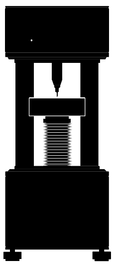
Application Note

Studying the concentration dependency of dynamic surface tension with MBP 200

Surface-active agents (surfactants) are commonly used compounds in both daily life and a wide range of industrial processes. They have a significant impact on the formation of droplets and films, which are crucial points for the quality of many products. It has been established that surfactants in solutions can react to changes in the available surface area in a matter of milliseconds,[1] which is crucial for their efficiency in washing processes or during spraying applications. It is therefore important to study the kinetics of surfactant adsorption at the gas/liquid interface, particularly for processes involving rapid wetting. ***Dynamic surface tension is an ideal parameter for understanding fast wetting processes. The MBP 200 Bubble Pressure Tensiometer manufactured by DataPhysics Instruments*** *is an ideal instrument for measuring dynamic surface tension, with the capacity to determine surface tension at* ***surface ages down to 5 milliseconds****. The following application note will showcase an automatic approach to determine the dynamic surface tension of Lutensol® solutions with different concentrations.*

Measurement device
Bubble Pressure Tensiometer – MBP 200



Measurement method
Maximum bubble pressure

Measured quantities
Dynamic surface tension

Environmental conditions
25 °C

Samples
Lutensol® solutions (non-ionic fatty alcohol surfactants in aqueous solution)

Industries
Washing
Printing
Spraying processes

dataphysics

MBP 200 Technique

The MBP 200 bubble pressure tensiometer, manufactured by DataPhysics Instruments (see Fig. 1), is a highly sophisticated measuring device which employs the maximum bubble pressure method to determine the dynamic surface tension of liquid solutions with great precision.[2] It is suitable for the determination of dynamic surface tensions in a range between 10 mN/m and 100 mN/m, over a surface age interval between 5 milliseconds and 200 seconds. The device is therefore ideal for the analysis of surface tensions of liquids, such as surfactant solutions, across a wide dynamic range.

Fig. 1: MBP 200 Bubble Pressure Tensiometer manufactured by DataPhysics Instruments

The maximum bubble pressure method enables the assessment of the dynamic surface tension at the newly formed surface of a bubble in a solution (Fig. 2).[3] The internal pressure (p_{in}) of a spherical gas bubble, as defined by the Young-Laplace equation, is dependent upon the radius of curvature (r_b) and the surface tension (σ) of the solution.[4]

As illustrated in Fig. 2(a), the formation of a gas bubble at the tip of a capillary causes an initial increase in curvature, which is subsequently followed by a decrease. This gives rise to a pressure maximum. The greatest curvature and therefore the greatest pressure are observed, when the radius of curvature is equal to the radius of the capillary. Once the radius of the capillary is known, the surface tension can be calculated from the pressure maximum (P_{max}). It is necessary to subtract the hydrostatic pressure (caused by the capillary's immersion). Accordingly, the surface tension (σ) can be calculated as follows:

$$\sigma = \frac{1}{2} \cdot \left(\Delta p_{mea,max} - \rho\, g\, h \right) \cdot r_{cap}$$

As depicted in Fig. 2(b), r_{cap} is the inner radius of the employed capillary, h is the set immersion depth, and ρ is the density of the studied liquid; g represents the local acceleration of gravity. The maximum possible pressure ($\Delta p_{mea.\,max}$) is determined by the device.

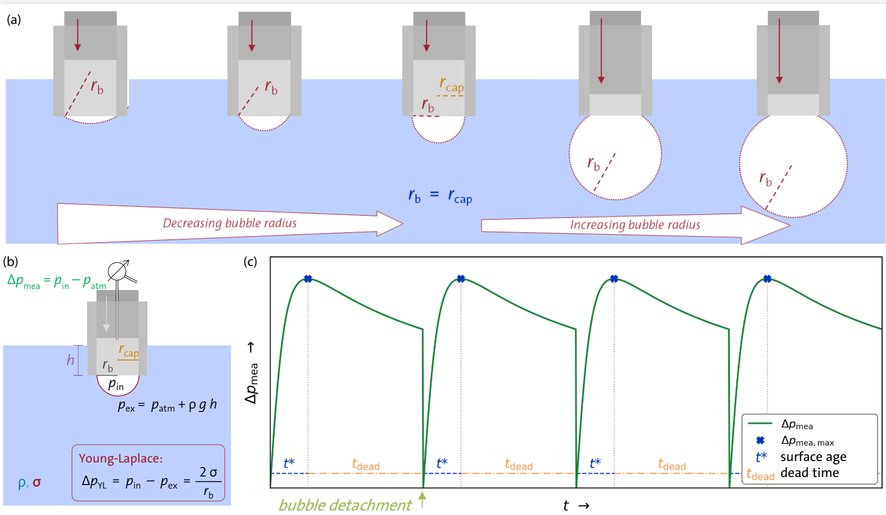


Fig. 2: (a) The formation of a gas bubble at the tip of a capillary (b) Determining the surface tension at maximum bubble pressure (c) Measured differential pressure in the dynamic experiment

