Surface Tension by Pendant Drop

I. A Fast Standard Instrument Using Computer Image Analysis

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An improved method has been developed for the determination of surface and interfacial tensions from primary drop shape data. In addition, wetting angles of sessile drops may be determined. The method has been built around a commercial pendant drop instrument and an IBM-compatible PC with a frame grabber card. In order to differentiate the drop profile, a filter routine using a local threshold and interpolation technique has been developed that is combined with an edge-tracing algorithm. The program for calculation of surface tension is divided into two parts. The first part is based on the traditional optical method and uses inflection of the drop profile. By means of several polynomial interpolations and curve fitting of theoretical profiles, the form factor β and surface tension γ are determined. The second part of the calculation utilizes the above values as a first estimate and then performs a further optimalization of γ by comparison between experimental and theoretical Young–Laplace profiles. With a PC AT with a 80287 mathematical coprocessor the measurements take about 5 s and the reproducibility is typically 0.01–0.03 mN/m for a wide range of known liquids. © 1991 Academic Press, Inc.

INTRODUCTION

The interfacial and surface tension characteristics of liquids are of importance for many processes in the chemical industry. There is a need for a rapid, easy, and low cost technique with satisfactory accuracy and reproducibility. Traditionally, instruments that employ the Du Noüy ring and Wilhelmy plate methods are in common use throughout the industry and in research laboratories.

The pendant drop method is traditionally very laborious. Nowadays video imaging facilities and mathematical coprocessors for personal computers are more readily available, and there is accordingly a great potential for improving this method. The Young–Laplace equation describing the drop profile of sessile, pendant, and ascending drops has resulted in some interest in the literature in improving the pendant drop method accordingly.

Pendant drop measurements are usually performed by photographing a drop in an optical bench arrangement, and then, from the copies, determining (a) the maximum diameter D_E and (b) the ratio between D_E and the diameter D_S at the distance D_E from the drop apex. This was first derived by Andreas *et al.* (1), while integration of the Young–Laplace differential equations was pioneered by Fordham (2) and Stauffer (3).

The Young–Laplace equation can be expressed as three dimensionless first-order differential equations, as shown by several workers (4–7). When video image processing is used, the drop profile typically consists of 500 to 1000 datapoints depending on the system. That Rotenberg's method is time consuming and sometimes inaccurate was pointed out by Anastasiadis *et al.* (5). Anastasiadis *et al.* have successfully used a video imaging system without any manual processing of data.

Most attention has been focused on sophisticated numerical methods for image analysis

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and integration. Although these methods may
sometimes produce excellent results, they are
too computation intensive to be applicable in
everyday instrumentation, requiring up to 10
min on a VAX 8000 series. Our objective has
been to construct a simple and fast instrument
having sufficient accuracy and reproducibility
to make this method useful in practical ap-
plications. In this paper we show that it is pos-
sible to perform image processing and com-
putation of interfacial tension from primary
drop shape data from a video imaging equip-
ment on a personal computer as rapidly as ca.
5 s and with satisfactory accuracy.

EXPERIMENTAL

(A) Chemicals

All organic liquids were analytical grade and
were used without further purification, except
for ethylbenzene, which was 99% pure grade
for synthesis. The water was purified by reverse
osmosis followed by ion exchange and filtra-
tion through active carbon (Millipore RO+Q
unit).

