Methods

WLM Preparation

This study uses the surfactant cetyltrimethylammonium bromide (CTAB, cetyl = hexadecyl, Alfa Aesar) dissolved in ^2H_2O (Cambridge Isotope Laboratories, 99.9% ^2H) and regulated at 45 °C with gentle stirring for 48 h. CTAB concentrations of 18.0, 19.0, 20.0, 21.0, 22.0, and 23.0 wt % (± 0.1 wt %) of total solution (0.67, 0.71, 0.76, 0.81, 0.86, and 0.91 M, respectively) are used for rheo-NMR studies. At least 24 h prior to experiments, samples are poured into a Couette cell, sealed with Parafilm, and allowed to rest at 40 °C. This ensures that measurements are not biased by shear history during cell assembly. Solutions are maintained above 25°C to prevent CTAB crystallization.

Rheo-NMR Spectroscopy

A Varian Unity NMR spectrometer (B_0 = 9.4 T, ν_{2H} = 61.395 MHz) applies a pulse-acquire sequence with 90° pulse of 25.0 µs. ^2H spectra are single acquisitions in order to accurately map sample behavior over time with ≤ 1 s time resolution. Typical FWHM linewidths in the ^2H spectra are ~ 2 Hz (shim limited). The custom rheo-NMR apparatus consists of a Couette cell (concentric cylinders) with rotation axis along B_0, comprised of a 10 mm O.D. NMR tube (9.03 mm I.D.) and a 7.45 mm O.D. NMR tube[31] separated by Delrin® spacers. CTAB sample is held in the 0.79 mm gap. This cell produces $\dot{\gamma}$ = 31.4 ±0.5 s^{-1} per 1 Hz revolution of the inner cylinder.[31] The length of the Couette cell is ~ 60 mm, ensuring that sample fills the RF coil. Shear rate ($\dot{\gamma}$) inside this cell is given by:

$$\gamma^{\bullet} = \nu_I \left(\frac{D_1 \pi}{D_2 - D_1} \right) \qquad (2)$$

where D_1 is the outer diameter of the inner cylinder, D_2 is the inner diameter of the outer cylinder, and ν_I is the rotation frequency of the inner cylinder. Douglass *et al.*[31] have estimated the maximum practical shear rate at ≈ 200 s^{-1}. Shear rate is varied using a computer interface (software: SMC60WIN SD130, v. 2.01; programmable driver: DPY50601, Anaheim Automation), which controls a stepper motor mounted above the NMR magnet. A brass drive shaft rotating on Teflon® bearings couples the stepper motor to the inner cylinder of the Couette cell. The cell's outer cylinder is fixed to the probe by a rubber annulus. Interchangeable stepper motors with varying gear ratios (1:1 motor #23YSG106S-LW8, 1:12.5 motor #23YSG106S-LW8-R12.5, and 1:100 motor #23YSG106S-LW8-R100, Anaheim Automation) allow access to over five decades of shear rate.