

Research News

Measuring Dynamic Surface and Interfacial Tensions**

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1. Introduction

Surfactants, defined as substances which reduce the interfacial tension of liquid surfaces often drastically, are of steadily growing interest in many fields of (bio)chemical technology and engineering. A precondition for the application of surfactants in many processes is a good qualitative and quantitative description of both their equilibrium as well as their dynamic properties at the interface. A lot of techniques have been developed to study static and dynamic interfacial tension. Of these, the drop volume method is one of the most frequently used.^[1-12] It has many advantages over other methods. Only small amounts of solution or solvent are necessary for a series of measurements in contrast to the ring or plate method, for which several hundred milliliters are usually needed.^[13] The accuracy and the reproducibility are as high as those of other methods, the accuracy being in the range of ± 0.1 mN/m. Important reasons for the use of the drop volume method are the easy sample handling and the simple temperature control over a broad temperature interval. The pendent drop technique shares all the above advantages except easy sample handling, and can also be applied to liquid/liquid interfaces without further modification. These factors have been responsible for making the drop volume method a very often used technique, although in the past only self-made set-ups were available.

With a newly developed automated version of the drop volume technique (TVT1 from "LAUDA") an apparatus is now available with all the mentioned advantages. In the present paper we discuss the range of application of the apparatus and its accuracy and reproducibility. Based on experimental studies it is demonstrated which information

on interfacial tensions and adsorption processes at fluid interfaces can be obtained from investigations with such an automated drop volume method.

2. Instrument Design and Construction

The principle of the drop volume technique is to measure the volume (or weight) of a drop detaching from a capillary with a circular cross-section. From the volume of the drop V and the capillary diameter $2r_{\text{cap}}$ the interfacial tension can be calculated.

The set-up of the automated drop-volume tensiometer is shown schematically in Figure 1. Drops at the tip of a capillary (1) are formed by a motor-encoder system (2) via a syringe (3) which is controlled by a microprocessor (4). A sensor (5) arranged below the capillary enables the registration of the moment of detachment of drops from the capillary. The connection to the computer (6) via an RS232C

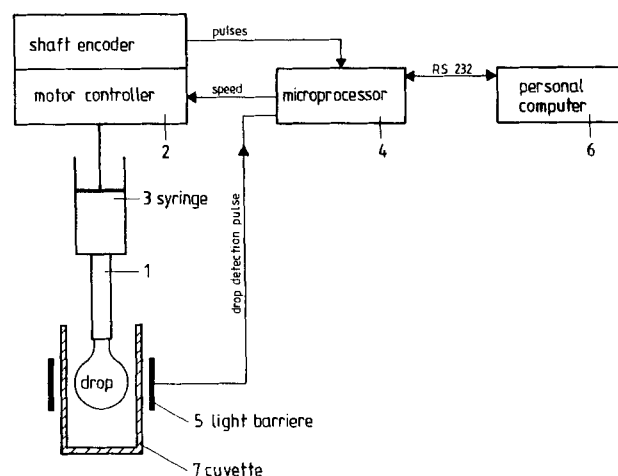


Fig. 1. Schematic of the set-up of the drop volume method.

interface allows the speed of the motor and the measuring procedure to be chosen, and the transfer of data about volume and time of measured drops into the computer for further interpretation. The detached drops are collected in a

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[**] The company LAUDA Dr. R. Wobser GmbH, Lauda-Königshofen, is gratefully acknowledged for making a prototype of the commercial product TVT1 available for the present studies. The support of the "Fonds der Chemischen Industrie" is gratefully acknowledged. [AM SC 131]

cuvette (7) from which the temperature can be controlled over a wide temperature interval.

2.1. Dosing System and Drop Volume Determination

The formation of drops is realized by a PLL (phase-locked loop) controlled DC motor directly connected to a high-resolution incremental shaft encoder which moves a syringe via two spindles. The volume of a drop is determined from the number of counts of the encoder, measuring the movement of the spindle, and from the diameter of the syringe. Taking into account the accuracy of the motor-encoder-system, the spindle and the syringe, the volume can be measured with a total accuracy of $\pm 0.01 \mu\text{L}$.

2.2. Drop Detachment Detection

The detachment of drops from the capillary is detected by an optoelectronic sensor which the drops pass initiating the registration of time generated by the computer. The drop formation time and drop volume are registered. Depending on the method of interpretation, the individual drop data as well as averaged data (the number of drops can be chosen) are stored and can be used for further study.

2.3. Temperature Control

The temperature control of the syringe and the cuvette is arranged by a water jacket connected to a liquid thermostat. The accuracy of the set-up is of the order of $< \pm 0.1^\circ\text{C}$. Temperature control is possible in the range of 5 to 60°C (with a special jacket even up to 90°C). The syringe, which is embedded into the water jacket, can be filled easily with the liquid to be measured, as this part is connected to the water circuit via a well-sealed coupler.

