Technical Note

Pendant Drop Measurements

Technical note:	TN316e
Industry section:	all
Author:	FT, TW
Date:	12/2010
Method:	
Keywords:	Methods, surface tension, interfacial tension, pendant drop

Drop Shape Analyzer – DSA100

Drop Shape Analyzer – DSA30

Determining the surface tension of liquids by measurements on pendant drops

Introduction

Among the numerous measuring methods for surface and interfacial tension between fluids, the optical pendant drop method is particularly elegant: It requires only a very small sample volume, not much apparatus, has few limiting conditions and is, when used correctly, a very accurate method. This article is intended to place current and future users of this method in the position of being able to achieve reliable results rapidly. KRÜSS customers with DSA100, DSA30 instruments and most of the EasyDrop versions already have access to this method with the help of a software module and minimal additional equipment.

Background

The pendant drop (PD) method is an optical method for determining the surface or interfacial tension of a drop of liquid by using the curvature of the drop profile.

An advantage when compared with the frequently used methods based on force measurement, such as the Du Noüy ring measurement or the Wilhelmy plate measurement, is the very small sample volume required (approx. 20-60 µL). In addition, measurements are possible throughout a wide pressure and temperature range (up to 690 bars and up to 400°C with KRÜSS equipment). Users of KRÜSS laboratory contact angle measuring instruments can utilize the method to evaluate the quality of the test liquids with very little effort by checking their surface tension values.

The main purpose of this article is to indicate the parameters that influence the accuracy of a PD measurement in order to place the user in a position of being able to avoid errors and obtain a reliable result.

Measuring principle

At the tip of a needle a suspended drop of a specifically heavier liquid generated within a specifically lighter phase (Fig. 1A). The lighter phase is either air (surface tension measurements) or another liquid (interfacial tension measurements).

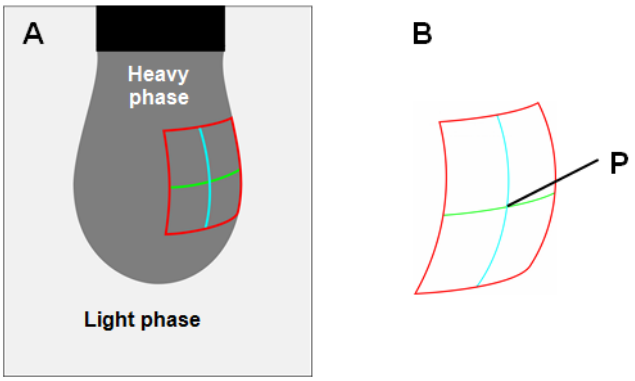

Fig. 1: Pendant drop (A); curved surface segment (B), the radii of the horizontal (green) and vertical (blue) circles of curvature define the surface curvature at point P.

Alternatively, the interfacial tension can be measured on an ascending drop, if the lighter phase is generated within a heavier one.

The interfacial tension between the inner and outer phases results in an increased pressure inside the drop. The relationship between the difference in pressure Δp and the interfacial tension is described by the Laplace equation (Eq. 1):

$$\Delta p = \sigma \cdot \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad \text{(Eq. 1)}$$

$\Delta p = p_{inner} - p_{outer}$ = Laplace pressure; σ = Interfacial tension; R_1, R_2 = Radii of horizontal and vertical circles of curvature.

Surface tension results in the drops assuming the smallest possible surface area; this means that without other forces acting upon them drops will be spherical. The effect of gravity deforms the drops, because their weight generates a hydrostatic pressure within the drop (Eq. 2) which makes a contribution to the inner pressure and therefore, in accordance with Eq. 1, influences the primary radii of curvature R_1 and R_2.

$$\Delta p_{Hyd} = \Delta \rho \cdot g \cdot l \quad \text{(Eq. 2)}$$

Δp_{Hyd} = Hydrostatic pressure; $\Delta \rho$ = Difference in density between heavier and lighter phase; g = Gravitational acceleration; l = Vertical distance between measuring point and needle opening.

As the hydrostatic pressure is height-dependent – it is minimal directly below the needle opening and increases in a vertical direction as the distance from the needle increases – the curvature of the drop surface also alters in a vertical direction. This results in the characteristic "pear shape" of a pendant drop.

The degree of variation from a spherical shape gives the relationship between the weight of the drop and its surface tension. If the difference in densities between the phases is known then the surface tension can be calculated from the drop shape [1]. The shape is not freely scaleable; the actual dimensions of the drop are used in the calculation.

During a measurement the magnification of the video image is first determined in order to be able to access the actual drop dimensions. The drop shape is then determined from the video image of the generated drop by gray level analysis. A numerical method is then used to vary a shape parameter known as B until the calculated drop shape coincides with the actual drop shape. The interfacial tension σ is then calculated from the difference in density $\Delta \rho$ and the adapted B parameter.

