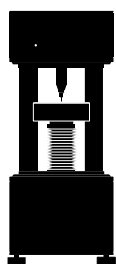


Application Note

Studying the dynamic surface tension of inks with MBP 200

Industrial inkjet printing applications are booming. Inkjet printers have become everyday products in homes and offices, and the market is growing rapidly. The development and optimisation of reliable inkjet inks with high permanence is a crucial and in-demand process. Static surface tension is a key quality parameter for inks, and it is essential to consider this in the formulation process. Nevertheless, it should be noted that wetting processes in inkjet printing, including internal printhead wetting, drop formation and interaction with the substrate, generally occur within a very short time frame, from microseconds to milliseconds.^[1] This is a significant difference from equilibrium conditions. **Dynamic surface tension is a more appropriate tool for understanding these ultrafast wetting processes than static surface tension.** By determining the dynamic surface tension, fast wetting processes of inks with different dispersants can be characterized, thereby enabling the production of high-quality pigmented inks for high-performance inkjet printing. The **MBP 200 Bubble Pressure Tensiometer manufactured by DataPhysics Instruments** is an ideal instrument for measuring the dynamic surface tension of liquid solutions. It can be used to determine dynamic surface tension at surface ages down to **5 milliseconds**. The following application note will demonstrate the technique using three inks with different formulations.

Measurement device
Bubble Pressure Tensiometer – MBP 200



Measurement method
Maximum bubble pressure

Measured quantities
Dynamic surface tension

Environmental conditions
25 °C

Samples
Three inks with different formulations

Industries
Ink manufacturing
Ink-jet printing applications

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.

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



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

culated 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:

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

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.

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 ($\sigma(t^*)$) is determined for the surface age (t^*). The subsequent time interval 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 ($\sigma(t^*)$) 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.

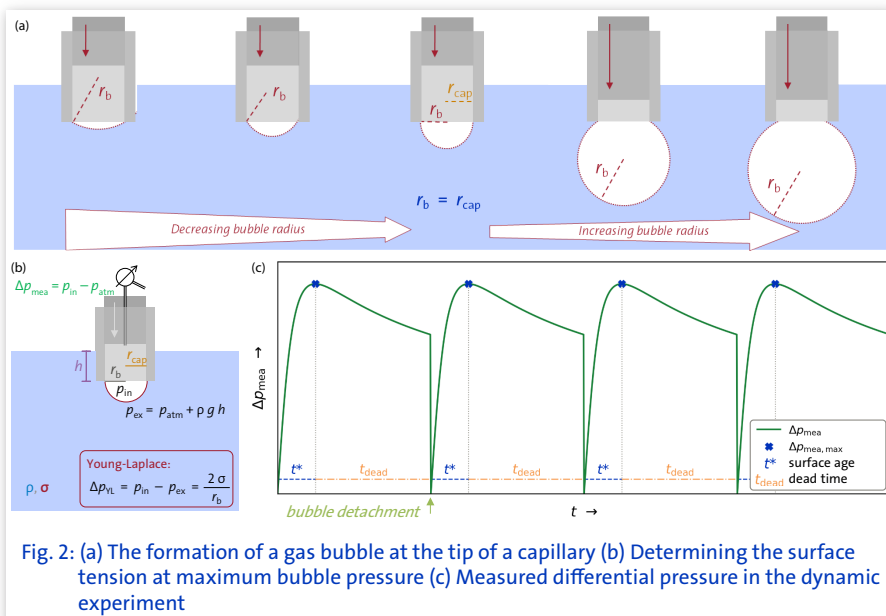


Fig. 2: (a) The formation of a gas bubble at the tip of a capillary (b) Determining the surface tension at maximum bubble pressure (c) Measured differential pressure in the dynamic experiment

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. The 'Surface Age Sweep' mode was used in this study.
3. Start the desired measuring method
4. 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