2.4. Capillaries

Needles supplied by "Hamilton" are used as capillaries. These needles are cylindrical steel needles with diameters in the range of 1.2 to 3.4 mm. Where the density of the liquid filled into the syringe is lower than that of the surrounding liquid, reverse capillaries can be used.

3. Measurement Procedure

The automated drop volume tensiometer TVT1 can be applied in two principal versions. The classic or dynamic version is based on a continuous liquid flow arranged by moving the piston of the syringe with a constant speed. After a drop has been formed and reached its critical weight (vol-

ume) it detaches and the next drop is formed. The dosing rate allows the control of the formation of drops in a drop time range of 0.3 s up to 30 minutes per drop of $10 \mu\text{L}$. As a result of these experiments, the interfacial tension as a function of drop formation time is obtained. For systems containing surface-active substances it should be noted that the drop information time is different from the effective age of the interface.^[14]

Another version is the so-called quasistatic procedure.^[4, 9, 15-19] It consists of a two-step process and is applicable only when the system contains surface-active substances, such as surfactants, polymers or mixtures of them. In the first step, a drop with a definite volume is formed very fast. This volume must be smaller than the critical volume corresponding to the actual interfacial tension at the drop surface. After the liquid flow into the drop stops, the drop has a constant volume and only the interfacial tension decreases due to further adsorption of surface active substances. Provided the volume chosen in the first step is not too small, the drop will detach after a certain interfacial tension has been reached which correlates to this volume. After the detachment from the capillary, the next drop is formed with the same or slightly different volume and the procedure starts again. Various strategies of choosing the drop volume for the consecutive drops exist. The procedure installed in the software of the TVT1 initially determines the interfacial tension using the dynamic version. Starting from that volume the volumes of the consecutive drops are decreased step by step by constant increments. The result of such experiments are comparable to those obtained with other quasistatic methods such as the ring or plate method.

4. Surface Tension Calculation and Expected Accuracy

The interfacial tension σ is calculated from the determined drop volume via Equation 1, where a is the capillary constant defined as shown in Equation 2, and $\Delta\rho$ is the density difference of the two adjacent phases, g is the acceleration constant, V is the drop volume and $2r_{\text{cap}}$ is the outer diameter of the capillary. The function $f(r_{\text{cap}}/a)$ denotes a correction function necessary to relate the surface tension to the volume of the detached drop. Initial theoretical attempts to determine the correction factors were made by Lohnstein.^[20-24]

$$\sigma = \frac{\Delta\rho g V}{2\pi r_{\text{cap}} f(r_{\text{cap}}/a)} \quad (1)$$

$$a = (2\sigma/\Delta\rho g)^{1/2} \quad (2)$$

The procedure to calculate the volume of a falling drop is based on the Gauss-Laplace equation of capillarity and the assumption that the contact angle of the critical drop, just before detaching from the capillary, is identical to that of the

residual drop remaining at the tip of the capillary. Further work was performed to determine these correction factors experimentally using capillaries with different diameters and various pure liquids.^[25-28]

The coincidence between the theoretical expected values of Lohnstein^[21] and the experimentally obtained data was satisfactorily good only in a small range of r_{cap}/a values. Later theoretical work by Hartland and Srinivasan^[28] explained the deviations between Lohnstein's and the experimental data. For the determination of actually used correction factors a fifth-order polynomial was fitted to the experimental data of Harkins and Brown^[27] plotted in the form of $r_{\text{cap}}/a = f(r_{\text{cap}}/V^{1/3})$ for $r_{\text{cap}}/V^{1/3}$ values in the range 0.3 to 1.2 with an accuracy in r_{cap}/a of less than ± 0.001 .

With the help of this polynomial the interfacial tension σ can be calculated for each $r_{\text{cap}}/V^{1/3}$ value, available from the experiment using Equation 3.

$$\sigma = a^2 \Delta \rho g / 2 \quad (3)$$

The total accuracy of the σ determination depends directly on the accuracy of the measurements of the drop volume V , the capillary diameter r_{cap} and the density difference $\Delta \rho$, and amounts to about $< \pm 0.1$ mN/m which coincides with the accuracy of other methods. At liquid/liquid interfaces this accuracy increases because of the substantially smaller density difference $\Delta \rho$.

