Surface Tensions from Detachment of Solid Rods

BJØRN LILLEBUEN

Universitetet i Trondheim, Norges tekniske høgskole, Institutt for uorganisk kjemi, N-7034 Trondheim-NTH, Norway

Two methods for making surface tension measurements in liquid systems are analyzed theoretically. Both the pin method and the method of Wilhelmy are so-called detachment methods; the force necessary to detach a metal rod (circular or rectangular) from the liquid surface is obtained experimentally. The theoretical analysis involves a calculation of the maximum volume of liquid that is held up by the rod being equal to the detachment force. The surface tension of the liquid is determined by the detachment force, the dimensions of the rod, and, in case of the pin method, the density of the liquid.

Surface tension is given as energy per unit area of surface, or equivalently force per unit length. If the force necessary to detach a metal rod from the liquid surface is measured together with the circumference of the rod, one might try to compute the surface tension of the liquid from the following relation:

$$\gamma = \frac{\Delta W_{\text{max}}}{A}$$  \hspace{1cm} (1)

Here

- $\gamma$: surface tension in dyne cm$^{-1}$
- $A$: circumference of the rod in cm
- $\Delta W_{\text{max}}$: detachment force in dyne

The pin method$^1$ (rod with circular endface) and the Wilhelmy method$^2,3$ (rod with rectangular endface) have both been used for measuring surface tensions of liquid systems at room temperature and up to about 1000°C. $\Delta W_{\text{max}}$ has been measured by slowly lowering the liquid surface and simultaneously recording the weight of the rod. This weight exhibits a definite maximum just before the contact between the surface and the rod is broken, and $\Delta W_{\text{max}}$ is given as the difference between this maximum weight and the weight of the rod after the contact is broken.

More than thirty years ago Freud and Freud$^4$ showed theoretically that relations like eqn. (1), containing only the detachment force and the circumference, do not apply when a ring is detached from the surface of a liquid. It is the purpose of this paper to analyze, theoretically, the detachment of a rod
(circular or rectangular) from a liquid surface. Previous investigators\textsuperscript{1-3} have calculated surface tension values from eqn. (1), taking \( A \) to be the actual circumference of the rod, or alternatively a calibration constant.

For pins we will show that the surface tension is not given by eqn. (1), but that it can be calculated from knowledge of the detachment force, pin radius, and density of the liquid. For rectangular rods eqn. (1) gives a correct result, if edge effects are neglected.

**THE PIN METHOD**

Using the method of Freud and Freud,\textsuperscript{4} the fundamental Laplace equation will be used to calculate the maximum volume of liquid that is held up above the surface by a circular rod. This volume is then connected to the experimental quantity, \( \Delta W_{\text{max}} \), through the relation

\[
\Delta W_{\text{max}} = V g \phi
\]

Here

\( V \) volume of liquid above undisturbed surface  
\( \phi \) density of the liquid  
\( g \) constant of gravity

The Laplace equation for the shape of a liquid surface is

\[
\frac{1}{R_1} + \frac{1}{R_2} = \frac{P}{\gamma}
\]

where \( R_1 \) and \( R_2 \) are the principal radii of curvature at a point on the surface, and \( P \) is the pressure at this point relative to the pressure on the undisturbed plane surface (which in this case is the surface at infinite distance from the rod).

For surfaces of revolution\textsuperscript{5}

\[
\frac{1}{R_1} = \frac{u}{x} \quad \text{and} \quad \frac{1}{R_2} = \frac{du}{dx}
\]

where \( u = \sin \alpha \), \( \alpha \) being the angle of the surface tangent with the \( x \)-axis. The level of the undisturbed surface coincides with the \( x \)-axis at an infinite distance from the rod, while the \( y \)-axis passes through the center of the rod.

The Laplace equation becomes:

\[
\frac{u}{x} + \frac{du}{dx} = -\frac{y \phi g}{\gamma}
\]

To obtain a general equation, the reduced variables \( y_r \) and \( x_r \) are introduced:

\[
y_r = y/(2\gamma g \phi)^{1/2}, \quad x_r = x/(2\gamma g \phi)^{1/2}
\]

Substitution into eqn. (4) gives:

\[
\frac{u}{x_r} + \frac{du}{dx_r} = -2y_r
\]
The largest reduced volume of liquid that can be held up above the surface by the pin is

\[ V_r = \frac{V}{(2\gamma/gq)^{3/2}} = \pi \int_{0}^{y_r'} x_r'^2 \, dy_r \]  

(7)

If the liquid wets the pin, the contact angle between the pin and the liquid surface will be zero. The integration, therefore, is performed from \( y_r = 0 \) to \( y_r = y_r' \), where \( u = 1 \) and \( x_r' = r \) (reduced pin-radius \( r = r/(2\gamma/gq)^{1/3} \)). See Fig. 1. Integration by parts of eqn. (7), and combination with eqn. (6) yields:

\[ V_r = \pi r^2 y_r' + \pi r_r \]  

(8)

In order to find \( y_r' \), eqn. (6) must be solved. Since it is impossible to integrate this equation by means of known functions, a Taylor expansion has been carried out. As initial values \( y_r = u = 10^{-5} \) were selected, while the initial values for \( x_r \) were in the region between 5.4 and 7.5. Lower initial values for \( y_r \) and \( u \) did not produce significant changes in the results.

