Colloid Polym Sci 274:643–647 (1996)

ORIGINAL CONTRIBUTION

Y. Hayami

The influence of asymmetry in drop shape on an interfacial tension measurement

Received: 15 November 1995
Accepted: 10 January 1996

Dr. Y. Hayami (✉)
Department of Home Economics
Chikushi Jogakuen Junior College
Dazaifu
Fukuoka 818-01, Japan

Abstract A requirement of the drop method for interfacial tension measurement is that the drop must have an axi-symmetry. The drop shape was measured as a function of the angle of the rod from which the drop was hanging. The deviation of the interfacial tension caused by asymmetry was calculated using the selected plane method in the pendant drop technique. A sharp maximum was seen in the interfacial tension vs angle curve when the rod was at the vertical point. The maximum value was concluded as being the true value of the interfacial tension. Both decreases in the pressure difference and in the curvature of the drop associated with an increase in the rod-angle are a counterpart with each other to satisfy the Bashforth and Adams equation. The underestimation of the interfacial tension seems to be caused by the apparent inconsistency between the decreases in the curvature and pressure difference terms. The rigorous mechanical setup demonstrated here is necessary to attain the true axi-symmetric condition, and thus obtain a reliable value for the interfacial tension.

Key words Asymmetry of drop shape – pendant drop measurement – selected plane method – interfacial tension – three-phase contact line

Introduction

It is well known that several methods used to measure the interfacial tension, i.e., plate, ring, capillary rise, etc, are influenced by the contact angle [1]. In fact, the plate method is one of the techniques used to measure the contact angle. There are many papers which show that the pendant and sessile drop methods are excellent techniques for static interfacial tension measurement. Both the pendant drop and sessile drop methods are believed to be contact angle independent. We have improved our apparatus for interfacial tension measurement so as to be able to calculate the interfacial thermodynamic quantities precisely and correctly. Many apparatus used for the pendant drop method described in recent papers use a video camera and a computer to readily obtain the interfacial tension from the image of drop [2]. To obtain a reliable interfacial tension value, the drop shape must have an axi-symmetry. Therefore, we have to check the influence of the asymmetry of the drop shape on the interfacial tension measurement to the same extent as has been done in the verification of the symmetrical setup in the optical apparatus.

In this paper, we report the extent of the influence of asymmetry in drop shape on the interfacial tension measurement in order to gain more quantitatively reliable values for the interfacial tension.

Materials and methods

Materials

Hexane (specially prepared reagent for spectrophotometric measurement) was obtained from Nacalai Tesque, Inc.

and was refluxed with metallic sodium for 20 h prior to distillation. The purity of the hexane was checked by gas–liquid chromatography. Water was distilled three times from an alkaline permanganate solution. The purity of water was checked using the value of its surface tension. The water and hexane were saturated with each other before measurements were made.

Apparatus

A block diagram of the experimental setup is shown in Fig. 1. All optical components and the sample cell were mounted on an aluminium table that was raised 20 centimeters above floor level to reduce vibration.

The three micrometer stages, each composed of a horizontal stage (Chuo Precision Industrial, LD-241) and a vertical stage (Chuo Precision Industrial, LS-241), were attached to a rotary stage (Optec, F1-200-M) which had levelling screws. Those micrometer stages were adjusted so that they could move perpendicular to each other. The microscope (Kyowa Kogaku, FMZ-A) was equipped with a video camera (Tokyo Electronic Industry, CS3320L) and a point sensor (Nikon Instec, point sensor PS-1) combined with the vertical stage. Thus, the microscope can be moved both horizontally and vertically by using the micrometer heads (Mitutoyo, MHD-25H) mounted on the stages. The value of the displacement of the stage was read to the order of 0.1 μm by the counter (Mitutoyo, ARC-17001 W) connected to the micrometer head. The (standard) glass scale was used to correct the value of the counter. The placement of the edge of the pendant drop was determined as the midpoint of the change in the light intensity measured by the point sensor, within an error of $\pm 0.2\ \mu$m. The video monitor (Tokyo Electronic Industry, 12M500A) was used to confirm the assignment of the placement of the edge.

A frosted glass diffuser was placed between the light source and the sample cell to obtain a uniform background light intensity. We observed that the error related to a change in the intensity of the light source during the assignment of the drop edge measured by the point sensor is 1/30 of that measured by the digitized pixel image with 10 gray levels.