Making a measurement

A pendant drop measurement is carried out simply and quickly. The following section describes the procedure and mentions some easy to avoid obstructions on the way to a reliable result.

1. Preparing for the measurement

1.1 Instrument location

Bright radiant light and vibrations that could cause the pendant drop to oscillate make drop shape analysis difficult or could lead to unwanted drop break-off from the needle. This means that the location should be as vibration-free as possible and that sunlight or bright room illumination should be screened off.

1.2 Choice of needle diameter

A deformation of the drop that is adequate for the measurement is only achieved when the drop is sufficiently large. This is why a large needle diameter should be selected in order to be able to generate correspondingly large drops. The KRÜSS standard needles for pendant drops have a diameter of about 1.8 mm and are suitable for most measurements. Narrower needles should only be used when, because of a low surface tension and/or a large difference in density, drop break-off from the standard needle occurs quickly.

1.3 Determining the image magnification

As the actual weight of the drop itself plays a major role in the calculation, in addition to the density and acceleration due to gravity (see below), the absolute size of the drop must also be known. This is determined from the image, and therefore the magnification of the image must be determined using an object whose dimensions are known before the measurement itself can be made. The magnification is a sensitive parameter whose determination should be carried out with the greatest care.

The outer diameter of the needle seen on the screen is normally used as the reference size. This diameter should be determined with an accuracy of at least 10 µm in the lower section of the needle used for determining the magnification in order to eliminate any possible height-dependent diameter variations. The tool used, for example an external micrometer, should be positioned so that the diameter is measured at right angles to the optical axis. In this way errors due to possible variation of the needle profile from a true circle can be eliminated.

The capillary tip must be located vertically on the screen and must not be tilted. Fig. 2 clearly shows that a needle tilted on the screen results in a considerable error in the magnification factor and therefore represents a significant source of error for the results.

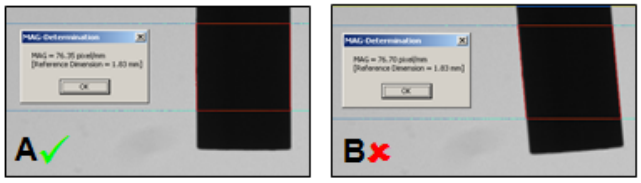

Fig. 2: Influence of tilted needle on the magnification factor. In (A) the correct factor is measured; in (B) the result varies by 0.5%.

The outline of the needle should be readily visible and the image should be sharp. For determining the magnification factor a rule of thumb states that the width of the needle outline should occupy at least 10% of the whole screen width. Otherwise the scale will be too small, and the size resolution for the measurement will be poorer.

The maximum width of the needle image is limited by the fact that the whole of the generated drop must also be visible on the screen.

The two measuring lines for determining the magnification should be at a distance of at least 20 pixels from one another (Fig.3), and should also be at the height at which the diameter was determined.

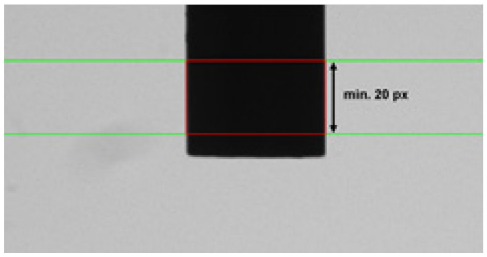

Fig. 3: Proper distance between the two measuring lines for determining the magnification

As the optimal needle width on the screen and the suitable image settings are frequently only known after drop generation, the determination of the magnification factor is often carried out after drop generation and image adjustment, directly before the measurement itself. In any case, each alteration to the image adjustment described below means that a new determination of the magnification factor is absolutely essential.

1.4 Generating the pendant drop and drop image optimization

For PD analysis the drop must be significantly deformed by the force of gravity; the drop shape must differ considerably from that of a true sphere. Normally the most favorable deformation is obtained when the drop is just before the point of break-off from the needle tip. In order to avoid premature drop break-off, the drop should be generated as slowly and vibration-free as possible. Fig. 4 shows a drop with a suitable deformation and one with an inadequate one.

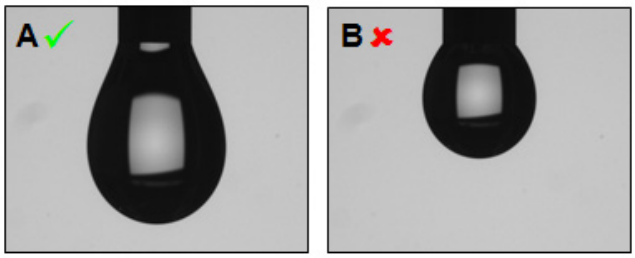

Fig. 4: Adequately (A) and inadequately (B) deformed pendant drops.

