Interfacial rheology: micro and macro illustrations

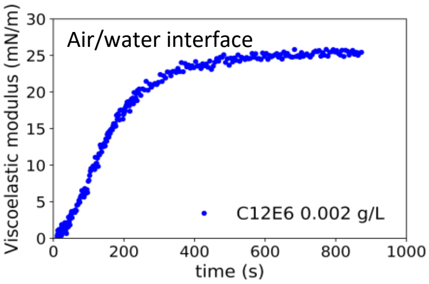
Introduction

Besides decreasing the value of interfacial tension, the presence of surface-active molecules at a fluid/fluid interface confers rheological properties radically different from the ones exhibited by the equivalent bare interface. The interfacial viscoelastic modulus is hence a powerful parameter for the characterization of fluid/fluid interfaces . At the macro-scale, the properties of foams, emulsions and bubbly liquids such as the stability, the transport and the mechanical behavior strongly depend on their composition and the properties (interfacial tension and viscoelastic modulus) of the fluid/fluid interfaces composing them [1, 2, 3]. In this context, examples at the micro and the macro scale are presented in the following to illustrate the usefulness of probing the interfacial rheology of fluid/fluid interfaces.

Microscopic scale: Molecular organization

E to probing the population density at a fluid/fluid interface

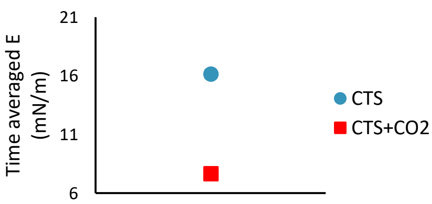
In the example below, an air bubble is generated in a C12E6 aqueous solution. The interfacial viscoelastic modulus at the air/ C12E6 aqueous solution is measured based on the response of surface tension to sinusoidal oscillations of the size of the interface.



The results show that the modulus increases as a function of time as a result of the increase of surfactant density at the interface. After this first phase, the modulus reaches a plateau and stabilizes.

E to monitor chemical reaction at the interface

During the viscoelastic modulus measurement of an oil/chitosan aqueous suspension interface, a decrease of the viscoelastic modulus was observed when CO_2 was dissolved in the water phase. This behavior can be explained by the decrease of the pH of the solution below the pKa of the $–NH_2/–NH_3^+$ chitosan groups (pKa = 6.5) which leads to the departure of chitosan nanoparticles from the interface to the bulk. At the scale on an emulsion composed of these interfaces, the dissolution of CO_2 in the aqueous phase destabilizes the system. In this case, measuring the viscoelastic modulus highlights the change in the interfacial composition induced by the departure of chitosan particles [4].

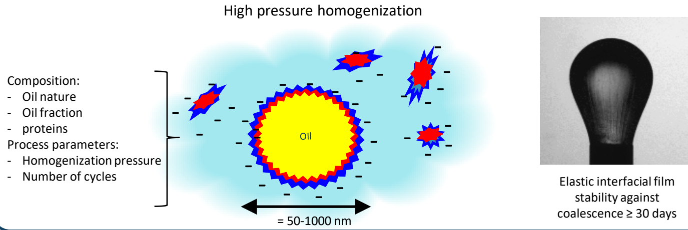


Time averaged dilatational elastic modulus (over 30 min). Data from [4]

Macroscopic scale: Material properties

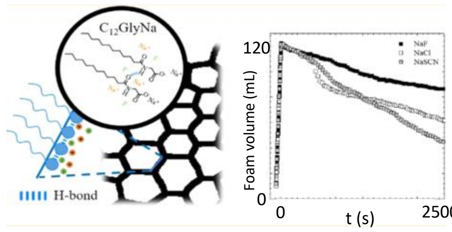
Link with emulsion storage stability

In the field of emulsions, observations suggest a link between long-term stability and the presence of a rigid membrane or a high viscoelastic interfacial modulus [5]. In this first example [6], the authors describe how interfacial rheology measurements can mimic weak droplet shocks due to Brownian motion under storage conditions. In this second example, the viscoelastic modulus is used as a criterion to measure the ability of a membrane to resist Ostwald ripening and coalescence events [7].



Link with foam stability

A few studies show that the higher the surface elasticity the better the foam stability [7, 8]. Obviously, other parameters play an important role in foam stability such as the presence of particles or liquid viscosity. To highlight how the molecular surface structure impacts the macroscopic properties, the authors of this article [8] carried out interfacial rheology and foam stability measurements on foaming solutions that differ only by the counter ions of salts: NaF and NaSCN. These counter ions are chosen because of their ability to promote or break H bonds. In this example, a higher foam stability and a higher viscoelastic modulus are found with NaF which promotes the H bond formation, promoting the surfactant/surfactant interactions unlike NaSCN.



References

[1] Langevin, D. (2000). Influence of interfacial rheology on foam and emulsion properties. Advances in colloid and interface science, 88(1-2), 209-222.
[2] Lucassen-Reynders, E. H. (1993). Interfacial viscoelasticity in emulsions and foams. Food Structure, 12(1), 1.
[3] Hemar, Y., Hocquart, R., & Lequeux, F. (1995). Effect of interfacial rheology on foams viscoelasticity, an effective medium approach. Journal de Physique II, 5(10), 1567-1576.
[4] Ren, D and al. CO2-switchable dispersion of a natural chitosan and its application as a responsive Pickering emulsifier. Colloids and Surfaces A: Physicochemical and Engineering Aspects 2018, 555, 507-514.
[6] Ali, A.; and al. β-lactoglobulin stabilized nanemulsions—Formulation and process factors affecting droplet size and nanoemulsion stability. International Journal of Pharmaceutics 2016, 500 (1-2), 291-304.
[5] H. Bouaouina, A. Desrumaux, C. Loisel, J. Legrand, Functional properties of whey proteins as affected by dynamic high-pressure treatment. International Dairy Journal 16, 275-284 (2006).
[7] A. Salonen, C. Gay, A. Maestro, W. Drenckhan, E. Rio, Arresting bubble coarsening: A two-bubble experiment to investigate grain growth in the presence of surface elasticity. EPL (Europhysics Letters) 116, 46005 (2017).
[8] Preisig, N.; Schad, T.; Jacomine, L.; Bordes, R.; Stubenrauch, C., How Promoting and Breaking Intersurfactant H-Bonds Impact Foam Stability. Langmuir 2019, 35 (47), 14999-15008.