The Method of Touching Drops as a New Way of Measuring the Surface and Interfacial Tension of Liquids Including Surfactant Solutions

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A new technique for measuring the surface and interfacial tension of liquids, the method of touching drops, has been elaborated. The method requires the measurement of only a single parameter, the height of one of the drops formed and is suitable for studying surfactant solutions. The theoretical grounding of the method, the apparatus construction, and the experimental procedure are described.

The measurement of surface tension is an important process in surface and colloid science. A wide variety of methods are currently available for measuring surface tension (detailed descriptions have been given[1]) including some of high precision. Among them, methods based on the analysis of meniscus profiles are most popular. These are the well-known methods of sessile and pendant drops and of capillary rise, *etc*. There are also rather attractive (although not so wide-spread) methods using a pair of menisci in place of a single meniscus: a pendant drop and a meniscus in a capillary tube[2] and a pendant drop coupled with a large (flat) sessile drop.[3] Such methods have two advantages. First, only vertical distances are measured in the course of the experiment, which can be performed with the aid of a one-dimensional cathetometer without needing more complex and expensive equipment (a two-dimensional measuring microscope, photo- or video-apparatus). Secondly, a quantity as obscure as the contact angle is not needed.

The method we suggest also belongs to the above group of methods,[2,3] but is even simpler in comparison since it is restricted by measuring only a single vertical distance in the experiment. The reason for this simplification is clear from a comparison of our method with the known one.[3] In the latter, the mutual location of two drops communicating with each other is such that the pendant drop is below the sessile drop (they are positioned at the upper and lower ends of, in fact, the same tube), whereas in our method there exists the reverse mutual location of the drops formed at the ends of two tubes (Fig. 1). The measurement is made at the moment when the drops, slowly pressed out towards each other, come into contact with their tops. The tops become at the same level and, hence, possess the same capillary pressure (the hydrostatic pressure difference in adjacent phases) and the same curvature radius *b*. As a result, the number of unknown parameters is reduced, and measurement of, *e.g.*, only the height of the sessile drop H_s is sufficient. In contrast with the previous method,[3] the condition $b = \infty$ for the shape of the sessile drop is not imposed in our method. Apart from the drop height measured in the experiment, the diameters of the tubes D_p and D_s, as well as the distance between the tube tips H, should be known. The quantities D_p, D_s and H are determined only once as the apparatus constants.

The scheme of the apparatus is shown in Fig. 1. The whole apparatus is made out of glass, but there are titanium tips at the ends of tubes 1 and 2 where a pendant drop and a sessile drop are formed. The titanium tips are thoroughly edged from within as shown in Fig. 1. We used pairs of tips of approximately equal diameters $D_p \approx D_s$ in the range 0.3–0.5 cm. The horizontal position of the lower tip is achieved by the regulation of the apparatus as a whole. A similar position for the other tip, as well as making the two tips coaxial, is accomplished by displacement of the tube 2 with a set of microscrews. The displacement of the tube 2 from one fixed position to another one is possible because of the sufficiently long and then readily deformed pipe-coil 3. The glass syringes soldered 4, 5 and 6 play the role of micropipettes and allow smooth dosing of a liquid on drop formation.

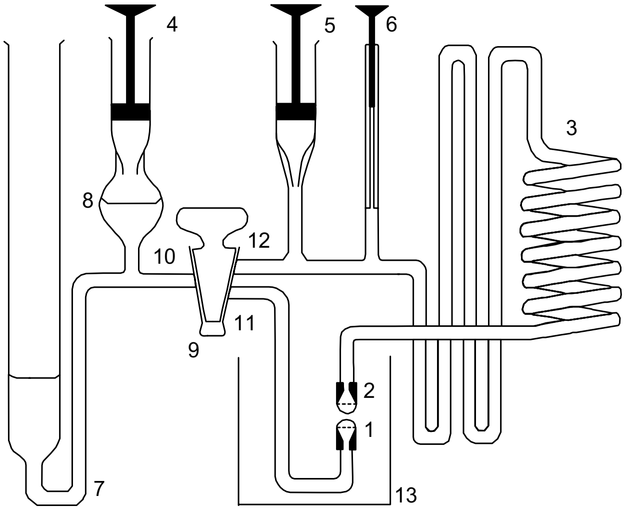

Fig. 1 The scheme of the apparatus: the tubes for forming drops (1, 2), the pipe-coil (3), the syringes (4, 5), the microsyringe (6), the U-shaped tube (7), the reservoir (8), the three-way cock (9), the tubes connected with the cock (10, 11, 12), the optical cuvette (13).

At the beginning of the experiment, the liquid under investigation is poured into the U-shaped tube 7 at the totally closed position of the three-way cock 9. Using the syringe 4, the right elbow of the tube 7 is filled including the reservoir 8 (the level of liquid in the left elbow is desirable to be set approximately at the level of the tip of tube 1). Then, the cock 9 joins the tubes 10 and 11, and the syringe 4 presses out the liquid in the tube 1 up to the formation of a small sessile drop. In the next stage, the cock is reset to the position 10–12, and the liquid is directed, through the coil 3, to the tube 2 to form a pendant drop. The drops become communicating with each other on joining the tubes 11 and 12 with the cock. After some spontaneous redistribution of the liquid between the drops, both the drops are smoothly pressed out, first with the syringe 5 and finally with the microsyringe 6, up to their moment of contact when the height of the sessile drop H_s is measured with the cathetometer.

