Rheology of protein-stabilized interfaces and their effect on the deformation behaviour of emulsion drops

Peter Fischer[1], and Philipp Erni[2]

[1] Institute of Food Science and Nutrition, ETH Zurich, Schmelzbergstrasse 9, LFO E20, 8092 Zurich, Switzerland (peter.fischer@ilw.agrl.ethz.ch)

[2] Hatsopoulos Microfluids Laboratory, Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

ABSTRACT

The small-deformation behaviour of Newtonian emulsion drops covered with a viscoelastic layer of adsorbed proteins (globular proteins and random coil protein) is investigated in shear flow and compared to emulsions prepared with a low molecular weight surfactant (SDS). Drop deformation experiments are performed with dilute emulsions in the rheometer using light microscopy as well as rheo-SALS [1, 2]. The relaxation behavior of emulsions with protein-stabilized interfaces are compared with those prepared using SDS [3, 4]. To obtain detailed information about the interfacial stress boundary condition of the drops, all proteins and surfactants are characterized using the following interfacial rheological properties: (i) transient and equilibrium interfacial tension or interfacial pressure; (ii) interfacial shear viscosity, dynamic storage and loss modulus, transient relaxation modulus, and creep compliance; in particular, combined time/frequency sweep data and stress relaxation loop tests are presented for the proteins; (iii) dynamic interfacial dilatational moduli; transient dilatational modulus after step deformation. An attempt is made to interpret the macroscopic drop deformation behaviour with the microrheology of the interfacial layers. The results show direct evidence for the important role of in-plane interfacial stresses of a viscoelastic protein network on the macroscopic drop deformation in comparison to the equilibrium interfacial tension.

INTRODUCTION

Interfacial phenomena such as interfacial tension are primarily discussed in terms of their relevance to applications involving emulsions and foams. However, interfacial rheology of viscoelastic and "soft-elastic gels" formed from self-assembled protein emulsifiers has a significant contribution to emulsion formation and stability. Recently we were able to show that droplets covered with network-forming globular proteins form "soft capsules" and do not behave in-line with common droplet deformation models [4]. This finding has important consequences on the understanding and application of emulsion because dispersing of emulsion stabilized with skins instead of soluble surfactant layers will directly effect engineering aspects.

The individual areas of interfacial shear and dilatational viscoelasticity [5], single emulsion drop dynamics [6] (e.g. in simple shear flow), rheology of emulsions and foams [7], and deformation of elastic membranes [8 - 10] have been studied in much detail for decades, both experimentally and theoretically. Significantly less work is published where these fields are

combined to clarify the role of in-plane interfacial stresses other than the equilibrium interfacial tension and the role of interfacial viscoelasticity in the deformation behavior of multiphase liquids [11 - 13]. A bridging approach for deformation of elastic membranes (without interfacial tension properties), deformation of "soft elastic skins" (membranes with interfacial tension), and deformation of soluble emulsifier layers with and with interfacial rheology (Taylor or Flumerfeld models [14]) is to our knowledge not existing. The concept of "soft elastic skins", i.e. membranes with interfacial tension that are bridging the cases of pure elastic and interfacial tension dominated surface aggregation is entirely new.

Emulsions, as well as immiscible polymer blends and phase-separated biopolymer mixtures, develop flow-induced morphologies when stresses due to the applied flow overcome the interfacial forces that favor the spherical drop morphology at rest [15, 16]. Drops can be subjected to deformation, breakup, and coalescence; all of these processes are associated with characteristic light scattering patterns [17]. Shape anisotropy of emulsion droplets in the micrometer size range can be studied by rheometer-based small-angle light scattering (Rheo-SALS) [18 – 20]. The flow and interfacial properties of the system can be combined into a dimensionless group, the Capillary number, defined as $Ca = \tau R/\sigma$, i.e., the ratio of hydrodynamic stress, τ, to interfacial stress, σ/R, where σ is the interfacial tension and R is the radius of the undeformed droplet.

