Measurement of Interfacial Tension between Immiscible Liquids with the Spinning Rod Tensiometer

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Received December 22, 1986; accepted September 8, 1987

A spinning rod interfacial tensiometer (U.S. Patent 4,644,782) is described and compared with the spinning drop tensiometers. The rod pierces the drop and can help to stabilize the rotating bubble, reducing spin up time and drift. The effects of contact lines at the rod end walls can be made negligible. The devices described accommodate liquids of all viscosities and are robust and inexpensive in design. Various tests of internal consistency are described. Values of interfacial tension for 13 pairs of liquids are given and, where possible, compared with literature values. © 1988 Academic Press, Inc.

1. INTRODUCTION

The spinning rod tensiometer is a device closely related to the spinning drop tensiometer. In the spinning rod tensiometer the drop is pierced by a small rod or wire which is centrally located and rigidly secured in the rotating cylinder. The rod is used to locate and stabilize the drop in a central position, to prevent drift, and to reduce spin up time. Very viscous liquids greater than 100, even 1000, poise as well as low viscosity liquids, can be conveniently loaded into the spinning rod tensiometer. Very viscous liquids (>100 poise) cannot be conveniently loaded into the spinning drop tensiometers used in commercial practice because they cannot be forced through the syringe used to load the instrument.

Three spinning rod tensiometer devices have been developed in our laboratory. One was briefly described by Joseph and Preziosi (1). They showed that the interface shape which minimizes the energy appropriate to the problem is a bubble when capillary effects of the contact line on the rod are neglected. The theory and experiments show that these effects are negligible when the rod is small (see also Fig. 2 of this paper).

The other two devices used in the experiments are described in this paper; a table giving the interfacial tension for pairs of liquids is presented, and various comparisons are made.

The technology of spinning drop and rod tensiometers is still under development and the validation of the instruments presently in use is still incomplete (see Manning (2)).

The spinning drop tensiometers described by Princen et al. (4), Cayias et al. (5), Torza (6), and Scriven et al. (7) and the spinning drop tensiometer marketed by Teckmar and manufactured in Germany differ in some important details but appear to share common problems.

(i) They cannot be used to measure interfacial tension of viscous liquids (>10 poise)
because they cannot be pushed through the syrings used to load the instrument.

(ii) The position of the rotating bubble is very sensitive to gravity. If the axis of the rotating cylinder is not perfectly level there is a strong tendency of the bubble to drift. The same problem can be exacerbated by certain types of vibration and frictional heating of bearings.

(iii) Even if the axis of the cylinder is level, gravity will force the bubble off the central axis and prevent it from assuming its equilibrium shape associated with the steady rigid body rotation. Gravity \( g \) is negligible when

\[
\Omega^2 D/2g = F \gg 1, \tag{1.1}
\]

where \( F \) is the Froude number. To suppress gravity, it is necessary to increase \( \Omega \), but evidently this will not ensure a good result; for example, Manning (2) says that \"drops should be measured when \( L/D > 4 \). However the drop should not be extremely long due to possible fluid dynamical complications.\" 

(iv) The spin up time can be a problem. The spin up time for a single fluid is very fast but the spin up time for two fluids can be slow due to the effects of gravity and the slow response for establishing equilibrium interfaces (7, 8).

Many of the problems which frustrate measurement of the interfacial tension with spinning drop tensiometers are alleviated by the stabilizing action of the central rod in the different spinning rod devices, discussed next.

2. THE SPINNING ROD Tensiometer, THEORETICAL.

The essential nucleus of the spinning rod tensiometer is a rotating bubble pierced by a rotating solid rod, as in Fig. 1. In principle, the spinning rod and spinning drop tensiometers are closely related, with differences arising only from the effects of the rod. In fact, the rod is very effective in stabilizing rotating bubbles, reducing instability, drift, and spin up time.

