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A new constitutive model for worm-like micellar systems – Numerical simulation of confined contraction–expansion flows

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ABSTRACT

This hybrid finite element/volume study is concerned with the modelling of worm-like micellar systems, employing a new micellar thixotropic constitutive model with viscoelasticity within network-structure construction–destruction kinetics. The work focuses on steady-state solutions for axisymmetric, rounded-corner, 4:1:4 contraction–expansion flows. This has importance in industrial and healthcare applications such as in enhanced oil-reservoir recovery. Material functions for the micellar models (*time-dependent, thixotropic*) have been fitted to match two different extensional configurations of the exponential Phan-Thien/Tanner (PTT) model (rubber *network-based, non-thixotropic*). This covers mild and strong-hardening response, and re solvent fraction, highly-polymeric ($\beta = 1/9$) and solvent-dominated ($\beta = 0.9$) fluids. Solution results are described through normalised Excess Pressure Drop (EPD), vortex intensity and stream function, stress (N_1 and N_2), and f-functional data. EPD predictions with the new micellar models prove to be consistent (at low rates, some rising) with Newtonian results, contrary to the base-reference modified Bautista–Manero (MBM) results. Markedly different vortex intensity trends are found in comparing micellar and EPTT solutions, which correspond with $N_2 - N_1$ and f data. In order to address the highly-elastic regime for thixotropic materials, a convoluted approach between EPPT and micellar models has been proposed. Here, numerically stable solutions are reported for impressively large *We* up to 300 and new vortex structures are revealed.

1. Introduction

This work is devoted to solve numerically the benchmark 4:1:4 rounded contraction/expansion flow of worm-like micellar systems using the Bautista–Manero constitutive approach [1–3]. Herein, a new approach is proposed that intimately introduces the viscoelasticity into the structure construction/destruction mechanism of worm-like micellar solutions. These non-Newtonian viscoelastic liquids present interactions of viscosity, elasticity, and breakdown and formation of internal structure. This spurns highly complex rheological phenomena, and manifests features associated with thixotropy, pseudo plasticity and shear-banding [1,5]. The versatility and complex rheological behaviour of viscoelastic wormlike micellar solutions render them an ideal candidate for varied applications. In viscoelastic surfactant form, they have been termed 'Smart Fluids', due to their ability to self-select their rheological properties to appropriately fit to change in alternative deformation environments. Processing and modern-day applications of such material systems range amongst additives in house-hold products (hard surface cleaners and drain-opener liquid plumber), paints, cosmetics, health care products (nutrient-carriers in shampoo and body wash), and under specific application fluid design such as with drag reducing agents in heating and cooling systems, and drilling fluids in enhanced oil-reservoir recovery (EOR) [6].

Significantly in modern EOR processes, which consist of hydraulic stimulation of oil wells to increase productivity, these fluid systems have become highly important given their adaptability in rheological characteristics [6]. Fracturing fluids are required in this operation, with the capability of transforming their rheological properties according to the prevailing flow conditions encountered. This involves transitions from low viscosity Newtonian fluids, when pumped into the oil-wells to fracture the rock-pores; passing through to gel-like form, with highly viscoelastic characteristics, capable of transporting proppants to keep fractures open and enhance rock-pores permeability in the oil-well; to finally, reverting into low viscosity fluids which degrade easily and unblock the fractures as the prerequisite pressure levels are realised. Wormlike micellar solution systems fulfil these requirements, being constituted of mixtures of surfactants – typically cetyltrimethylamonium bromide (CTAB) or cetylpyridinium chloride (CPyCl) [7] – and salts – sodium salicylate (NaSal) – in water.

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These mixtures arrange themselves into physically bonded units and change their network-structure characteristics with temperature, surfactant and salt concentration [8]; but also with the forces and deformations they experience. The wormlike micelles are elongated surfactant groups that, under suitable conditions, can entangle and impart viscoelasticity to the fluid. Their behaviour is highly complex, although similar to that observed for polymer solutions and melts; hence their naming "living polymers" [8]. Unlike the covalently bonded polymer backbone, these micelles lie in thermodynamic equilibrium with the solvent and continuously break and reform under Brownian fluctuations. Therefore, additionally to reptation, wormlike micelles provide a mechanism for stress relief and entanglement elimination, creating and destroying temporary branch points, known as "ghost-like crossing" [8].

Furthermore, wormlike micelles are particularly viable for industrial application, since (a) fewer additives than for polymer-based fracturing fluids are required in their production, which render them a cheaper option [6]; (b) in EOR, chemical-breakers are unnecessary, since after contact with crude oil, wormlike micelles systems rearrange into small spherical micelles (c.a. 10–50 nm). These are simpler and smaller physical arrangements, which finally form a low viscosity microemulsion. Additionally, (c) wormlike micelles are more environmentally friendly and more easily biodegradable than polymer-based fracturing fluids [6].

