

Happy 2022!

TECLIS Scientific team wishes you a year 2022 full of great experiments and successful projects!

SCIENCE

Interfacial rheology: a tool to probe interfaces at molecular scale

On the initiative of the academic scientific community of Lyon, the seminar "Only Lyon rheologie!" will take place on January 27-28, 2022.



Only Lyon Rhéologie !

Two days workshop dedicated to rheology where Jean-Luc Bridot will introduce the interfacial rheology on January 28th.

Related to the event we are posting a new series of applications notes dedicated to Interfacial dilatational Rheology with TRACKER™.

- Interfacial rheology: a tool to probe interfaces at a molecular scale. How to measure the interfacial rheology of an interface ? Why should you measure interfacial rheology ?
- Impact of frequency, amplitude and concentration on interfacial viscoelastic modulus. How the viscoelastic modulus is not an intrinsic property of an interface or a molecule, but rather characterizes the behavior of the monolayer in response to a particular solicitation characterized by the frequency and the amplitude at a given concentration.
- Illustrations of the usefulness of probing the interfacial rheology of fluid/fluid interfaces:
 - At microscale to study Molecular organization
 - At macroscale as a criteria to evaluate ageing of liquid dispersions.

✉ contact@teclis-scientific.com

New Defoamer Tester

New JETSCAN™ has been designed to measure defoaming agents' efficiency and persistence on foams produced by liquid jet circulation.

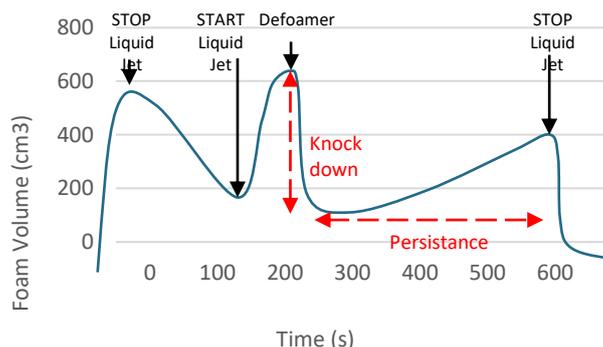
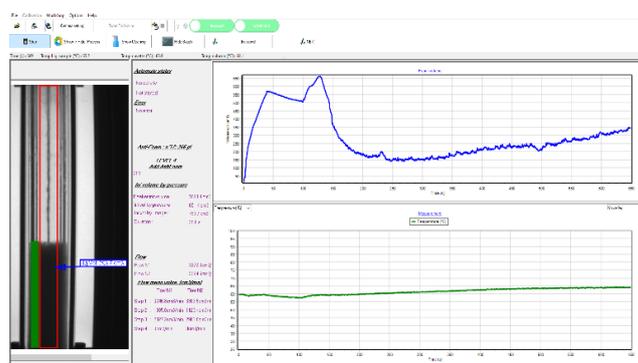


Fig1 Experiment profile Procedure

The experiment Protocol (Fig1) has been specially designed to test defoamers:

- effectiveness (knock down effect): from the ratio of the foam volumes after defoamer introduction.
- Persistence: by the time needed on reaching the maximum foam height with the presence of defoamer

JETSCAN™ software controls experiments parameters, collects and injects defoamer samples, measures foam volumes, manages cleaning process to ensure perfect reliability of the measurements.



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Surface tension is not enough to characterize interfaces...

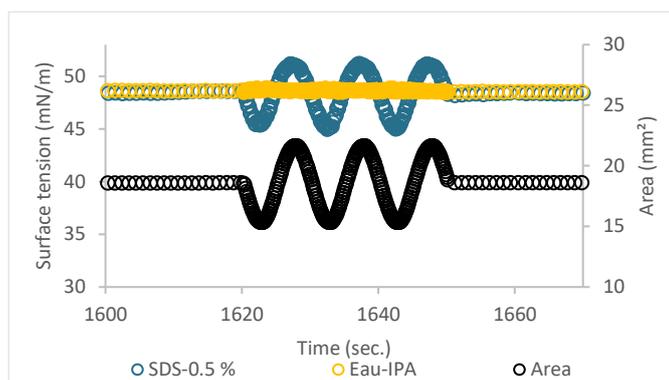
Interfacial tension is a major parameter in the characterization of the interfacial activity of a molecule. Monitoring Interfacial tension allows, among other parameters:

- to determine if the molecule is surface-active
- to characterize the adsorption kinetics to the interface of the molecule
- in some cases, to determine the interfacial concentration of this molecule.