In a similar way to the needle width on the screen, a sufficiently large drop image is required for accurate measurements, because as the magnification of the drop shape increases, the number of pixels available for the analysis also increases. This is why the drop and needle together should occupy as much of the screen in a vertical direction as possible (Fig. 5).

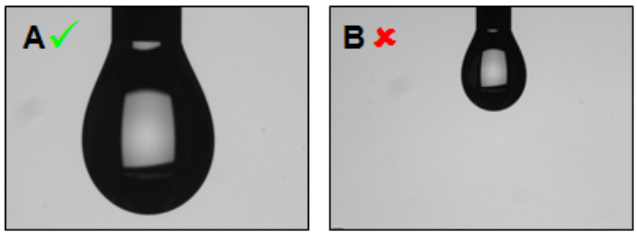

Fig. 5: Drops with correct (A) and too low (B) magnification.

After the magnification the sharpness of the image should be optimized, as fuzziness results in less accurate profile recognition by the software. Fig. 6 shows a correctly focused image and a fuzzy one.

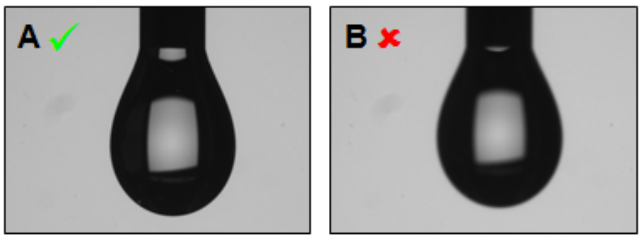

Fig. 6: Correct (A) and incorrect (B) focus setting.

The brightness of the background illumination should also be optimized. If the light intensity is too dark then the contrast between the background and the drop will also be too weak; this means that profile recognition by the software will be incorrect or even impossible. In contrast, too bright background illumination can lead to over-illumination of the drop, which then appears narrower than it actually is. Fig. 7 shows the influence of the illumination on the contrast between the drop and background.


Fig. 7: Drop image with suitable (A), too dark (B) and too bright (C) background illumination.

As a suitable guideline for the illumination intensity the gray level value of the dark part of the drop should have a maximum of 40 and the surrounding phase should have 170-200 (Fig. 8).

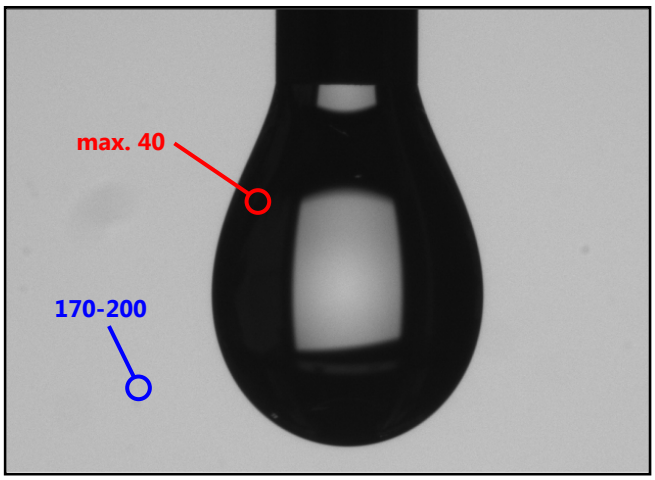

Fig. 8: Gray level values of the drop and surrounding phase under optimal illumination.

1.5 Excluding evaporation effects

Preventative measures against evaporation should be taken with volatile liquids or sample components, as otherwise the drops will be reduced in volume and may also lose their optimally deformed shape. In addition, with solutions of surface-active substances their surface concentration and therefore their surface tension can alter, so that a constant measured value cannot be obtained.

Help is provided by carrying out the measurement in a covered glass cuvette, on whose base several drops of the liquid to be analyzed are placed. As the vapor pressure in the filled cuvette corresponds approximately to that of the drop surroundings, evaporation is reduced. Measurement in a cuvette also protects the drop against vibrations caused by air movements and can therefore also be a good idea for non-volatile samples.

1.6 Recording the stationary value

The variation of surface tension with time mentioned above can also occur without evaporation for surfactants which only migrate slowly to the boundary. The slow flow rate of high-viscosity liquids means that the formation of the final drop shape can take some time. In such cases we recommend that the interfacial or surface tension is measured as a function of time and that the stationary value is regarded as being the result.

2. Carrying out the drop shape analysis

Measurement irregularities can also result from incorrect software settings or occur when carrying out the drop shape analysis itself. The following sections show where the sources of error are to be found when making a measurement.

