

The scientific background to tensiometric measurements

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The choice of the most appropriate method and instrumentation for the determination of surface or interfacial tensions depends not only on the nature of the sample being tested, but also on an understanding of the scientific principles behind the methods used. This article reviews the most commonly-used methods.

The understanding and evaluation of the tensiometric properties of materials, both solids and liquids, is vital in many processes and development programs, particularly whenever surface-modifying compounds such as surfactants are being used. Surfactants are ubiquitous in the modern world, with their applications ranging from use as wetting and spreading agents, emulsifiers, foam stabilisers, dispersant, lubricants, washing agents and waterproofing agents. The continuing use of surfactant products in these fields requires the use of tensiometers, which by definition must be capable of being able to perform adequately in the individual fields in which they are being applied. Such fields range from the analytical laboratory, R&D departments and QC laboratories.

Typical studies carried out in the analytical laboratory range from the characterisation of emulsifiers and flotation additives, through the analysis of the dissolution properties of powders and tablets to the adsorptive behaviour of proteins and bio-surfactants. In R&D, tensiometers could be used for the optimisation of the wetting properties of coatings, for the study of amphiphilic molecules and for the development of cleaners, washing agents and sprays that contain surfactants. In QC, tensiometers are used for a variety of purposes, such as the monitoring of the surfactant content in aqueous solutions and cleaning agent residues.

The choice of the optimal model of tensiometer depends on the particular application in which it will be used. However, since the operation of tensiometers depends on some clearly defined physico-chemical laws, it is clear that an understanding of these basic laws and the principles behind the different types of measurement systems is essential for the appropriate choice of instrument for a given application.

In general, the methods used for the measurement of surface and interfacial tensions can be subdivided into static and dynamic methods.

Static methods

Surface and interfacial tensions are known as “static” or “quasi-static” whenever their values do not change, stop changing or change very slowly when the external conditions are kept con-

stant. The system is therefore at, or very close to, thermodynamic equilibrium. The two methods that are most often used for the determination of static interfacial tensions are the Wilhelmy method, based on the use of a solid plate and the Du Nouy method, based on a ring.

Wilhelmy method

This method can be used not only to determine the surface tension of liquids, but also the contact angle on solids. In this method, a solid plate whose weight has previously been established and tared is brought into contact with the liquid to be measured. The meniscus weight is measured until the measurement values are constant, at which point the surface tension can be calculated (Figure 1). It is imperative that in this system the contact angle is 0° C, which can be achieved by scrupulous cleaning of the metal plate or by annealing. Typical samples that are suitable for measuring by this approach are pure liquids, and both polar and non-polar liquids, as well as liquids with low surfactant concentrations.

The contact angle, and therefore the wettability of a solid, can itself be calculated from the known surface tension, σ , and the measured weight of the liquid meniscus. This is done by bringing a tared solid into contact with the liquid. The solid is then automatically moved up and down. The recording of the force against distance results in a hysteresis force curve from which both the advancing and receding angles can be calculated. This method can be applied for the determination of the surface energy of solids, for example, in foils, films, painted surfaces, silicone wafers and any other specially treated surfaces.

Du Nouy ring method

This method uses a solid ring structure whose weight is known and tared. The ring is dipped completely into the liquid to be analysed (Figure 2). It is then slowly withdrawn from the liquid until maximum force (F_{\max}) is attained. The surface and interfacial tensions are calculated from the maximum force:

$$\sigma = \frac{F_{\max}}{4\pi R f_{\text{CORR}}(r, R, \rho)}$$

where f_{CORR} is a ring correction factor depending on the precise geometry of the ring and the density of the liquid.

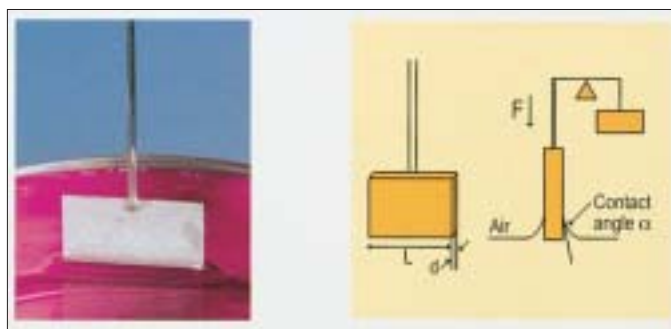


Figure 1. The principle of the Wilhelmy method for determining surface tensions.

