

COUPLING A IONIC SURFACTANT AND A DRUG SALT: EQUILIBRIUM CHARACTERISTIC PARAMETERS & STRAIN HARDENING IN START-UP FLOW

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ABSTRACT

Surfactant solutions containing Cetylpyridinium Chloride (CPyCl), a classical ionic surfactant, and Sodium Diclofenac (Diclo), a non-steroidal anti-inflammatory drug, were investigated in a wide range of compositions using rheology and Cryo-EM. Solutions were made at three different concentrations of CPyCl, i.e. 5.0, 16.7 and 33.0 mM. The ratio between the salt and the surfactant concentrations, $R = \text{CPyCl}/\text{Diclo}$, was within the range $0.4 < R < 1.4$. Linear viscoelastic rheology was performed at 25°C using a stress controlled DHR-2 Rheometer (TA instruments), equipped with sandblasted 40 mm diameter parallel plates, a Peltier system to control the temperature, and a solvent trap to avoid evaporation. The use of dilute solutions allowed to examine their microstructure via cryo-EM imaging, e.g. avoiding high density of micelles. High-resolution images of vitrified specimens were recorded with a Glacios FEG electron microscope (Thermo Fisher) at 200 kV. Nonlinear rheological experiments were performed at 25°C with a strain-controlled ARES rheometer (TA instruments, USA), using a 50 mm – 0.017rad cone-plate geometry.

We discovered that by tuning R it is possible to achieve completely different microstructures, with variable persistence and contour lengths, and unexpected behaviours in nonlinear start-up flow.

LINEAR RHEOLOGY AND MICROSTRUCTURE

By following the zero-frequency viscosity evolution as a function of Diclo content, it was possible to identify various regions, characterized by a completely different rheological response.

By matching the frequency sweep data with the cryo-EM images, we were able to connect these regions to specific morphological transitions: from spherical micelles to very long and entangled wormlike micelles, to branched networks and eventually well-defined vesicles.

For some systems, we were able to measure the entire spectrum of relaxation times, including the shortest characteristic Rouse time at high frequencies, usually reached only by Diffusive Wave Spectroscopy¹. This allowed for the evaluation of some important microstructural parameters, such as entanglement, contour, and persistence lengths, taking advantage of available models^{2,3}. We were able to quantitatively correlate the above microstructural parameters with the information disclosed by the cryo-EM analysis. A very good quantitative agreement was found between the extracted parameters and the cryo-EM data. The combination of dilute solution rheology and microscopy shed a new light on the role of the binding salt in the morphological transitions of these peculiar micellar solutions.

START UP EXPERIMENTS

For the more entangled systems, the transient behavior in shear flow was investigated through startup measurements, performed at different shear rates so as to cover a wide range of the Weissenberg number, Wi . The long-time response allowed also to build up the flow curves for each sample.

During the transient regime, some samples show flow instabilities and strain hardening phenomena at $Wi > 1$, a phenomenon already detected before on surfactant solutions⁴. Other solutions do not show the same features, behaving like ordinary linear polymers in fast shear flows, that is, exhibiting pronounced overshoots followed by tiny undershoots of the transient shear viscosity, before approaching steady-state⁵. We tried to rationalize this behavior, by identifying the most important parameters, i.e. number of entanglements, characteristic micellar lengths, relaxation times etc., and by clarifying their role in the transient dynamics.

A possible mechanism for the onset of flow singularities is suggested and discussed in terms of a modified rubber network theory, applied recently on similar micellar networks⁶.

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