Many approaches have been pursued to model wormlike micelles flow behaviour. Bautista et al. [1,2,4] proposed a rheological modelling approach for wormlike micelle solutions, the Bautista–Manero–Puig (BMP) model. This equation of state consists of the upper-convected Maxwell constitutive equation to describe stress evolution, coupled to a kinetic equation that takes into account structural changes induced by the flow, based on the rate of energy dissipation. This theory has demonstrated accuracy in the description of shear-banding [4,9,10], pulsating flows of wormlike micelle solutions [11], characterisation of associative polymers [12], and for evaluating the negative wake flow past a sphere [13] and drag correction [14]. Some years later, Boek et al. [3] corrected the BMP model, given its unbounded extensional viscosity in simple uniaxial extensional flow – thus producing the Modified Bautista–Manero (MBM) model. This has been utilised to model the transient flow of wormlike micellar solutions in planar 4:1 contraction flow setting [15], being a forerunner in wormlike micellar simulations for complex flows, along with others based on the principles of mesoscopic Brownian dynamics [16]. The VCM model, based on a discrete version of the 'living polymer theory' of Cates, has been tested in simple flows, where rheological homogeneity prevails [17,18], and under conditions of shear-banding [19]. Another approach, consists of using the Johnson–Segalman model, modified with a diffusion term for the extra/polymeric stress (so-called d-JS model [16,20–22]). This model has been tested against experimental data in simple shear flows and shear-banding conditions. The Giesekus model has also been used in the representation of wormlike micelles under simple shear scenarios, whilst using the non-linear anisotropy coupling parameter to introduce shear-banding conditions [23–28]. For this purpose, the appropriate Giesekus model parameters, for both banding and non-banding conditions, have been determined through Large Amplitude Oscillatory Shear (LAOS) [24] experiments in a coaxial-cylinder Couette geometry [23]. In addition, whilst using parallel plate geometries, and adjusting temperature, salt concentration and shear rate, shear-banding and non-banding conditions have been studied by Rheo-small-angle 1ight scattering (Rheo-SALS) [25], and flow-small angle neutron scattering (flow-SANS) [26]. In this respect, findings reveal shear-induced separation into an isotropic low-shear band and another flow-aligned nematic high-shear band.

The surfactant:salt concentration of these fluid-systems dictates their nature and rheological response, providing a classification into three (or more) basic types. As such, the so-called 'salt curve' provides the dependency of the zero-shear viscosity η_{p0} on the surfactant:salt concentration. Studies on the composition of wormlike micellar solutions and their rheological implications [29–31], provide evidence that these solutions (i) have η_{p0} close to the Newtonian solvent *at low salt concentration*; this range is characterised by *spherical micelles*. (ii) When the salt concentration is increased to *moderate/semi-dilute levels*, the solution demonstrates a dramatic increase in its zero-shear viscosity, reaching η_{p0} peaks as large as six times the solvent zero-shear viscosity [30,31]; this range manifests the formation-growth *of wormlike structures* and beginnings of their *entanglement*, causing shear-thinning and normal stresses in shear [31]. (iii) *Further increase of the salt concentration* generates *longer wormlike micelles*, which form an entangled network [31]. This is reflected in a steep decline in η_{p0} given by the proliferation of stress-relaxation points at the entanglement junctions [30]. The work presented in this manuscript is based around the Bautista–Manero approach [1–3,4], and aims to represent wormlike micellar systems in the second–third type-stage, with significant pseudoplastic and elastic characteristics. This theory originated to represent semi-dilute concentrations of micellar solutions in water, composed of erucyl bis-(hydroxyehtyl)methylammonium chloride (EHAC) as surfactant, and sodium salicylate (NaSal) as counterion [32]. In addition, such theory has proven effective more broadly to describe other micellar systems, such as cetylpyridinium chloride–sodium salicylate (CPCl) as surfactant, and brine as counterion; and cetyltrimethylammonium tosylate (CTAT), dodecyltrimethylammonium bromide (DTAB), Pluronics P103 as surfactants, with NaSal as counterion [33].

The contraction–expansion flow has become a standard benchmark problem in experimental and computational rheology [34]. Two of the most outstanding aspects to this configuration are the kinematics of flow, and the pressure drop measurement and its numerical estimation. The former is given by vortex activity in the re-entrant corner and the lip of the contraction. Here, diverse manifestations of the nature of the fluid can be outlined related in vortex size and evolution (extensional viscosity) and structure formation and numerical tractability (sharp/rounded corners) [15,35–37]. The pressure drop measurement, which reflects the energy expended in the flow, is often studied through an EPD measure [38,39], and offers a significant challenge to computational rheology [34,38].

Taking the experience gained in our prior work on modelling of wormlike micellar solutions [15], we subsequently deploy a new micellar approach, driven by phenomenological observation (EPD attainment) in the axisymmetric rounded-corner 4:1:4 contraction/expansion domain, for which there is a dearth of comparable work available – micellar fluid solutions in complex flows. This study also sheds light on some other key related topics – that is limiting *We* (We_{lim}) and vortex dynamics – all absent in simple viscometric flows [15,16]. We proceed to demonstrate that this new constitutive approach provides: (i) consistent EPD values at low *We* regimes – vital for oil-well rock-bed permeability estimation in EOR; (ii) larger We_{lim} in numerical solution reached through the explicit presence of the elasticity (*We*) in the structure equation; and (iii) attainment of rising EPD trends at high elasticity levels.

2. Governing equations, constitutive modelling and fluids considered

Under transient, incompressible and isothermal flow conditions, the relevant mass conservation and momentum equations for viscoelastic flow, may be expressed in non-dimensional terms (see definitions below; where here for conciseness the * notation on dimensionless variables is omitted) as:

$$\nabla \cdot \boldsymbol{u} = 0 \tag{1}$$