5. Hydrodynamic Effects on Drop Formation and Detachment

Depending on the value of the capillary constant $a = (2\sigma / \Delta \rho g)^{1/2}$ which controls the absolute size of a drop for a given capillary, the present apparatus allows the measurement of the interfacial tension of drops over a time interval of about 0.1 seconds to some hours. Especially at very low drop times the dynamic version of the method based on continuously growing drops cannot be applied without further corrections. The volumes of drops at the interface of pure liquids increase with decreasing drop formation time. This effect has been discussed in detail by Jho and Burke^[29] and van Hunsel.^[30] Without giving a physical interpretation, an equation was derived to compensate these hydrodynamic effects (Eq. 4), here V_e and S are undisturbed drop volume and a regression coefficient from a linear regression of experimental data obtained for different liquids and capillaries, respectively. An effect of the viscosity of the liquids was not observed.

$$V(t) = V_e + S t^{-3/4} \quad (4)$$

Systematic studies of the dependence of drop times on the drop volume were performed recently using capillaries with different diameter and various liquids and their mixtures, having viscosities in the range of 0.5 to 450 mm²/s.^[31] The

interpretation of experimental data was made on the basis of the following physical description: A drop which has reached its critical volume starts to detach. This process of detachment takes a limited time which should be a function of the interfacial tension σ , the viscosity of the liquid, and the diameter of the capillary. During drop detachment there is still a connection with the liquid reservoir and because of the continuous liquid flow into the drop an additional amount of liquid V_a is pumped into the detaching part of the drop (Eq. 5) where F is the liquid flow per time. The flow rate results from the experimental conditions and can be defined as shown in Equation 6.

The final relation used to describe the dependence of the drop volume on the drop formation time has the form^[31] shown in Equation 7. The experimental data indicated that there is a remarkable effect from the capillary radius as well as from the viscosity μ of the liquid but no significant effect from the surface tension on the drop detachment time t_o . From linear regressions of experimental data the drop detachment time $t_o(r_{\text{cap}}, \mu)$ was calculated using Equation 8 where α and β are linear functions of the viscosity. The hydrodynamic correction is assumed to be equivalent also for surfactant-containing systems and has to be applied in each case.

$$V_a = t_o F \quad (5)$$

$$F = V_e / (t - t_o) = V(t) / t \quad (6)$$

$$V(t) = V_e (1 + t_o / (t - t_o)) = V_e t / (t - t_o) \quad (7)$$

$$t_o = \alpha(\mu) + \beta(\mu) r_{\text{cap}} \quad (8)$$

6. Experimental Results and Discussion

The present setup was tested by performing measurements with pure liquids and surfactant solutions at water/air and water/organic solvent interfaces.

6.1. Surface Tension of Pure Liquids

Results of surface tension measurements at the water/air interface show that the reproducibility between single drops is very high and coincides with the expected accuracy of the method of $< \pm 0.1$ mN/m.

The temperature dependence of the surface tension of water is shown in Figure 2. For comparison, data from other authors are introduced as well. The results of the present study are within the scattering of data obtained by others and it is hard to decide which of the data are most reliable.^[32-35]

The application of the drop volume technique to volatile liquids is possible because for drop formation times of up to

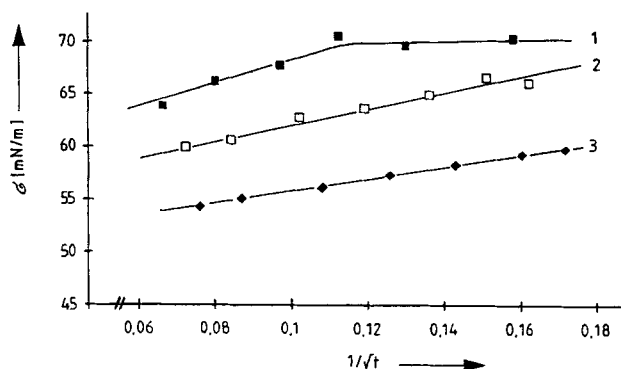


Fig. 2. Temperature dependence of the surface tension of water: 1-measured with the present set-up, 2-Gittens [32], 3-R. Cini et al. [33].

30 minutes there is no significant increase in σ indicating that there is no noticeable leakage of the syringe or the cuvette.

changing the drop formation time, dynamic tensions can be obtained. Such data can be interpreted using several theories in order to obtain information about adsorption mechanisms.^[35–39] The dynamic surface tensions of three solutions of dodecyl dimethyl phosphine oxide are shown in Figure 3. The linear dependence over broad $1/t^{1/2}$ ranges is in accordance with diffusion controlled adsorption kinetics.^[39]

Dynamic surface and interfacial tensions of surfactant solutions can be measured also by using the quasistatic procedure which was first applied by Addison et al.^[15–19] and later by other authors.^[4, 9, 30] The procedure consists of a two-step process. A drop of a definite volume is created at the tip of the capillary, and then the time is measured until the drop detaches. This happens because of the decrease of the surface or interfacial tension due to adsorption, unless the chosen drop volume was too small. The resulting dynamic surface tensions are shown in Figure 4 for the same surfactant solution as in Figure 3.

