

Determination of Surface Tension

Using the Stirrup Method

1. Goal

The aim of this experiment is to study the surface tension of liquids. This done using the stirrup method, where the ratio of a water-ethanol mixture and the temperature of olive oil are determined.

2. Incentive

Surface tension is a common, natural phenomenon with far-reaching consequences. It appears in the form of droplets from liquids on their surfaces or in falling raindrops. A well-known example are also water striders, insects that can walk on the surface of water easily. The surface tension of liquid mixtures depend on the ratio of their composition, which is why in heavily polluted ponds or lakes the surface tension is too low and water striders are not able to live there.

3. Theory

Forces act on the surfaces of liquids and solids striving to minimize their surface area. In nature, the existence of these forces is most notably observed in liquids, as liquid molecules move around well in opposite directions. Accordingly, the effect of these forces forms surfaces in the smallest possible size (for example, water droplets).

3.1 Cohesion and Adhesion

We distinguish between two types of forces:

Cohesive forces are attractive forces between the atoms or molecules of the same material

Adhesive forces are attractive forces between different atoms or molecules of different solid or liquid bodies.

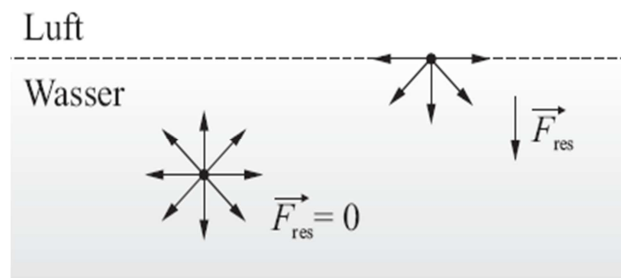


Fig. 1: Cohesion forces in liquids

The cause of these (macroscopic) forces are at the microscopic level, such as van der Waals and dipole-dipole interactions or hydrogen bonds. These forces diminish rapidly over distance, so that in this model, only neighbouring molecules interact.

We consider the forces acting on two molecules of a liquid: one molecule lies inside the liquid and the other on the surface, which is accepted as the boundary layer of the liquid to air (see Fig. 1). Cohesive forces act on the inside of the liquid exclusively, which after a time will balance out since no direction is preferred over another. This means over time there is no net resulting force F that acts in a molecule.

On the surface molecule acts an adhesive force between liquid and air in addition to the cohesive force. However, since this is negligibly small, the focus is only on cohesive forces. They act exclusively within the liquid or along its surface, so do not cancel each other out completely. Unlike inside the liquid, the surface has a non-zero net force which spans across the liquid.

3.2 Specific Surface Energy

If the particles of a liquid should be brought from inside to the surface, work ΔW is performed due to the specified forces. Due to the transition of these particles, the surface of the liquid A is increased by ΔA . The following quotient is called the *specific surface energy* or *surface tension*.

$$\sigma = \frac{\text{Work required to increase surface area}}{\text{Increase in surface area}} = \frac{\Delta W}{\Delta A}$$

3.3 Dependency of Surface Tension on the Mixing Ratio of Substances

In a mixture of two liquids, the liquid having the smaller surface-tension accumulates in the boundary layer, i.e. a mixture of two liquids with a spatially inhomogeneous mixing ratio is obtained. This is due to the reduction in surface energy and thus the total energy of the system. As the ratio of the mixture varies spatially, no linear correlation between surface tension σ and concentration c exists (see Fig. 2). Instead, the relationship follows *Szyskowski*:

$$\sigma_{Mish}(c) = \sigma(0) - A \cdot \log(1 + B \cdot c)$$

With:

- σ_{Misch} : Surface tension of the mixture
- c : Concentration of the mixture with the reduced surface tension
- A, B : Constants (A small and B strong material dependency)

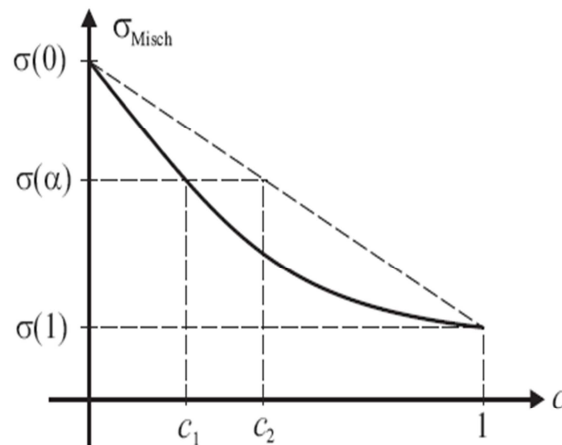


Fig. 2: Surface tension dependent on the mixture ratio

3.4 Temperature Dependency of the Surface Tension

When a liquid is heated, the kinetic energy of the molecules increases. In such an agitated state, less work ΔW is required in order to bring a particle to the surface. The surface tension decreases in order for the dependent critical temperature T_k of the material of all liquids to reach 0. The critical temperature is the temperature of a substance, beyond which the distinction between gas and liquid phase cannot be determined.

