Application Report

Stretching Exercises for Drops

Application note: 246e

Industry section: Printing, chemicals, food, petroleum technology

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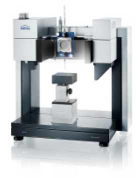
Date: 2005



Method: Drop Shape Analyzer – DSA100R

Keywords: Surface rheology, viscoelasticity, foaming, surfactant, elastic modulus, loss modulus

Stretching Exercises for Drops

Abstract

Some unwelcome effects in the production of inks or paints such as foams or bubbles relate to the surface viscous behaviour of added surfactants. KRÜSS offers a scientific instrument that helps to master problems in fast processes and the tendency of foaming: the EDM/ODM module for surface rheologic measurements with the measuring system DSA100.

Introduction

Panta rhei – everything flows. This saying – attributed to the Greek philosopher Heraclites – defines water to be the symbol of all changes. The science of rheology, in its name still showing this Greek root, analyses the behaviour of liquid substances – their viscosity and elasticity. The area of surface rheology investigates the effects that a size change of a surface has on its surface tension.

Everything flows, but what does it mean when we speak of the flowing of a surface? For so-called Newtonian liquids such as water, the flowing behaviour on the surface is not interesting. If the surface expands, water molecules from inside the liquid take their place immediately and the surface tension does not depend on time and speed. This changes as soon as surface active agents are included in the liquid: a time dependent behaviour is initiated and the work of the surface rheologist begins.

Surfactants and other surface-active substances have a hydrophobic part in their molecular structure and therefore, they accumulate at the water surface. By doing so, they reduce the surface tension and increase the affinity of the liquid solution to hydrophobic solids and fluids. This property makes surfactants very useful. For example surfactant addition can improve the wetting of a solid material. The formula of water-based inks, paints and lacquers therefore always includes surfactants. However, surfactants also show unwanted secondary effects such as foaming.

Fig. 1: Foaming – not always as desired as here

A lot of motions on the surface

The quantity of these molecules at each surface area is the surface concentration and is specified by the symbol "Γ". Gibb's Elasticity (E_G) defines the dependence of the surface tension (σ) on the surface concentration:

$$E_G \equiv -\frac{\delta\sigma}{\delta \ln \Gamma}$$

With an insoluble surface-active substance, the surface concentration will decrease when the surface area is increased. Imagine a spotted balloon: the number of dots per area unit decreases as the balloon is blown up. For a fluid, this means that the surface tension depends on the size (A) of the surface. The thermodynamic technical term for this effect is "surface elasticity" E_A:

$$E_A \equiv -\frac{\delta\sigma}{\delta \ln A}$$

In case of the chosen example of insoluble material, changes of area and concentration go hand in hand, and both elasticities, E_G and E_A, are in accordance with each other. However, if the fluid includes soluble particles, which applies to soluble surfactants, the molecules from inside the bulk material take the available place at the surface (see figure 2) or vice versa: if it gets crowded on a contracted surface, particles will move in the other direction until the old, equilibrium surface concentration has been achieved again. Suddenly, surface tension is not a constant value anymore but depends on the degree and the speed of the area change and on the mobility of the dissolved molecules.

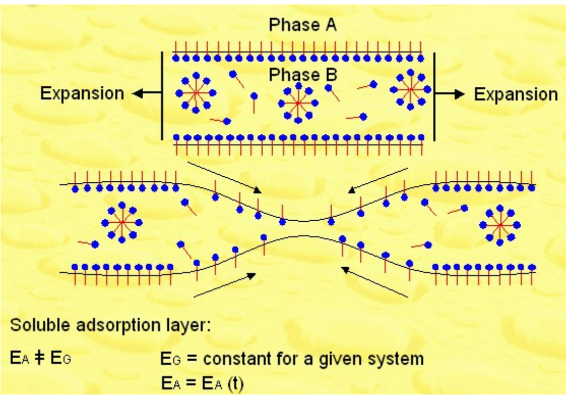


Fig. 2: Available area for new molecules after expansion

Surfactants: Agents with risks and side effects

In the manufacturing process of inks and paints, surfactants are used, among other additives, to decrease the surface tension and to mediate between ink and solid material – as for example between printer ink and paper.
In high-speed processes, however, they lose some of their efficiency because molecules do not reach the place, i.e. the surface, fast enough where they become active. A second property of surfactants is also highly unwanted in the manufacturing of inks: their disposition to foaming. The cosmetic industry tries to achieve mechanically stable foams by using suitable surfactants whereas in colour manufacturing foams and bubbles should vanish into thin air as fast as possible. Often so-called "defoamers" are used to suppress foaming. Of course, each additional component increases the cost of production and each substance added leads to more unwanted synergy effects. It is, therefore, important to carefully choose surfactants with a minor disposition to foaming.

