Experiment 446.1

SURFACE TENSION OF LIQUIDS

Theory

To create a surface requires work that changes the Gibbs energy of a thermodynamic system.

$$dG = -SdT + VdP + \gamma dA \qquad (1.1)$$

where γ is the surface tension, the free energy per unit surface area. Since a surface always involves two phases, the surface tension depends on the nature of the two substances between which the surface is formed. If surface segregation of material occurs in a solution, then the surface tension of the solution may depend on concentration in complex ways. Like other thermodynamic variables, surface tension depends on conditions such as the temperature. Eq. (1.1), for example, shows that the temperature derivative of γ is given by the following Maxwell equation:

$$\left(\frac{\partial \gamma}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial A}\right)_T \qquad (1.2)$$

where the derivative on the right is known as the surface entropy. One can evaluate the surface entropy by investigating the manner in which the surface tension varies with temperature.

Reports of surface tension are often given for the situation in which the second phase is air or the vapor of the material. Thus, for example, at 20°C, the reported surface tension of benzene against air is 28.85 dyne/cm, whereas the reported surface tension of benzene against its vapor is reported to be 28.89 dyne/cm. In Table 1.1 are data on the surface tension of water against air. Surface tensions for liquids against liquids are called **interfacial tensions**. Such interfacial tensions can be very different from the surface tensions of liquids against air. For example, the interfacial tension of water against benzene is 35 dyne/cm at 20°C, whereas its value against air is 73.05 dyne/cm, and that of benzene against air is 28.85 dyne/cm.

Surface tension produces several observable phenomena. The rise of a liquid in a capillary is the result of surface tension. The spreading of a film of oil on water is another example of the effect of surface tension, something first reported by Benjamin Franklin, although it probably was known in antiquity.

Consider the simple situation depicted in Fig. 1.1, in which the end of a capillary tube of radius, *r*, is immersed in a liquid. For sufficiently small capillaries, one observes a substantial rise of liquid to height, *h*, in the capillary, because of the force exerted on the liquid due to surface tension. Equilibrium occurs when the force of gravity balances this force due to surface tension. The balance point can be used as a means to measure the surface tension:

$$\gamma(2\pi r) = \rho\, h\, (\pi r^2)\, g \qquad (1.3)$$

Table 1.1. Density and Surface Tension of Water Against Air at Various Temperatures[a]

Temperature (°C)	Density (gm/cm^3)	γ (dyne/cm)	Temperature (°C)	Density (gm/cm^3)	γ (dyne/cm)
0	0.99987	75.6	30	0.99567	71.18
5	0.99999	74.9	40	0.99224	69.56
10	0.99973	74.22	50	0.98807	67.91
15	0.99913	73.49	60	0.98324	66.18
18	0.99862	73.05	70	0.97781	64.4
20	0.99823	72.75	80	0.97183	62.6
25	0.99707	71.97	100	0.95838	58.9

[a] Source: R. C. Weast and M. J. Astle, Eds., CRC Handbook of Physics and Chemistry, 63rd Edition, CRC Press, Boca Raton, Florida, 1982.

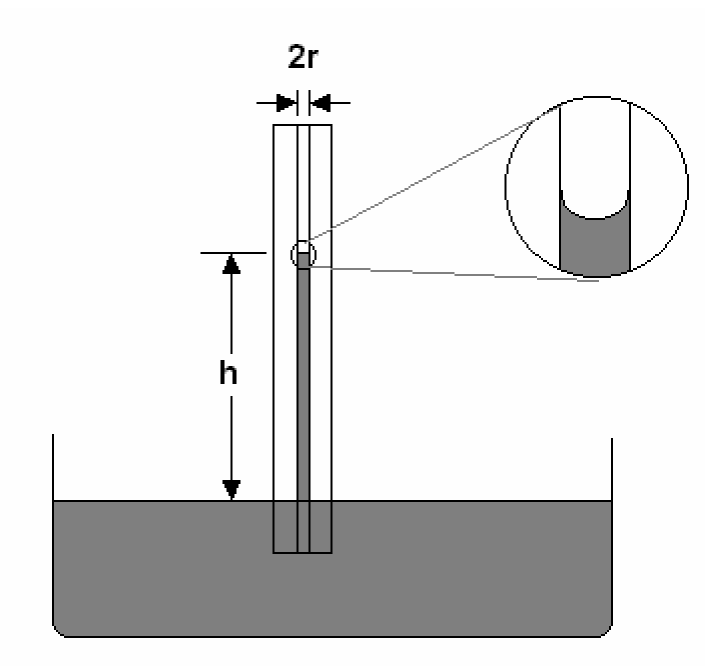

Figure 1.1. Capillary rise due to surface tension.