The pendant drop, suspended from the end of the syringe, was housed in the quartz cell with the windows. Usually a capillary tube or tip connected to the syringe is used for drop formation [3]. However, in that event we observed the displacement of the drop in the upward or the downward direction, depending on the humidity in the cell and the volume of liquid in the syringe. The velocity of the displacement was usually 1 μm per minute. This was caused by the increase or decrease of the drop volume originating from evaporation of the drop liquid or a leak of the liquid from the syringe to the drop through the rubbing. We used a small glass rod of 3 mm diameter fused to the end of the glass syringe as a support for the drop in order to eliminate the change in drop volume. Due to the complete wetting of water on the glass surface, a drop of water is formed on the outside of the glass rod. A small hole bored at the end of the syringe near the glass rod was useful in the drop formation process and also served to isolate the drop from the liquid in the syringe. Several conditions concerned with the three-phase contact, i.e., the verticality of the glass rod, the homogeneity of the glass-rod surface against wetting with the liquid making a drop, and the completeness of the circular cross-section of the glass rod, are strictly required to make an axi-symmetric drop. We used a glass rod with a diameter which was uniform to within $\pm 2\ \mu$m per 10 mm length.

Interfacial tension measurement

The interfacial tension was measured to within an experimental error of 0.04 mN m^{-1} by use of the selected plane method in the pendant drop technique [4]. The angle of

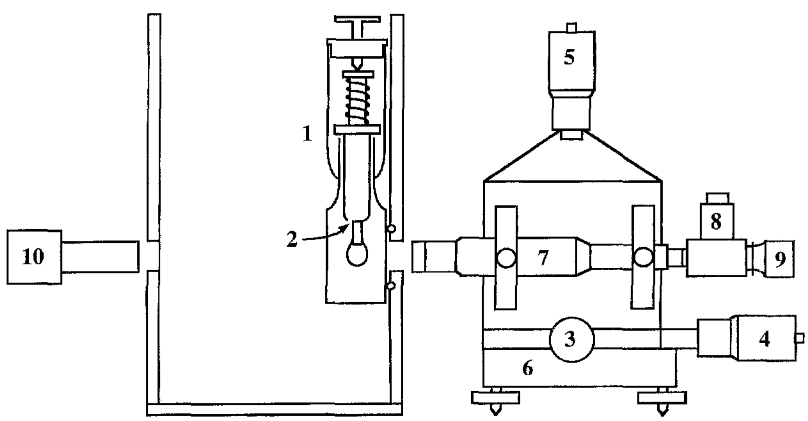

Fig. 1 Schematic of the experimental setup of the pendant drop measurements: 1) quartz cell, 2) pin hole, 3) x-direction micrometer stage, 4) y-direction micrometer stage, 5) z-direction micrometer stage, 6) rotary stage, 7) microscope, 8) point sensor, 9) video camera, 10) lamp house

inclination of the rod θ shown in Fig. 2 was measured to within a precision of 0.02°, using the same method as was used for the measurement of the drop diameter. Figure 2 also indicates the three-phase contact line on the glass-rod surface. The pendant drops were allowed to stand for 30 min to establish the thermodynamic equilibrium and a further 10 min for the attainment of mechanical equilibrium after each inclination. The temperature was controlled to within 0.01 K.

Results and discussion

In the selected plane method, the shape factor S is defined as

$$S = \frac{d_s}{d_e} \tag{1}$$

where d_e is the maximum (equatorial) diameter of the pendant drop and d_s is the diameter of the pendant drop in a selected plane at a distance d_e from the apex of the drop as shown in Fig. 2. Those two diameters were measured as a function of the angle of inclination θ at constant temperature T under atmospheric pressure. Figure 3 shows the dependence of d_e and d_s on the angle θ. Also in Fig. 3, we have plotted the value of the shape factor S multiplied by a factor of 6 in order to adjust the magnitude to the same order as the diameter. As shown in Fig. 2, $\theta = 0°$ means that the glass rod is vertical. The two diameters d_e and d_s, and the shape factor S gradually increase with an increase in the inclination of the glass rod.

To explain this phenomenon we briefly reform the Bashforth and Adams equation within the axi-symmetrical condition

$$\Delta p_0 + \Delta \rho g z = \gamma(1/r_{1,z} + 1/r_{2,z}) , \tag{2}$$

where Δp_0 is the pressure difference due to the curvature at the apex of the drop; $\Delta \rho$ is the density difference between two fluids, and is always negative for a pendant drop; z is the vertical coordinate measured from the apex [5]. Here, we use a three-phase contact line as a reference point, z_0, instead of an apex. Then we have

$$\Delta p_0 = \gamma(1/r_{1,z_0} + 1/r_{2,z_0}) , \tag{3}$$

where r_{1,z_0} and r_{2,z_0} are the two radii of curvature of the interface at the point of three-phase contact. We assign the radius of curvature of the meridian at the three-phase contact line, clearly connected by the contact angle of the drop, as r_{1,z_0} and the radius of curvature related to the radius of the glass rod and the contact angle as r_{2,z_0}. In this experiment, r_{1,z_0} is negative and r_{2,z_0} positive. Substituting Eq. (3) into Eq. (2), we have

$$\gamma(1/r_{1,z} + 1/r_{2,z}) = \gamma(1/r_{1,z_0} + 1/r_{2,z_0}) + \Delta \rho g z . \tag{4}$$