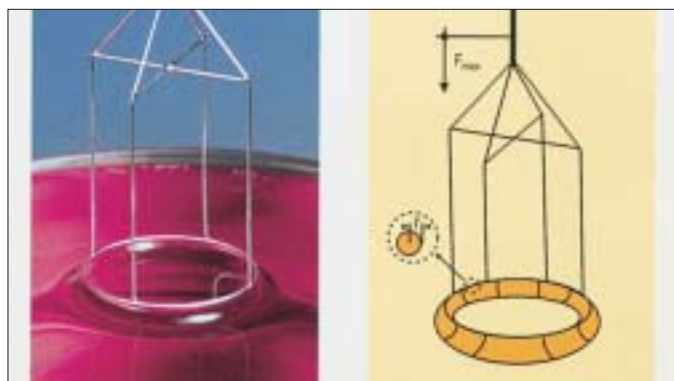


Figure 2. Principle of the Du Nouy ring method.

The Du Nouy ring method can be applied for static surface and interfacial tension measurements and for the automated determination of critical micellar concentrations (CMC). Typical samples that can be handled by this method are pure liquids and both polar and non-polar liquids or those with low surfactant concentrations.

Dynamic methods

Surface and interfacial tensions are known as “dynamic” when their values decrease significantly with time, despite the fact that external conditions are held constant, i.e. they are not in thermodynamic equilibrium. The most familiar methods for the determination of such dynamic methods are the drop volume method and bubble pressure methods. As the name suggests, in the drop volume method the dynamic surface or interfacial tension is calculated from the volume of a falling drop, while in the bubble pressure method, the pressure in a small gas bubble is used to determine the dynamic surface tension. In both methods the time scale can be varied, thus enabling specific dynamic effects to be investigated. Such dynamic methods are necessary for the analysis of solutions containing high concentrations of surfactants.

Surfactants at interfaces

Surface-active substances, because of their structure, prefer to migrate to surface or interfacial regions. The migration characteristics of these molecules mean that their concentration in the surface/interfacial regions steadily increases with time. Consequently the surface/interfacial tension decreases with time. However, at the same time there is a certain number of surfactant molecules which despite the attraction to the surface induced by their chemical structure, nevertheless manage to leave the surface area. If the

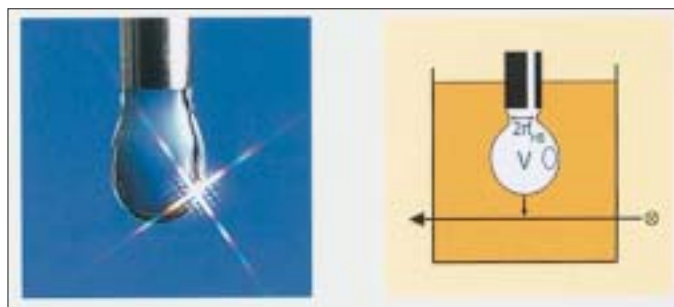


Figure 3. Principle of the drop volume method of determination of dynamic interfacial tension.

number of molecules leaving is equivalent to those arriving, then of course a stable value of surface/interfacial tension is established. Whether a stable or dynamic situation is obtained depends on the previously poorly understood surfactant properties. In many analyses carried out by so called general tensiometers based on the ring or plate methods as described above, such effects can be particularly important and can lead to significant measuring errors. Awareness of the dynamics of the sample is particularly important in time-controlled surfactant actions such as those involved in rapid coating processes, droplet formation in sprays and liquid jets, wetting processes or emulsion stability. Drop volume and bubble pressure methods are the methods of choice for recording these dynamic changes.

