

Interfacial Tension Measurement of Immiscible Liquids Using a Capillary Tube

N. Rashidnia

Sverdrup Technology Inc., Brookpark, OH 44142

R. Balasubramaniam

NASA Lewis Research Center, Cleveland, OH 44135

D. Del Signore

Mechanical Engineering Dept., University of Toledo, Toledo, OH 43606

The interfacial tension of immiscible liquids is an important thermophysical property that is useful in the behavior of liquids both in microgravity (Martinez et al., 1987; Karri and Mathur, 1988) and in enhanced oil recovery processes under normal gravity (Slattery, 1974). Many techniques are available for its measurement, such as the ring method, drop weight method, spinning drop method, and capillary height method (Adamson, 1960; Miller and Neogi, 1985). According to Karri and Mathur, many of the techniques use equations that contain a density difference term and are inappropriate for equal density liquids. They reported a new method that is suitable for both equal and unequal density liquids, in which a capillary tube forms one of the legs of a U-tube. The interfacial tension is related to the heights of the liquids in the cups of the U-tube above the interface in the capillary. Our interest in this area arose from a need to measure small interfacial tensions (around 1 mN/m) for a vegetable oil/silicone oil system that was used in a thermocapillary drop migration experiment (Rashidnia and Balasubramaniam, 1991). In our attempts to duplicate the method proposed by Karri and Mathur, we found it quite difficult to anchor the interface inside the capillary tube; small differences of the liquid heights in the cups drove the interface out of the capillary.

We present an alternative method using a capillary tube to measure the interfacial tensions of liquids of equal or unequal density. The method is based on the combined capillary rises of both liquids in the tube, with air being the medium above the liquids. This way of using the capillary tube differs from those used previously, such as by Clarkson (1984). Also, in this method, no difficulties are encountered in anchoring the interface inside the capillary tube as in our attempts to duplicate the method by Karri and Mathur.

Principle

A simple sketch of the combined capillary rise method is shown in Figure 1a. A large container contains the two immiscible liquids, one on top of the other. A capillary tube is

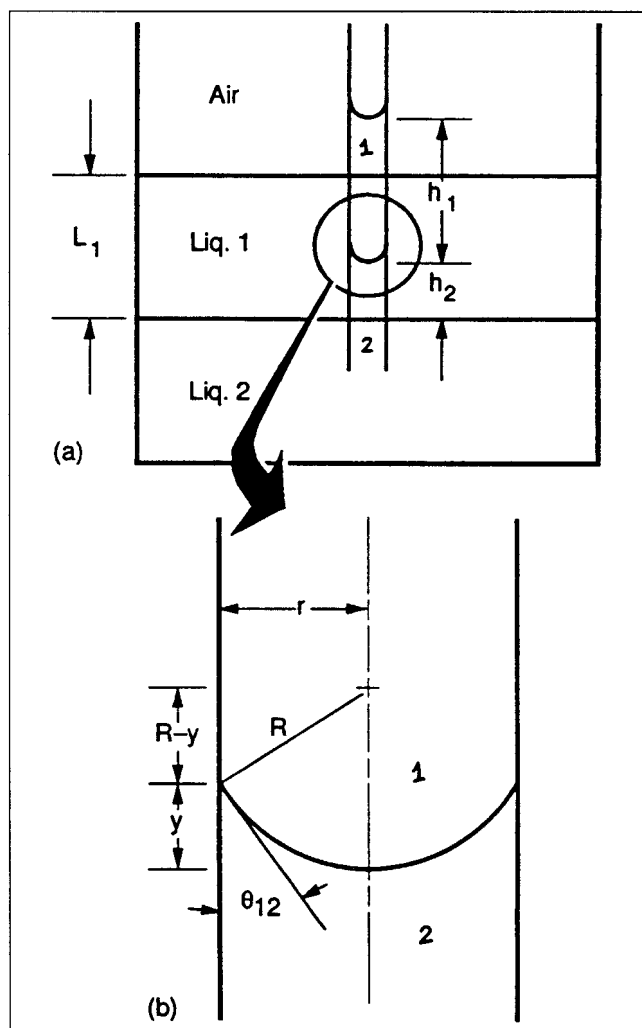


Figure 1. Principle of the combined capillary rise method.