From analytical geometry, the radii of curvature at point z are given by

$$r_1 = [1 + (dz/dx)^2]^{3/2}/(d^2z/dx^2) \tag{5}$$

and

$$r_2 = x[1 + (dz/dx)^2]^{1/2}/(dz/dx) . \tag{6}$$

Substitution of Eqs. (5) and (6) into Eq. (4) yields

$$(d^2z/dx^2) + (dz/dx)\,[1 + (dz/dx)^2]/x = [1/r_{1,z_0} + 1/r_{2,z_0} + \Delta \rho g z/\gamma][1 + (dz/dx)^2]^{3/2} . \tag{7}$$

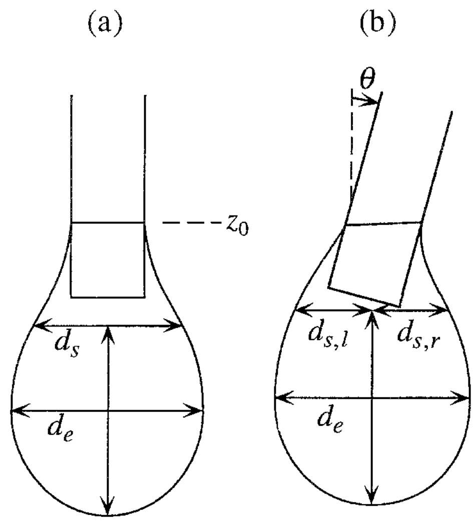

Fig. 2 Diameters of the selected plane of a pendant drop: (a) $\theta = 0°$, (b) $\theta \neq 0°$

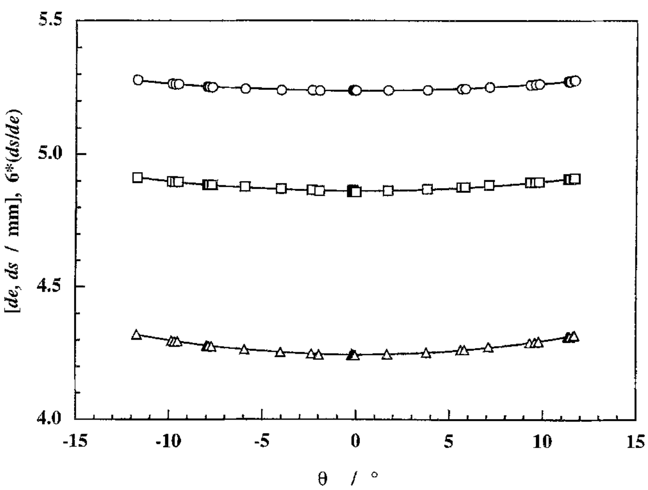

Fig. 3 Diameters d_e and d_s, and shape factor (d_s/d_e) vs glass-rod angle curves: (○) d_e; (△) d_s; (□) 6* (d_s/d_e)

Equation (7) means that the drop shape and size are the same and do not depend on the drop volume as long as the drop is formed from the same sample and supported by the same glass rod and the three-phase contact line is placed above the end of the glass rod. Actually, we can draw only one fitting curve for each plot of d_e, d_s, and S in Fig. 3, though each experimental point was obtained using a different drop volume. Additionally, we obtained other values of d_e, d_s, and S with another size of glass rod, these results are not indicated in Fig. 3.

If the angle of inclination of the glass rod θ changes from 0°, then the shape and size of the drop varies with the alteration of the values of r_{1,z_0} and r_{2,z_0}. The values of d_e, d_s, and S depend on the angle θ as shown in Fig. 3. However, we can still observe from Fig. 3 that they are not dependent on the drop volume.