Both effects, dependency on speed and the disposition to stable foaming need to be investigated. Classic tensiometry, such as the plate method of the KRÜSS K100 Tensiometer, is important to analyse the auxiliary material but cannot help to know more about the surface behaviour of fast changes. In order to investigate more close into this, the KRÜSS BP2 Tensiometer (bubble pressure) is used.

The surface tension is measured by the maximum pressure of a bubble formed in a test fluid. The speed of bubble formation is varied and the surface tension in dependent of the age of the bubbles that are formed. However, bubble pressure measurements do not allow direct statements about foam stability. These are only possible with a surface rheologic approach.

When Loss means Gain

Surface rheology differentiates between two effects which appear in changing the surface and which have different influence on the processing behaviour: The dependency on the degree of area change and the dependency on the speed of expanding or reducing the surface. The former is called surface elasticity and the latter surface viscosity. Put into a formula, the change in surface tension called surface stress (τ) is divided into the components τ_{vis} and τ_{el}. The following applies:

$$\tau = \tau_{vis} + \tau_{el}$$

Important figures for the characterisation of surfactants are the storage modulus E' (elastic component) and the loss modulus E'' (viscous component; see figure 3). These figures and the stability of a foam bubble are coherent. At a high surface elasticity, the produced foam reacts just like a spring. This phenomenon can be seen for example when pressing the foam crown in a bubble bath and the foam getting back to more or less the same shape immediately. If, however, the loss modulus is high and the storage modulus small, foam will dissolve and bubbles will burst by even little mechanic influence from outside.

Storage and loss moduli are therefore important results from EDM/ODM measurements which help to define the role of a surfactant in the working process.

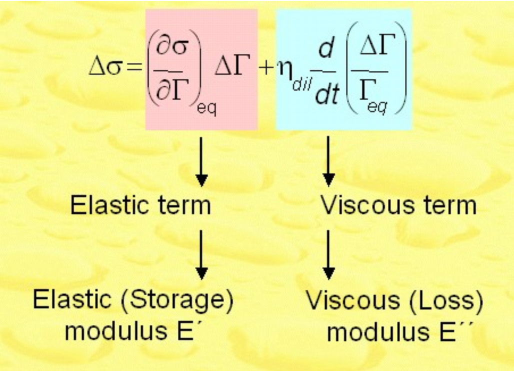


Fig. 3: The two components of tension change

Two parameters relevant for surface rheology are the elasticity or storage modulus E' and the viscous or loss modulus E''. Both values are obtained from the signal of a sinusoidaly oscillating drop; information can be obtained from the amplitude and from the phase shift of the resulting oscillation.

The analogy of these names to the volume rheologic parameters G′ and G′′ is no coincidence, both fields of science investigate the response of a system to external deformation influence.

Feel and See with EDM/ODM

The degree of area change and its speed hence show different effects. At first sight, this sets a difficult task: How can two parameters that always occur together be recorded separately in one measurement? It is best to make use of two "Senses".

With the KRÜSS EDM/ODM module ("E" standing for Expanding and "O" standing for Oscillating Drop Method) the sample is located between the membranes of a piezo pump. The liquid is pumped through a capillary where a drop is formed at the tip. The precise control of the pump allows the expansion and contraction of the drop to a desired size or the oscillation of the drop with a predefined amplitude, frequency or waveform.

The two "senses" are a camera and a highly sensitive pressure transducer. The video camera monitors the picture of the drop and transmits it to the frame grabber picture of the measuring software where it can be analysed. Knowing the picture scale, the exact dimensions of the drop can be defined and thus the changes of the surface.

The pressure detector registers the measurement of the pressure, providing data results at any point of the measurement. If the pressure diagram and the optical analysis of the drop image are combined, the required surface rheological data can be calculated.

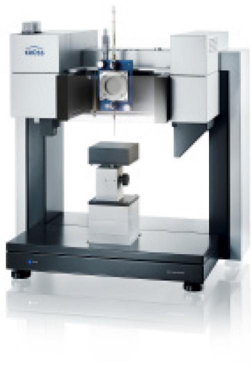


Fig. 4: Responsible for drop expansion – the EDM/ODM Module

The heart of the system is situated between the camera and light source. This includes the pressure device with piezo pump, capillary and pressure transducer. Video and pressure sensor data is reported to a connected computer. The software guides the user through the analysis, including a large number of scientific methods for static and dynamic measurements of interfacial and surface tensions.