Table 1. Interfacial Tensions of Liquid Pairs

Liquid Pair	Density kg/m ³	Measured Interfacial Tension mN/m		Lit. Value of Interfacial Tension mN/m
		mean	Std. Dev.	
Anisole/ Distilled Water	996 998	25.2	0.34	35*
Diethyl Adipate/ Distilled Water	1,009 998	12.9	0.18	18*
Benzonitrile/ Distilled Water	1,010 998	19.0	0.31	28*
<i>p</i> -Anisaldehyde/ Ethyleneglycol	1,119 1,114	3.4	0.28	—
3-phenyl-1-propanol/ Distilled Water	998 998	7.9	0.17	0*
2-Octanol/ Distilled Water	819 998	8.71	0.2	9.6**
Benzaldehyde/ Distilled Water	1,044 998	13.4	0.27	14.78*, 15.51**
Cyclohexane/ Distilled Water	779 998	48.0	0.65	50.2**
Carbontetrachloride/ Distilled Water	1,583 998	43.5	0.38	44.3*, 45.0**

*Karri and Mathur (1988).

**Girifalco and Good (1957).

dipped into the upper liquid (liquid 1) to measure its surface tension with air (σ_{1a}). Then, the capillary tube is pushed further down into the lower liquid (liquid 2) so that a liquid-liquid interface is present in it. This is accomplished best by using a pinch cork attached to a flexible tube connected to the top of the capillary before pushing it down into liquid 2. Upon releasing the pinch cork, the liquid-liquid interface naturally rises into the capillary (for wetting liquids). One may also establish 1a and 12 interfaces inside the capillary tube without having the two liquids in contact in the outer container. This is accomplished by dipping the capillary tube first into liquid 1, and subsequently, without allowing the column of liquid 1 to drain, by dipping it into a container of liquid 2. This is, in fact, the preferred approach especially for equal-density liquids and is used in the experiments reported here. For this case, the height L_1 (Figure 1a) is zero. Assuming the interface 12 and 1a to be spherical, the following equation may easily be derived for the interfacial tension:

$$\sigma_{12} = -\sigma_{1a} \frac{\cos\theta_{1a}}{\cos\theta_{12}} + \frac{gr}{2\cos\theta_{12}} (\rho_1 h_1 + \rho_2 h_2 - \rho_1 L_1) \quad (1)$$

where

σ = interfacial tension

θ = contact angle

g = earth's gravitational acceleration

r = capillary tube radius

ρ = liquid density

Various liquid heights are defined in Figure 1a. In deriving the above equation, the curvatures of both interfaces in the container are assumed to be zero. While this is easily realized for unequal density liquids, it is not necessarily the case for equal-density liquids. For the data reported here, L_1 is zero and so this situation does not arise. Specializing Eq. 1 for equal-density liquids, the following equation may be obtained:

$$\sigma_{12} = -\sigma_{1a} \frac{\cos\theta_{1a}}{\cos\theta_{12}} + \frac{\rho gr}{2\cos\theta_{12}} (h_1 + h_2 - L_1) \quad (2)$$

Equations 1 and 2 involve both the contact angles θ_{1a} and θ_{12} . If the capillary tube is itself used to measure σ_{1a} , θ_{1a} drops out of Eq. 1, because the capillary rise measured is:

$$h = (2\sigma_{1a}\cos\theta_{1a})/(\rho_1 gr) \quad (3)$$

which may be used directly in Eq. 1. θ_{12} may be obtained from the geometry of the interface within the capillary (Figure 1b). Assuming a spherical interface:

$$\theta_{12} = \cos^{-1}[2k/(k^2 + 1)] \quad (4)$$

where $k = y/r$. If θ_{12} is less than ten degrees, the error in assuming it to be zero in Eq. 1 or 2 is less than 1.5%. The working equation used to calculate σ_{12} for the case with $L_1 = 0$ is:

$$\sigma_{12} = gr[\rho_1(h_1 - h) + \rho_2 h_2]/(2\cos\theta_{12}) \quad (5)$$

Experimental Procedure

Pyrex-glass capillary tubes with an ID of 1.15 mm and length of 10 cm are used. The liquids are contained in quartz cells of inner dimensions $1 \times 1 \times 4.5$ cm and a thickness of 1.25 mm. All the measurements reported are at room temperature (around $21^\circ\text{C} \pm 2^\circ\text{C}$; the room temperature was steady during the course of every experiment to $\pm 0.5^\circ\text{C}$). The top end of the capillary is connected via a rubber tubing to a suction device. The apparatus is mounted on an optical table; no vibration isolation is provided.

