

Surface Tension

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2.1.1 Surface tension

- ◆ Surface tension is a fundamental property by which the gas–liquid interfaces are characterized. The zone between a gaseous phase and a liquid phase looks like a surface of zero thickness. The surface acts like a membrane under tension.
- ◆ Let us consider a liquid in contact with its vapor, as illustrated in Fig. 2.1.1.

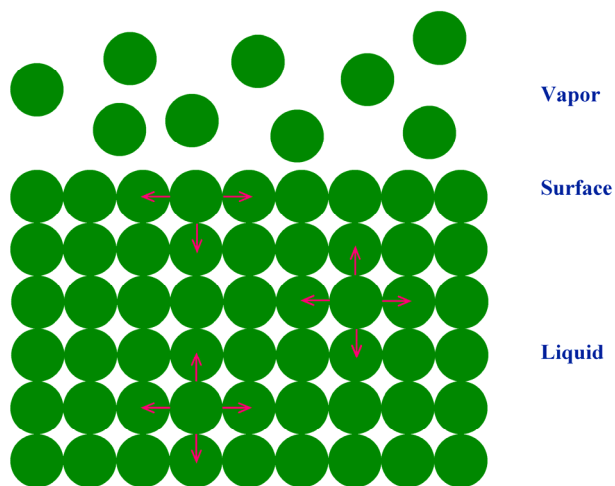


Fig. 2.1.1 Origin of surface tension.

- ◆ A molecule in the bulk liquid is subjected to attractive forces from all directions by the surrounding molecules. It is practically in a uniform field of force. But for the molecule at the surface of the liquid, the net attraction towards the bulk of the liquid is much greater than the attraction towards the vapor phase, because the molecules in the vapor phase are more widely dispersed.
- ◆ This indicates that the molecules at the surface are pulled inwards. This causes the liquid surfaces to contract to minimum areas, which should be compatible with the total mass of the liquid. The droplets of liquids or gas bubbles assume spherical shape, because for a given volume, the sphere has the least surface area.
- ◆ If the area of the surface is to be extended, one has to bring more molecules from the bulk of the liquid to its surface. This requires expenditure of some energy because work has to be done in bringing the molecules from the bulk against the inward attractive forces. The amount of work done in increasing the area by unity is known as the *surface energy*. If the molecules of a liquid exert large force of

attraction, the inward pull will be large. Therefore, the amount of work done will be large.

- ◆ Surface energy is the amount of work done per unit area extended. Its unit is J/m^2 (which is equivalent to N/m). For example, the amount of work required to create 1 m^2 surface is about $72.8 \times 10^{-3} \text{ J}$ for water.
- ◆ Surface tension is defined as the force at right angle to any line of unit length in the surface. Therefore, surface tension = force/distance. It is expressed in N/m .
- ◆ Therefore, it is apparent that the units of surface energy and surface tension are identical. Surface energy can be determined by measuring the surface tension.

Exercise 2.1.1: Explain why the drops of a liquid or gas bubbles tend to assume spherical shape.

Solution: Among all three dimensional bodies with a given surface area, the sphere has the largest volume. In other words, for a given volume, the area will be minimal when the body has spherical shape. It can easily be proved from the isoperimetric inequality, according to which,

$$A^3 \geq 36\pi V^2$$

where A is the surface area and V is the volume. The least surface area for a certain volume will be obtained when the equality condition is satisfied, which applies if the body is a sphere.

A detailed proof of the above conclusion is available in the reference: P. Ghosh, *Colloid and Interface Science*, PHI Learning, New Delhi, 2009, pp. 97–100. The details of isoperimetric inequality are available in the reference: R. Osserman, “The Isoperimetric Inequality”, *Bull. Am. Math. Soc.*, **84**, 1182, 1978.

2.1.2 Equivalence between surface tension and surface energy

- ◆ The natural tendency of the surface of a liquid is to contract to minimize the surface area. Therefore, if we attempt to increase the area, work will be required.

- ◆ Consider a thin film of liquid, $ABCD$, contained in a rectangular wire-frame, as shown in Fig. 2.1.2.