Two systems with the same interfacial tension can show extremely different behaviors. For example, the addition of surface-active molecules such as sodium oleate (soap) to water lowers the value of interfacial tension at the solution-air interface and enhances the foamability of the solution while the addition of alcohol to water, lowers the interfacial tension but does not give the solution the ability to form foams. As an illustration, 2 solutions, a water/IPA mixture at 3 wt% and an aqueous SDS solution at 0.5 g/L show a similar liquid-air interfacial tension (around 48 mN/m) but very different macroscopic behaviors. Indeed, the aqueous SDS solution foams strongly while the hydroalcoholic mixture does not.

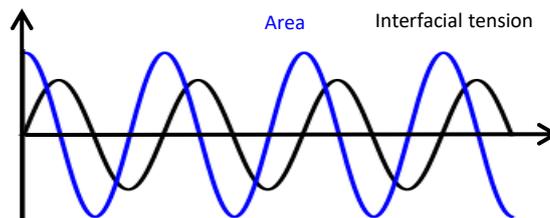
In addition to this macroscopic difference, the rheological properties of the two systems are different. While surface tension stays constant (orange symbols) during interfacial area variation (black symbols) for the hydroalcoholic mixture (orange dots), a strong correlation between surface tension and area is observed for the SDS solution (blue dots). Indeed, an increase in tension is observed when the interfacial area increases and when the area decreases, interfacial tension also decreases.

This dependence between the values of interfacial tension and interfacial area can be interpreted as a 2D viscoelasticity.



How to measure the interfacial rheology of an interface ?

Most commonly, the elastic modulus and the phase angle difference φ between the area and surface tension are obtained based on the response of surface tension to sinusoidal oscillations of the size of the interface.



Therefore, $E = |E^*| = \frac{dy}{d \ln A}$, $E' = |E^*| \cos \varphi$ and $E'' = |E^*| \sin \varphi$

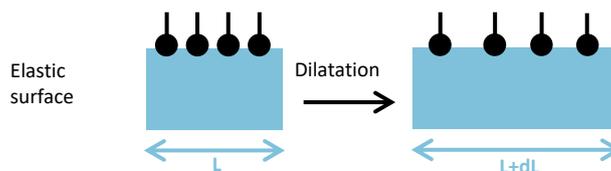
Definitions

Interfacial dilatational rheology defines a relationship between stress, deformation, and strain rate thanks to elastic and viscous coefficients. In practice, the interfacial viscoelastic modulus can be written as :

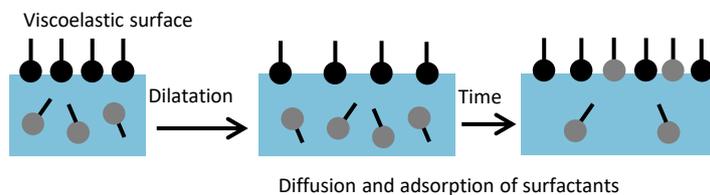
$$E^* = E' + iE''$$

With E' the elastic modulus and E'' the viscous modulus.

- E' can be interpreted as the elastic counterforce of the system. The system behaves as if the surfactants are only at the interface, so no equilibration of their concentration occurs.



- E'' describes how fast the initial value of surface tension is restored after deformation. If there are surfactants in the bulk phase, diffusion to the interface and adsorption occur leading to a time-dependent process [1]



Why should you measure interfacial rheology ?

Emulsion, foams and bubbly liquids are dispersed media used in many industrial applications (food, cosmetics, oil and gas, etc.). At the macro-scale, their properties such as the stability, the transport properties and the mechanical behavior strongly depend on their composition and the properties of the fluid-fluid interfaces composing them [2, 3, 4].

