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Elastic properties of a dilute surfactant solution in the shear induced state

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Abstract  The first normal stress differences \( N_1 \) of a highly dilute cationic surfactant solution are investigated in a cone-and-plate rheometer. In continuation of a previous paper (Nowak 1998), where the buildup of a shear induced structure in such a solution was attained after a reduced deformation, the \( N_1 \) turned out to be in proportion to the square of the shear rate \( \dot{\gamma} \) reduced by a critical value \( \dot{\gamma}_c \) in a first range above \( \dot{\gamma}_c \). At higher shear rates the \( N_1 \) tend to lower values than predicted by this relation.

Relaxation experiments were performed in the same geometry to determine the characteristic time scales of the shear induced state’s decay. In the lower range above \( \dot{\gamma}_c \) the stress decay is a monoexponential process, while a second time constant has to be introduced to describe the relaxation in that range, where the \( N_1 \) deviate from the parabolic dependence of the reduced shear rate.

Key words  Dilute cationic surfactant solution · Shear induced state · First normal stress difference · Relaxation

Introduction

In rheometric flows dilute surfactant solutions show unsteady changes in their rheological properties. Dilute in this context means that the concentration is high enough to ensure that rodlike micelles are present in the quiescent solution, but well below the overlap concentration \( c^* \). Much work is done to characterize the rheological behavior of surfactant solutions well above \( c^* \). In this semi-dilute concentration regime the linear rheological behavior of a surfactant solution can be described by a Maxwell model, i.e., a zero shear viscosity and a relaxation time (Rehage and Hoffmann 1991; Butler et al. 1996). In contrast to the shear-thinning behavior of a semi-dilute solution, those in the dilute concentration range show a quasi-Newtonian viscosity slightly above that of the solvent at low shear rates. Beyond a critical shear rate \( \dot{\gamma}_c \) the viscosity \( \eta \) increases many times over the value at low shear rates. In the literature, this shear-thickening behavior is described as a transition into a shear-induced state (SIS). The critical shear rate and the extent of the viscosity increase \( \Delta \eta \) not only depend on the temperature and the solution’s surfactant and counterion concentration and type, but also on the geometry of the rheometer and the so-called sweep-time (Ohlendorf et al. 1986; Wunderlich and Brunn 1989; Hu and Matthys 1995), required to pass the whole shear range. That means that e.g., \( \dot{\gamma}_c \) decreases and \( \Delta \eta \) increases with wider gap of a Couette cell or larger diameter of a capillary viscometer and longer sweep-time. No transition to a SIS is found in solutions subjected to oscillatory strain (Rehage et al. 1986).

The influence of the sweep-time can be explained by the chronological evolution of the rheological properties in a stress buildup experiment (Fig. 1). Although the results shown in this figure are obtained with the surfactant system tetradecyl trimethyl ammonium salicylate (C14TASal) used in this study, the qualitative behavior seems to be of some generality for highly dilute surfactant solutions with rodlike micelles. Below \( \dot{\gamma}_c \) the viscosity is constant in time. Beyond \( \dot{\gamma}_c \) the solution becomes rheopectic after a certain induction time \( t_{\text{ind}} \).
For longer times in the order of minutes, Wunderlich et al. (1987) measure significant elastic properties under oscillatory strain, if the fluid is subjected to a steady shear flow above \( \dot{\gamma}_c \) prior to the dynamic measurements. In such cases they find a broad spectrum of relaxation times of the order of 20 min.

Hu and Matthys (1995) investigated a highly dilute system, only slightly different from the one used here, containing equimolar amounts of a ternary ammonium salicylate with a C_{18} carbon chain. From an exponential fit of the \( N_1 \) relaxation data over approximately 100 s after cessation of the flow they get two relaxation times in a range of seconds differing by half an order of magnitude. The longer relaxation time, supposed to quantify the decay rate of the SIS, decreases with increasing applied shear. This is attributed to smaller structures induced at higher shear rates. Hoffmann et al. (1994) needed at least three time constants to fit their shear stress relaxation data obtained in a C_{16} pyridinium salicylate system well below the overlap concentration.

Usually one of these times is equated with the characteristic time scale of the shear-induced structure's decay, although the stresses relax within a few seconds and the decay of the shear-induced structure lasts for several minutes (Wunderlich et al. 1987; Nowak and Urban 1996).

**Experiments**

The solutions were prepared out of equimolar amounts of tetradeyl trimethyl ammonium bromide, also referred to as C_{14}TAB or TTAB, and sodium salicylate, NaSal, dissolved in deionized water to give a concentration of 2.4 mmol/l. At a temperature of 20 °C the transition concentration \( c_t \), beyond which the monomers assemble into rodlike micelles, is about 0.8 mmol/l, whereas the overlap concentration \( c^* \) is reached at approximately 5 mmol/l for this surfactant system.

The normal forces were measured in a PC-controlled rotational rheometer Physica Rheolab MC 20. With the measuring device Mvk-Nf the forces were measured without displacement in the axial direction. As there is no internal temperature control, the experiments were carried out in an air-conditioned room at a temperature of (22.3 ± 0.1) °C.

The applied measuring system MK 98 is of cone-and-plate type with a cone angle of 2.3° and a radius of 50 mm of both the rotating cone and the stationary plate. The cone point truncation \( x \) is 50 μm, and the fluid volume in the gap 10.5 ml. The shear rate-dependent normal stress differences were determined by recording the axial normal forces in stress buildup experiments at constant revolution number of the measuring system as a function of time over a period of 1200 s. Two sequences of 60 s each at the beginning and the end of the experiments respectively permit a null balance and the recording of the fluid's relaxation behavior after the cessation of the strain.

Considering the reproducibility of the acquired data, the experiments were repeated at least three times at each shear rate each with a fresh solution to avoid memory effects. Several authors (e.g., Hu and Matthys 1997; Lu et al. 1998) allowed the samples to relax for a period, presumably long enough to eliminate memory effects before reusing the same probe. In the experiments presented here the use of a fresh solution seems to be the only way to exclude...