(B) Instrumentation

A block diagram of the apparatus for pen-
dant drop surface tension measurements ap-
pears in Fig. 1. All parts are commercially
available. In addition to the NRL contact angle
goniometer including microsyringe attach-
ment and environmental chamber (Ramé–
Hart Inc.), there is also a supplementary com-
plete stage support. This is necessary in order
to adjust the video camera properly. The video
camera (JVC Model GX-N7E color video
camera with removable lens), is equipped with
a lens system (Olympus Optical Co.) consist-
ing of a V-OM video camera adapter, a teles-
copic auto extension tube, and a macro 80-
mm F4 lens. The signal from the camera is
fed to a video cassette recorder (Mitsubishi
HS-710 EZ(S)) and further via a frame grab-
ber (Data Translation DT2803-50) to a per-
sonal computer (IBM AT compatible) with
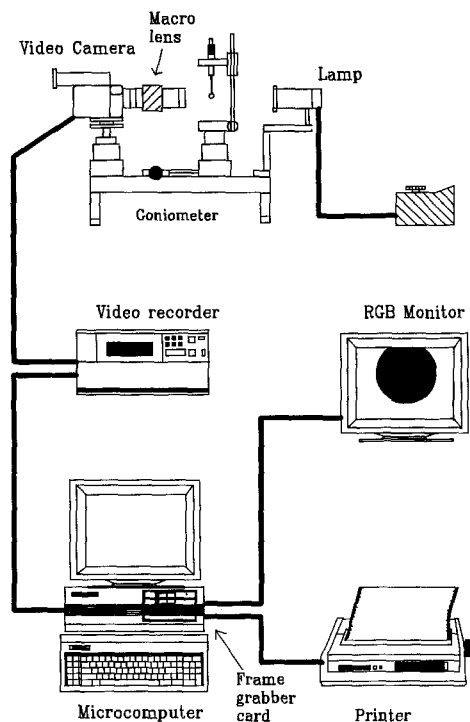an 80287 numeric coprocessor. The frame

FIG. 1. Schematic setup of the instrument.

grabber card is connected to an additional
RGB monitor (Digital Equipment VR241).

It was found that the best way to minimize
the errors from interference rings around the
drop is to use a diffuse white lit background.
This is achieved by using a piece of white paper
in the rear window of the environmental
chamber, between the light source and the
drop.

The optical bench was finely adjusted to ex-
act horizontal position, then the tilting of the
camera was adjusted until a horizontal glass
slide stayed at the same level in the camera
(and on the monitor) independent of the po-
sition of the focal plane. The sideways tilting
of the camera was adjusted until a vertically
suspended metal wire was depicted along one
single line of pixels on the monitor.

As support for the pendant drops, steel nee-
dles of different diameters were used. The wet-
ting angle between the steel and the liquids is
not very important, as long as wetting is rel-

atively uniform along the needle rim. The needle was adjusted so that it did not appear in the video picture. The needles were cleaned with solvents chosen according to the type of liquid that had been used, and finally five times in the actual liquid. The needle diameter was varied according to the measured system, in order to give shape factors in the most sensitive region ($0.2 < \beta < 0.5$).

The magnification was found by measuring a cylinder (usually the syringe needle) with an accurately determined diameter at the same magnification as the drop. The same profile tracing method as used on the drop pictures was utilized together with linear curve fitting in order to obtain good accuracy. The ratio of magnification in the vertical direction to that in the horizontal direction was recorded once and kept as an instrument constant. This ratio (Lx/Ly) was determined by the measurement of a microscope grating both horizontally and vertically at the same magnification.

DROP PROFILE ANALYSIS

(A) Contour Tracing

The video image consists of 256×256 pixels, each with 64 levels of light intensity (gray levels). The filter routine for detection of the drop profile is a simple edge-tracing routine with increased accuracy compared to global thresholding and maximum gradient techniques. The two latter techniques were tested and rejected. In order to discriminate the drop interface we use a local threshold and interpolation routine. The coordinates of the drop profile are found by linear interpolation to a given fraction, F, between the local maximum and minimum of light intensity, i.e.,

$$I_{threshold} = F \times (I_{max} - I_{min}). \qquad [1]$$

From analysis of the gray levels in the neighborhood of the drop interface, as exemplified in Fig. 2, we have used 0.67 as a suitable value for this fraction. However, as the value has considerable influence on the final result (see below) a comparison of this
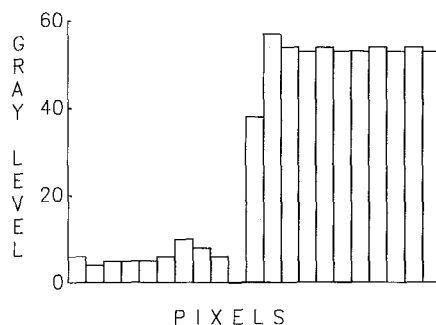

FIG. 2. Typical intensity profile across the drop boundary.

method against liquids of known surface tension will indicate the optimum value. One of the coordinates for each point is an integer (0–255) and the other will be a decimal number because of the interpolation routine. The accuracy is thus considerably improved compared to simple global thresholding or maximum gradient routines that give both coordinates as integers.