In liquid foams for example, the dilatation of interfaces when bubbles migrate to the free liquid-gas interface as a result of Buoyancy and interact with other neighboring bubbles leads to a decrease of surfactant coverage. To achieve equilibrium, surfactant molecules migrate to the stretched area and induce a flow of the subphase toward the thin part. Thanks to this effect called "Gibbs-Marangoni", the thinning is stopped, and the foam is stabilized [5].

References

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 [3] Lucassen-Reynders, E. H. (1993). Interfacial viscoelasticity in emulsions and foams. Food Structure, 12(1), 1.
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Introduction

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Most commonly, the viscoelastic modulus and the phase angle difference φ between the area and surface tension are obtained based on the response of surface tension to sinusoidal oscillations of the size of the interface.

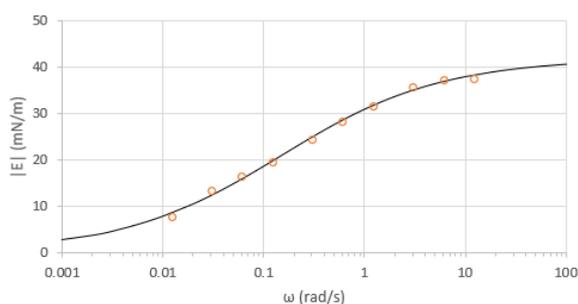
Therefore, $E = |E^*| = \frac{dy}{d \ln A}$, $E' = |E^*| \cos \varphi$ and $E'' = |E^*| \sin \varphi$

Interfacial rheology measurement is driven by 3 experimental parameters: **the frequency** and **the amplitude** of the stress applied and **the concentration** of the solution. As illustrated below, the value of the viscoelastic modulus will depend on each of those parameters.

Effect of the frequency

In this illustration, the dilatational rheology of amphiphilic polysaccharides derived from dextran is characterized at the oil/water interface by applying oscillations at various frequencies. While the elastic modulus increases with the frequency, the opposite has been observed for the viscous modulus. These experimental results can be well-described by the Lucassen-van den Tempel model which assumes diffusion-limited adsorption of surfactants.

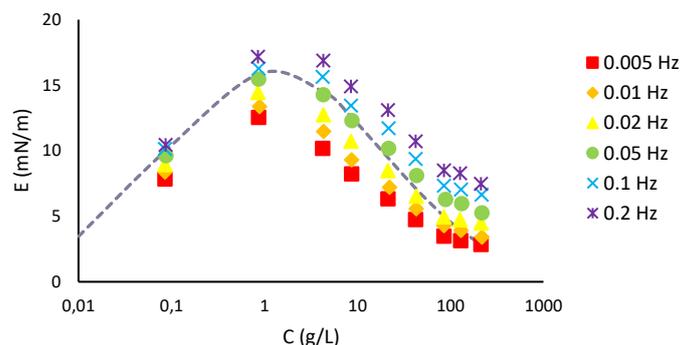
In comparison, similar experiments with Tween 80 showed a linear variation of $\log E$ with $\log \omega$ which could be attributed to the fast exchange of surfactant molecules between the interface and the micelles in the bulk aqueous phase [1].



Lucassen and van den Tempel model fitting parameters

$\omega_0 =$	0.2 rad/s
$E_0 =$	42 mN/m

Experimental data (C12E6) illustrating the dependency of E to the oscillation frequency.

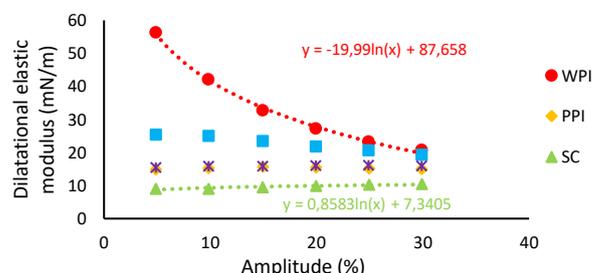


Viscoelastic modulus E as functions of concentration of AOSB537 bitumen-intoluene/NaHCO₃ with increasing frequency. Data from [2]. The dotted curve represents the schematic evolution of E as a function of C [3]

Effect of the amplitude

For this last illustration, the behavior of plant-dairy protein blends at an air/water interface is investigated. The elastic modulus is deduced by applying oscillations at different amplitudes. While the elastic modulus for two proteins and proteins-blends didn't seem to depend on the amplitude, a strong strain dependence is observed for the remaining two.