The drop volume method

This method is suitable not only for the determination of dynamic surface tension, but also the interfacial tension between immiscible liquids. For the measurement of surface tension, the principle is as follows: Drops of the liquid are generated using a suitable tube and device (Figure 3, left side). Such drops continue to grow as long as their weight is less than the holding force of the capillary. Once the weight of the drop reaches the equivalent of the holding force, the drop falls. With suitable instrumentation, the volume of the drop can then be calculated. The surface tension is then calculated from this volume :

$$s = \frac{g\rho V}{2\pi r_{HB}}$$

For the measurement of interfacial tension, drops of a liquid with relatively high density, e.g. water, are generated in a liquid with relatively low density, e.g. oil. Both fluids should be immiscible. As soon as the weight of the submerged drop, minus its buoyancy, reaches the same magnitude as the holding force, the drop will sink. Using suitable instrumentation, the volume of the sinking drop can be measured and the interfacial tension calculated by a modification of the formula used above for the surface tension:

$$s = \frac{g(\rho_1 - \rho_2) V}{2\pi r_{HB}}$$

Typical samples that are analysed by the drop volume method are solutions, oils and viscous systems containing surfactants. The method is particularly suitable for emulsifiers, “average speed” surfactants and average surfactant concentrations.

Maximum bubble pressure method

In this method, air is caused to flow under controlled conditions through a capillary tube into the liquid being measured. The pressure in the gas bubble that is formed at the end of the capillary tube rises as more air passes into the bubble. The pressure reaches a maximum when the bubble has reached a hemispherical shape (Figure 4). At this stage, the radius of the hemispherical bubble is equivalent to the radius of the capillary tube. Once the hemispherical shape is exceeded, the increasing pressure caused by the continuing air flow only serves to expand the bubble until it detaches itself. The surface tension can be calculated from the maximum bubble pressure and the radius of the bubble using the Laplace equation:

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

where: h = immersion depth
 r = sample density
 g = gravitational force
 σ = surface tension
 r_{kap} = internal radius of the capillar tube
 ΔP_{\max} = maximum pressure

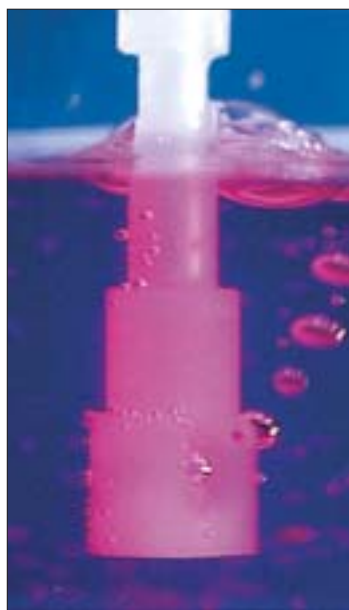


Figure 4. Principle of the maximum bubble pressure method for the determination of the surface tension of liquids.

In practice, the accurate measurement of the maximum bubble pressure as well as the extremely rapid recording of pressure changes can pose severe challenges to the instruments being used for the analysis. Only well-designed and carefully constructed instruments incorporating precision engineering and sophisticated electronics can be depended on to generate reliable results (Figure 5).

Glossary

The definition of some selected, commonly-used terms in tensiometry:

Critical Micelle Concentration (CMC)

At this concentration, surfactant solutions undergo a sudden change in their physical properties, due to the formation of organised aggregates (micelles). The structure of the micelles depends on the nature of the solvent and the structure of the surfactant molecules.

Measurement of CMC

This is the determination of the surfactant concentration at which surfactant molecules begin aggregating and can be calculated from the relationship of the measured surface tension with the surfactant concentrations.

Interfacial energy

This is the sum of the free energy of all the molecules present at

The time that elapses from the start of bubble formation to the stage of maximum pressure (when the hemispherical shape is attained) determines the surface age corresponding to the surface tension. The time taken for the bubble to pass from the stage of maximum pressure (the hemispherical shape) until the bubble detaches itself from capillary tube is known as the dead time and is not relevant or useful for the extraction of further information.



Figure 5. The generation of reliable results depends on choosing the method most appropriate to the characteristics of the sample and the use of a well-designed and carefully constructed instrument. The Lauda TVT2 instrument shown above is one model in the extensive range of specially designed instruments supplied by the Lauda company.

the interface between different materials. The interface between a liquid and a gas is known as a surface and the corresponding interfacial energy known as surface energy.

Surface age

The age of a surface since its creation. In bubble pressure tensiometry, this is the period from the beginning of bubble formation until the bubble reaches its hemispherical shape. In drop volume tensiometry, this is the period between the creation and separation of a drop.

Dynamic measuring process

This is the process used to calculate the surface/interfacial tension dependent on surface age.

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