Measurement of Interfacial Tension of Immiscible Liquids of Equal Density

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The use of two immiscible liquids of equal density offers the possibility of eliminating the buoyancy forces and thus simulating microgravity environment on earth. This technique can be used to study microgravity fluid physics such as:

1. Interfacial tension driven flows (Marangoni effect) on earth, for example, drop migration in a liquid matrix with temperature gradient
2. Two-phase (vapor-liquid) flow regimes (Karri and Mathur, 1987) likely to occur in microgravity

For the study of microgravity fluid physics, one of the most important liquid properties is the interfacial tension. In the absence of gravity force, interfacial forces play an important role in determining the thermocapillary flows driven by a temperature gradient and type of flow regimes in the case of two-phase flow. In order to use this technique, it is essential to know the interfacial tension between two immiscible liquids of equal density. The measurement of interfacial tension in such liquid systems is quite complex because of the absence of a liquid density difference. The equations used in the traditional interfacial tension measurement techniques such as the capillary height method (Reynolds, 1921), ring method (Zuidema and Waters, 1941), and drop weight method (Harkins and Humphrey, 1916), contain a density difference term and, therefore, become invalid as the density difference approaches zero. In short, since two equally dense liquids forming an interface represent a relatively gravity-free situation, these classical measurement techniques cannot be used, as they use the resultant gravity force at the interface giving rise to a density difference term in the final expression.

In this paper, we present a new approach that was originally developed by Bartell and Miller (1928) to measure the interfacial tension between two liquids of equal density. They used this method to measure the interfacial tension of dark liquids with water since they were unable to observe a falling drop in the dark liquid as required with the drop weight apparatus, or to delineate the meniscus once the capillary was wetted with the dark liquid as in the capillary rise method.

Principle of the Method

The simple device shown in Figure 1 is based on the capillary rise principle. The apparatus consists of two cups, *A* and *B*, connected by a U-shaped tube, one leg of which is a capillary tube. Liquid *b* is added to cup *B* until it reaches the end of the U-tube at the bottom of cup *A*. Liquid *a* is then added slowly from a buret to cup *A*, so that liquid *b* is forced back until the liquid meniscus enters the lower end of the capillary and finally stabilizes at some reference point *C*. The heights h_a and h_b of liquids *a* and *b*, respectively, above this reference point or meniscus, are measured using a cathetometer. The forces acting on the meniscus are:

Gravity force

$$F_g = \pi r^2 (\rho_a h_a - \rho_b h_b) g \tag{1}$$

where r = capillary radius, and ρ the corresponding densities (F_g is acting in the downward direction)

Vertical force due to interfacial tension

$$F_{int} = 2\pi r \gamma_{ab} \tag{2}$$

Equating Eqs. 3 and 4 for the mechanical equilibrium condition at the meniscus, one obtains:

$$\gamma_{ab} = 1/2\, gr (\rho_a h_a - \rho_b h_b) \tag{3}$$

It is noteworthy that the term $(\rho_a h_a - \rho_b h_b)$, which contains the difference between the products of corresponding density and height, does not approach zero even for equal-density liquids. This method is general and therefore can be used to measure the interfacial tension of any combination of two immiscible liquids irrespective of their densities.

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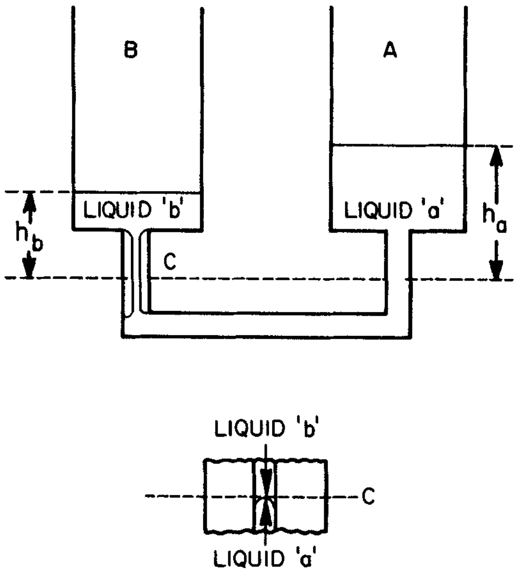

Figure 1. Apparatus for interfacial tension measurement of equal density fluids.