In a more detailed description, the drop supported by the inclined glass rod does not have a circular cross-section in the horizontal plane, but also there is no axi-symmetry of the meridian in the vertical plane. The former is caused by the elliptical shape of the horizontal cross-section of the inclined glass rod and is related to the alteration in r_{2,z_0}, the latter is caused by the deviation of the symmetrical axis of revolution in accordance with the displacement of the three-phase contact line from the horizontal plane to the inclined plane and is related to the asymmetrical change in r_{1,z_0}. The change in r_{1,z_0} on the right-hand side, $r_{1,z_0,r}$, and on the left-hand side, $r_{1,z_0,l}$ of the glass rod in the plane containing the direction of inclination are shown in a qualitative sense in Fig. 4. The influence of the inclination on the change in r_{1,z_0} is dependent on the location along the three-phase contact line, and the opposite logic applies in Fig. 4. Actually, we did not measure the curvature at the three-phase contact line of the pendant drop. However, we may detect the influence of the inclination of the glass rod on the shape of the drop by observing the change in d_s.

As shown in Fig. 2, if d_s is divided by a vertical line extending from the middle point of d_e, then $d_{s,r}$ and $d_{s,l}$ is the right and the left part of d_s, respectively. The value of $d_{s,r}$ and $d_{s,l}$ are plotted against the inclination angle in Fig. 5. A glance at Fig. 5 shows the influence of the inclination as an asymmetry in the value of d_s. Both curves of $d_{s,r}$ and $d_{s,l}$ have an asymmetrical shape about the line corresponding to the angle 0. Naturally, they are mirror images of each other about the vertical line. It seems to be related to the two opposite changes in the curvature described in Fig. 4, but we do not discuss this point in any further detail.

Let us now consider the inclination of the glass rod suspending the same drop, i.e., keeping the drop volume constant. By using Eq. (2), we describe both cases of $\theta = 0°$

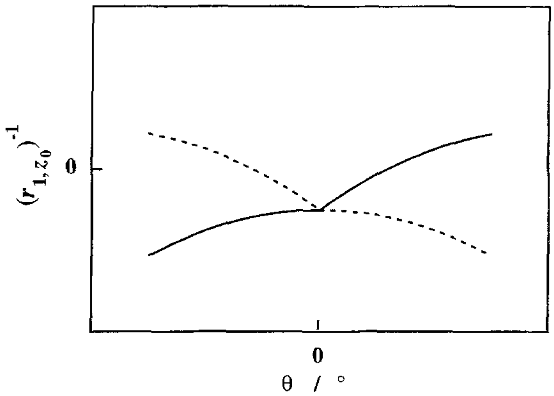

Fig. 4 Sketch of the dependence of curvature $1/r_1$ at z_0 on the glass-rod angle: (———) $(r_{1,z_0,l})^{-1}$, (- - - - - -) $(r_{1,z_0,l})^{-1}$

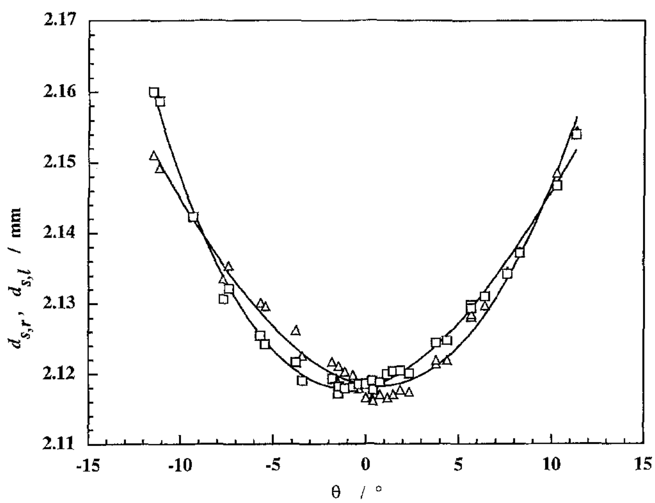

Fig. 5 $d_{s,r}$ and $d_{s,l}$ vs glass-rod angle curve: (□) $d_{s,r}$; (△) $d_{s,l}$

and $\theta \neq 0°$ at the apex as follows

$$\gamma(1/r_{1,z_a} + 1/r_{2,z_a}) = p_{i,z_0} - p_{e,z_0} + \Delta\rho g(z_a - z_{a'}) + \Delta\rho g(z_{a'} - z_0) \quad (8)$$

and

$$\gamma(1/r_{1',z_{a'}} + 1/r_{2',z_{a'}}) = p_{i',z_0} - p_{e,z_0} + \Delta\rho g(z_{a'} - z_0), \quad (9)$$

where the subscripts i and e means the interior and the exterior of the drop, respectively, the subscript a means the apex, and the superscript' denotes the inclined drop. Here we assume that the displacement of the three-phase contact line from the horizontal plane is small enough to have