![Fig. 1. Rotating bubble \( \Delta \rho = \rho_2 - \rho_1 > 0 \) is the density difference. A solid rotating rod of radius \( a \) pierces the drop in the spinning rod tensiometer. A central rod is not used in the spinning drop tensiometer.](image)

The ideas behind the rotating rod tensiometers were formulated in the papers by Joseph et al. (9) and Joseph and Preziosi (1). The problem considered in the first of these papers is as follows: two liquids occupy the region between two coaxial cylinder which rotate with constant common angular velocity \( \Omega \). They started with the Navier–Stokes equations and the usual interface conditions, neglected gravity, looked for spatially periodic solutions, and found rigorously that rigid motions of two fluids are unconditionally stable and that the configuration of flow minimizes a potential

\[
M = \int_0^{2\pi/a} dx \int_0^{2\pi} \left\{ T[R^2 + R_y^2 + R^2 R_x^2]^{1/2} - \frac{\Delta \rho \Omega^2}{8} \left[ R^2 - d^2 \right]^2 \right\} d\phi \tag{2.1}
\]

which, in retrospect, can be identified as a potential studied by Beer (10). Here \( R(\phi, x) \) is a periodic function of \( x \) and \( \phi \), with mean value \( d = \bar{R} \). Periodic minimizers of \( M \), with

\[
J = \frac{\Delta \rho \Omega^2 d^3}{T}, \tag{2.2}
\]

where \( \Delta \rho \) is the density difference and \( T \) is the interfacial tension, are perfect right circular cylinders of constant radius \( d \). When \( J < 4 \), the interface cannot be a cylinder of constant radius, though rigid motions are still stable, but instead is a nonconstant minimizer of the potential \( M \).

Joseph and Preziosi (1) showed that relative minimizers of the potential are always unstable in the sense that kinematically admissible dis-
turbances with a large dissipation will always destabilize a relative minimum, driving it to a lower, finally a global minimum. They showed using the method of Beer (10), neglecting capillarity at solid surfaces, that minimizers touch the axis of rotation in a plane perpendicular to the axis. Solutions that touch the axis may be regarded as limiting cases of periodic solutions, a periodic array of drops \((J < 0)\) identical to the drops studied by Chandrasekhar (3) or the bubbles \((J > 0)\) studied by many persons starting from Beer (10).

It is interesting that the equality in [2.2] cannot be achieved for free bubbles; \(J \geq 4\) cannot be achieved because the bubble will elongate as \(\Omega\) is increased in such a way that the effective mean radius

\[
d \approx \left\{ \frac{4T}{\Delta \rho \Omega^2} \right\}^{1/3}\quad [2.3]
\]

is a decreasing function of \(\Omega\). On the other hand it is very easy to achieve \(J \geq 4\) by restraining the increase in the length of the bubble using, say, end plates. \(J = 4\) is the asymptotic solution, \(d \to 0\) of the long bubble treated by Vonnegut (11) and Princen et al. (4).

Minimizing solutions that touch the axis of rotation will certainly touch the inner cylinder. Cylinder-touching solutions are of two types. The interface between the two fluids intersects the cylinder at lines of contact or the interface has a tangent or higher order contact with the cylinder. Both situations occur but, in fact, the second case has no line of contact. Instead one fluid tenaciously wets the rod so that physical touching of the cylinder is impossible. This appears to be true for oils coating rods rotating in air. The oil has higher order contacts with the wetted rod (see Figs. 7–11 in Joseph and Preziosi (1)). Lines of contact seem always to appear when there are two liquids. The presence of capillarity at the line of contact of the bubble and the rod, which might at first appear to be a serious problem, appears to be of no consequence for the measurement of the interfacial tension. The effects of capillarity at lines of contact will be small when the ratio of rod to bubble radius is small or when the angle at the rod is the same as when there is no rod (see (1) and appendix for a mathematical demonstration). In these limiting cases, one of which is easily achieved by design, the presence of a rod does not affect the diameter \(D\) needed in [2.5]. Comparisons of theory and experiment are exhibited in Figs. 6–7 of the paper by Joseph and Preziosi (1) and Fig. 2. In this figure the dots represent the theory; they give the values of an axisymmetric bubble \(R(x)\) which minimizes the potential \(M\) given in [2.1] when the maximum diameter and the aspect ratio are prescribed. The effects of capillarity prevents one from determining the aspect ratio from the experiments. The aspect ratio is iterated to produce a best fit. Each iterate gives a different value for

\[
J_d = \Delta \rho \Omega^2 d^2 / T,\quad [2.4]
\]

where \(d\) is the mean radius. The value of

\[
J_D = J_d D^2 / 8 d^3\quad [2.5]
\]

is relatively insensitive to these iterations when the aspect ratio \(L/D > 4\).