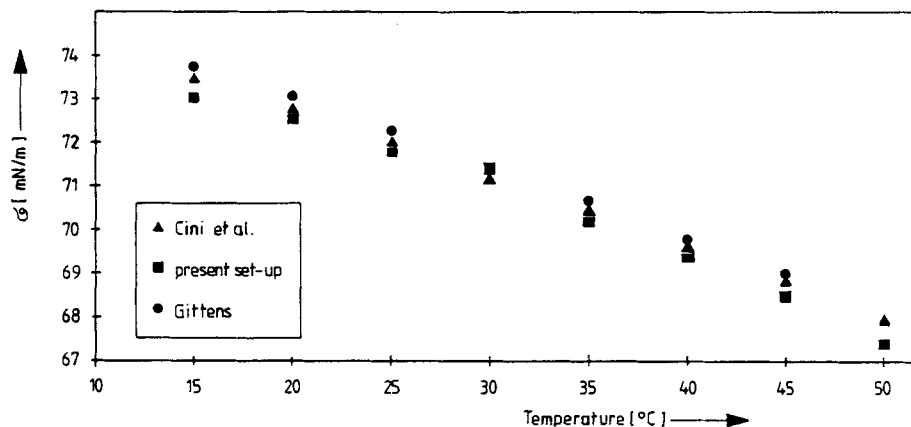


Fig. 3. Dynamic surface tension of *n*-dodecyl-dimethylphosphine oxide solutions using the dynamic version of the drop volume technique at 25 °C: $c_0 = 2 \times 10^{-8}$ (1), 3×10^{-8} (2), 5×10^{-8} (3) mol/cm³.

6.2. Interfacial Tension of Pure Liquids

The drop volume technique is one of the few methods which is also usefully applicable to liquid/liquid interfaces. The advantage is the small amount of liquid necessary for the experiments and the absence of any wetting problems. In cases where the drop forms at the inner circumference of the capillary the material has to be changed to a more hydrophobic one in order to ensure that the drops are formed at the outer surface, which is usually easier to control.

The results of interfacial tension measurements at the water/chloroform (31.6 ± 0.1 mN/m) and water/decan interface (51.2 ± 0.2 mN/m) are in agreement with literature data.^[35] The interfacial tension becomes independent of the drop formation time at values higher than 50 seconds and is not affected by any leaking of the volatile solvents.

6.3. Dynamic Surface Tension of Surfactant Solutions

The drop volume technique is also useful for measuring the surface and interfacial tension of surfactant solutions. By

7. Comparison of Both Measurement Procedures

Both the classic and the quasistatic versions of the drop volume method produce dynamic surface and interfacial tensions. The interpretation of these dynamic values has to be performed in a different way because the conditions of the

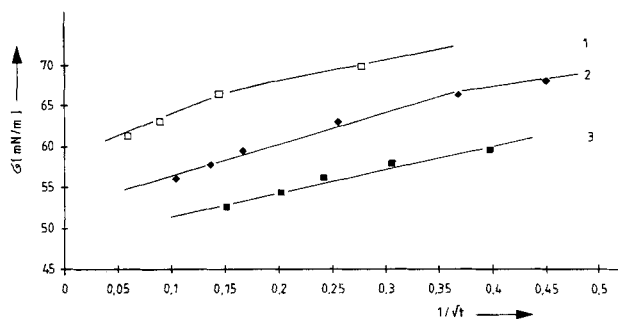


Fig. 4. Dynamic surface tension of *n*-dodecyl-dimethylphosphine oxide solutions using the quasistatic version of the drop volume technique at 25 °C: $c_0 = 2 \times 10^{-8}$ (1), 3×10^{-8} (2), 5×10^{-8} (3) mol/cm³.

experiments are different. While the area of the drop is constant over the longest part of the experiment in the case of the quasistatic version, it increases continuously with the increase of the drop volume in the classical version. Therefore, in the first case it is allowed to apply the theories developed for a static interface,^[40, 41] but for the latter case the area increase as well as the flow inside the drop have to be considered.^[12, 30, 42] For the same surfactant solutions both experimental procedures were applied and the resulting dynamic surface tension data were interpreted by the appropriate theories. The results obtained indicate diffusion-controlled adsorption kinetics assuming a common mean diffusion coefficient of $D = 3.8 \cdot 10^{-6} \text{ cm}^2/\text{s}$.

8. Conclusions

The accuracy of measurement in the drop volume method is comparable with other methods, such as the ring or the plate method. The temperature control and the sample handling of the drop volume method are very easy and the use of the method for studies of liquid/liquid interfaces is possible without any modifications, in contrast to ring or plate tensiometry. As the theories for the interpretation of adsorption kinetics data are available for different measuring procedures the drop volume method can be effectively used to study adsorption mechanisms at fluid interfaces.

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