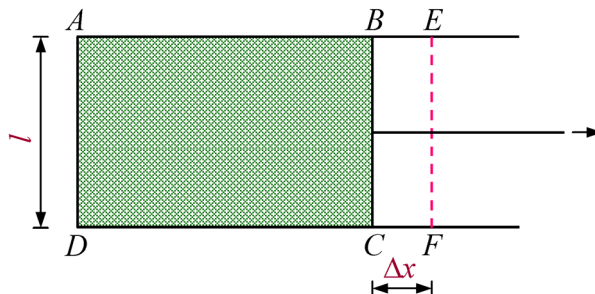


Fig. 2.1.2 Illustration of the work done in increasing the surface area.

- ◆ The boundary BC (length = l) is movable. Imagine now that the film is stretched by moving the boundary BC by Δx to the new position EF . If γ be the surface tension, the force acting on the film is $2\gamma l$, because the film has two surfaces. The work done in stretching the film is,

$$W = 2\gamma l \Delta x = \gamma \Delta A \quad (2.1.1)$$

where $\Delta A = 2l\Delta x$ is the change in total area on the two sides of the film. Therefore,

$$\gamma = \frac{W}{\Delta A} \quad (2.1.2)$$

This depicts the equivalence between surface tension and surface energy.

2.1.3 Surface tension of liquids

Surface tension of some liquids at 293 K is presented in Table 2.1.1.

Table 2.1.1 Surface tension of liquids

Substance	Surface Tension (mN/m)	Substance	Surface Tension (mN/m)
Acetic acid	27.4	Mercury	476.0
Acetone	23.3	Methyl acetate	24.8
Aniline	42.9	Methyl alcohol	22.6

Benzaldehyde	40.0	Methyl ethyl ketone	25.1
Benzene	28.9	<i>m</i> -Xylene	28.9
Bromobenzene	36.5	<i>n</i> -Butyl alcohol	24.5
Bromoform	41.5	<i>n</i> -Decane	23.9
Carbon disulfide	32.3	<i>n</i> -Heptane	20.4
Carbon tetrachloride	26.8	<i>n</i> -Hexane	18.4
Chlorobenzene	33.3	Nitrobenzene	43.4
Chloroform	27.2	<i>n</i> -Octane	21.8
Cyclohexane	25.5	<i>n</i> -Pentane	16.0
Cyclohexanol	32.7	<i>n</i> -Propyl alcohol	23.8
Dichloromethane	26.5	<i>o</i> -Nitrotoluene	41.5
Ethyl acetate	23.8	<i>o</i> -Xylene	30.0
Ethyl alcohol	22.3	<i>p</i> -Xylene	28.3
Ethyl mercaptan	23.2	Toluene	28.5
Iodobenzene	39.7	Water	72.8

2.1.4 Calculation of surface tension

2.1.4.1 Parachor method

- ◆ Sugden (1924) proposed the following equation to calculate surface tension from the physical properties of the compound.

$$\gamma = \left[\frac{\wp (\rho_l - \rho_v)}{M} \right]^4 \quad (2.1.3)$$

where ρ_l and ρ_v are the densities of the liquid and vapor, respectively, and M is the molecular weight. $\wp$ is known as *parachor*, which means *comparative volume*.

- ◆ If we neglect the density of vapor in comparison with the density of the liquid, we have, $\wp = \bar{v}_l \gamma^{1/4}$, where $\bar{v}_l$ is the molar volume of the liquid.
- ◆ A comparison of the parachors of different liquids is equivalent to the comparison of their molar volumes under the condition of equal surface tension.

- ◆ ϕ is a weak function of temperature for a variety of liquids over wide ranges of temperature, and generally assumed to be a constant. Additive procedures exist for calculating ϕ .
- ◆ Equation (2.1.3) suggests that surface tension is very sensitive to the value of parachor and the liquid density. The structural contributions for calculating ϕ are given in Table 2.1.2. The total value of ϕ for a compound is the summation of the values of the structural units.