In this contribution, anisotropy in dilute emulsions under flow is studied by Rheo-SALS and the effects of adsorbed protein layers with interfacial rheology are assessed. Emulsions were prepared with either excess surfactant, sodium dodecyl sulfate (SDS) or a surface-active globular protein, β lactoglobulin. The SDS was used far above its critical micelle concentration (cmc), and hence the interfacial stress condition of the droplets can be approximated by a pseudo equilibrium interfacial tension. That is, shear and dilatational interfacial stresses, including interfacial concentration gradients, are absent, or they are balanced on a timescale much faster than our experimental observation time. In contrast, the deformation of emulsion droplets stabilized with β-lactoglobulin is expected to be governed by the solid-like behavior of the adsorbed protein layer, the properties of which are studied with interfacial rheometry.

INTERFACIAL RHEOLOGY, DROPLET DEFORMATION, AND RHEO-SALS

The interfacial shear moduli were measured using a biconical disc interfacial rheometer, as described in detail elsewhere [21]. A Physica MCR 300 rheometer (Anton Paar, Germany) was adapted for interfacial rheometry.

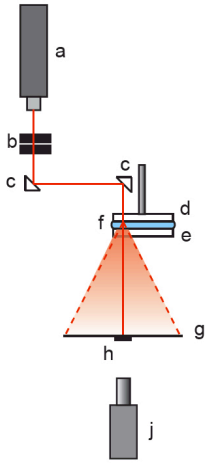

Figure 1: Arrangement for the Rheo-SALS experiments: (a) He–Ne laser; (b) aperture and neutral density filter; (c) prisms; (d) rotating glass plate; (e) base plate containing circulating heating/cooling water and glass window; (g) translucent screen; (h) beam stop; (j) CCD camera

To study the effects of an adsorbed protein layer on the deformation of single drops suspended in a sheared continuous phase, we used an optical shear cell with

real-time control of the drop position. The device is a modification of Taylor's classic band apparatus and is described in Birkhofer et al. [22].

The Rheo-SALS measurements were performed with the device described by Herle et al. [2]. The apparatus is based on the stress-controlled DSR rheometer (Rheometric Scientific, USA). The light source is a monochromatic 5 mW He–Ne laser (Melles-Griot, USA) with a wavelength of 632.8 nm, guided through the transparent parallel-plate geometry by two prisms. The plate diameter is 40 mm and the gap between the two quartz glass plates is 1 mm (see Figure 1).

SINGLE DROP STUDIES

A simple but very effective incubation method was used to create model drops with tailored interfacial properties using both globular and flexible surface-active proteins. The small-deformation behavior of single Newtonian oil drops covered by an adsorbed viscoelastic protein layer was investigated in optical flow cells. Figure 2a compares the deformation of a clean oil drop subjected to shear flow with the one of the identical drop after it has been covered with a protein layer. For the uncovered drop the expected deformation to an ellipsoidal shape is in agreement to the Taylor model. In contrast, the protein-covered drop behaves highly irregular: while from the Taylor theory a larger overall deformation would be expected, the viscoelastic interface clearly restricts the average deformation to a smaller value and causes the drop shape to oscillate. To address the problem of reduced deformation and shape oscillation two existing models are utilized: Flumerfelt's extended small-deformation theory and the Barthès-Biesel & Sgaier model for capsule deformation [8, 14]. From Figure 2b it is clear that the measured deformation values are far below Flumerfeld's prediction. On the other hand, shape oscillations are predicted by Barthès-Biesel & Sgaier for capsules in shear flow for the case of a highly viscous membrane and moderate modified Capillary numbers $\tau R/(Eh)$, where Eh is a dimensionless Young modulus of the membrane material multiplied with the membrane thickness [9, 10]. A fundamental difference to drop deformation theories is the absence of a static interfacial tension: the membrane is seen as a thin layer of a viscoelastic solid, expressed in terms of constitutive laws known from solid material mechanics. We are able to compare the data for the β-lactoglobulin drop with the perturbation analysis of the Stokes equations for a capsule provided by Barthès-Biesel & Sgaier model as shown in Figure 2b.

