The "Hollow Cylinder" Method for Surface Tension Measurements

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Two detachment methods for making surface tension measurements in liquids have recently been analyzed theoretically.¹ It was shown that both the detachment of a circular rod (pin method) and the detachment of a rectangular rod (Wilhelmy method) can be utilized for absolute surface tension determinations, without any calibration in reference liquids. This paper deals similarly with the detachment of a hollow cylinder from a liquid surface. The method has been applied in several high temperature liquids.³ but no satisfactory theory has as yet been proposed. In the present paper it is shown that a suitable modification of the equations developed for the pin¹ proves successful.

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In the earlier paper, 1 the maximum reduced volume of liquid that can be held up above the undisturbed surface by the pin was found to be:

$$V_{\rm r}(1) = \pi R_{\rm r}^2 y_{\rm r}' + \pi R_{\rm r} \tag{1}$$

where the subscript r denotes the reduced parameters

$$y_{\rm r}' = y' / \sqrt{a}$$
, $R_{\rm r} = R / \sqrt{a}$, $V_{\rm r}(1) = V(1) / a^{3/2}$
 $a = 2\gamma / g\varrho$

V(1): Maximum volume of liquid above undisturbed surface.

y': Maximum height of liquid above undisturbed surface.

R: Radius of the pin.

y: Surface tension of the liquid.

q: Density of the liquid.

g: Constant of gravity.

Since the pin is a solid cylinder, two modifications are necessary in the case of a hollow cylinder: First, the hollow cylinder will act as a capillary. Any standard treatment of this effect ³ reveals that the liquid volume that is lifted is given by the equation:

$$V(2) = 2\pi r \gamma \cos \theta / g \rho \tag{2}$$

 θ is the contact angle between the cylinder walls and the liquid, and r is the inner

radius of the cylinder. In the moment of detachment, it will be assumed that the wetting is perfect, and thus $\cos \theta = 1$, and

$$V(2) = 2\pi r \gamma / g_0 \tag{3}$$

which gives

$$V_{\rm r}(2) = \frac{V(2)}{a^{3/2}} = \frac{2\pi r \gamma}{g \gamma (2\gamma/g \varrho)^{3/2}} = \frac{\pi r}{\sqrt{a}} = \pi r_{\rm r} \ (4)$$

Secondly, both $V_r(1)$ and $V_r(2)$ will contain the volume given by the expression

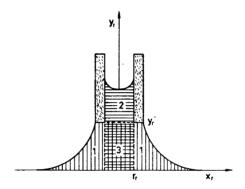


Fig. 1. The detachment of a hollow cylinder from a liquid surface. 1: The volume $V_{\mathbf{r}}(1)$. 2: The volume $V_{\mathbf{r}}(2)$. 3: The volume $\pi r_{\mathbf{r}}^{2} y_{\mathbf{r}}'$.

 $\pi r_r^2 y_r'$. The maximum reduced volume of liquid that can be held up by the cylinder is therefore (see Fig. 1):

$$V_{r} = V_{r}(1) + V_{r}(2) = \pi r_{r}^{2} y_{r}' \tag{5}$$

By means of eqns. (1) and (4) we obtain:

$$V_{r} = \pi R_{r} + \pi r_{r} + \pi y_{r}' (R_{r}^{2} - r_{r}^{2})$$
 (6)

where $R_{\rm r}$ is defined as the outer reduced radius of the cylinder. This expression can now be utilized for surface tension calculations. As a starting point, the simplest and most intuitive relation for the detachment of a hollow cylinder is given by setting the detachment force equal to the forces originating from breaking the surface films on the two perimeters with radius R and r:

$$\Delta W_{\text{max}} = 2\pi (R+r) "\gamma" \tag{7}$$

We denote the surface tension obtained in this way by " γ " to indicate that this is only an approximate value.

A correct value for the surface tension is obtained by setting the detachment force equal to the weight of the volume lifted:

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$$\Delta W_{\text{max}} = V g \varrho \tag{8}$$

Converting to reduced parameters:

$$\Delta W_{\text{max}} = V_{\text{r}} (2\gamma/g\varrho)^{3/2} g\varrho \tag{9}$$

It is then possible to write eqn. (8) in the following form by using eqn. (6):

$$\frac{\gamma}{\frac{\Delta W_{\text{max}}}{2\pi(R+r)}} = \frac{1}{1 + (R_{\text{r}} - r_{\text{r}})yr'}$$
(10)

The expression $1/[1+(R_r-r_r)y_r']$ is then, insofar as its deviation from unity is concerned, a measure of the deviation from the approximate eqn. (7). Since y_r' is a function of R_r only, given in the earlier paper as

$$y_{\rm r}'(R_{\rm r}) = -1.282R_{\rm r} + 4.878R_{\rm r}^{\frac{1}{2}} - 4.770R_{\rm r}^{-1/8} + 1.914R_{\rm r}^{-1/4}$$

it is possible to calculate surface tension values by means of eqn. (10), which may be rewritten:

$$\frac{\gamma}{\frac{\Delta W_{\text{max}}}{2\pi(R+r)}} = \frac{1}{1 + R_{\text{r}} \left(1 - \frac{r_{\text{r}}}{R_{\text{r}}}\right) y_{\text{r}}'(R_{\text{r}})}$$
(11)

Thus, when $\Delta W_{\rm max}$, R, r, and ϱ are known, the surface tension value may be calculated by eqn. (11). Since $R_{\rm r}$ and $r_{\rm r}$ contain γ as a factor, an iteration procedure is necessary. A suitable starting value for γ is obtained from eqn. (7). The iterations may be avoided by introducing the dimensionless factors R^3/V and r/R. The resulting computation procedure proves, however, more complicated than the iteration procedure, which can easily be undertaken by a computer.

Acknowledgement. I express my gratitude to Professor Kai Grjotheim, Dr. Jan Lützow Holm and Dr. Harald A. Øye for their continuous interest and help during the preparation of this manuscript. Financial support from Norsk Hydro A/S is gratefully acknowledged.

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Received October 8, 1970.

Fortran Editions of Haltafall and Letagrop

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The complete Algol versions of HALTA-FALL¹ and LETAGROP ²⁻⁷ appeared in 1967—1970. Since then there has been a demand for the Fortran versions of these programs. The present Fortran programs are straightforward translations of the corresponding Algol versions. We have till now made copies, working on the following computers: CDC 3600, IBM 360/75 and CDC 6600.

Acknowledgements. We are obliged to Dr. Klaus Appel, Mr. Björn Kleist and Mr. Karl-Einar Sjödin for their valuable help. The financial support of The Swedish Natural Science Research Council is gratefully acknowledged.

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Received October 14, 1970.

Acta Chem. Scand. 24 (1970) No. 8