numerical computations of steady state values of $N_1(\dot{\gamma})$, the first normal stress difference, as a function of shear rate in *Taylor-Couette* flow do not agree with results obtained in *cone–plate* experiments for shear rates in the shear banding region [7]. This latter discrepancy may be due to the geometrical differences, but may also be due to the simplicity of the kinetics describing the reforming rate of the VCM model, a simplification made in part to highlight the controlling role of micellar breakage in the observed dynamics. In [31], the VCM model was modified, allowing temporal and configuration dependent changes of the equilibrium breakage rate and of the relaxation rate of the long species in order to account for gel-like structure formation that can be observed in some micellar solutions at very high deformation rates [32,33].

As noted above, building on the VCM model success, a thermodynamically consistent two species model has recently been derived [26]. In this new model the nonlinear breakage and reforming rates have different functional forms than those of the VCM model. Preliminary simulations of the modified model in a homogeneous viscometric flow showed a multi-valued underlying rheological constitutive relation (flow curve) similar to those of the VCM model. Results for inhomogeneous flows of this new model have not yet been reported. One advantage of the new model is that there is no free nonlinear parameter, on the other hand this distinction may well restrict the ability of the model to be fitted to experimental data for different micellar concentration.

In the present paper we carry out a comprehensive investigation of the full VCM model in shearing deformations including transient analysis from initial start up to steady state for a Taylor-Couette flow geometry. We compile a number of disparate existing results describing the VCM model predictions, and also provide new computational results; for example the effect of changing flow geometry on the predicted steady state curve