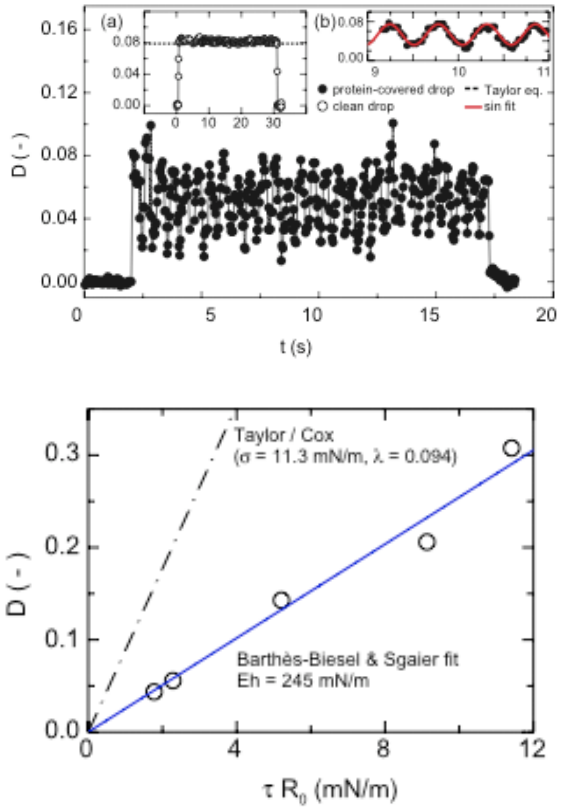

Figure 2a: Deformation experiments performed with a clean, surfactant-free drop and with the identical drop covered with a protein layer after adsorption during 60 minutes in a lysozym solution. 2b: Deformation data for b-lactoglobulin-covered drops described with the capsule deformation model. The membrane Young modulus Eh is used as the fitting parameter (Solid line: least squares fit of the capsule model; dashed line: prediction of the Taylor or Cox theories $D = (1/\sigma)\tau R_0$).

EMULSION RHEOLOGY

A typical set of results for the frequency-dependent storage and loss moduli of the dilute emulsion in the absence of surface rheological effects is shown in Figure 3. If both the disperse phase and the continuous phase are Newtonian, we observe a 'relaxation shoulder' in the elastic modulus centered above a characteristic frequency related to the shape relaxation of the droplets. The related relaxation timescale is influenced by the interfacial tension, the continuous phase viscosity, the viscosity ratio, and the droplet size. For the latter, a mean radius derived from the droplet size distribution can be used. Emulsion rheological models, such as those by Palierne [23] or Yu et al. [24] can be used to describe emulsion rheological data with shape relaxation. In Figure 3(c) calculated values for G'(ω) are included (dashed line). The discrepancy above the relaxation shoulder is due to the use of a mean droplet diameter rather than the full size distribution.

In Figure 4 the storage moduli of dilute emulsions (ϕ = 4.5 vol.%) prepared with excess SDS or β-lactoglobulin are compared. We note the absence of a characteristic relaxation shoulder for interfaces stabilized by the protein. If the (static) interfacial tension alone would govern the stress boundary condition between the oil and water phases, we would expect comparable shape responses at comparable Capillary numbers. Therefore, the difference between the surfactant and the protein data appear to be qualitative in nature: it appears that in the protein system the deformation of the micrometer-sized droplets is completely suppressed.

To probe the morphology of the emulsions under flow, we use light-scattering patterns obtained at the maximum deformation rate during an oscillation experiment. For the emulsions stabilized with excess SDS, a characteristic distortion of the light-scattering patterns in the vorticity direction is observed.