The EDM/ODM Module is just one component of the universal drop shape analysis system DSA100 of KRÜSS. Some simple manipulation and the system is changed into an instrument to measure the surface tension of solids. The bottom part of the instrument then consists of a three-dimensionally movable sample stage on to which drops of different liquids can be dosed automatically.

A Lot on the Ball!

Conventional surface rheological analysis uses the method of the "pendant drop" from image analysis just as KRÜSS did for the characterisation of interface and surface measurements. This method produced reliable results for all static measurements. However, for dynamic surface tension measurements this is not the best and shortest way. This is mostly due to the characteristic, pear-shaped form of the drop. If such a drop is expanded, another relative area change at each position is obtained and a correlation between area and surface tension is not possible.

This implies the following solution: a ball-shaped drop is needed. Nevertheless, up to now, gravity impeded all efforts in this respect. As soon as the drop is big enough to be analysed by the pendant drop method, it already deviates far from the ideal spherical form. Only the evaluation of the pressure signal allows to measure the surface tension of a small, ball-shaped drop.

O for Oscillation

To measure both the storage modulus (E´) and the loss modulus (E´´) a mathematically defined waveform is needed: the sine wave. In the case of spherical drops, we are able to change not only the volume but also the drop surface at any drop position sinusoidally over time. At a surfactant measurement of a solution of Brij 58 against hexadecane, we demonstrate how interfacial tension behaves with such a drop oscillation (figure 5):

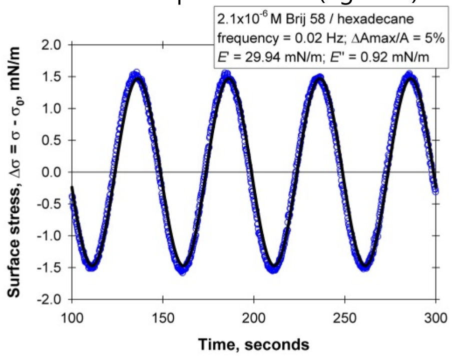


Fig. 5: ODM-Measurement of a surfactant solution

The change of interfacial tension during the wave run at a frequency of 0.02 Hz is a race against time. As one can see, the system gives a sine form answer. This effect can only be seen in case of a surface viscous liquid. In case of a pure solvent, no change of the surface tension would be seen; the reply would be identical to the 0-level of the y-axis. From the ratio of the results of E´ (29.94 mN/m) and E´´ (0.92 mN/m) we can detect that the surfactant solution shows an extreme surface elastic behaviour leading to the conclusion of the formation of very stable bubbles and foams.

E for Expansion

Also interesting for a surface rheologist is the run-up and relaxation behaviour of a solution. This is the point when the EDM-measurement becomes important. The drop is expanded or contracted at an exactly defined rate and then held at a constant surface area. The time dependent run of surface and interfacial tension is being recorded.

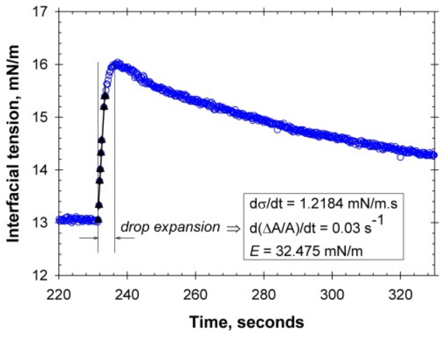


Fig. 6: EDM-Measurement of a surfactant solution

The EDM measurement in figure 6 is done for the same solution as in the earlier ODM measurement. One can very clearly see how interfacial tension abruptly mounts during expansion and relaxes after it. Relaxation of the system, however, is (as one can see) not a matter of split seconds. Surfactants are big, immobile molecules which need a long time to wander from the inside of a solution to the sub-surface (diffusion) and to "integrate" into the surface (adsorption). Also important is the run-up behaviour. At the very beginning of the measurement, surface and interfacial tension change linearly with the time. From the slope of the linear stress the start-up modulus E can be calculated. This gives information about the interdependency between the molecules at the surface.

Science meets business

The EDM/ODM module is one more important tool to expand material testing in an application laboratory by analysing surface-active substances. In addition, it complies with high scientific claims. An evaluation tool, included in the software package, provides analyses.

This gives way to a large scale of molecular parameters – from the above mentioned E´, E´´ and E to the dilatational surface viscosity to adsorption and diffusion coefficients. Documentation takes the user by the hand and demonstrates the significance and limits of the individual mathematical models.

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