Table 2.1.2 Structural contributions for calculating the parachor

Structural unit	$\phi \times 10^6$	Structural unit	$\phi \times 10^6$
C	1.600	R-[CO]-R', R + R' = 2	9.123
H	2.756	R-[CO]-R', R + R' = 3	8.714
CH ₃	9.869	R-[CO]-R', R + R' = 4	8.447
CH ₂ in -(CH ₂) _n , n < 12	7.113	R-[CO]-R', R + R' = 5	8.233
CH ₂ in -(CH ₂) _n , n > 12	7.166	R-[CO]-R', R + R' = 6	8.056
1-Methylethyl	23.704	R-[CO]-R', R + R' = 7	7.842
1-Methylpropyl	30.569	-CHO	11.737
1-Methylbutyl	37.646	O (not mentioned above)	3.557
2-Methylpropyl	30.818	N (not mentioned above)	3.112
1-Ethylpropyl	37.255	S	8.731
1,1-Dimethylethyl	30.302	P	7.202
1,1-Dimethylpropyl	36.899	F	4.641
1,2-Dimethylpropyl	36.970	Cl	9.816
1,1,2-Trimethylpropyl	43.301	Br	12.092
C ₆ H ₅	33.716	I	16.058
-COO-	11.345	Double bond, terminal	3.397
-COOH	13.124	Double bond in 2,3-position	3.148
-OH	5.299	Double bond in 3,4-position	2.899
-NH ₂	7.558	Triple bond	7.220

–O–	3.557	3-membered ring	2.134
–NO ₂	13.159	4-membered ring	1.067
–NO ₃	16.538	5-membered ring	0.533
–CONH ₂	16.307	6-membered ring	0.142

Note: The unit of $\wp$ in this table is in $\text{kg}^{1/4} \text{m}^3 \text{s}^{-1/2} \text{mol}^{-1}$.

Example 2.1.1: Estimate the surface tension of ethyl alcohol at 298 K using the parachor data. Given: the density of ethanol is 800 kg/m^3 .

Solution: The surface tension is given by,

$$\gamma = \left(\frac{\wp \rho_L}{M} \right)^4$$

For ethyl alcohol: $\text{CH}_3\text{CH}_2\text{OH}$, $\wp = (9.869 + 7.113 + 5.299) \times 10^{-6} = 22.281 \times 10^{-6}$

$$\therefore \gamma = \left(\frac{22.281 \times 10^{-6} \times 800}{0.046} \right)^4 = 0.0225 \text{ N/m} = 22.5 \text{ mN/m}$$

This value is very close to the experimental value at 293 K, i.e., 22.3 N/m.

2.1.4.2 Effect of temperature on surface tension

- ◆ The surface tension of most liquids decreases with increasing temperature. Since the forces of attraction between the molecules of a liquid decrease with increasing temperature, the surface tension decreases with increasing temperature.
- ◆ One of the classical equations correlating the surface tension and temperature is the Eötvös–Ramsay–Shields equation,

$$\gamma(\bar{v}_l)^{2/3} = k_e(T_c - T - 6) \quad (2.1.4)$$

where $\bar{v}_l$ is the molar volume of the liquid, T_c is the critical temperature and k_e is a constant. For non-associated liquids, the value of k_e is 2.12, and for associated liquids, its value is less than this value.

- ◆ According to this equation, the surface tension will become zero at a temperature six degrees below the critical temperature, which has been observed

experimentally. Theoretically, the value of surface tension should become zero at the critical temperature, since at this temperature, the surface of separation between a liquid and its vapor disappears. However, it has been observed that the meniscus disappears a few degrees below the critical temperature for some liquids.

- ◆ The Brock–Bird correlation relates surface tension to the critical properties of the liquid by the relationship,

$$\gamma = P_c^{2/3} T_c^{1/3} Q (1 - T_r)^{11/9} \quad (2.1.5)$$

where Q is given by,

$$Q = 5.55134 \times 10^{-8} \left[1 + \frac{(T_b/T_c) \ln(P_c/101325)}{1 - T_b/T_c} \right] - 1.295 \times 10^{-7} \quad (2.1.6)$$

where T_b is the normal boiling point of the liquid, P_c is the critical pressure and T_r is the reduced temperature.

- ◆ The quantity $\gamma P_c^{-2/3} T_c^{-1/3} k^{-1/3}$ (where k is Boltzmann's constant) is dimensionless. It was suggested by van der Waals that this group may be correlated with the quantity, $(1 - T_r)$. This method of estimation of surface tension is also known as *corresponding states method*.
- ◆ The Brock–Bird method is not suitable for liquids which exhibit strong hydrogen bonding (such as alcohols and acids). Sastri and Rao (1995) have presented the following correlations for surface tension of such liquids.
- ◆ For alcohols, they proposed,

$$\gamma = 1.282 \times 10^{-4} P_c^{0.25} T_b^{0.175} \left(\frac{1 - T/T_c}{1 - T_b/T_c} \right)^{0.8} \quad (2.1.7)$$