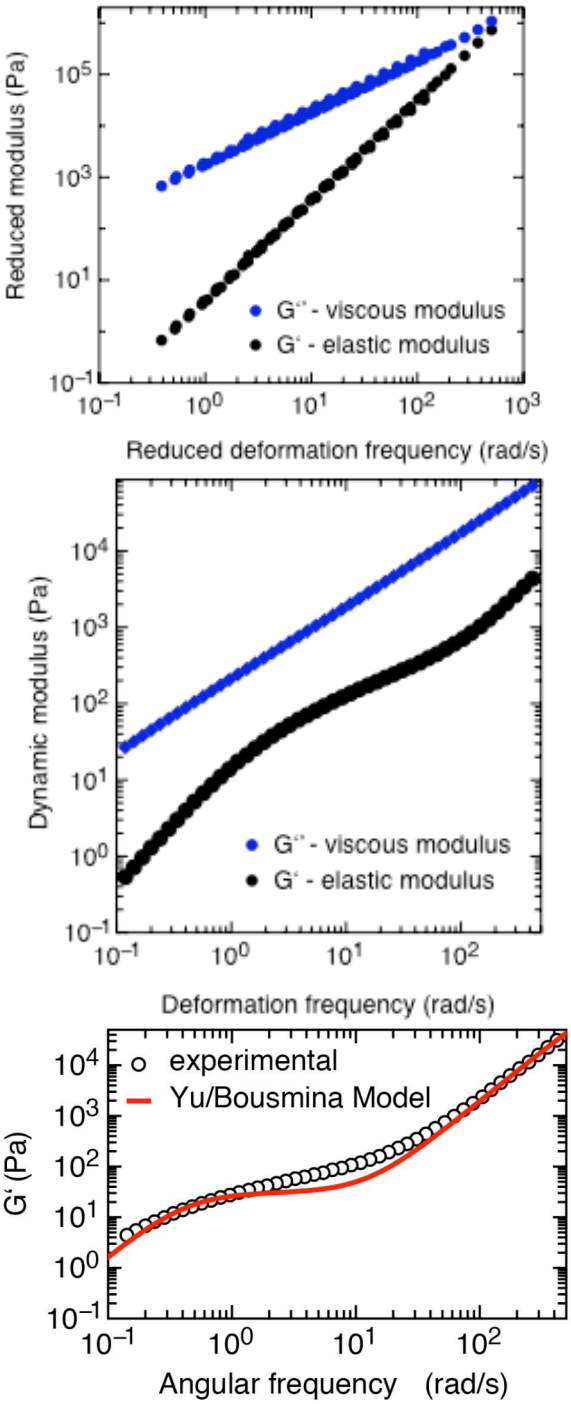

Figure 3: Frequency-dependent dynamic moduli of emulsions with dominant shape relaxation stabilized by excess SDS. (a) Reduced storage and loss moduli, G' and G'', of the continuous phase. (b) G' and G'' at 20°C of an emulsion prepared with SDS (oil phase fraction ϕ = 4.5 vol.%). The arrow indicates the characteristic relaxation shoulder of the storage modulus, caused by shape relaxation of the deformed

droplets. (c) Comparison of experimental G'(ω) data with calculated values (dashed line, [24]) based on measured interfacial tension, individual phase moduli and mean droplet diameter from laser diffraction.

The scattering anisotropy can be assumed to be due to deformation of the droplets in the flow direction. For the emulsion stabilized with β-lactoglobulin, the scattering patterns are isotropic throughout the frequency spectrum. This indicates the absence of any detectable droplet deformation, a result in line with the missing relaxation shoulder in the G'(ω) curve.

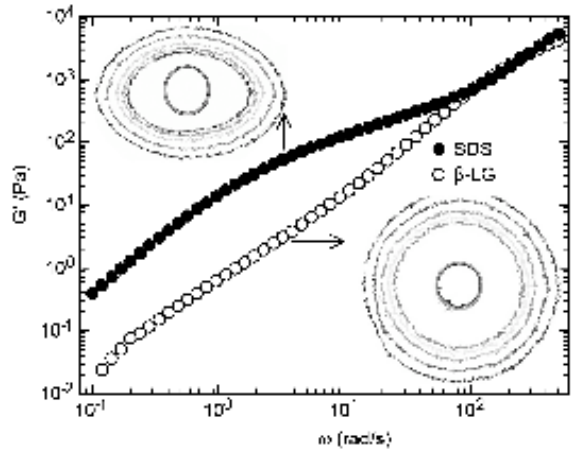

Figure 4: Comparison of the frequency-dependent storage modulus G'(ω) for emulsions stabilized with either SDS or β-lactoglobulin (b-LG) (droplet phase fraction $\phi = 4.5$ vol.%). Note the absence of a pronounced relaxation shoulder for the protein system. The insets show contour plots of Rheo-SALS patterns obtained for the same emulsions, but with a lower droplet phase volume fraction of $\phi = 0.1$ vol.%. The innermost ring of the scattering patterns is from the beam stop.

SUMMARY

The results found for the case of globular protein adsorption layers (β-lactoglobulin or lysozyme) have the potential to significantly change the way in which protein-based emulsifiers used in industry are understood: common fluid mechanical models for emulsion drop behavior in flows are not able to describe the experimental data if a globular protein is present at the oil/water interface, even if these models account for the presence of surface-active species with considerable surface tension gradient effects or surface viscosities. However, we found that another class of models, namely those originally developed for *microcapsules* with solid membrane layers can quantitatively describe the deformation behavior. This result suggests to view such systems as "soft capsules" rather than emulsifier-covered drops, a result in line with the findings that β-lactoglobulin or lysozyme layers possess properties of *soft solids* or *particulate gels*.