where r is the radius of the capillary, h is the capillary rise, ρ is the liquid density, g is the acceleration due to gravity[1], and γ is the surface tension of the liquid. Rearrangement gives a simple expression for the surface tension:

$$\gamma = \frac{1}{2}\rho g r h \qquad (1.4)$$

A careful look at the boundary shows that the surface is not perfectly flat. Instead it curves up (or sometimes down) at the wall to form a meniscus, as shown in the inset in Fig. 1.1. The material in this region also contributes to the force of gravity, so one often finds a correction to Eq. (1.4) to yield

$$\gamma = \frac{1}{2}\rho g r \left(h + \frac{r}{3}\right) \qquad (1.5)$$

where the contact angle (the angle between the surface of the liquid and surface of the glass) has been assumed to be 0°.

Procedure

In this experiment you determine the surface tension of liquids against air by the method of capillary rise. To get good results, you must pay attention to cleanliness and procedure. If the

[1] The standard acceleration due to gravity is defined by the International Committee on Weights and Measures to be 980.665 cm/sec^2. Where exceptional accuracy is required, the acceleration due to gravity (in cm/sec^2) at various places on the surface of the Earth can be found from Helmert's equation:

$$g = 980.616 - 2.5928 \cos(2\phi) + 0.0069 \cos^2(2\phi) - 3.086\times10^{-6} H,$$

where ϕ is the latitude and H is the elevation above sea level in centimeters.

capillary tube has not been cleaned recently, it should be soaked in hot nitric acid for several minutes, following by washing with deionized water. The capillary should be stored in the polyethylene bottle containing deionized water when not in use.

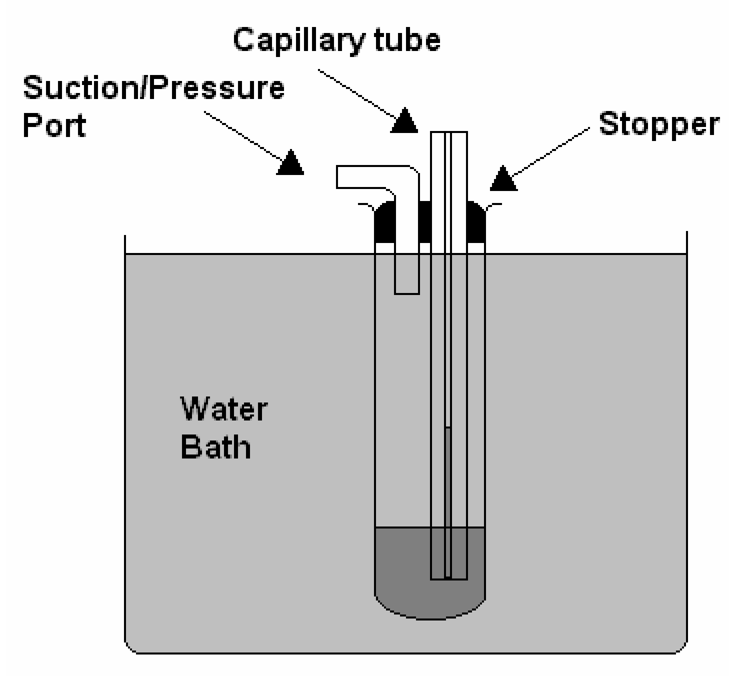

Figure 1.2. Schematic of the device for measuring capillary rise.

The apparatus is shown in Fig. 1.2. A test tube is fitted with a two-hole stopper. Through one hole is fitted the capillary tube (a length of a thermometer cut to expose the capillary at both ends). This is fitted through a glass sleeve and held in place by a piece of rubber tubing. In the second hole is a tube through which pressure or suction can be applied. This whole apparatus is immersed in a water bath to allow control of temperature. The water bath should be set initially at 25±1°C (if room conditions allow).

The measurement technique is straightforward. You use the cathetometer[2] to determine the rise above the level of the material in the test tube. Record the height of the liquid in the test tube and then the height of the liquid in the capillary; the difference of these is the capillary rise. Do this measurement at least four times on each sample. Each measurement should be made after the system is disturbed and allowed to return to equilibrium. Use the pressure/suction port or the top of the capillary to drive the system away from equilibrium in both directions. **You should raise and lower the liquid in the capillary several times (by means of the suction and pressure) before making the first reading** to ensure proper coating of the capillary walls. Be certain that the cathetometer is level and that the hair is set at the level of liquid in the test tube (and at the bottom of the meniscus for reading the height) in the capillary when making readings. Do not allow bubbles to form in the capillary, as this causes a substantial error in the reading of the capillary rise. Your result for each measurement will be an average of at least four evaluations for each sample at each temperture.

