

Physical Chemistry Laboratory (CHEM 336)

EXPT 6-2: Surface Tension

THEORY

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

$$dG = -SdT + VdP + \gamma dA \quad (1)$$

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.

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 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, 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:

Table 1. Density and Surface Tension of Water Against Air at Various Temperatures^a

Temperature (°C)	Density (gm/cm ³)	g (dyne/cm)	Temperature (°C)	Density (gm/cm ³)	g (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	72.72	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.

$$\gamma(2\pi r) = \rho h(\pi r^2)g \quad (2)$$

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, and γ is the surface tension of the liquid. Rearrangement gives a simple expression for the surface tension:

$$\gamma = \frac{1}{2} \rho g r h \quad (3)$$

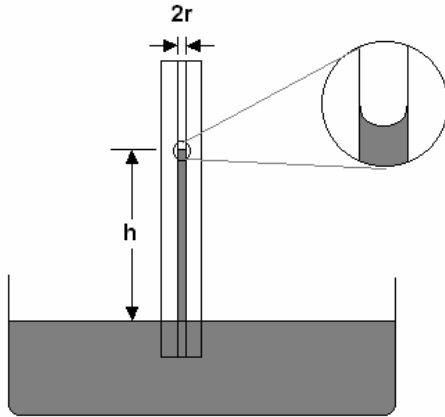


Figure 1. Capillary rise due to surface tension.

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. The material in this region also contributes to the force of gravity, so one often finds a correction to Eq. (3) to yield,

$$\gamma = \frac{1}{2} \rho g r \left(h + \frac{r}{3} \right) \quad (4)$$

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

The *surface concentration* of a solute, Γ , represents the excess of solute per unit area of the surface over what would be present if the internal (bulk) concentration prevailed all the way to the surface. For a perfect solute (solutions at low concentrations), Γ can be calculated from the following equation (see Garland et al, 7th Ed, pg. 295 for a derivation),

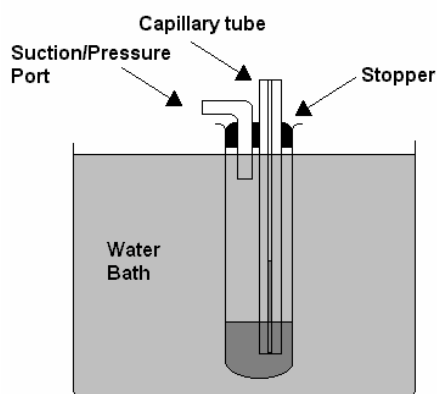
$$\Gamma = - \frac{1}{2.303RT} \frac{d\gamma}{d(\log c)} \quad (5)$$

where c is the concentration of all solute species.

Polar organic solutes have the ability to reduce the surface tension of water. Such solutes tend to accumulate at the surface and form unimolecular films of adsorbed molecules. A plot of the surface tension of the solution against the logarithm of the bulk concentration should be linear.

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 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.



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 $25 \pm 1^\circ\text{C}$ (if room conditions allow). The measurement technique is straightforward.

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. 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 temperature.

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.

2. Prepare a 250 ml stock solution of 0.8 M *n*-butanol and using the procedure above measure the capillary rise for this solution. Dilute precisely the stock solution to three quarters the concentration and repeat until eight concentrations have been used (i.e. 0.8, 0.6, 0.45, 0.34, 0.25, 0.19, 0.14, 0.11 M solutions). After all measurements are made, rinse the capillary thoroughly with deionized water and replace it in the storage tank.

CALCULATIONS

1. For each measurement on water and the alcohol, calculate the average and standard deviation of the capillary rise.
2. Use the results for water and its known surface tension to determine the effective radius of the capillary. [You should interpolate to obtain the density at the conditions appropriate to your measurements.]
3. Use Eq. 4 to estimate the radius of the capillary from the water data.
4. Calculate the surface tension of the butanol solutions using Eq. 4. Assume the densities of the solutions are the same as that for pure water.
5. Plot the surface tension of butanol solutions versus the logarithm of the bulk concentration c and determine the slope in order to calculate Γ (in units of mol cm⁻² or mol m⁻²) using Eq. 5.
6. Express the surface concentration in molecules per square Angstrom and obtain the “effective cross-sectional area” per molecule of adsorbed butanol in Å².

REFERENCES

Garland et al. Experiments in Physical Chemistry 7th Ed, pp 292-301