Apparatus and Measurement

The apparatus shown in Figure 1 is constructed with Pyrex glass. The two cups, *A* and *B*, are about 0.022 m ID and 0.12 m in height. These are connected by U-type glass tubing, one arm of which is a capillary tube of approximately 0.75 mm radius. The diameter of the capillary is determined from the weight difference between capillary tube filled when with mercury and when empty.

For constant temperature conditions, the apparatus is immersed in a constant-temperature water bath with plane glass sides for visibility and recording. For the determination of interfacial tension, liquid *b* (organic liquid or oil) is slowly added to the cup *B* until it fills just below the top of the U-tube in the bottom of cup *B*. It is important to ascertain that there are no air bubbles caught along the wall of the U-tube including the capillary. Liquid *a* (water) is then slowly added from a buret to cup *A* until the meniscus or interface is forced downward along the U-tube and stabilizes in the capillary at some reference point *C*. The height of each liquid above this reference point is then readily measured by means of a cathetometer.

The density of liquid *b* is measured using a specific-gravity bottle. Knowing the densities and heights, the interfacial tension can readily be calculated using Eq. 3.

Experimental Results

Several liquid systems of unequal densities with known interfacial tension were used for calibration of the apparatus. The results, presented in Table 1, are within acceptable accuracy. The chemicals used were of analytical grade purity. The use of high-purity chemicals may have reduced the percent error. For ordinary accuracy requirements, no capillary corrections for meniscus height readings are necessary, as indicated by Bartell and Miller (1928).

This apparatus has been used to measure the interfacial tension of eleven different systems of approximately equal densities. Water was used as liquid *a* throughout the experiments. Liquids *b* used in the experiments were either pure organic liquids or oils. In the cases of heavy mineral oil and silicone oil, a small amount of carbon tetrachloride was added to adjust the density. All *b* liquids had densities almost equal to that of water. The temperature of the apparatus was maintained at 25°C. The apparatus was cleaned with acetone followed by washing with NOCHROMIX solution. The washed apparatus was rinsed with distilled water and dried overnight at about 110°C. Table 2 presents the experimental results for eleven different liquid systems. Densities and interfacial tensions are also listed.

Table 1. Interfacial Tension of Various Systems of Unequal Densities at 25°C

System	Density of Organic Liquid kg/m^3	Interfacial Tension, N/m		Error
		Measured	Literature	
Aniline -Water	1,022	0.00541	0.00577	−6.3
Benzaldehyde -Water	1,050	0.01478	0.01551	−4.7
Carbon tetrachloride-water	1,583	0.0443	0.045	1.6

The liquid systems were so selected that the measured interfacial tension would cover a wide range of values. In the case of the 3-phenyl-1-naphthyl amine and water system, the densities are almost equal and the measured heights were about the same, giving an interfacial tension of about 0 N/m. The highest interfacial tension, of about 0.047 N/m, was obtained for the liquid system of Dow Corning 200 silicone fluid (50 cSt at 25°C) (+CCl_4) and water. The apparatus is sensitive enough to measure interfacial tension ranging from 0 to 0.05 N/m. From Table 1, the accuracy of this method is within ±6% error for liquids of unequal densities. Since the interfacial tension of liquid systems of equal density is unknown, it is anticipated that the accuracy of this instrument would be within ±10% error.

This device can be used to measure the interfacial tension as a

Table 2. Interfacial Tension of Various Systems of Equal Densities at 25°C

System	Density of Organic Liquid Oil kg/m^3	Interfacial Tension N/m
Amyl benzoate-water	988	0.033
Anisole-water	993	0.035
Benzonitrile-water	1,002	0.028
Butyl benzoate-water	1,002	0.034
Diethyl adipate-water	1,004	0.018
Diethyl Dimethylmalonate-water	1,018	0.019
n,n-Diethyl-1-naphthyl amine–water	1,075	0.016
3-Phenyl-1-propanol–water	998	0
Polypropylene glycol-2000–Water	1,003	0.005
Heavy mineral oil (+CCl_4)-water	998	0.031
Silicone oil (+CCl_4)-water	998	0.047

function of temperature for two liquids exhibiting equal or unequal density. This can be achieved by immersing the apparatus in a constant-temperature water bath, maintaining the temperature at any desired value.

Notation

a, b = subscripts denoting liquid a, b
F_g = gravity force, N
F_{int} = interfacial force, N
g = acceleration due to gravity, m/s^2
h = height of liquid from a reference point, m
r = capillary radius, m
ρ = density of liquid, kg/m^3
γ_{ab} = interfacial tension between two liquids, N/m

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