



Viscoelastic retardation spectra of interfaces formed by water/glycerol monostearate crystals in canola oil dispersions



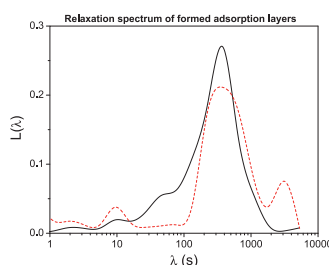
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HIGHLIGHTS

- Viscoelastic retardation spectrum of water/oil interfaces with particles was studied.
- Creep compliance data was fitted using regularization method.
- Dominant retardation times increase with decreasing particle content.

GRAPHICAL ABSTRACT



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ABSTRACT

The applicability of a phenomenological theory of viscoelasticity for processing and analyzing mechanical data of adsorption interfaces is explored in this work. Based on this theory, a retardation spectrum was generated by the application of Tikhonov regularization techniques to data obtained from creep compliance experiments. To this end, 2% or 3% (w/w) glycerol monostearate (GMS) was put into canola oil (CO) at 70 °C, and the dispersions were cooled down to 30 °C (cooling rate of 1 or 10 °C/min), for obtaining GMS crystals in CO dispersions (CD_{x,y}). The viscoelastic retardation spectrum was estimated from creep compliance mechanical tests of the formed interfaces. The interpretation of the results in terms of the distribution of retardation modes λ and their relative intensity $L(\lambda)$ was found to reflect the main features of the viscoelastic properties of water/oil adsorption layers. In particular, the creep dynamics were dominated by relatively slow (400–700 s) dynamics, which can be related to the reconfiguration of the adsorption layer, induced by diffusion and adsorption/desorption mechanisms in the vicinity of the water/oil interface. Reconfiguration of the adsorption layer as a consequence of applied shear was more pronounced for relatively small concentrations of dispersed particles, suggesting that a saturation of the adsorption layer contributes to its stability.

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1. Introduction

The recent demand of non-hazardous natural surfactants for use in the food, biomedical and pharmaceutical industries has increased the investigation of the way in which these materials promote interface stabilization. In this scenario, different forms of interface stabilization involving biomaterials have emerged as

a reliable alternative for surfactant-free dispersed systems where interface stabilization is achieved by the adsorption of solid particles at the interface and the formation of 3D networks for impeding creaming and coalescence [1–4]. Two main mechanisms can be identified in the stabilization of these systems: (i) the formation of an adsorbed dense film (monolayer or multilayer) in the vicinity of the interface, and (ii) the formation of 3D particle network in the continuous phase, limiting droplet coalescence and mobility [5,6].

Particles interface stabilization offers some economical and functional advantages over conventional surfactant-based stabilization [7,8], and can present distinctive interfacial rheological

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properties features that can be explored for a systematic formulation of products with prescribed functionalities [9]. Characterization of the shear rheology of interfacial layers arises as a relevant issue given that the flow behaviour of emulsions is controlled by the presence of the solid particles inducing changes in the system viscoelasticity. Results in this line should provide insights about the physical and chemical mechanisms taking place in the conformation and evolution of mono- and multi-layered structures in the vicinity of immiscible fluids.

Mechanical tests are commonly used for characterizing the molecular mechanisms controlling the viscoelastic behaviour of interfaces [10,11]. During mechanical (e.g., creep compliance and frequency sweep) tests, the interface is subjected to shear stress disturbances for expressing a broad spectrum of viscoelastic retardation modes [12]. Similar to polymeric materials, the structure of the underlying viscoelastic retardation spectrum (VRS) reflects the mechanisms involved in interface formation and reconfiguration. In polymeric materials, the shape of the VRS is often linked to specific molecular architectures [13]. It has been pointed out that, similar to the so-called relaxation spectrum, the VRS provides a correct view of the main characteristic of viscoelastic behaviour of complex material [14]. The rationale is that the mobility of liquid and solids in the vicinity of the interface is expressed in the VRS.

The VRS is not accessible for direct measurements, so it should be estimated on the basis of dynamic mechanical experiments. Creep compliance (i.e., shear stress step) response is the most common approach for retardation spectrum estimation [15–18]. Given the creep dynamics, the method involves solving a Fredholm integral equation of first kind [19] by the application of Tikhonov regularization procedure on continuous Maxwell model. The resulting spectrum can be interpreted in terms of the retardation modes linked to different stabilization mechanisms. In this way, the estimated VRS can be used for, e.g., proper selection of stabilization material and the formulation of emulsions with tailored characteristics.