On measuring the equilibrium surface tension of surfactant solutions, especially of dilute ones, there can be a danger that no adsorption–desorption equilibrium occurs at the drop surface at the moment of drop contact. To avoid this situation, the procedure of "pseudo-touching" the drops is used: the tubes 1 and 2 are placed aside from the common axis maintaining the horizontal position of the tip cross-sections. Direct contact of the drop tops becomes impossible in this position, but drop tops at the same level can be easily registered with the aid of the horizontal hair-line of the cathetometer eyepiece, provided both the drop tops are visible simultaneously. The advantage of such a position is that a drop can be made somewhat larger than at the drop-top contact and then returned to the drop-top contact size to verify equilibrium attainment. The drops are pressed out slowly until their tops reach a common horizontal, and the height H_s is measured. Then, the drops are pressed out further (but, naturally, not to their contact) and drawn back by sucking out the liquid with the microsyringe 6, and the height H_s is measured again. If both the values of H_s coincide, this provides evidence for the equilibrium value of the surface tension.

On measuring the interfacial tension at the liquid-liquid boundary, a second lighter liquid is poured into the optical cuvette 13 up to the level when the ends of tubes 1 and 2 are immersed entirely into the liquid.

The calculation of surface (interfacial) tension from the H_s value measured is realized by means of the computer program elaborated PEN)(SES.† By solving numerically the differential equations of capillarity (modern personal computers perform this operation in several seconds), the dimensionless coordinates $\xi_s \equiv x_s c^{1/2}$ and $\zeta_s \equiv z_s c^{1/2}$, as well as the drop-top radius b, can be determined, where x and z are the Cartesian coordinates of the drop profile (with the origin at the drop top, Fig. 2) and x_s and z_s are their values at the end points of the profile ($x_s = D_s/2$, $z_s = H_s$) and c is the capillary constant:

$$c = (\rho_1 - \rho_2)g/\gamma \tag{1}$$

(ρ_1 and ρ_2 are the density of the liquid under investigation and of the surrounding phase, respectively, g is acceleration due to gravity, γ is surface tension). Using, *e.g.*, ξ_s, the surface tension is found from the identity:

$$\gamma = (\rho_1 - \rho_2)gD_s/2\xi_s \tag{2}$$

To estimate the accuracy, we obtain from equation (2) an expression for the relative error $\Delta\gamma/\gamma$:

$$\gamma/\gamma = [(\rho_1 + \rho_2)/(\rho_1 - \rho_2)] + g/g + D_s/D_s + \xi_s/\xi_s \tag{3}$$

We confine ourselves to considering rather typical systems with $\rho_1 \approx 1$ g cm^{-3} and $\rho_2 \approx 0.001$ g cm^{-3} at $\rho_1 = \rho_2 = 0.0001$ g cm^{-3}, as, *e.g.*, the air/aqueous surfactant solution system. We assume $D_s = 0.1 \pm 0.0001$ cm for the tube 1 (the problem of a precise treatment of the tip edges arises for more narrow tips). The rigorous analysis of ξ_s/ξ_s is rather difficult since ξ_s is implicitly dependent on all the experimental quantities including D_p, H and H_s (Fig. 2). However, it is reasonable to suppose that ξ_s/ξ_s does not exceed the worst of the errors H_s/H_s which is 0.001 at the minimum height of sessile drops $H_s = 0.1$ cm (smaller drops are scarcely practical) and $H_s = 0.0001$ cm (the cathetometer accuracy). Putting the above values into equation (3) with $g \approx 1000$ cm s^{-2} and $g \approx 0.01$ cm s^{-2} yields $\gamma/\gamma \approx 0.002 = 0.2\%$.

The above estimated accuracy of the method is also confirmed by our experiments with water chosen as a standard liquid. In average, the value of surface tension 72.63 dyne cm^{-1} was obtained at 20 °C, which is in a good agreement with the literature data (72.75 dyne cm^{-1},[4]). For the sake of illustration, we represent a typical set of data obtained in the course of a single experiment: $\rho_1 = 0.9982$ g cm^{-3}; $\rho_2 = 0.0012$ g cm^{-3}; $g = 981.93$ cm s^{-2}; $D_s = 0.4282$ cm; $D_p = 0.4055$ cm; $H = 0.3417$ cm; $H_s = 0.2430$ cm; $\gamma = 72.67$ dyne cm^{-1}.

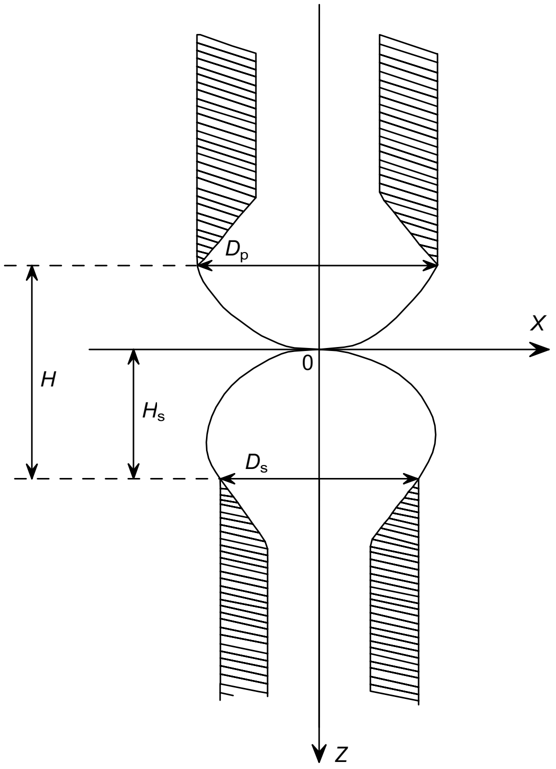

Fig. 2 The profiles of a pendant drop and a sessile drop at the moment of their contact.

References

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† A diskette with the program may be ordered from the authors.