Before each experiment, the capillary tubes and the quartz cells are cleaned as follows. They are immersed in a micro-

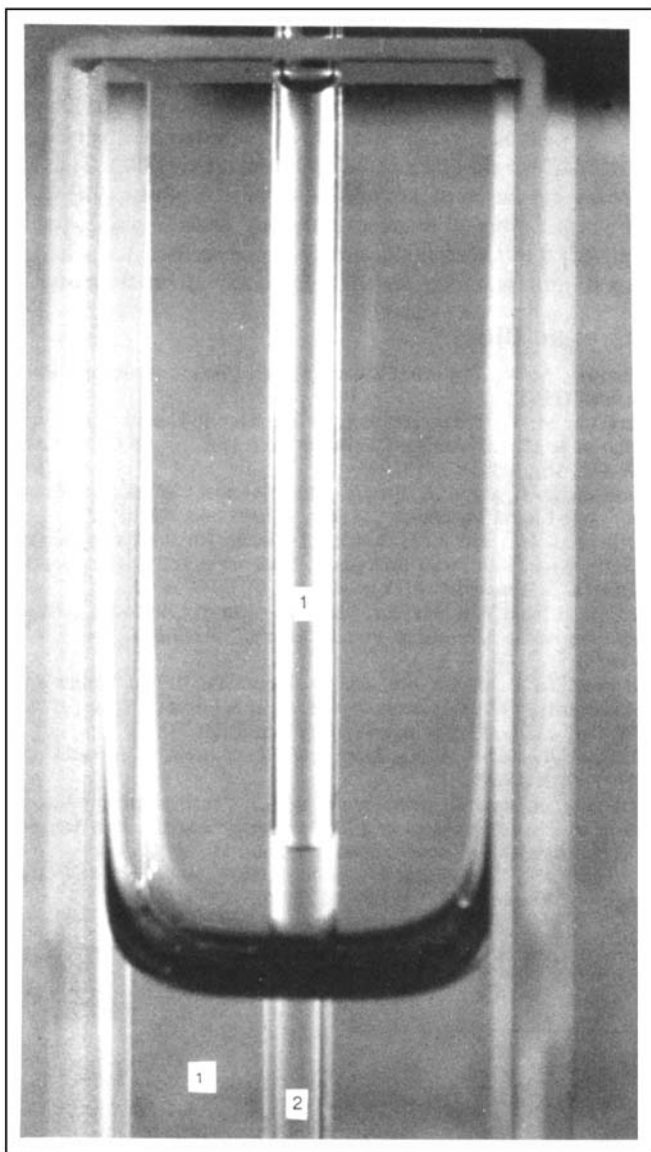


Figure 2a. Combined capillary rise method for cyclohexane/water system.

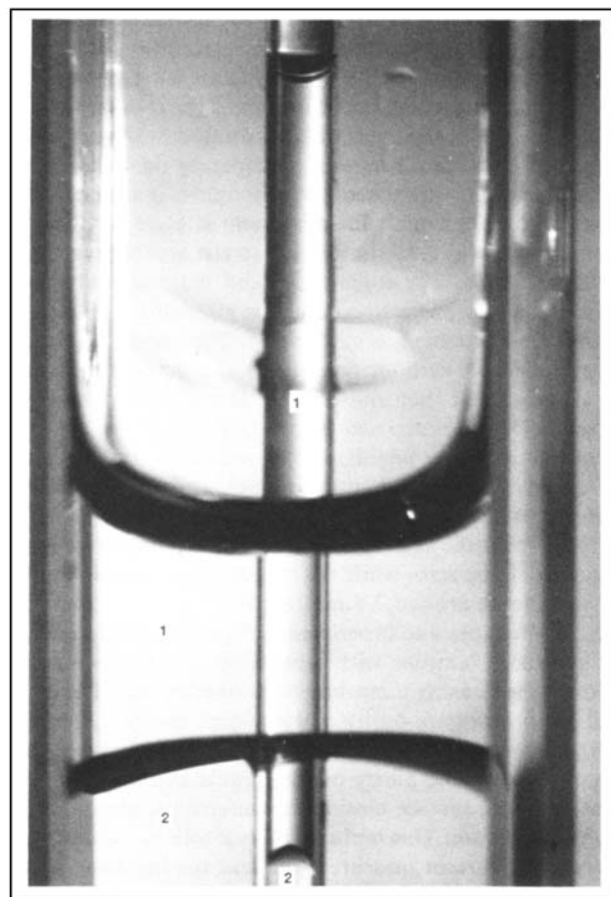


Figure 2b. Combined capillary rise method for benzaldehyde/water system.

ameter of the capillary tube (diameter is 1.15 ± 0.015 mm) and the lengths required to calculate θ_{12} .