Once a point on the drop profile has been found, the search for the next point is limited to the nearest point on the next line. In the bottom part of the drop the search direction is switched from horizontal to vertical. However, for ascending drops the routine automatically starts from the bottom of the picture.

Most drop profiles consist of from 400 to 700 points. On the average the routine uses from 2 to 3 s for these calculations. The same filter routine is used in determining the drop interface when the apparatus is used for contact angle measurements.

(B) Determination of Initial Size Parameters

Surface tension is determined in a two-step process. First, the size parameters R_0 and β are determined from the drop profile, after which surface tension is calculated from these parameters by the well-known equation

$$\gamma = \Delta\rho g R_0^2 / \beta. \qquad [2]$$

Here $\Delta\rho$ is the mass density difference between the drop and the surrounding medium, g is

the gravitational constant, R_0 is the radius of curvature at the drop apex, and β is the shape factor, as defined by this equation.

In the traditional method developed by Fordham (2), β is calculated from the ratio $\sigma = D_S/D_E$. Fordham has tabulated this function, so that β may be read from the tables. Girault et al. (6) have made a polynomial approximation of Fordham's table, giving the equation

$$\beta = 0.02664 + 0.62945\sigma^2. \qquad [3]$$

It was felt that this method of calculating β could be improved upon by using polynomial regression analysis on σ-data produced from theoretical profiles.

The equations describing the drop profile are derived from the Young–Laplace equation and may be represented in dimensionless form as described by several workers. We have utilized the form presented by Rotenberg et al. (4)

$$\frac{d\Theta}{dS} = 2 - \beta Y - \frac{\sin\Theta}{X} \qquad [4]$$

$$\frac{dX}{dS} = \cos\Theta \qquad [5]$$

$$\frac{dY}{dS} = \sin\Theta. \qquad [6]$$

The coordinates X, Y, S, and Θ are illustrated in Fig. 3. S is the distance along the drop profile from the drop apex. X, Y, and S are dimensionless parameters made by dividing x, y, and s, respectively, by R_0. The negative sign in front of β corresponds to a hanging drop with a positive $\Delta\rho$. Theoretical dimensionless profiles were calculated from $\beta = 0.1$ to 0.5, in steps of 0.001 by means of a Kutta–Merson numerical integration algorithm with automatic step length adjustment. The maximum relative error was set to 10^{-4}. Each profile was measured mathematically by determining D_E by third-order polynomials through the four points closest to the maximum and D_S from the four points closest to the distance D_E from the apex. In this way the σ-ratios could be cal-
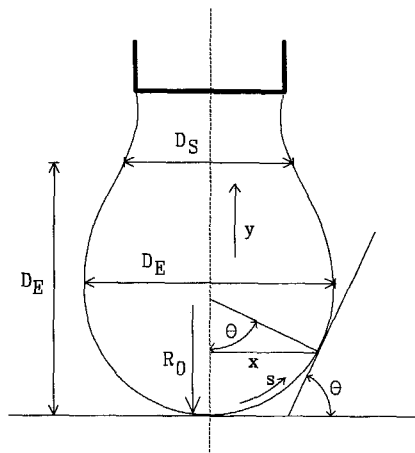

FIG. 3. Geometry of pendant drop with variables.

culated for each of the 400 values of β. From these values an improved equation for β was calculated by the method of least squares,

$$\beta = 0.12836 - 0.7577\sigma$$
$$+ 1.7713\sigma^2 - 0.5426\sigma^3. \qquad [7]$$

This equation gives a better fit than a second-order polynomial without the first-order term, and all the coefficients have good significance. The maximum error in the regression is $\Delta\beta = 0.0008$. This corresponds to a typical error of 0.1 mN/m in γ. From the same data, an equation for $D_E/2R_0$ was found by the same numerical method for $0.1 < \beta < 0.5$,

$$D_E/2R_0 = 0.9987 + 0.1971\beta$$
$$- 0.0734\beta^2 + 0.34708\beta^3. \qquad [8]$$

These values are only slightly different from those of Girault et al. The maximum error in this expression is 0.0003.