These numerical solutions of eqn. (6) made possible the determination of \( y_r' \) as a function of \( r \) from a least squares treatment:

\[ y_r' = -1.282 r + 4.878 r^{1/3} - 4.770 r^{1/3} + 1.914 r^{1/4} \]  

(9)

Standard deviation < 0.5 % when

\[ 8 \times 10^{-3} < r_r < 7 \times 10^{-1} \]

According to eqns. (8) and (9), \( V_r \) is now a function of \( r_r \) only.

The relationship between the experimental quantity, $AW_{\text{max}}$, and the maximum volume of liquid that is held up above the surface by the pin, is:

$$\Delta W_{\text{max}} = Vg\varepsilon = (2\gamma/g\varepsilon)^{3/2} V_r \varepsilon g$$  \hspace{1cm} (10)

Introducing $r_r = r/(2\gamma/g\varepsilon)^{1/4}$ in eqn. (10), and rearranging yields:

$$\frac{\gamma}{(\Delta W_{\text{max}}/2\pi r)} = \frac{\pi r_r}{V_r}$$  \hspace{1cm} (11)

The quantity $\pi r_r/V_r$ is, insofar as its deviation from unity is concerned, a measure of the deviation from the simple, intuitive relation

$$\gamma = \Delta W_{\text{max}}/2\pi r$$  \hspace{1cm} (12)

This is illustrated in Fig. 2.

It is seen that eqn. (11) may be applied to compute the surface tension value if $\Delta W_{\text{max}}$, $\varepsilon$ and $r$ are known. Since $r_r$ contains $\gamma$, an iteration procedure is necessary. The calculations are, however, greatly simplified if the dimensionless quantity $r_r^3/V_r$ is considered:

$$\frac{r_r^3}{V_r} = \frac{(r/(2\gamma/g\varepsilon)^{1/4})^3}{V} = \frac{r^3}{V} = \frac{\Delta W_{\text{max}}}{g\varepsilon}$$  \hspace{1cm} (13)

Therefore, $\pi r_r/V_r$ has been calculated as a function of $r_r^3/V_r$ by a least squares treatment, and is given as:

$$\pi r_r/V_r = 0.992 + 2.564 \times 10^{-6}/(r_r^3/V_r) - 6.605 \ (r_r^3/V_r) + 73.25 \ (r_r^3/V_r)^2$$
$$-454.0 \ (r_r^3/V_r)^3$$  \hspace{1cm} (14)

Standard deviation $<0.1\%$ when

$$4 \times 10^{-4} < r_r^3/V_r < 6 \times 10^{-2}$$

Thus, the surface tension can be calculated directly from $r$, $\varepsilon$, and $\Delta W_{\text{max}}$, by means of eqns. (14), (13), and (11).

THE WILHELMY METHOD

When a rod with a rectangularly shaped endface is withdrawn from a liquid surface, the surface around the rod will no longer be a surface of revolution. Eqn. (6) is therefore not valid in this case.

If the assumption is made that the length $L_r$ of the rectangle is much greater than the width $B$, we may write the following expression for the maximum reduced volume that is held up by the rod:

$$V_r' = 2 \int \int_{0}^{\infty} y_r \, dx_r \, dL_r$$  \hspace{1cm} (15)

The $x_r$-axis coincides with the level of the undisturbed surface at an infinite distance from the rod. The $y_r$-axis passes through one of the short sides of the rectangle, and is normal to the rectangle (see Fig. 3). As before $1/R_1 =$
$$\frac{du}{dx}$$, but now \(1/R_2 = 0\) because the sides of the rectangle are without curvature \((R_2 \to \infty)\). The transformed and reduced Laplace equation in this case is:

$$\frac{du}{dx} = 2y_t$$  \hspace{1cm} (16)

(Strictly, the right side of eqn. (16) should be \(-2y_t\), but the sign is not important in the following calculations.)

Combination of eqns. (16) and (15) gives:

$$V_t' = \int_0^L \frac{1}{0} du \int_0^L dL_t = L_t$$  \hspace{1cm} (17)

The total reduced volume that can be held up by the rod is therefore:

$$V_t = L_t + B_t$$  \hspace{1cm} (18)

The only approximation implicit in eqn. (18) is that the edge effects have been neglected. Further:

$$\frac{\gamma}{\Delta W_{\max}/2(L + B)} = \frac{2\gamma(L + B)}{V_{\text{eq}}} = \frac{2\gamma(L + B)}{(L_t + B_t)(2\gamma/\rho g)^{1/2}g \rho}$$

$$= \frac{2\gamma(L + B)}{[(L + B)/(2\gamma/\rho g)^{1/2}g \rho]^2} = 1$$  \hspace{1cm} (19)

Thus:

$$\gamma = \Delta W_{\max}/2(L + B)$$  \hspace{1cm} (20)

The surface tension can consequently be calculated from \(\Delta W_{\max}\), \(L\), and \(B\), by means of eqn. (20). The density of the liquid does not need to be known.

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