2.1 Required system parameters

In order to be able to make a PD measurement the densities of the heavy and light phases as well as the value of the acceleration due to gravity must be entered in the software. The values at the particular measuring temperature must be used for the densities of the participating phases. For surface tension measurements the density of the surrounding air which despite of its low value still has an influence on the result, should also be entered.

For the acceleration due to gravity the international standard value of 9.80665 m/s^2 is entered in the software as the default value. This should be replaced by the local value at your location; this can normally be obtained from your national physical institute.

2.2 Sensibility of profile recognition in the analysis software

The sensitivity of the profile recognition is expressed by the determined difference in gray levels that is considered as the transition between the drop and the surrounding phase. For sharp drop images with a good contrast a value of around 30 is recommended – this is the default setting for "profile detection" in the KRÜSS software. With poorly recognizable phase transitions the value can be reduced. If the sensitivity is set incorrectly then the software cannot determine the drop profile, or cannot determine it correctly (Fig. 9). If this is the case then the value in the software must be adapted until the drop profile is recognized correctly.

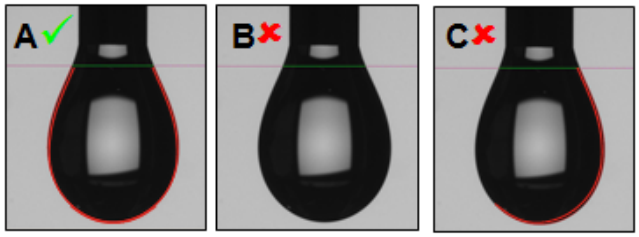

Fig. 9: Influence of the "Profile Detection" value on profile recognition: (A) Correct value, profile found completely; (B) Value too low, no profile found; (C) Value too high, profile only partly found.

2.3 Setting the baseline for the analysis

The baseline is used to define which part of the drop profile will be used for the drop shape analysis. This means that a reliable result can only be obtained when this line is applied to the drop profile at the correct height. In principle, the baseline should be placed as near as possible to the needle tip, but far enough away from it so that it excludes that part of the drop profile whose shape is influenced by contact with the needle.

Whether the baseline has been applied correctly can be evaluated by seeing whether the fit line generated by the software corresponds exactly to the profile of the whole drop (Fig. 10A). If this is the case then it can be assumed that the profile analysis will be reliable.

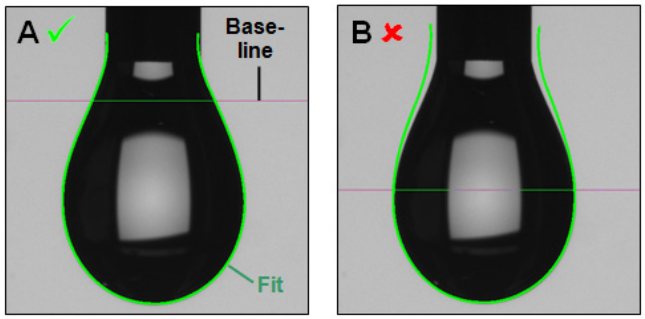

Fig. 10: (A) Fit depicts drop profile correctly and provides an accurate result; (B) Fit clearly varies from drop profile and provides an inaccurate result.

If there are significant variations between the fit and drop profile (Fig. 10B) the position of the baseline should be altered until the variations disappear.

In order to assure reproducibility it is recommended that all quantities influencing the result are included in the measurement report: the gravitational acceleration, the density values of the two phases, the needle diameter and the magnification.

Summary

As an optical method, the pendant drop measurement is an accurate method which can be carried out with little exertion. It is based on the analysis of the profile of a pendant drop deformed by the force of gravity. With the aid of a numerical adaptation of the shape parameter B the interfacial or surface tension can be calculated from the drop shape.

The dosing needle is used as the reference object for determining the actual drop dimensions from the drop image. The exact determination of its diameter, image size and vertical position influence the accuracy in the same way as the size, sharpness and brightness of the drop image.

The real size of the drop is also of crucial importance. Only when it weighs enough the deformation required for the measurement, the variation from a true sphere will be sufficient.

Physical limiting conditions, such as the density of the drop liquid and the surrounding phase and the local value of the acceleration due to gravity must be determined exactly. Influences that falsify the measurement, such as vibrations, interference from light or sample evaporation can be avoided by suitable setup conditions and working inside a cuvette.

For the profile analysis itself a suitable sensitivity for determining the phase transition must first be set. A good height must be found for the baseline, which separates that part of the drop deformed by contact with the needle from the region to be analyzed. The most important criterion for this is the degree of agreement between the optical and calculated profile line.

Literature

[1] Song B, Springer J.: J Colloid Interface Sci. 1996 Dec 1;184 (1):77-91.

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