In order to monitor the internal pressure of the gas bubbles, the MBP 200 incorporates a highly sensitive pressure sensor. Fig. 2(c) illustrates that the generation and subsequent expansion of gas bubbles occur continuously until the point of detachment from the capillary tip. The formation of a new bubble is initiated immediately following the detachment of a previous bubble. A time interval of t* elapses until the growing bubble attains a half-spherical shape and the recorded pressure attains its maximum value, $\Delta p_{mea,max}$. Accordingly, the surface age is identical to the time span t*, which is the time elapsing between the moment the bubble surface was formed and the instant of half spherical bubble shape. The dynamic surface tension (σ) is determined for the surface age (t*). The subsequent time until bubble detachment is defined as the dead time. As the length of the time interval (t*) depends on the regulation of the gas flow rate, it follows that the dynamic surface tension (σ(t*)) can be determined for varying surface ages (t*) by modifying the gas flow rate. To achieve different surface ages in measurement, the MBP 200 is equipped with a valve arrangement that can generate varying gas flow rates.

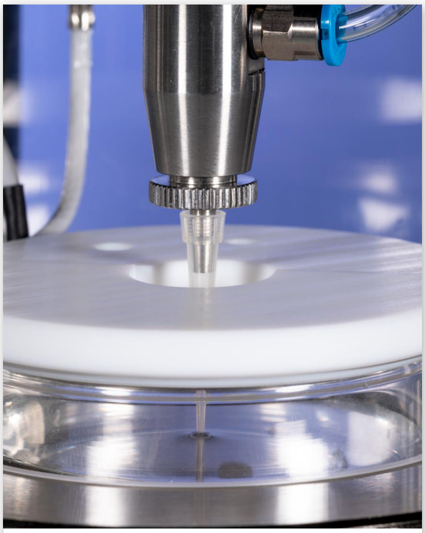


Fig. 3: Disposable capillaries utilised in MBP 200 with PTFE cover

Experiment

To ensure high accuracy, the capillary used in the measurements is calibrated with high purity water. The measurement is done in two steps:

I. Calibration measurement for the used capillary

1. Place the desired capillary in capillary mount (Fig. 3).
2. Position a clean vessel with pure water on the sample stage.
3. Start the calibration measurement.
4. A calibration file is generated and automatically used for subsequent measurements.

II. Studying the dynamic surface tension of the samples

1. Position a vessel with the sample liquid on the sample stage.
2. Specify the density of the sample liquid in the software.
3. The 'Automatic Concentration Series' mode was used in this study. **The automatic titration function utilizing the LDU 25 liquid dosing unit from DataPhysics Instruments (Fig. 4) was used.**
4. Start the desired measuring method
5. Live display of measuring values and results in the software where they can be further analysed.

The MBP 200 is equipped with a number of features that are worthy of note. Of particular note is the **automated surface contact detection system**, which initiates the immersion process at the pre-set depth. The design incorporates a **collision protection mechanism** that safeguards the capillary and the measuring device from damage. A **splash guard with a PTFE cover** (Fig. 3) prevents liquid from splashing out of the sample vessel, thereby reducing the effort required for cleaning. During immersion, an airflow mechanism prevents liquid from entering the capillary. **The gas flow rate is automatically regulated** to achieve the desired surface age at the detected pressure maxima. Additionally, the device features a **"purge" function** that facilitates the removal of residual liquid from the capillary.

Results & Discussion

Thank to **the automatic titration function utilizing the LDU 25 liquid dosing unit, the 'Automatic Concentration Series' mode in MBP 200 software enables consecutive determination of the sample liquid's dynamic surface tension for a series of different surface ages as a function of concentration automatically.** The surface age and the dynamic surface tension are averaged over a number of individual bubbles, typically around 15. The experimental error was found to be less than ±0.5 mN/m even at low surface ages.