Values for R_0 and β were found from the profile data by several numerical smoothing techniques. First the central axis of the drop was determined by a first-order regression line through all data points, using the y-values as the independent and the x-values as the dependent variable (Fig. 3). The lowest point of the drop, i.e., the point where the central axis intersects the drop profile, was found by fitting

a fourth-order polynomial without the first- and third-order terms to all data points in the bottom profile up to a limit of $y/x = 0.44$ (in scaled coordinates). This function is symmetrical around the central axis, and the accuracy is 0.03% (relative to R_0, found by fitting theoretical profiles). The data points on one side of the drop were inverted, and the x- and y-axes exchanged, so that the rest of the calculations were performed on a single half-profile.

The maximum diameter D_E was found by first finding the (40) points closest to the point of inflection of the curve by the secant method, and then fitting a second-order polynomial through these points, thereby enabling an analytical derivation. A similar technique was used to find the diameter D_S at the distance D_E from the apex. From the values of D_E and D_S, β and R_0 were found from Eqs. [7] and [8], and γ was determined from Eq. [2].

(C) Fitting of Profile Data

In order to achieve even better accuracy and reproducibility of surface tension data, it is necessary to utilize all the profile data in a least-squares parameter optimization. Because the initial values of β and R_0 are already quite close to the optimal values, a relatively simple, yet effective, method of second-order interpolation/extrapolation—or response surface method—was chosen. To decrease computing time further, a database of theoretical profile data has been produced. This database contains (dimensionless) X- and Y-coordinates for all profiles for $0.1 < \beta < 0.5$ in steps of $\Delta\beta = 0.001$ (400 data sets). The database was produced in the same way as described above, and stored in an indexed disc file. The objective function used in the optimalization was the mean square deviation between theoretical and experimental points,

$$\Delta f = \sum (y - \hat{y})^2 / N, \qquad [9]$$

between $X = 0.5$ and the maximum value in the data set. N is the number of data points. The theoretical value, $\hat{y}$, was calculated at each

experimental x-value by interpolation by using a third-degree polynomial through the four closest theoretical data points (two on each side).

The optimalization was performed by first calculating the mean square deviation at 9 (3 × 3) grid points in the β–R_0-plane around the starting point. The distance between the grid points was 0.001 in both directions. The mid-β-value was the one closest to the starting value (i.e., maximum deviation is 0.0005). From three dimensionless profiles, nine scaled profiles were calculated by multiplying each by the three values of R_0. Through these nine points, a second-order response surface was used to find the minimum. Because the starting point is very close to the optimum, and the distance between the grid points is small, a second-order surface makes almost an exact fit. This method is both fast and accurate in finding the optimum, most of the computing time being spent in calculating the mean square deviation. The optimalization procedure may be repeated with the new values as the starting point, but experiments show that very little improvement in the value of γ is achieved.

(D) Measurement of Contact Angles

Because of the general applicability of the filter routines, it was found that contact angles could also be usefully measured in the same instrument. While this, at least with respect to the pure optical measurement, is a relatively trivial task, a video-enhanced method is both faster and more accurate. Also the instrument need not be dismantled in order to measure both the surface tension and the contact angle in the same experimental setup.

The method was constructed to show a horizontal line on the screen, along which the solid surface is aligned. The filter routine then will give a properly aligned drop profile. The contact angle is easily calculated by numerical derivation of the profile at the contact point. Because of reflection in the substrate and some diffraction, the two to three data points closest

to the contact point must be neglected. Different methods of numerical derivation give considerably different results because of the extrapolation involved. Presently a travelling secant method, with linear extrapolation to the contact point, seems most robust. This gives values between a pure linear derivation, which underestimates the contact angle, and higher-order methods, which usually tend to overestimate.

An alternative method for determination of contact angles is to fit the sessile drop profile (as suggested by Rotenberg *et al.*). This method should theoretically give more accurate values, and will definitely be much more time consuming, especially because a larger span in β has to be covered. Presently this method has not been implemented here, and we believe the general difficulties in the reproducibility of contact angles, mainly surface inhomogeneity and the difference between approaching and receding contact angles, make the value of the additional effort it takes to utilize this method questionable.