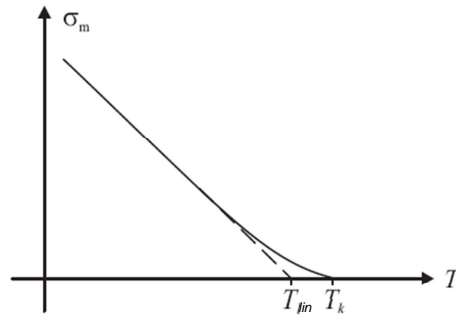


Fig. 3: Molar surface tension dependant on temperature.

Experimentally, the following linear dependency for the molar surface tension σ_m can be found in a further temperature range (Fig. 3):

$$\sigma_m(T) = k_\sigma(T_{lin} - T)$$

Where σ_m is somewhat inconveniently defined over the molar volume V_m : $\sigma_m = \sigma \cdot V_m^{2/3}$. Eötvös's rule states that the temperature coefficient k_σ is the same size for almost all liquids:

$$k_\sigma \approx 2.1 \cdot 10^{-7} J / K \cdot mol^{2/3}$$

4. Stirrup Method

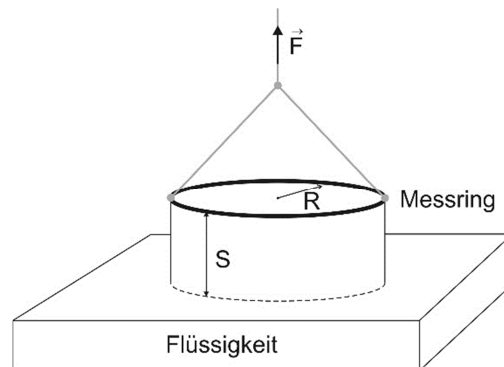


Fig. 4: Measuring ring with increased surface area through adhesion

In the experiment to be performed, a metal ring (hereinafter referred to as a measuring ring) is carefully pulled out of a liquid by means of a dynamometer. As shown schematically in **Fig. 4**, the liquid adheres to the metal ring and forms a liquid film or cylinder as it is extracted. This increases the surface area, which requires work.

$$\Delta W = F \cdot s$$

Here, F is the force with which the metal ring is pulled out of the liquid, and s the height of the liquid film. In a first approximation, we can take F to be a constant force along s . The force F is then measured at the point in which the liquid film gives way under the metal ring. The increase in surface area is given using the following formula.

$$\Delta A = 2 \cdot 2\pi \cdot R \cdot s$$

Since the ring has two surfaces, one on the inside of the liquid film and the other on the outside, the formula has a factor of 2. R denotes the average of the outer and inner radius of the ring.

Corrections to the measured force by the weight of the raised amount of liquid is negligible, since the bottom of the ring has a sharp edge and the liquid film is very thin. Thus, the specific surface energy is obtained using:

$$\sigma = \frac{\Delta W}{\Delta A} = \frac{F \cdot s}{2 \cdot 2\pi \cdot R \cdot s} = \frac{F}{4\pi \cdot R}$$

This shows that in determining the surface tension, only the force F at the breaking point of the film is needed, which proves to be quite convenient.

5. Experiment

5.1 Material and Experimental Assembly

A torsion force measurer (accurate to 0.1 mN) measures the force F , which is required along with the measuring ring (diameter $D = 2R = 19.65$ mm) to deform the surface of a liquid (see **Fig. 4**). The liquids include olive oil, demineralized water and ethanol.

5.2 Task

Determine using the experimental setup above:

- a) The surface tension of a water-methylated spirits mixture, its composition depending on the mixing ratio in the range from 0 to 100% in 5% increments (pipettes and a summary table are available for the mixture)
- b) The surface tension of olive oil as a function of the temperature in a range from 13-30°C in 5°C increments

5.3 Method

The measuring ring is carefully degreased with methylated spirits, thoroughly rinsed in distilled water and then drained and secured with a silk thread on the left arm of torsion force measurer. The pointer of the dynamometer is set to '0' and compensates for the weight of the measuring ring with the screws on the lever arm, so that the lever arm is in the white field between the cutting indicators.

The test liquid is poured into the carefully cleaned petri dish and the measuring ring completely submerged.

In order to make a measurement, the petri dish, which sits upon a tripod of variable height, is lowered at the same time that the measuring ring is hoisted with the torsion force measurer. The arm of the dynamometer must always remain horizontal. Here, the liquid film is pulled up with the measuring ring. After the liquid film tears, the required force is read off of the torsion force measurement tool. It must be ensured that no vibrations occur during measurements, as this may lead to premature tearing of the film and thus to errors in the determination of the breakaway force. In determining the temperature dependence, the liquid is heated on a hot plate, the measured values are recorded during the subsequent cooling.

It should be noted that cooling from a high temperature happens very fast and the recording of the first points of data can be a bit difficult.

Safety notice: During the experimental procedure goggles are to be worn!

5.4 Protocol

The protocol should contain a concise description of the physical principles and concepts. Copying of this introduction is not necessary.

The experimental setup and the implementation will be described in detail - also in view of any

possible sources of error.

The results will be shown graphically and compared with theory. If the data appears faulty, the cause of the error will be discussed.

Literature:

- [1] Walcher, W.: *Praktikum der Physik*, 5. Auflage, Teubner Verlag, Stuttgart (1985)
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