

When $N_1 = |N_2|$: A potential new class of model highly viscoelastic micellar fluids based on functionalised-Dipeptide solutions

Osama M. Maklad,^a Kate McAulay,^b Dave J. Adams^b and Robert J. Poole^a

^aSchool of Engineering, University of Liverpool, Liverpool, L69 3GH, U.K.

^bSchool of Chemistry, University of Glasgow, Glasgow, G12 8QQ, U.K.

Low molecular weight gels (LMWG) are used in a wide range of applications, including optoelectronics, directing cell growth and controlled drug release. Here, we investigate the rheological properties of a LMWG based on a functionalised-dipeptide (“2NapFF”) [1] which appears to behave as a surfactant at high pH in the “precursor” phase (*i.e.* prior to a gelation phase caused by a pH or temperature change). This new hydrogel exhibits very “stringy” behaviour and has been shown to have extremely high relaxation times using capillary breakup extensional rheometry (CaBER) [1]. Believing that it should be possible to vary the micellar aggregates formed from this gelator, and hence the rheology, by varying simple parameters such as the nature of the counterion we prepared solutions of 2NapFF at a pH of 11 using one of a number of hydroxide salts (LiOH, NaOH, KOH, RbOH, CsOH or tetrabutylammonium hydroxide (TBAOH)) to deprotonate the terminal carboxylic acid (all at a fixed concentration of 10mg/mL). We then characterised the rheology of the resulting solutions in small amplitude oscillatory shear, steady shear and extension (CaBER). Using a cone-and-plate geometry and a dedicated protocol [2] we are able to measure the first normal-stress difference N_1 and using a parallel-plate geometry to measure $(N_1 - N_2)$. In so doing, we find for these systems that they are highly elastic (e.g. for shear rates greater than 10s^{-1} $N_1 > 10\tau$ where τ is the shear stress) and also, in contrast to polymeric solutions and all other reported wormlike micelles in the literature, we find that N_2 is very large and equal in magnitude to N_1 (*i.e.* $N_1 = -N_2$). Given this highly elastic and unique behaviour, we propose that these solutions have the potential to be used as a new class of model highly viscoelastic fluids.

References:

- [1] E. R. Draper, M. Wallace, R. Schweins, R. J. Poole, and D. J. Adams, “Nonlinear Effects in Multicomponent Supramolecular Hydrogels,” *Langmuir*, vol. 33, no. 9, pp. 2387–2395, 2017.
- [2] R J Poole (2016), Measuring normal-stresses in torsional rheometers: a practical guide. The British Society of Rheology, Rheology Bulletin. 57(2) pp 36-46 .