COMPUTER PROGRAM–USER INTERFACE

To make the use of both this instrument and the mathematical methods involved as convenient and fast as possible, a user-friendly PC interface was built around the core subprograms. A menu-driven interface was chosen, a block diagram of which is shown in Fig. 4. The menus facilitate input and storage of data such as densities and sample information and makes operator control of the frame grabber board relatively easy.

Measurements carried out with this system are based upon experimental methods, created and edited through the menu system. A method describes the data source (video or disk file), time interval between measurements, number of measurements in a series, if data should be stored and in what form (bitmap or profile data), how results should be presented, and whether the full profile should be utilized in calculations. By using the meth-

ods for running experiments, up to 100 unattended measurements in a series are possible. The method system facilitates easy operation by technical assistants. However, the system also contains options for closer control of data capture and manipulation through the test routines and data manipulation menus. Storage of raw data (bitmaps), profile data, and recalculation is possible. The program is written entirely in Pascal.

RESULTS AND DISCUSSION

This instrument may be used for different types of measurements on surface and interfacial tensions. In this paper we have concentrated on measurements on pure substances in order to check the accuracy and reproducibility of the instrument and the mathematical methods. Also some checking of the calibration method was performed. A systematic variation in the threshold fraction F was performed on one particular drop image (stored), taking the variation on both the calibration and the drop profile into account. The sensitivity for water in air is typically $d\gamma/dF = 2.0$ mN/m. This will be somewhat dependent on the needle diameter and the magnification, but it clearly shows the importance of correct profile determination. Also reproducibility in the single contour points and the optical aberration in the system was checked by plotting the x-values in the calibration of a 3-mm glass tube at two magnifications. The calculated standard deviation is 0.023% (0.06 pixel) and the difference between the edges (upper and lower) and the middle of the picture is 0.06% (0.15 pixel). It can be concluded that the reproducibility is good and the optical aberration can be neglected.

Table I gives the surface tension of 13 different pure liquids against air. Also given are literature data for these liquids (8, 9). The measured values correspond well with the literature data within a range of 1–2 mN/m. While this is not completely satisfactory from a quantitative viewpoint, the measured values
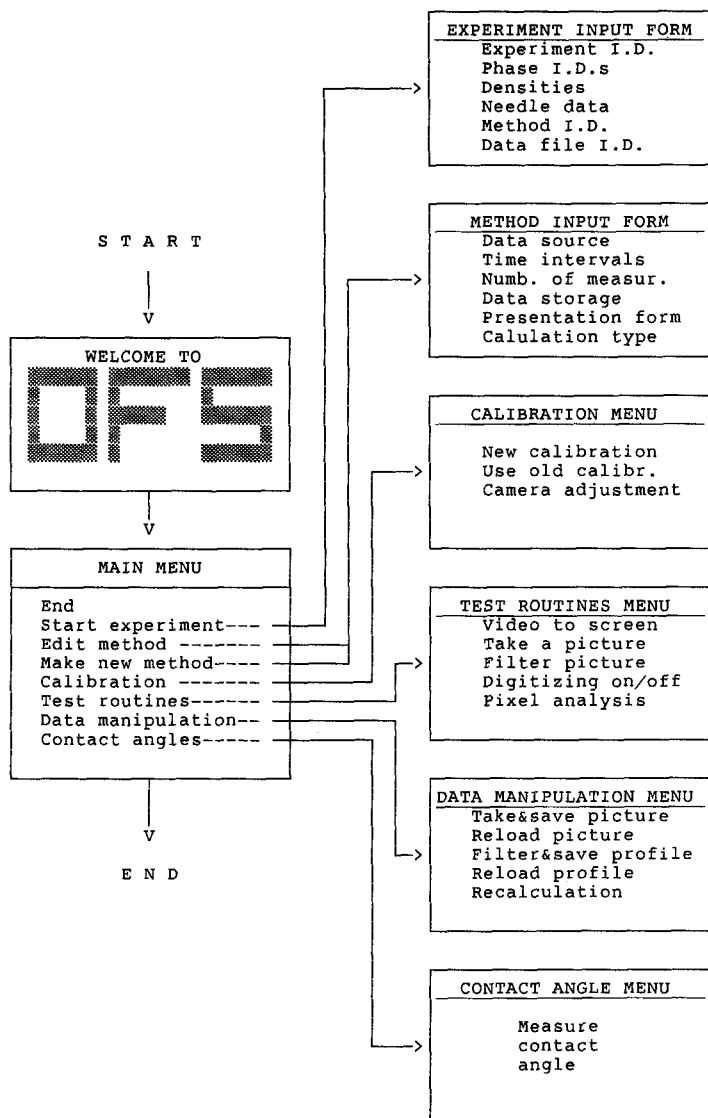
FIG. 4. Block diagram of the OFS menu system for pendant drop.