Preziosi (12) gave the values of minimizing parameter for \(M\), expressing results in terms of \(d\) (with \(r_2 = D\) and \(\lambda = L\)). Their table is basically the same as tables of Princen et al. (4) and Cayias et al. (5) for rotating bubbles when the different parameters used in different studies are converted. The tables given by all the aforementioned authors do not give values

Fig. 2. A rotating bubble of olive oil in glycerin at 103 rad/s. The dots represent the shape of the bubble predicted by the theory with contact lines conditions neglected.
for $L/D > 4$. In Table I, we give the values of minimizing parameters over the complete $L/D$ range and we show the values of $J_d$ and $J_D$ side by side. Inspection of this table shows that $J_d$ is still rapidly varying for $L/D > 3.5$, whereas $J_D$ is slowly varying, having nearly attained a constant value near its asymptotic, $L/D \rightarrow \infty$ value, $J_D = 4$. This implies that $J_d$ is a better parameter to specify the bubble shape and $J_D$ is a better parameter for computing interfacial tension.

The measurement of interfacial tension with spinning drop or spinning rod tensiometers is frequently made ambiguous by the appearance of small air bubbles. Careful loading procedures can suppress this problem and air bubbles which do not touch the bubble can be ignored. Small air bubbles which enter into the liquid bubble of low density whose interfacial tension is the point at issue can frustrate the measurement. If the gravity were absent, or if the speed $\Omega$ was high enough to produce small air bubbles, their presence would have no effect on the measurement of the interfacial tension between two liquids.

To be precise about the remark just made, we made note that if the volume of each of two liquids and the total volumes of the two liquids plus the gas is preserved, the gas must preserve its volume. The compressibility of the air then plays no role. Suppose that there are two liquids plus air in the cylindrical container with the central rod. Suppose further that the air is enclosed entirely by the light liquid and that the light liquid is enclosed entirely by the heavy liquid. Then there are two interfaces, $\Sigma_1$ between air and the light liquid and $\Sigma_2$ between the light and heavy liquid, and $\Sigma_1$ is entirely enclosed by and makes no point of contact with $\Sigma_2$. Then, following procedures introduced by Joseph et al. (9), we find that rigid motions are globally stable and that $\Sigma_1$ and $\Sigma_2$ minimize the potential

$$M = M_1 + M_2,$$

where $M_1$ is the potential for $\Sigma_1$ and $M_2$ is the potential for $\Sigma_2$. The potential is to be minimized among all nonintersecting interfaces ($\Sigma_1$, $\Sigma_2$) periodic in $x$ and $\phi$ or the limiting bubbles arising from this prescription of periodicity subject to the constraint that the volume of each constituent is preserved.

Apart from the condition that $\Sigma_1$ and $\Sigma_2$ are disjoint sets, the potentials $M_1$ and $M_2$ are independent. Minimizers for $M$ which leave $M_1$ and $M_2$ disjoint minimize $M_1$ and $M_2$ separately. Each minimizing interface is a nested sequence of bubbles of unduloid type. A min-
imizing interface of this type is shown in Fig. 2.

3. THE SPINNING ROD TENSIOmeter, EXPERIMENTAL

The schematic of the experimental apparatus is shown in Fig. 3. The precision bore Pyrex glass has an inner radius of 0.5-in., with a surface eccentricity within ±0.001 in., an outer radius of 0.6 ± 0.01 in., and a length of 6.5 in. Various sizes of rods were tested in our experiment, including a thin wire. The wire is replaced after each run, while the rod is checked to assure its concentricity and is changed if needed.