The results presented above demonstrate that viscoelastic protein layers adsorbed at the oil water interface restrict the deformation of emulsion droplets under flow, and that Rheo-SALS is a suitable method to study such effects for droplets in the micrometer size range. At identical Capillary numbers, the flow-induced anisotropy is significantly smaller for protein-covered droplets as compared to drops with an adsorbed small-molecule surfactant. Additionally, protein-covered emulsion droplets, once broken down to their final sizes in the micrometer range, do not deform anymore, especially if the continuous fluid is of low viscosity. Consequently, these droplets should be considered as 'solid' dispersed spheres covered with a charged polymer adsorption layer similar to the results found in the single droplet deformation experiments.

ACKNOWLEDGMENTS

We thank Bruno Pfister, Daniel Kiechl, Christoph Eschbach and Martina Haug at ETH, and Patrick Heyer, Jörg Läuger and Victor Kusnezov at Anton Paar/Physica. Parts of this project were supported by the Swiss National Science Foundation (SNF project no. 200020-108052) and by ETH Zurich.

REFERENCES

[1] Erni P, Fischer P and Windhab EJ: Appl. Phys. Lett. 87 (2005) 244104.
[2] Herle V, Fischer P and Windhab EJ: Langmuir 21 (2005) 9051 - 9057
[3] Erni P, Fischer P and Windhab EJ: Langmuir 21 (2005) 10555 - 10563
[4] Erni P, Herle V, Fischer P and Windhab EJ: In Food Colloids - Self Assembly and Material Science, Dickinson E and Leser M (Editors), The Royal Society of Chemistry, London, 2007
[5] Edwards DA, Brenner H, Wasan DT: Interfacial Transport Processes and Rheology, Butterworth-Heinemann, Stonheam 1991.
[6] Stone HA: Annual Review of Fluid Mechanics 26 (1994) 65-102.
[7] Larson RG: The Structure and Rheology of Complex Fluids, Oxford University Press, Oxford, 1999.
[8] Barthes-Biesel D, Sgaier H: J. Fluid Mech. 160 (1985) 119-135.
[9] Chan KS, Olbricht WL: J. Fluid Mech. 250 (1993) 609-633.
[10] Walter A, Rehage H, Leonhard H: Colloids Surf. A 183 (2001) 123-132.
[11] Van Hemelrijck E, Van Puyvelde P, Velankar S, Macosko CW, Moldenaers P: J. Rheology 48 (2004) 143.
[12] Williams A, Janssen JJM, Prins A: Colloids Surf. A 125 (1997) 189.
[13] Gunning PA, Mackie AR, Gunning AP, Woodward NC, Wilde PJ, Morris VJ : Biomacromolecules 5 (2004) 984-991.
[14] Flumerfelt RW: J. Colloid Inter. Sci. 76 (1980) 330-349.
[15] Scholten E, Sprakel J, Sagis LM and van der Linden E: Biomacromolecules 7 (2006) 339.
[16] Ziegler VE and Wolf BA: Macromolecules 38 (2005) 5826.
[17] Tucker CL and Moldenaers P: Ann. Rev. Fluid Mech. 34 (2002) 177.
[18] Antonov YA, van Puyvelde P and Moldenaers P: Biomacromolecules 5 (2004) 276.
[19] van Puyvelde P, Moldenaers P, Mewis J and Fuller GG: Langmuir 16 (2000) 3740.
[20] Vermant J, van Puyvelde P, Moldenaers P, Mewis J and Fuller GG: Langmuir 14 (1998) 1612.
[22] Birkhofer B, Eischen JC, Fischer P and Windhab EJ: Ind. Eng. Chem. Res. 44 (2005) 6999.
[21] Erni P, Fischer P and Windhab EJ: Langmuir 21 (2005) 10555.
[23] Palierne JF: Rheol. Acta 29 (1990) 204.
[24] Yu W, Bousmina M, Grmela M and Zhou C: J. Rheol. 46 (2002) 1401.