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Methodology to estimate the yield stress applied to ultraconcentrated detergents as model systems

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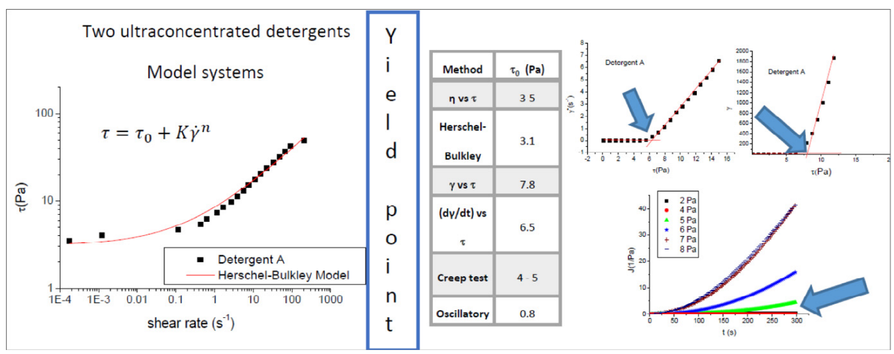
HIGHLIGHTS

- Two gel detergents have been studied to estimate yield stress using different methods.
- The systems may be considered as different models due to its different flow behaviour.
- Yield stress value depends on the methodology followed to estimate it.
- The system, the purpose and the test time are the keys to select one specific method.

GRAPHICAL ABSTRACT



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ABSTRACT

Two commercial highly-concentrated detergents have been studied as model systems in order to estimate the yield stress using different methodologies. Both exhibit clear viscoelastic properties with long relaxation times; the elastic component being dominant on the viscous one. They show different yield stress and time-dependent flow properties.

While one of them exhibits apparent thixotropy, the other shows a thixotropy/antithixotropy transition, which predicts the occurrence of complex shear-induced microstructural transitions and the need to strict process control. Their flow curves illustrate the different fluidity of both gel detergents, which show standard shear thinning and "very shear thinning" properties, respectively.

1. Introduction

The yield stress has been always a very controversial parameter. It is noted that in the last ten years, yield stress or yield stress have been cited more than 40,000 times in the general scientific literature (Scopus data base, 2006 to present). Originally, the yield stress was defined as the stress that must be applied to the sample so that it starts to flow. Below the yield stress, the sample deforms elastically and above it, the sample flows as a liquid (Larson, 1999). However, rheometers became more sensitive over time and it could be clearly detected that there is often a small range of stress over which the flow properties change abruptly (an apparent yield stress). For structured liquids, this transition is from very high viscosity to mobile liquid (very low viscosity) with a difference of some decades (Barnes, 1999). Thus, yield stress is usually defined as the highest stress at which no flow is detectable within the test. Hence, the yield stress measured may vary depending on the patience of the experimentalist and the experimental protocol (Møller et al., 2006). This should not cause huge problems for practical applications. From a practical point of view, the yield stress is

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still very useful in a whole range of applications, such as quality control, development of new formulations or the study of stability against phase separation. Well-known examples of fluids with yield stress are shaving foam, ketchup, wet and dry sand as well as toothpaste.

Several techniques have been used to determine the yield stress (Balhoff et al., 2011; García et al., 2016, 2015). However, different values of the yield stress can be obtained depending on the experimental procedure (Nguyen and Boger, 1992; James et al., 1987; Barnes, 1997; Barnes and Nguyen, 2001).

The overall goal of this project has been the application of different methodologies such as multi-step protocol for steady-state flow curves, quick stress ramps, creep tests and stress sweeps in order to estimate the yield stress. For this purpose, two commercial gel-like detergents exhibiting different flow properties have been studied as model systems. In addition, the time-dependent and viscoelastic properties of the two systems were also explored. Recently, the commercial importance of liquid detergents is increasing in western countries, especially gel-type concentrated detergents. This kind of systems contain surfactant concentrations higher than 35 wt%. They have some advantages such as they are easy to transport by suppliers and the consumer, they save industrial water consumption, and they need less store space than powder detergents. Heavy duty liquid detergents and the so-called structured gel-like detergents display a fascinating variety of rheological properties (Rounds, 2006). The knowledge of the rheological behaviour of these products provides relevant and useful information for the development of new formulations, stability studies and processing parameters.

2. Materials and methods

2.1. Materials

Two highly-concentrated commercial gel detergents have been studied, which will be referred to as A and B in this paper, respectively. Detergent A possesses 40 wt% anionic surfactant, 5 wt% non-ionic surfactant, 8.6 wt% soap and 24 wt% water. Detergent B contains 34 wt% anionic surfactant, 8 wt% non-ionic surfactant, 5 wt% soap and 33 wt% water. The anionic surfactants are typically sodium linear alkylbenzene sulfonate and sodium alkyl ether sulfate and the non-ionic surfactant is an alcohol ethoxylate (Sachdev et al., 2006). Both detergents have other typical components of detergents such as coadjuvants, enzymes, brighteners, and perfumes.