A travelling microscope with an eye piece was used to measure the diameter and the length of the drop. The lens distortion and the effect of refractive indexes in different materials require a magnification factor to obtain the true diameter of the drop. Using the thin lens theory, one can relate the true diameter of the drop to the measured one by

\[ D = \frac{D_{\text{app}}}{n} \]  \[3.1\]

where \( D_{\text{app}} \) is the measured drop diameter and \( n \) is the refractive index of the heavier fluid.

The drop length can be monitored over time to determine its steady state. The equilibrium state is reached when the drop length remains unchanged. Capillarity at lines of contact between the fluid and the rod are critical to the measurement of the drop diameter. Resistance to motion of the contact line produces higher values of the interfacial tension which actually increases with the speed of rotation. An indirect test for this unwanted effect is to measure the interfacial tension at different speeds. An unique value of interfacial tension obtained at different speeds indicates that contact lines do not affect the measured tension. To eliminate the capillarity, one can decrease the rod diameter for a fixed volume of the lighter fluid. The advantages of the rod are to decrease the spin up time of the fluid to a rigid motion, especially when the density difference is small, and to stabilize the drop from oscillating or drifting in the axial direction.

The following is an outline of the procedure used in each run.

(i) The cylinder is loaded with working fluids whose density difference has been determined. The cylinder is spun up to a speed at which the Froude number is sufficiently large.

(ii) The lighter fluid is usually broken into full bubbles and half bubbles as shown in Fig. 4. The constant diameters of bubbles are verified experimentally to be the same when capillarity effects at contact lines are negligible. A particular bubble is selected and monitored with time to determine its equilibrium state.

(iii) The constant diameter of the drop and the rotational speed of the cylinder are obtained at the equilibrium state and the interfacial tension is computed using the formula

\[ \sigma = \frac{4\pi r^2}{2L} \]

Fig. 4. Possible drop configurations.

Fig. 3. The schematic of the experimental apparatus.
\[ T = \frac{\Delta \rho \Omega^2 (D_{\text{app}})^3}{8n^2 J_D (L/D)} \]  

where \( \Delta \rho \) is the density difference (g/cm³), \( \Omega \) is the rotational rate of the cylinder (s⁻¹), \( D_{\text{app}} \) is the measured drop diameter (cm), \( n \) is the refractive index of the heavy fluid, and \( L/D \) is the aspect ratio, i.e., the ratio of the drop length to its diameter; the correction factor \( J_D (L/D) \) is given in Table 1 for \( L/D < 4 \) and is equal to 4 when \( L/D \geq 4 \).

4. THE SPINNING ROD TENSIOMETER, RESULTS AND DISCUSSION

We have already remarked about the contact line effects of a small rod. Even large effects are confined to a region near the line of contact and do not cause significant changes in the diameter of \( D \) of long drops, say \( L/D > 4 \). The localized effects of capillarity are shown theoretically and were demonstrated experimentally for bubbles on spinning rods in Figs. 6–7 in the paper by Joseph and Preziosi (1) and in Fig. 2 of this paper. These comparisons seem to establish that the presence of the rod does not introduce new uncertainties in the measurement of interfacial tension from the shape of rigidly rotating long bubbles. The rod does have some deleterious effects on the measurement of interfacial tension using shorter bubbles for which the correction \( f(L/D) = 4/J_D \) is significantly larger than one (see Table I). The reason is that capillarity prevents the precise determination of \( L \). However, the stabilizing effect of the rod is such that long bubbles with very large \( L/D \) ratios can be achieved rapidly and stably without major restriction on the viscosities of the two fluids. For these long bubbles \( f = 1 \) is within experimental error.