Distilled water is used as liquid 2 in all the cases except for the anisaldehyde/ethylene glycol pair, for which liquid 2 is ethylene glycol. For many cases, there is density inversion within the capillary; however, no instability is observed and the 1a and 12 interfaces are stable in all the experiments reported.

Results and Discussion

Interfacial tensions of nine liquid pairs (Table 1) have been measured using the combined capillary rise method proposed here (with $L_1 = 0$). They cover a fairly wide range of values of the interfacial tension and the density difference between the liquids. Figures 2a and 2b show the interfaces obtained in the quartz cell and in the capillary tube for cyclohexane/water and benzaldehyde/water systems, respectively (in these pictures $L_1 \neq 0$). Representative measurements of the contact angle (θ_{12}) for all the systems in Table 1 revealed that θ_{12} is less than ten degrees; hence, θ_{12} has been assumed to be zero in Eq. 5 for computing the interfacial tensions.

Table 1 presents the results for the interfacial tensions. The sample standard deviations are less than 0.5 mN/m (typically around 2% of the mean); thus, the data are very reproducible. The accuracy of the cathetometer used is 0.01 mm. The in-

cleaning solution mixed with water and allowed to stand overnight. They are then cleaned and rinsed with distilled water. This is followed by rinsing with acetone, methanol and distilled water, in that order. Finally, they are dried in a vacuum oven at 120°C for an hour.

The capillary tube is first dipped into liquid 1 and then into liquid 2 to establish liquid 1/air and liquid 1/liquid 2 interfaces within it. To ensure that the interfaces are in equilibrium locations and the capillary tube is wetted by the liquids, a small suction followed by a release to atmospheric pressure is applied a few times to the top of the capillary. The equilibrium locations are stable and repeatable. The interfaces are established quite rapidly (a few minutes maximum) using the present method. The various heights needed for the measurement of σ_{1a} and σ_{12} are obtained using a cathetometer. Typical heights are on the order of 3 to 15 mm, and the cathetometer resolution is 0.01 mm. A stereo microscope is used to measure the di-

terfaces, however, appear thicker in the cathetometer field of view due to refraction effects; hence, placement of the cross-hairs has an inherent error. If we assume a worst-case error of 0.1 mm in measuring liquid heights in the capillary (typical heights are 3 to 15 mm), this would indicate a 2–3% cumulative error in the interfacial tension. Comparing the measured interfacial tensions with those in the literature, it is seen that for nonequal density liquids the agreement is good, with a maximum deviation of 9.3% for octanol/water and benzaldehyde/water interfaces. The experiments did indicate that benzaldehyde was very prone to coating the glassware with crystals; it is not clear whether this plays a role. The interfacial tensions for cyclohexane, carbontetrachloride and octanol with water are slightly lower than those in the literature (Donahue and Bartell, 1952; Girifalco and Good, 1957).

For equal-density liquids, the agreement of our data with the results of Karri and Mathur is much worse. The maximum deviation is 32% for benzonitrile/water interface. Karri and Mathur report the interfacial tension of 3-phenyl-1-propanol with water to be zero, while the measurements herein indicate the value to be around 7.9 mN/m. We found that the cleanliness of the tubes and experiment cells are crucial to measure the interfacial tensions with repeatability; hence, we strictly followed the cleaning procedure mentioned earlier. The liquids used are of ordinary purity and not high purity. Other than general laboratory precautions, no additional steps have been taken to ensure the purity of the liquids and the interfaces. Thus, as in all surface tension measurements, cleanliness remains as an issue. This perhaps plays a role in the deviations between the current measurements and the literature values. In view of large deviations, independent measurements are needed to confirm the accuracy of the interfacial tensions of the equal-density liquids in Table 1.

While the lowest interfacial tension measured with the combined capillary rise technique is reported to be around 3.4 mN/m in Table 1, lower values around 1 mN/m have also been measured for the neutral-density liquid pair comprising silicone oil and vegetable oil to measure $d\sigma/dT$ in the temperature range 20 to 50°C (Rashidnia and Balasubramaniam, 1991). Thus, it appears that the combined capillary rise technique can be used for a broad range of interfacial tensions. Additional testing is required to establish the accuracy of the method for a larger class of immiscible liquid pairs, especially of equal density.

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