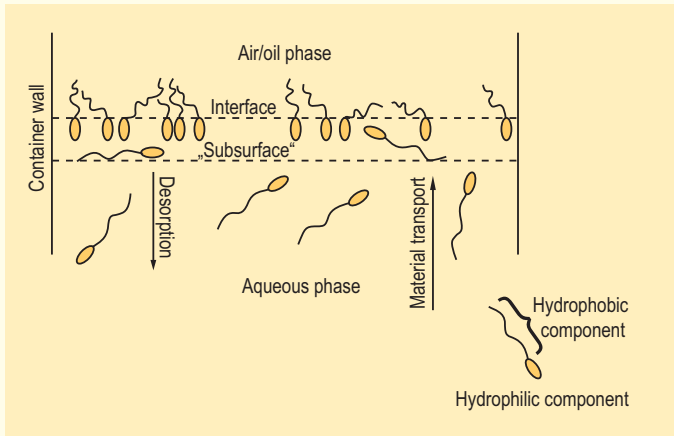


Dynamic methods

Surface and interfacial tensions are called “dynamic” when their values, despite constant external conditions, decrease significantly with increasing age, i.e. when they are not in thermodynamic equilibrium. The most familiar methods for determining

these dynamic values are the drop volume and bubble pressure methods. In the drop volume method, the dynamic surface or interfacial tension is determined from the volume of a falling drop.

Surfactants at interfaces



Origin of the “dynamics”

Surface-active substances, because of their structure, prefer to migrate to surface or interfacial regions. The migration characteristics of these molecules mean that, over time, they enrich the surface/interfacial regions. This constantly decreases the surface/interfacial tension. At the same time, a few molecules manage to leave the surface/interfacial regions. If the number of molecules arriving equals those leaving, then a stable surface/interfacial tension value is reached. These dynamic effects are based on previously poorly understood surfactant properties. In many analysis cases using so-called general tensiometers (ring/plate), this effect

can lead to serious measuring errors. The analysis of these effects is particularly important in time-controlled surfactant actions, such as, e.g. rapid coating processes, droplet formation in sprays and liquid jets, wetting processes or emulsion stability. The drop volume and bubble pressure methods are particularly suitable for recording these dynamic changes.

The drop volume method

Determination of the dynamic surface tension and the interfacial tension between immiscible liquids

Surface tension:

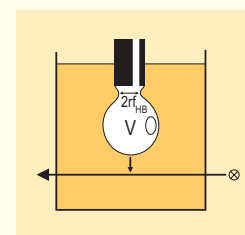
Drops are generated using a suitable device. These drops grow as long as their weight is less than their holding force on the capillary. As soon as this weight has reached the same magnitude as the holding force, the drop falls and the volume of the falling drop is measured. The surface tension is then calculated from this volume.

$$\sigma = \frac{g\rho V}{2\pi r f_{HB}}$$

Interfacial tension:

Drops of a liquid with a high density, e.g. water, are generated in a liquid with low density, e.g. oil. Both fluids are immiscible (water/oil). As soon as the weight, minus buoyancy, reaches the same magnitude as the holding force, the drop will fall. The volume of the falling drop is measured and the interfacial tension calculated.

$$\sigma = \frac{g(\rho_1 - \rho_2)V}{2\pi r f_{HB}}$$



Preferred applications:

- For surface and interfacial tension
- Particularly suitable for dynamic interfacial tensions

Examples of typical samples:

- For solutions, oils and viscous systems that contain surfactants
- Particularly suitable for emulsifiers, “average-speed” surfactants and average surfactant concentrations

Equipment suitable for this method:

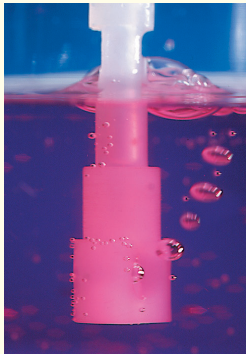
- The LAUDA Tensiometer TVT 2 – easy to use, robust and PC controlled (see P. 18 ff.)

In the bubble pressure method, the pressure in a small gas bubble is used to determine the dynamic surface tension. The age of the drop/bubble can be varied in both the drop volume and bubble pressure methods. This enables specific dynamic effects to be investigated. The LAUDA Tensiometers TVT 2 and MPT 2 work with very wide time ranges that overlap. Absolutely precise

determination of the dynamic surface tension with surface aging up to less than 1 ms is possible with the LAUDA Bubble Pressure Tensiometer MPT 2, thanks to the specially developed procedure. The Drop Volume Tensiometer TVT 2 enables measuring of interfacial tension with surface aging up to several hours.

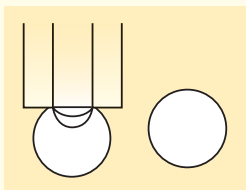
Maximum bubble pressure method

Determination of the surface tension of liquids



Measuring principle:

Air is blown through a capillary into the liquid being measured. The pressure in the gas bubble formed on the end of the capillary rises. Maximum pressure is reached when the bubble reaches the hemispherical shape. At this point in time, the radius of the hemispherical bubble corresponds to the radius of the capillary. Once the hemispherical shape is exceeded, the pressure only serves to expand the bubble until it detaches itself. The surface tension can be calculated with the Laplace equation from the maximum bubble pressure and the bubble radius. The time from the start of bubble formation to the hemispherical shape (maximum pressure) is the surface age corresponding to the surface tension. The time from the hemispherical shape until the bubble detaches is the dead time. It is not relevant for the measurements.



This process generally causes measuring technology problems in other bubble pressure tensiometers, e.g. during the precise determination of the maximum bubble pressure or the extremely rapid recording of pressure changes. These problems do not occur with the MPT 2, thanks to its special construction and measuring process.

$$\Delta P_{\max} = \frac{2\sigma}{r_{\text{kap}}} - \rho \cdot g \cdot h$$

h: immersion depth · *ρ*: sample density · *g*: acceleration due to gravity · *σ*: surface tension · *r_{kap}*: capillary, internal radius · *ΔP_{max}*: maximum pressure

Preferred applications:

- Dynamic surface tension
- For systems containing surfactants

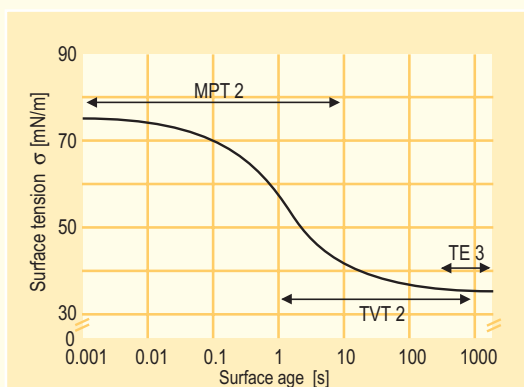
Examples of typical samples:

- Very “rapid” surfactants and/or high surfactant concentrations

Equipment suitable for this method:

The PC controlled Bubble Pressure Tensiometer MPT 2: it enables precise determination of dynamic surface tension with surface ages measured from fractions of milliseconds up to 50 s (see P. 24 ff.).

LAUDA Tensiometers supplement each other



If depicted in a logarithmic way the surface tension/surface age is a S-shaped curve which is characteristic for each surfactant and its concentration. Each of the LAUDA Tensiometers covers a certain range of the surface age for physical-technical reasons. The range defined by the application is therefore the deciding criteria in selecting the equipment. Using the combination of different LAUDA Tensiometers provides nearly complete coverage of the time range.