1. Calibration of the apparatus is done by determining the capillary rise of deionized water, for which the temperature-dependent surface tension is well known. Add enough water to the bottom of the test tube so that the bottom of the capillary can easily be immersed in it. Install the stopper with the capillary in it and clamp the whole setup so all parts of the apparatus containing water (including the water in the capillary) are immersed in the water bath. To bring water into the measurement vessel, open the two stopcocks on it

[2] A cathetometer is a devise for precisely determining height. It consists of a telescope with crosshairs mounted on a graduated bar. By moving the telescope up and down to line the cross hairs with the point to be measured, one can read the height very precisely. Ask the laboratory instructor for instruction in reading the scale and focusing the instrument.

simultaneously. You may have to adjust the amount of openness of the bottom stopcock to make the water level stable, so watch it carefully. Wait a few minutes to allow everything to come to a constant temperature. Record the temperature of the bath from the thermometer, as well as the levels.

Be careful with the water flow in the thermostatting bath. If the level rises, it will spill over onto the desk, making a mess. Adjust the bottom stopcock to create a steady level. You may have to change this as you change the temperature. When starting the flow, open BOTH stopcocks simultaneously. When shutting the system down, close BOTH stopcocks simultaneously.

2. Make measurements at a number of temperatures between 25 and 40°C. Change the bath temperature slowly between experiments, allowing time for equilibration.[3] Always allow time for thermal equilibration of the material before making a measurement. Measure the capillary rise of water and the alcohol assigned to you at each temperature, doing it first at a temperature near 25°C. [Check with the laboratory instructor after you have determined the capillary rise of water at that temperature before you continue.] It is important that, when adding a new material, you rinse the capillary thoroughly. That means you have to add fresh material and pull it into the capillary several times. Repeat this with three aliquots of material. After the third rinse, make a set of repeated measurements of the capillary rise.
3. After all measurements are made, rinse the capillary thoroughly with deionized water and replace it in the storage tank. The final state of the water bath should be near 25°C.

Table 1.2. Density of Alcohols at Various Temperatures (gm/cm^3)

Temperature (°C)	Methanol	Ethanol	Propanol
0	0.8100	0.8065	0.8193
10	0.8008	0.7979	
20	0.7915	0.7894	0.8035
30	0.7825	0.7810	
40	0.7740	0.7722	0.7875
50	0.7650	0.7633	
60	0.7555	0.7541	0.7700
70	0.7460	0.7446	
80	0.7355	0.7348	0.7520
90	0.7250	0.7251	0.7425
100	0.7140	0.7157	0.7325

Source: H. Landolt, R. Boernstein and W. Roth, *Physikalische-Chemische Tabellen*, Springer Verlag, Berlin, 1912, 5. Auflage.

[3] I advise you to make all measurements at a particular temperature before changing to another temperature; the water is used as a calibration. If you are measuring a particular alcohol at several temperatures, measure the water at each temperature as you go, rather than doing all of the water measurements at different temperatures first. This saves time because heating the water bath is the rate-limiting step.

Calculations

1. For each measurement on water and the alcohol, calculate the average and standard deviation of the capillary rise. It is convenient to report rises along with the associated error as a function of temperature for water and the alcohol in a table.
2. Use the results for water and its known surface tension to determine the effective radius of the capillary at each temperature with equation (1.4). [You should interpolate to obtain the density at the conditions appropriate to your measurements.]
3. Use Eq. (1.5) to estimate the radius of the capillary from the water data. Does this equation give a value that is measurably different from that by using equation (1.4)? Explain the answer. If it is different, then use Eq. (1.5) in the following calculations. If not, you may use equation (1.4) in what follows.
4. Using the known densities of water and the alcohol assigned to you, calculate the surface tension of the alcohol at the various temperatures with either Eq. (1.4) or (1.5), whichever is appropriate. Assume the known surface tension of water allows a calibration of the apparatus at each temperature. Be sure to report uncertainty.
5. From the data on the surface tension of the alcohol as a function of temperature, determine the surface entropy.
6. Determine the surface energy of the alcohol at each temperature at which you made a measurement.

Discussion Questions

1. Compare your data to literature data for the surface tension of the alcohol. [This means you have to spend some time in the library looking through books to find “old” measurements!]
2. Did you notice any effect of hysteresis in this apparatus? Explain your answer.
3. Does the surface entropy of your alcohol depend on temperature? Explain.
4. Describe changes you might make in the design of the experiment to make the measurement more precise. Explain your reasoning.
5. Is the surface tension of an alcohol higher or lower than that of water? Give a possible physical reason why this is so.
6. What is a contact angle? In this experiment, what contact angle does one have or assume? How will this assumption affect the results? Is it important?
7. Briefly describe (in one paragraph) other methods one might use to measure surface tension of a liquid against air.