Table II gives the value of the interfacial tension at room temperature for 17 different pairs of liquids. We have compared our values with published values wherever possible. The

### TABLE II

<table>
<thead>
<tr>
<th>Fluid–fluid system</th>
<th>Spinning rod tensiometer ( T ) (dyn/cm)</th>
<th>Table values ( T ) (dyn/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octane/water</td>
<td>55.60 ± 0.587</td>
<td>51.0&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Decane/water</td>
<td>45.7 ± 1.41</td>
<td>46.0&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Silicone oil 20 cS/water</td>
<td>24.35 ± 0.338</td>
<td>24.34 ± 0.2&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>Silicone oil 100 cS/water</td>
<td>24.67 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>Silicone oil 12.5 S/water</td>
<td>27.11 ± 0.164</td>
<td></td>
</tr>
<tr>
<td>Silicone oil 100 S/water</td>
<td>43.525 ± 0.578</td>
<td></td>
</tr>
<tr>
<td>Crisco oil/silicone oil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 cS</td>
<td>3.59 ± 0.17</td>
<td></td>
</tr>
<tr>
<td>20 cS</td>
<td>1.413 ± 0.029</td>
<td>1.65 ± 0.18&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>100 cS</td>
<td>1.43 ± 0.07</td>
<td>1.25 ± 0.12&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>500 cS</td>
<td>1.40 ± 0.06</td>
<td></td>
</tr>
<tr>
<td>1000 cS</td>
<td>1.25 ± 0.12</td>
<td></td>
</tr>
<tr>
<td>Crisco oil/water</td>
<td>3.385 ± 0.093</td>
<td></td>
</tr>
<tr>
<td>Castor oil/water</td>
<td>14.85 ± 0.49</td>
<td></td>
</tr>
<tr>
<td>Olive oil/water</td>
<td>16.42 ± 0.256</td>
<td></td>
</tr>
<tr>
<td>Olive oil/glycerin</td>
<td>10.456 ± 0.860</td>
<td></td>
</tr>
<tr>
<td>Motor oil SAE 30/water</td>
<td>9.22 ± 0.448</td>
<td></td>
</tr>
<tr>
<td>STP oil treatment/water</td>
<td>30.075 ± 0.559</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> CRC table.
<sup>b</sup> Sessile drop method.
<sup>c</sup> Spinning drop method.
<sup>d</sup> Spinning drop method (from our laboratory).
measurements reported in the table were limiting values for sequences of measurements in which \( \Omega \) was progressively increased. A typical set of results and calculations is given in Table III and shows that the method gives unique values of \( T \) over a wide range of \( \omega \). In general, limiting values could clearly be identified. High precision may or may not be attainable with the relatively inexpensive instruments we used to construct the tables (see Section 3). In any event we regard the validation of our tensiometer as only secondarily concerned with high precision. We are striving to determine the conditions under which low precision value may be reproduced again and again. Exactly the same problems of validation apply to the spinning drop tensiometer and they are somewhat alleviated, but not relieved, by state-of-art technology (see Manning (2, Chap. III)).

(i) We have verified that the value of interfacial tension which we measured using a long bubble with \( L/D > 5 \) is independent of rod diameter for small diameters because capillarity has a negligible effect on \( D \). The interfacial tensions of various liquids were measured using different rod diameters and materials and these data are given in Table IV.

(ii) We also verified experimentally that long bubbles and long half bubbles which were attached to the side wall give the same value of interfacial tension.

(iii) Stable rigid motion may be achieved with a round interface between the liquids when the central rod is bent. In fact, the central rod could have been a square cross section, provided that it rotates rigidly. The rod has a passive stabilizing effect and does not interfere with bubble dynamics.

Some points of comparison of spinning drop and spinning rod tensiometers are listed below. We have numbered the list in the same sequence as the sections to describe problems associated with the spinning drop tensiometer.

(i) Since a syringe is not used to load the rod tensiometers, the measurement of interfacial tension is not restricted to low viscosity fluids.

(ii) The rod stabilizes the position of the bubbles, suppresses the effects of gravity, and eliminates the problem of drift. Measurements of interfacial tension for Crisco oil/silicone oil interfaces for 5-, 100-, 500-, and 1000-CS silicone oils were taken in the same apparatus with and without a rod. The measurements of the bubble without a rod could not be carried forward at high angular speeds because the drift of the free bubble was badly exacerbated. High speeds without drift are easy to obtain with the rod but the accuracy is diminished at low speeds.