In this case, the modulus decreases as the amplitude increases which indicates that the interfacial network weakened upon deformation. Note that these experiments probed both the linear (deformation up to 5-8%) and the non-linear regime [4].



Apparent dilatational elastic moduli at the air-water interfaces stabilized by proteins and protein blends as a function the applied deformation (frequency, 0.01 Hz). Data from [4]

Conclusion

The viscoelastic modulus is not an intrinsic property of an interface or a molecule, it rather characterizes the behavior of the monolayer in response to a particular sollicitation characterized by the frequency and the amplitude at a given concentration. Hence, the experimental protocol needs to be determined carefully depending on the sollicitation regime of interest.

References

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Effect of the concentration

In this case, the dilatational rheology of bitumen-in-toluene/sodium bicarbonate solution interface is characterized at different bitumen concentrations and different frequencies.

The results presented below show that, for each frequency, the viscoelastic modulus increases to a maximum and then declines as bitumen concentration increases. This behavior suggests that the interfacial mobility increases as concentration increases beyond the maximum modulus. Similar bell-shaped curves are predicted theoretically when adsorption and desorption processes are modeled[2-3]

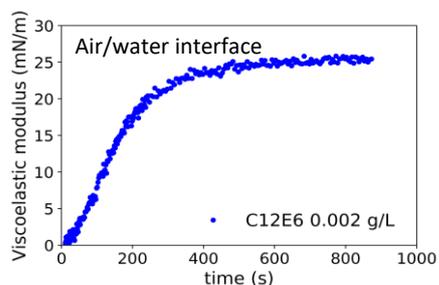
Introduction

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 probe 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.

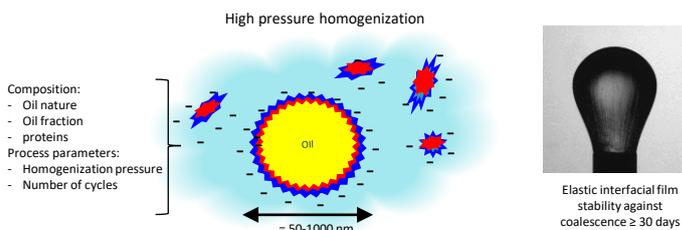


The results show that the modulus increases as a function of time as a result of the increase of surfactant density at the interface. After this first phase, the modulus reaches a plateau and stabilizes.

Macroscopic scale: Material properties

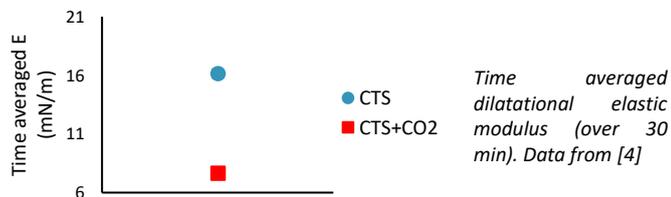
Link with emulsion storage stability

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].



E to monitor chemical reaction at the interface

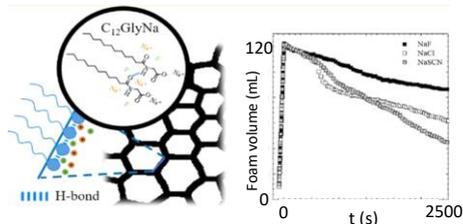
During the viscoelastic modulus measurement of an oil/chitosan aqueous suspension interface, a decrease of the viscoelastic modulus was observed when CO₂ was dissolved in the water phase. This behavior can be explained by the decrease of the pH of the solution below the pKa of the -NH₂/-NH₃⁺ chitosan 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 CO₂ 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]

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

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