2.2. Methods

Rheological tests were performed with two controlled-stress rheometers (Haake MARS, Thermo-Scientific, Germany; Haake RS-100, Thermo-Scientific, Germany) using a cone-plate geometry. Flow curves and stress ramps were carried out using RS100 rheometer with the cone-plate geometry (35 mm diameter, 0.07 rad angle). Creep tests and Small Amplitude Oscillatory Shear tests (SAOS) were conducted using Haake MARS II with a cone-plate (60 mm diameter, 0.035 rad angle). All the measurements were performed at 20 ± 0.1 °C with a DC-30/K10 (Thermo-Fisher) and C5P Phoenix circulator (Thermo-Scientific, Germany). A cover was used in order to reduce the potential water loss. All the rheological tests were repeated three times for each sample. All samples were kept at the measuring position at the same temperature for 10 min in order to have the same recent past thermomechanical history. The samples were at the set temperature when loaded on the measuring geometry.

All the measurements used a controlled-stress (CS) protocol. A stepwise CS protocol was used for steady state flow curves from 3 to 40 Pa. In addition up-down stress ramps (0–45 Pa, 300 s for each ramp) followed by constant stress stage (45 Pa for 300 s), trapezoidal protocol, were carried out to detect the possible occurrence of hysteresis loops, and hence, the existence of thixotropic and/or antithixotropic behaviours (Mezger, 2006).

Different results obtained from (a) mathematical fitting of flow curves, (b) study of the shear rate and strain dependence with shear stress from quick up stress ramps (120 s), (c) creep tests and (d) stress sweeps at 1 Hz have been compared in order to estimate the yield stress.

Finally, viscoelastic properties have been evaluated by mean of frequency sweeps (from 0.1 to 100 rad/s) selecting a stress within the linear viscoelastic range.

3. Results and discussion

3.1. Steady state shear flow

Figs. 1A and 1B show flow curves of two commercial highly-concentrated gel-like detergents. Fig. 1A presents the results using a viscosity *vs* stress plot whereas Fig. 1B exhibits a viscosity *vs* shear rate plot. Fig. 1A shows the dependence of viscosity on shear stress. An abrupt decrease of viscosity at a specific shear stress is presented for detergent A. This fact is less marked for detergent B. It could be an evidence of the apparent yield stress for detergent A. Fig. 1B reveals the influence of shear rate on viscosity for both detergents. Experimental results of Fig. 1B reveal a shear-thinning behaviour in all shear rate range studied for both systems. However, the flow curve for the detergent A should be carefully analysed since a very shear-thinning behaviour can be distinguished (Roberts et al., 2001). The log-log plot for the detergent A allows a lack of information of viscosity in two decades of shear rate to be detected. This result is a consequence of a high increase in shear rate within a narrow shear stress range (3–5) Pa, which provokes a sharp decrease of viscosity above a certain critical stress. Detergent A possesses high viscosity at very low shear rate below the critical stress. The term "creep flow" has been previously used to describe this slow flow (Barnes, 1999). The slope of the log-log viscosity-shear rate plot is −0.94, which is relatively close to −1. The previous analysis reveals that this shear stress range (3–5 Pa) can be associated with the yield stress of this detergent (Barnes, 2007). This detergent flow indicates a structural collapse

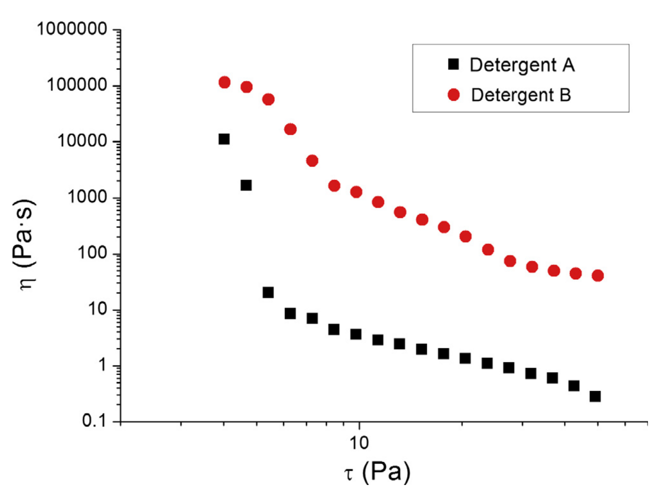

Fig. 1A. Influence of shear stress on viscosity for detergent A and B using a stepwise protocol.