Application Note

Impact of frequency, amplitude and concentration on interfacial viscoelastic modulus

Introduction

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.
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.

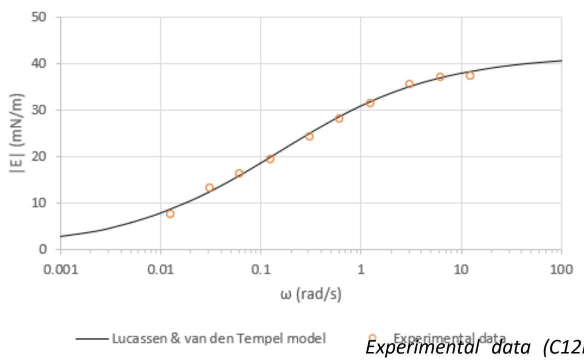
Therefore, $E = |E^*| = \frac{d\gamma}{d \ln A}$, $E' = |E^*| \cos \varphi$ and $E'' = |E^*| \sin \varphi$

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 logE with logω which could be attributed to the fast exchange of surfactant molecules between the interface and the micelles in the bulk aqueous phase [1].



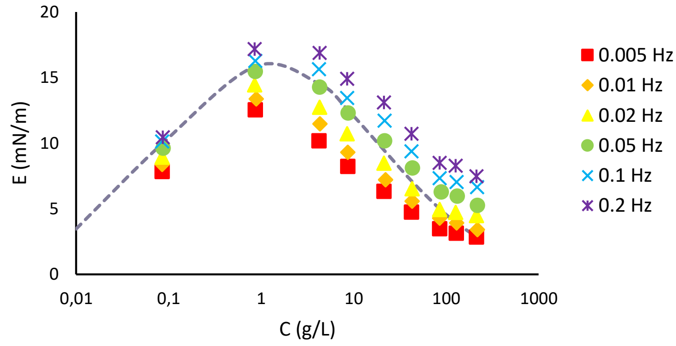
Lucassen and van den Tempel model fitting parameters	
ω0 =	0.2 rad/s
E0 =	42 mN/m

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

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 visco-elastic 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]

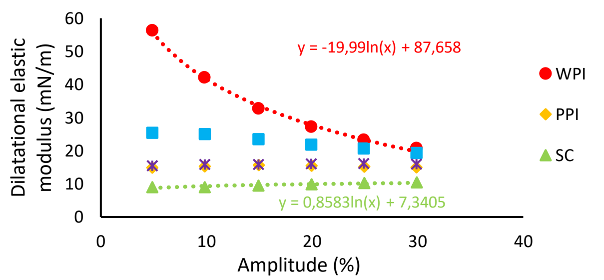


Viscoelastic modulus E as functions of concentration of AOSB537 bitumen-in-toluene/NaHCO3 with increasing frequency. Data from [2]. The dotted curve represents the schematic evolution of E as a function of C[3]

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 solicitation characterized by the frequency and the amplitude at a given concentration. Hence, the experimental protocol needs to be determined carefully depending on the solicitation regime of interest.

References
[1] Desbrières, J., López-Gonzalez, E., Aguilera-Miguel, A., Sadtler, V., Marchal, P., Castel, C., ... & Durand, A. (2017). Dilational rheology of oil/water interfaces covered by amphiphilic polysaccharides derived from dextran. *Carbohydrate polymers*, *177*, 460-468.
[2] Angle, C. W., & Hua, Y. (2012). Dilational interfacial rheology for increasingly deasphalted bitumens and n-C5 asphaltenes in toluene/NaHCO3 solution. Energy & fuels, 26(10), 6228-6239.
[3] Boos, J., Preisig, N., & Stubenrauch, C. (2013). Dilational surface rheology studies of n-dodecyl-β-d-maltoside, hexaoxyethylene dodecyl ether, and their 1: 1 mixture. Advances in colloid and interface science, 197, 108-117.
[4] Hinderink, E. B., Sagis, L., Schroën, K., & Berton-Carabin, C. C. (2020). Behavior of plant-dairy protein blends at air-water and oil-water interfaces. Colloids and Surfaces B: Biointerfaces, 192, 111015.