themselves are very reproducible. It is believed that the main reason for the difference between measured and literature data is the purity of the liquids and temperature differences; the measurements were performed at room temperature (ca. 23°C). The deviation between these results and literature data does not seem to follow any particular trend, indicating that the calibration of the instrument and the choice of constants is satisfactory. Neither do there appear to be particular trends in the difference between γ-values calculated from initial size parameters and those calculated from the full profile data. It is therefore difficult to determine from these results which of the methods gives the most fully correct answer. The reproducibility, however, is ca. 10 times better with the full profile method, leading to

TABLE I

Comparison of Literature Data (8, 9) and Measured Values of Interfacial Tension

Type of liquid	Literature (mN/m)	Method 1		Method 2	
		γ (mN/m)	SD (mN/m)	γ (mN/m)	SD (mN/m)
Water (21°C)	72.60	71.4	0.2	71.16	0.03
Formamide	58.2	59.0	0.3	59.05	0.03
Sulfuric acid	55.1	55.1	0.1	57.73	0.01
Ethylene glycol	47.7	46.8	0.1	47.46	0.01
Aniline	42.9	42.8	0.1	41.77	0.02
Pyridine	38.0	36.6	0.2	36.52	0.01
Dimethylformamide	37.7	35.8	0.2	36.23	0.01
Ethylbenzene	29.20	28.6	0.2	28.21	0.06
2-Ethoxyethanol	30.0	27.8	0.2	28.58	0.05
Toluene	28.5	28.6	0.2	28.77	0.02
Tetrachlormethane	26.95	27.2	0.1	26.14	0.04
Cyclohexane	25.5	25.1	0.2	24.31	0.05
Hexane	18.43	19.6	0.3	17.72	0.04

Note. Method 1 values are calculated from initial size parameters. Method 2 values are obtained from fitting full profile data. Standard deviation is calculated from 10 consecutive measurements on the same drop.

the conclusion that this method is better in removing random noise in the profile data points. This noise is believed to be mainly due to (mostly invisible) vibrations of the drop in air, and should be less apparent when measuring interfacial tensions. It should be noted

TABLE II

Reproducibility of Measurements on Separate Drops of Formamide and Cyclohexane at Different Magnifications

Meas. No.	Formamide		Cyclohexane	
	γ	SD	γ	SD
1	58.60	0.03	24.84	0.04
2	58.59	0.03	24.71	0.03
3	58.10	0.02	24.66	0.07
4	59.52	0.02	25.08	0.07
5	58.77	0.02	25.05	0.05
Mean	58.8		24.9	
SD (single)	0.5		0.2	
SD (mean)	0.2		0.1	

Note. The full profile method was used.

that these standard deviations do not measure reproducibility between drops. To check this further, five different drops of formamide and cyclohexane in air were measured at somewhat different magnifications and thus with separate calibration before each drop. This corresponds to the accuracy that would be representative of a typical everyday use of the instrument for single surface tension measurements. The results are given in Table II. It is seen that reproducibility between drops is ca. 1% (standard deviation), a value considerably above that of a single drop (Table I) with the same calibration. We believe further improvement of accuracy is possible, but this requires both better control of drop conditions (temperature, purity, evaporation) and possibly more tedious calibration methods.

It can be concluded that this instrument and software, as implemented at the present time, is a fast and fully accurate method for determining the surface tension of liquids by pendant drop. More experimental work will be carried out in the future when time-dependent processes such as adsorption and mass transfer

in particular will be investigated and contact angle measurements reported.

ACKNOWLEDGMENTS

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