- ◆ For acids, the Sastri–Rao correlation is,

$$\gamma = 3.9529 \times 10^{-7} P_c^{0.5} T_b^{-1.5} T_c^{1.85} \left(\frac{1 - T/T_c}{1 - T_b/T_c} \right)^{11/9} \quad (2.1.8)$$

- ◆ For any other type of liquid, the following correlation was suggested by them.

$$\gamma = 4.9964 \times 10^{-7} P_c^{0.5} T_b^{-1.5} T_c^{1.85} \left(\frac{1 - T/T_c}{1 - T_b/T_c} \right)^{11/9} \quad (2.1.9)$$

Example 2.1.2: Estimate the surface tension of acetic acid at 293 K using Brock–Bird and Sastri–Rao correlations. Given: $T_c = 591.95$ K, $P_c = 5.74 \times 10^6$ Pa and $T_b = 391.1$ K. The experimental value of surface tension of acetic acid is 0.0274 N/m.

Solution: From Brock–Bird correlation:

$$Q = 5.55134 \times 10^{-8} \left[1 + \frac{(391.1/591.95) \ln(5.74 \times 10^6 / 101325)}{1 - 391.1/591.95} \right] - 1.295 \times 10^{-7} = 3.6239 \times 10^{-7}$$

$$\gamma = (5.74 \times 10^6)^{2/3} (591.95)^{1/3} Q (1 - 293/591.95)^{11/9} = 0.0423 \text{ N/m}$$

From Sastri–Rao correlation:

$$\begin{aligned} \gamma &= 3.9529 \times 10^{-7} (5.74 \times 10^6)^{0.5} (391.1)^{-1.5} (591.95)^{1.85} \left(\frac{1 - 293/591.95}{1 - 391.1/591.95} \right)^{11/9} \text{ N/m} \\ &= 0.0268 \text{ N/m} \end{aligned}$$

- ♦ Estimation of surface tension using the parachor data usually gives good results. Its simplicity makes it a popular method for calculating surface tension. Escobedo and Mansoori (1996) have suggested that $\wp$ is a function of temperature. They proposed the following temperature-dependence for $\wp$.

$$\wp = \wp_0 f(T_r), \quad T_r = T/T_c \quad (2.1.10)$$

where $\wp_0$ is independent of temperature, but depends on the physical properties of the compound, such as its critical temperature, pressure, normal boiling point and molar refraction.

2.1.5 Measurement of surface tension

- ◆ The surface tension of liquid can be experimentally measured by several methods. The drop-weight method, du Noüy ring method, Wilhelmy plate method and the maximum bubble pressure method are discussed in this module.

2.1.5.1 Drop-weight method

- ◆ In this method, a drop is allowed to form slowly at the end of a tube having a fine capillary inside it. Then it is slowly released and collected in a container. Several drops (e.g., 100 drops, at the rate of one drop in about 200 s) are collected in the same manner and the weight of the liquid is measured. From this weight, the average weight of a drop is calculated.
- ◆ The classical instrument for carrying out this measurement in the laboratory is *Stalagmometer*. Now days, computer-controlled instruments can form precise drops.
- ◆ The principle behind the drop-weight method is as follows. As the size of the drop at the tip of the tube grows, its weight goes on increasing. It remains attached to the tube due to surface tension, which acts around the circumference of the tube in the upward direction. When the downward force due to gravity acting on the drop becomes slightly greater than the surface tension force, the drop detaches from the tube. Therefore,

$$\text{Upward force} = 2\pi r_o \gamma \quad (2.1.11)$$

$$\text{Downward force} = mg \quad (2.1.12)$$

where r_o is the outer radius of the tip of the tube.

- ◆ At the point of detachment,

$$mg = 2\pi r_o \gamma \quad (2.1.13)$$

Equation (2.1.13) is known *Tate's law*.

- ◆ The use of this equation requires the value of r_o . To avoid this, a relative method is usually used. A liquid whose surface tension is known is used as a *reference liquid*. Highly-purified water or an ultrapure organic liquid may be used for this purpose. The surface tension is calculated from the following equation.

$$\gamma = \left(\frac{m}{m_{\text{ref}}} \right) \gamma_{\text{ref}} \quad (2.1.14)$$

where γ_{ref} is the surface tension of the reference liquid, and the weight of a drop of this liquid is m_{ref} .