(iii) High \( \Omega, L/D \), and small \( D \) are easily and stably obtained. This means that extremely long bubbles (say \( L/D > 10 \) or more) can be used with the rod tensiometer without possible fluid mechanical complications.

(iv) The measurement of bubble lengths on spinning rods is ambiguous or not possible.

We cannot yet specify a users program for
measuring interfacial tension with rod tensiometers which yield the same value every time for every fluid. It seems to us that this as yet unsolved problem is common to rod and drop tensiometers and may in part be due to the sensitivity of tension to small contamination.

APPENDIX: THEORY

The equation governing \( \sigma(x) = R(x)/d \), where \( d \) is the mean radius, is

\[
\frac{1 + r' - r'^2 r}{(1 + r^2)^{3/2}} + \left[ \frac{1}{2} J(r^2 - 1) - \lambda \right] r = 0, \quad [A.1]
\]

where \( \lambda \) is a Lagrange multiplier associated with the constraint (equivalent to constant volume) that \( d \) is the mean value of \( R \) over \( x \).

After changing variables, \( v = \cos \psi \), where \( \psi \) is the local angle between the tangent to the curve \( r = r(x) \) and \( x \), we find a first integral

\[
r(v - 1) = (r_2 - r)f(r, \theta, r_2, a, J), \quad [A.2]
\]

where \( \theta \) is the prescribed contact angle \( J = J_d \), \( r_2 = x_{\text{max}} r(x) \), \( a \) is the rod radius, and

\[
f = \frac{J}{8} (r^2 - a^2)(r_2 - r)
\]

\[
- \frac{r_2 - a \cos \theta}{r_2^2 - a^2} (r_2 + r) + 1 \leq 0 \quad [A.3]
\]

because \( r_2 > r \) and \( v = \cos \psi \). Equation \([A.2]\) is a first-order differential equation, \( \cos \psi = 1/\sqrt{r_2^2 + 1} \), which is to be integrated from \( x = x_1 \), where \( (r, r') = (a, \tan \theta) \) to \( x = x_2 \), where \( r' = 0 \). \( f \) is a cubic in \( r \) and it has two points \( \partial f/\partial r = 0 \), one of which is negative. It follows that when \( a < r < r_2 \), \( f \) is a decreasing function of \( r \) with a maximum at \( r = a \) or \( r = r_2 \) is a single minimum in \( a < r^2 < r_2 \) and \( f \) is maximum at the end point \( r = a = r = r_2 \). We can verify that \( f(a, \theta, r_2, a, J) \leq 0 \) automatically, and

\[
f(r_2, \theta, r_2, a, J) \leq 0 \text{ if and only if}
\]

\[
J \leq 4 \frac{r_2^2 + a^2 - 2r_2 a \cos \theta}{r_2(r_2^2 - a^2)^2}. \quad [A.4]
\]

For long bubbles, \( v - 1 \sim -\psi^2/2 \) and \( r_2 - r \sim \psi' \) and \( f(r, \theta, r_2, a, J) \to 0 \) with \( \psi \) implying the equality in \([A.4]\) for long bubbles. We can compute surface tension \( T \) when the bubble is long and \( r_2 \) and \( \cos \theta \) are known.

The working formula for the spinning rod tensiometer \( f = 0 \) may be replaced with the working formula \( J = 4/r_2^3 \) for the spinning drop

\[
\frac{1}{r_2^2} \left[ \frac{r_2^2 + a^2 - 2r_2 a \cos \theta}{r_2(r_2^2 - a^2)^2} \right] - 1
\]

\[
= \frac{2x \cos \theta}{1 + x^2 - 2x \cos \theta} = \frac{g(x, \cos \theta)}{1} \leq 1,
\]

\[
[A.5]
\]

where \( x = a/r_2, g(0, \cos \theta) = g(x, 1/2(3 - x^2)) \) = 0. We may ignore the rod when \( a \) is small, \( r_2 \) is large, or the contact angle at the rod is near to the angle on the bubble without the rod at the same radius. The ratio \( x \) is easy to control in practice.

REFERENCES