Comment on "Evidence of a Sponge-to-Lamellar Phase Transition under Shear by X-Ray Scattering Experiments in a Couette Cell"

In a recent Letter [1] Mahjoub, Bourgaux, Sergot, and Kleman (MBSK) reported an apparent shear-induced sponge (L_3) to lamellar (L_α) transitions in the cetylpyridinium chloride (CPCl)/hexanol membrane in brine system. At unexpectedly low shear rates ($<50\ \mathrm{s}^{-1}$) for the relatively concentrated solutions studied ($\sim$10 membrane vol %), they reported lamellar phase nucleation in the perpendicular "*a*" orientation and a subsequent parallel "*c*" reorientation at higher shear. Long relaxation times were reported for the "*a*" oriented phase, while the lamellar phase induced at higher shear was "stabilized" [*sic*] and showed no evidence of relaxation to the sponge phase. Here we suggest a simple alternative explanation: the reported observations are due to composition-driven phase transitions caused by hexanol cosurfactant evaporation.

This Letter attracted our attention since these shear rates are well within the accessible range for the Poiseuille shear neutron scattering cells [2] used in our studies on complex fluid systems under flow near a surface. For good neutron contrast, measurements were to be carried out on a D_2O substituted heavy brine system. Since this could be expected to slightly alter the shears at which transitions occur, we repeated the Couette shear cell measurements of MBSK on the National Institute of Standards and Technology NG3 small angle neutron scattering spectrometer [3].

We were able to replicate the observations of MBSK [4]. However, transitions did not occur at reproducible shear rates and scattering changes actually depended more consistently on time spent in the cell. In every case where a transition was observed, samples recovered from the cell were now clearly in a biphasic state (L_α/L_3), and would remain so even if stirred. Furthermore, the recovered samples could be returned to the sponge phase by adding a very small drop of hexanol. To us this clearly suggested that the observed effects were due to hexanol evaporation rather than shear. Therefore we instituted a protocol of progressively increasing the shear rate until a transition was observed, then stopping and replacing the sample with a fresh sample and starting again at the previously attained apparent transition shear. In no case was the transition immediately repeated. In a linked series of such measurements the sponge system's shear response from rest to $10\,000\ \mathrm{s}^{-1}$ showed no true shear-induced transition. Finally, with an improved vapor barrier Couette cell we measured single samples over this range without observing any shear-induced transition or distortion of the correlation scattering ring characteristic of the isotropic sponge phase structure [5].

A previous paper by this group [6] discussing preliminary scattering data indicated that while water evaporation was carefully controlled in their experiments that of hexanol was essentially ignored on the grounds that its vapor pressure is much lower. However, inspection of their phase diagram [6] shows that while the sponge phase is maintained over a 20% in water content only a small change in the hexanol to CPCl ratio will make the system biphasic. MBSK observed transitions only for L_3 samples close to the phase boundary with the biphasic L_α/L_3 state, where only very little hexanol evaporation is required to drive the system biphasic. Our results are consistent with theoretical estimates [7] that shear-induced transition should occur for a critical shear rate $\dot{\gamma}_c \sim k_B T/\xi^3 \eta$, where ξ is the characteristic dimension of the sponge ($\sim$33 nm for a 10 membrane vol % sample [1]), and η the solvent viscosity ($\sim$1 cP). A transition would not be expected before shear rates $\sim 100\,000\ \mathrm{s}^{-1}$, some 4 orders of magnitude higher than those reported by MBSK. Composition driven thermodynamic transitions to biphasic or fully lamellar states also explain MBSK's (and our) other observations. The "reversible" transitions at lower shear rates are due to small amounts of the less dense lamellar phase component floating out of the beam. At longer times, when a stabilized shear-induced lamellar phase is reported, the lamellar phase component constitutes a large (or full) fraction of the solution sufficient to extend into the beam at rest. This will, of course, fail to relax to the supposed thermodynamic equilibrium sponge state.

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