- ◆ When Eq. (2.1.13) is used to measure surface tension, corrections need to be applied because only a portion of the drop (the larger portion) falls from the tube. A significant amount of liquid (up to 40%) may remain attached to the tip of the tube. A correction factor, χ , known as *Harkins–Brown factor*, is used to correct the surface tension obtained from Eq. (2.1.13).

$$\gamma = \frac{\chi mg}{2\pi r_o} \quad (2.1.15)$$

where χ is a function of $r_o/V^{1/3}$ (V = volume of the drop), which has been verified experimentally using different liquids and tips of different radii.

- ◆ It has been found that χ does not depend upon the viscosity of the liquid. The variation of χ with $r_o/V^{1/3}$ is shown in Fig. 2.1.3.

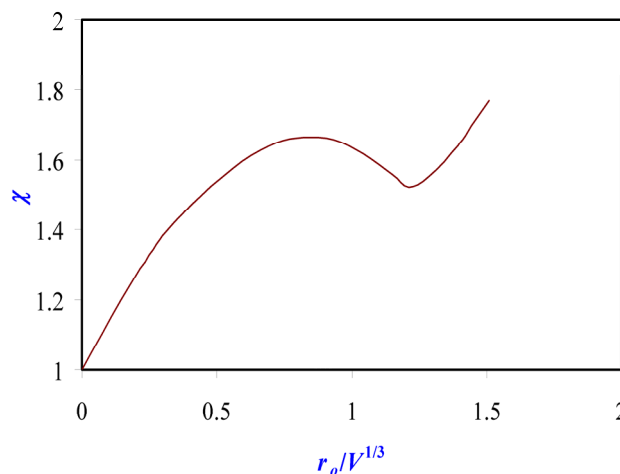


Fig. 2.1.3 Harkins–Brown correction.

- ◆ The radius of the tip should be chosen such that χ is least sensitive on the variation of $r_o/V^{1/3}$. The correction factor can be quite large. Since the value of V can differ from liquid to liquid, χ may differ from one liquid to another, even

when the same tip is used. Therefore, the ratio of correction factors in the relative method may not be unity.

Precautions:

- ◆ The liquid should either completely wet the tip or do not wet it at all. In the latter case, the internal radius of the tip should be used as r_o .
- ◆ The tip must be very clean. The presence of a very small amount surface active substance can cause significant error in the measurement.

2.1.5.2 du Noüy ring method

- ◆ This is one of the most widely-used methods for measuring the surface tension. It is named after the French physicist who developed it in the late 1800's.
- ◆ The advantage of the ring method is that it is rapid, very simple and does not need to be calibrated using solutions of known surface tension. When applied to pure liquids with due precautions, the error can be reduced to $\pm 0.25\%$.
- ◆ The measurement is performed by an instrument known as *Tensiometer*. This instrument has an accurate micro-balance and a precise mechanism to vertically move the sample liquid in a glass beaker. The modern tensiometer has a computer-controlled arrangement that can move the table holding the liquid very slowly ($\sim 100 \mu\text{m/s}$). The procedure is illustrated in Fig. 2.1.4.
- ◆ The ring is usually made of an alloy of platinum and iridium with well-defined geometry. The measurement procedure is as follows. The ring hanging from the hook of the balance is first immersed into the liquid and then carefully pulled up by lowering the sample vessel.

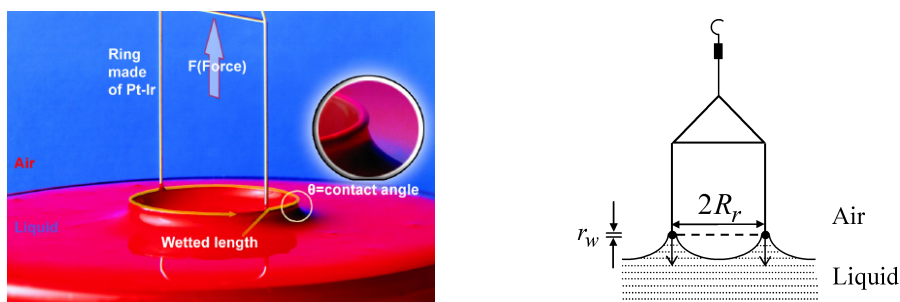


Fig. 2.1.4 The du Noüy ring method for measuring surface tension.