The viability of interfaces stabilized with biopolymers depends of different factors, including particle size and concentration, as well as of the electrostatic charges displayed by particles. The way these factors affect the interface stability should be reflected in the estimated VRS as derived from mechanical tests. This work considers interfaces formed by water/glycerol monostearate crystals in canola oil dispersions for evaluating the effects of particle concentration, cooling rate and ageing time in the shape of retardation spectrum. The VRS was estimated from creep compliance mechanical tests of the formed interfaces. The interpretation of the results in terms the distribution of retardation modes λ and their relative intensity $L(\lambda)$ was found to reflect the main features of the viscoelastic properties of water/oil adsorption layers.

2. Materials and methods

In a previous paper, the formulation and characterization of glycerol monostearate dispersions and the corresponding water/oil interfaces were reported in terms of crystal shape, size and concentration [20]. For completeness of presentation, a brief description of the crystal dispersion preparation and rheological measurements will be given below.

2.1. Materials

Canola oil (CO) purchased from a local grocery store and stored at room temperature was used as the oil phase. Deionized water was used for all experimental runs. Glycerol monostearate (GMS)

with >95.0% purity was provided by Industria Química del Centro S.A. de C.V. (Mexico City, Mexico).

2.2. Crystal dispersions preparation

Canola oil was heated up to 70 °C, and added with grinded GMS to two different concentrations (2 and 3%, w/w). Once homogeneous CO-GMS dispersions were obtained, the mixtures were cooled down to 30 °C, using two different cooling rates (1 and 10 °C/min). The resulting GMS crystals dispersions in CO were coded as $CD_{x,y}$, where the x stands for the GMS concentration (2 or 3%, w/w) and y for the cooling rate (1 or 10 °C/min) employed in their preparation.

2.3. Interfacial creep compliance data

Physica MCR 300 (Physica Meßtechnik GmbH, Stuttgart, Germany) modular compact rheometer was adapted for carrying out the interfacial shear measurements. The interfacial creep compliance was carried out by subjecting the interfacial films (developed in a thermostated acrylic vessel, with inner radius, R_c , of 27 mm, inserted in the measuring plate of the rheometer) to a constant interfacial torque (M_{int}) of 0.5 μ Nm during 15 min (applied with a stainless steel biconical disc, of radius, R_b , of 15 mm and double angle, 2α , of 10°), after which M_{int} was withdrawn, and the stress relaxation of the interfacial film was followed for further 15 min. The change in the angular displacement of the disc with time (θ_b) was monitored every 2 s with the rheometer software. Inertial effects can affect the functioning of controlled-stress rheology, especially in step-stress and impulse-response tests. In such cases, the angular acceleration of the fixture is retarded by the moment of inertia I of the spindle of the torsional rheometer, and the attached geometry. The coupling between the moment of inertia I and the fluid viscoelasticity is seen in the general equation of motion of the fluid in step-stress experiments:

$$\frac{I}{b} \ddot{\gamma}_{int} = H(t)\sigma_{int,0} - \sigma_{int}(t) \quad (1)$$

where γ_{int} is the strain, $H(t)$ is the Heaviside function, $\sigma_{int,0}$ is the magnitude of the applied step, and σ_{int} is the retarding stress exerted by the sample on the fixture. If the moment of inertia I is large enough, then $H(t)\sigma_{int,0} - \sigma_{int}(t) \approx 0$ after a relatively small time after the application of $\sigma_{int,0}$. In this way, it can be ensured that $\sigma_{int,0} \approx \sigma_{int}(t)$ for $t \geq \varepsilon$, for a small positive number ε . For the rheometer used in this study, $I = 1.03 \times 10^{-3} \text{ mN s}^2$, which is sufficiently small for ensuring that $\sigma_{int,0} = \sigma_{int}(t)$ for the sampling time of 2 s. On the other hand, the parameters M_{int} and θ_b were converted to interfacial shear stress ($\sigma_{int} = 0.3553 \text{ mN m}^{-1}$) and the interfacial shear strain (γ_{int}), respectively, with the following equations [21]:

$$\sigma_{int} = \frac{M_{int}}{2\pi r^2} \quad (2)$$

and

$$\gamma_{int}(t) = \frac{2R_b^2}{R_c^2 - R_b^2} \theta_b(t) \quad (3)$$

where r is the radial location between the disc and the vessel ($R_b \leq r \leq R_c$). The interfacial creep compliance of the films as function of time was obtained as $J(t) = (\gamma_{int}(t)/\sigma_{int})$ [22,23].

The appearance of shear banding was noted when protein/polysaccharide adsorbed films were subjected to interfacial shear, finding that the shear localization at the interface coincided with the onset of non-linear viscoelasticity [24]. In this work, in order to discard potential shear-banding effects, we performed

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