Fig. 5 illustrates the dynamic surface tension of Lutensol® solutions with different concentrations over a surface age, ranging from 15 ms to 20000 ms. At a Lutensol® concentration of 0.000 g/l, i.e. pure water, the dynamic surface tension is stable at 72.5 mN/m. There is almost no change in the dynamic surface tension of the Lutensol® solution when the concentration is lower than 0.007 g/l. The dynamic surface tension decreases drastically at a surfactant concentration of 0.016 g/l. A clear decrease of the dynamic surface tension is observed even at short surface ages (below 100 ms) when the surfactant concentration is higher than 0.071 g/l. This suggests that the higher the concentration of Lutensol®, the faster the surfactants reduce the surface tension. Thus, higher concentrations of Lutensol® may provide excellent wetting even at low surface ages.

Fig. 4: The LDU 25 liquid dosing unit allows operators to change the concentration inside the studied solution automatically.

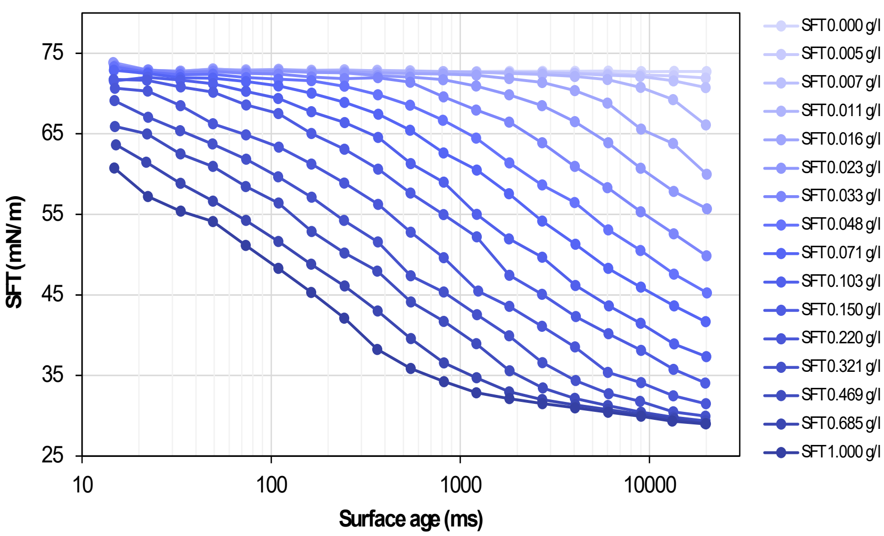


Fig. 5: The dynamic surface tension of Lutensol® solutions with different concentrations at different surface ages from 15 ms to 20000 ms

Furthermore, it has been demonstrated that the dynamic surface tension reaches equilibrium at concentrations exceeding 0.321 g/l, exhibiting a nearly identical value of approximately 29 mN/m. This indicates that those surfactant concentrations are greater than the critical micellization concentration (CMC) of the Lutensol® solution. However, noticeable differences of the dynamic surface tension are observed during short surface ages, i.e. less than 100 ms. This is particularly significant in the study of rapid adsorption, a phenomenon that is characteristic of surfactant concentrations that are both near and above the CMC.

Summary

The MBP 200 Bubble Pressure Tensiometer from DataPhysics Instruments can measure dynamic surface tension at very short surface ages in the **millisecond time scale**. Combined with the automatic titration function using the **LDU 25** Liquid Dosing Unit, the MBP 200 can **automatically** determine the dynamic surface tension of samples as a function of concentration for a range of different surface ages. As described in this note, it can automatically determine the difference of the dynamic surface tension at short surface ages, i.e. less than 100 ms, at different surfactant concentrations, even near and above the CMC. This is particularly important when studying fast surfactants.

The MBP 200 is therefore an ideal instrument for analysing liquids such as surfactant solutions, understanding super-fast wetting processes and optimising formulations with good dynamic wetting performance.

Reference

[1] Yuan, X. H.; Rosen, M. J. Dynamic surface tension of aqueous surfactant solutions. *J. Colloid Interface Sci.* **1988**, *124,* 652–659.

[2] https://www.dataphysics-instruments.com/products/mbp/

[3] Mysels, K. J. Improvements in the maximum-bubble-pressure method of measuring surface tension. Langmuir. **1986**; *2(4)*: 428-32.

[4] Holcomb, C. D.; Zollweg, J. A. Improved differential bubble pressure surface tensiometer. *J. Colloid Interface Sci.* **1992**; *154(1)*: 51-65.

[5] https://www.dataphysics-instruments.com/products/mbp/accessories/

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