

Surface tension is not enough to characterize interfaces...

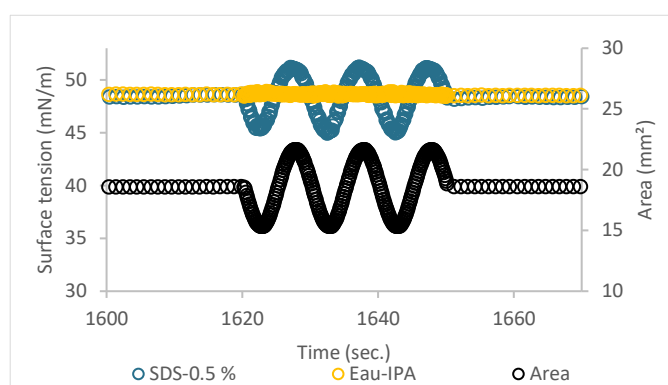
Interfacial tension is a major parameter in the characterization of the interfacial activity of a molecule. Monitoring Interfacial tension allows, among other parameters:

- 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.

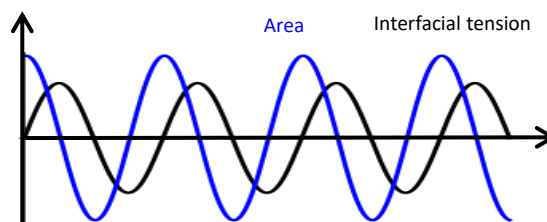
In addition to this macroscopic difference, the rheological properties of the two systems are different. While surface tension stays constant (orange symbols) during interfacial area variation (black symbols) for the hydroalcoholic mixture (orange dots), a strong correlation between surface tension and 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.



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

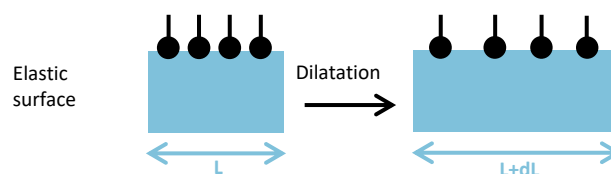
Definitions

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 :

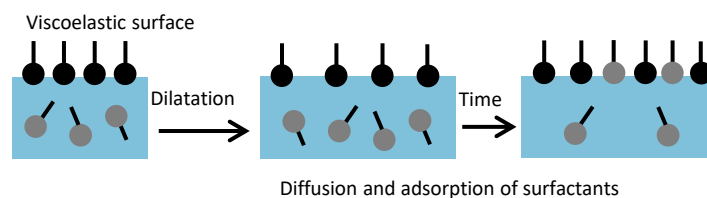
$$E^* = E' + iE''$$

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

- [1] Hutin, Anthony. (2019). Application Notes – Theory: 5. Compression & dilatation interfacial rheology.
- [2] Langevin, D. (2000). Influence of interfacial rheology on foam and emulsion properties. *Advances in colloid and interface science*, 88(1-2), 209-222.
- [3] Lucassen-Reynders, E. H. (1993). Interfacial viscoelasticity in emulsions and foams. *Food Structure*, 12(1), 1.
- [4] 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.
- [5] Marangoni, Carlo. "Sul principio della viscosita' superficiale dei liquidi stabilito dalsig. J. Plateau." *Il Nuovo Cimento* (1869-1876)5.1 (1871): 239-273.