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

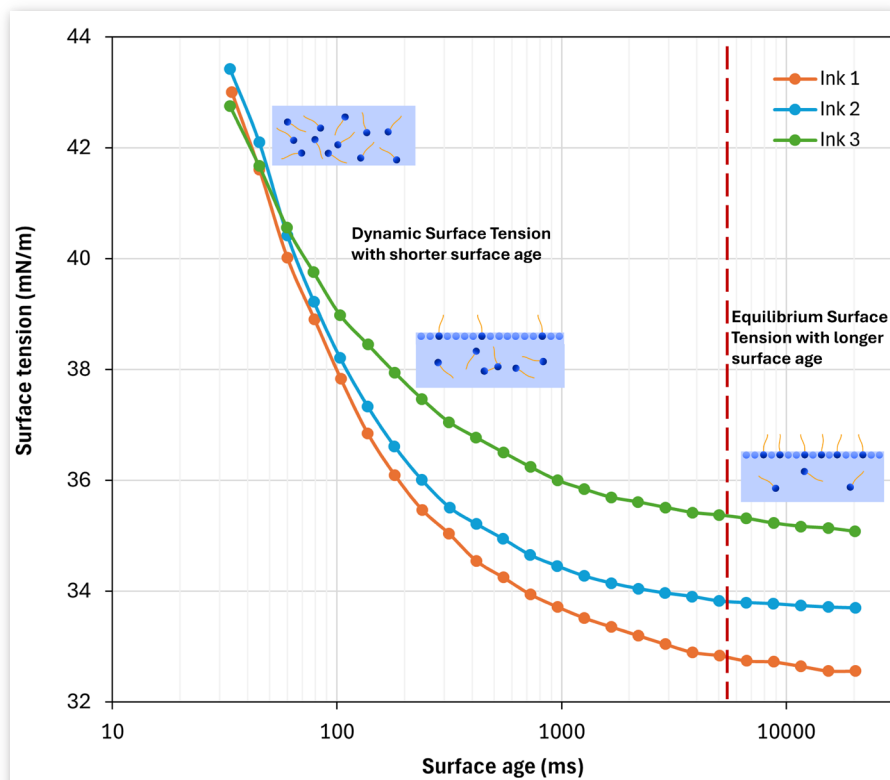


Fig. 4: Dynamic surface tension of three inks with different formulations at the surface ages from 30 ms to 20000 ms

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

The 'Surface Age Sweep' mode in the MBP 200 software enables the consecutive determination of the dynamic surface tension of a sample liquid for a series of different surface ages within a specified range. The surface age and the dynamic surface tension are typically 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.

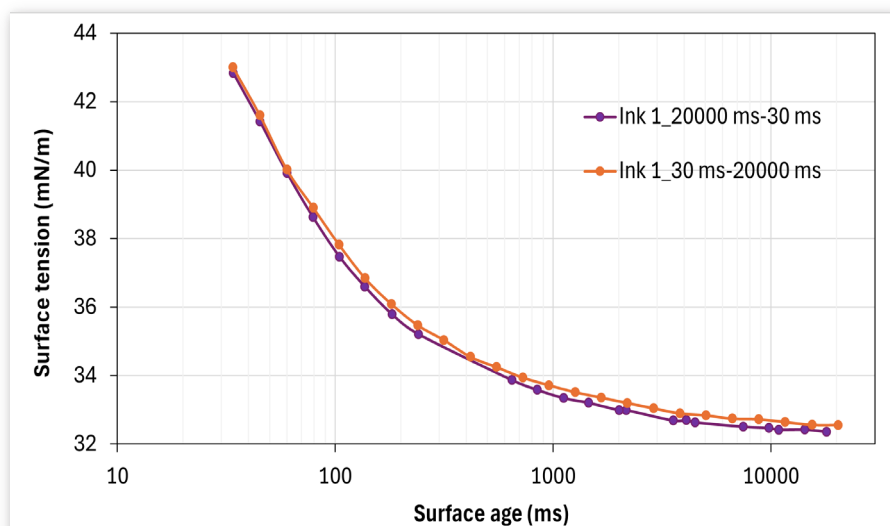


Fig. 5: Dynamic surface tension of Ink 1 determined by surface age sweeps from 30 ms to 20000 ms and from 20000 ms to 30 ms, respectively

Fig. 4 illustrates the dynamic surface tension of three inks with optimised formulations over the surface age, spanning a range from 30 ms to 20000 ms. The dynamic surface tension of the three ink formulations was found to be similarly low in the relevant time frame (below 100 ms), indicating the presence of fast surfactants. At the surface age of 100 ms, Ink 1 exhibits the lowest dynamic surface tension, with a value of 37.48 mN/m. In contrast, Ink 3 displays the highest dynamic surface tension, with a value of 40.11 mN/m. This suggests that the three samples may exhibit a comparable dynamic wetting behaviour, but that Ink 1 may possess the best wetting properties. The equilibrium surface tension can be observed at longer surface ages, which also demonstrate that Ink 1 has the lowest surface tension. This provides further evidence that Ink 1 may possess the best wetting properties. In comparison to a classical surface tension test, which would only have yielded an equilibrium surface tension, MBP 200 is capable of measuring not only equilibrium surface tension, but also dynamic surface tension at a millisecond scale. This is very helpful for understanding rapid wetting processes.

Furthermore, the impact of the direction of the surface age sweep (measuring from short surface ages to long surface ages and vice versa) on the dynamic surface tension was investigated. Fig. 5 shows that the dynamic surface tension curves of Ink 1 varies slightly when measuring sweeps over the specified surface age range of 30 ms to 20000 ms, and 20000 ms to 30 ms. This indicates that the direction of the surface age range has a negligible effect on the dynamic surface tension measurement for these three

inks. Nevertheless, it is important to do these kind of inverse surface age sweep studies since especially samples that tend to foam can be deeper understood when data from both sweep direction is available.

Summary

The MBP 200 bubble pressure tensiometer from DataPhysics Instruments is capable of measuring dynamic surface tension at very short surface ages in the millisecond time scale. This makes the instrument ideal for analysing liquids containing fast surfactants, such as printing inks. By measuring the dynamic surface tension, the wetting processes can be characterized and ink formulations with good dynamic wetting performance can be achieved.

Reference

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