$$p_{i,z_0} = p_{i',z_0} \,. \quad (10)$$

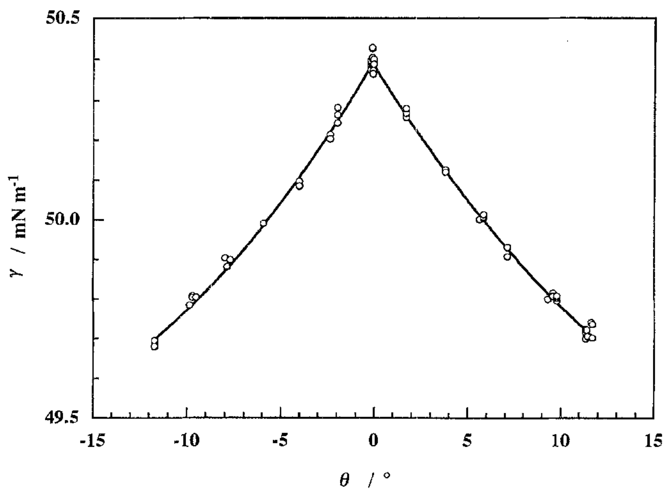

Fig. 6 Interfacial tension vs glass-rod angle curve of the hexane/water system

As described in Fig. 3, both values of d_e and d_s increase with increasing θ. Thus the vertical distance between the apex and the three-phase line decreases with an increase in θ, because the drop volume is kept constant in the case of using the same drop. The decrease in the vertical length of the drop means there is a decrease in the pressure difference, $\Delta\rho g(z_a - z_{a'})$, at the apex of the drop in Eq. (8). Also, the pressure difference at identical heights above the apex of the drop decreases with an increase in θ. On the other hand, the value of the shape factor S increases with an increase in θ as shown in Fig. 3. The increase in the value of S indicates a decrease in the curvature of the drop. Both decreases in the pressure difference and in the curvature of the drop associated with an increase in θ are necessary to satisfy Eq. (2), because the interfacial tension remains constant in this experiment.

Next, let us evaluate the interfacial tension γ by using the following relation

$$\gamma = \Delta\rho g(d_e)^2 \left(\frac{1}{H}\right), \tag{11}$$

where $1/H$ is a function of shape factor S. We used $1/H$ in the form of polynomial function of S derived by Misak [6]. Thermodynamically, the interfacial tension should not change under our experimental conditions. Strictly speaking, we cannot obtain the true value of the interfacial tension by applying Eq. (11) to our experimental data, because the condition of axi-symmetry of the drop would fail under our experimental conditions, except at the angle $\theta = 0°$. In practice, however, we can obtain useful information about the influence of asymmetry in drop shape on the interfacial tension measurement from this evaluation.

The interfacial tension value of the pure hexane/water interface at 298.15 K is plotted against the angle of inclination in Fig. 6. Clearly, the interfacial tension is underestimated owing to the asymmetry in drop shape. The curve is seen to have not a cusp point but a sharp maximum at the angle $\theta = 0°$, because there is no cusp point in either of the curves of d_e and d_s in Fig. 3. Naturally, the maximum value was identical to the interfacial tension value published in the reliable literature [7–9]. The underestimation seems to be caused by the apparent discrepancy between the decrease in the term of curvature and in the term of pressure difference. Thus, we have confirmed that the establishment of the symmetry of the drop shape is very important, in addition to the rigorous requirements of the optical setup.

Acknowledgment The present work was supported by a Grant-in Aid for Scientific Research (No. 63780132) from the Ministry of Education, Science and Culture.

References

1. Adamson AW (1982) Physical Chemistry of Surfaces. 4th ed, Wiley-Interscience, New York
2. Li D, Cheng P, Neumann AW (1992) Adv Colloid Interface Sci 39:347–382
3. Ambwani DS, Fort Jr T (1979) In: Good RJ, Stromberg RR (eds) Surface and Colloid Science, Vol 11. Plenum Press, New York and London, pp 93–119
4. Andreas JM, Hauser EA, Tucker WB (1938) J Phys Chem 42:1001–1019
5. Padday JF (1969) In: Matijević (ed) Surface and Colloid Science, Vol 1 Wiley-Interscience, New York, p 84
6. Misak MD (1968) J Colloid Interface Sci 27:141
7. Aveyard R, Haydon DA (1965) Trans Faraday Soc 61:2255–2261
8. Motomura K, Iyota H, Aratono M, Yamanaka M, Matuura R (1983) J Colloid Interface Sci 93:264–269
9. Ikeda N, Aratono M, Motomura K (1992) J Colloid Interface Sci 149:208–215