- ◆ The micro-balance continuously records the force applied on the ring when it pulls through the air–liquid interface. The surface tension is the maximum force needed to detach the ring from the liquid surface. The detachment force is equal to the surface tension multiplied by the periphery of the surface detached. Therefore, for a ring,

$$F = 4\pi R_r \gamma \quad (2.1.16)$$

where R_r is the radius of the ring. The force measured by the balance includes the weight of the ring. In actual practice, the weight of the ring is first recorded before it is immersed in the liquid. Sometimes, a calibration is made with a known weight.

- ◆ Usually the results obtained from Eq. (2.1.16) are in error. Harkins and Jordan (1930) derived a correction factor f such that the correct surface tension can be obtained from the following equation.

$$\gamma = \left(\frac{F}{4\pi R_r} \right) f \quad (2.1.17)$$

The correction factor appears due to the weight of the liquid film immediately beneath the ring, which is also raised when the ring pulls.

- ◆ The correction factor depends upon the complex shape of the meniscus during the detachment of the ring, density of the liquid, radius of the ring (R_r) and the radius of the wire (r_w) with which the ring is made.

- ◆ Huh and Mason (1975) have graphically presented the variation of f with R_r^3/V and R_r/r_w .
- ◆ The correlation given by Zuidema and Waters (1941) for f is given below.

$$f = 0.725 + \left[\frac{0.00363\gamma_{\text{Expt}}}{\pi^2 R_r^2 \Delta\rho} + 0.04534 - 1.679 \left(\frac{r_w}{R_r} \right) \right]^{1/2} \quad (2.1.18)$$

In Eq. (2.1.18), the radii R_r and r_w are expressed in cm, $\Delta\rho$ is expressed in kg/dm^3 and γ_{Expt} (the experimentally measured value of surface tension) is expressed in mN/m. The Zuidema–Waters correlation gives accurate results when $\gamma_{\text{Expt}} < 35 \text{ mN/m}$ and $\Delta\rho > 0.1 \text{ kg/dm}^3$.

- ◆ Both Huh–Mason and Zuidema–Waters corrections are used by the tensiometer manufacturers.

Precautions:

- ◆ Equations (2.1.17) and (2.1.18) assume that the contact angle (θ) is zero, i.e., the liquid should completely wet the ring. To ensure this, the platinum–iridium ring is cleaned by burning it in a Bunsen burner.
- ◆ The ring is quite delicate and prone to distortion during use. Such distortions should be avoided, and it must be ensured that the ring lies flat on a quiescent surface.
- ◆ When used with the surfactant solutions, the ring must be cleaned thoroughly with pure water since the presence of small amounts of surfactant can cause a significant amount of error in the measurement. If the ring is used with viscous oils such as silicone oil or crude petroleum, it must be cleaned with a good solvent (such as acetone) to dissolve and remove the oil.

2.1.5.3 Wilhelmy plate method

- ◆ This method is named after the German chemist Ludwig Wilhelmy. It is similar to the du Noüy ring method. However, it is simpler and does not require the correction.
- ◆ In this method, a thin plate (usually made of platinum and iridium) is used. It is dipped into the liquid whose surface tension is to be measured, as shown in Fig. 2.1.5. The vessel containing the liquid is gradually lowered and the force measured by the balance at the point of detachment (F) is noted.

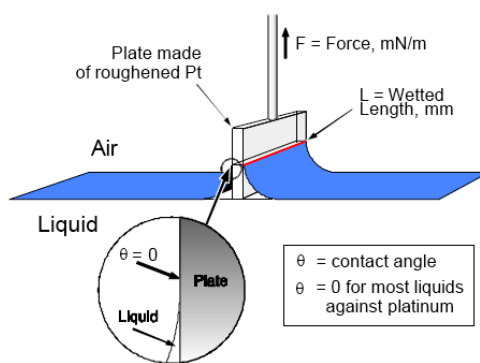


Fig. 2.1.5 Wilhelmy plate method for measuring surface tension.

- ◆ The Wilhelmy plate is sometimes used in another way. In this approach, the liquid level is raised until it just touches the hanging plate. The force recorded on the balance is noted.
- ◆ The Wilhelmy equation is,

$$\gamma = \frac{F}{P \cos \theta} \quad (2.1.19)$$

where P is the wetted perimeter of the plate, and θ is the contact angle.

- ◆ The contact angle is reduced to near-zero values (so that the liquid wets the plate completely) by cleaning the plate by burning it in the flame of Bunsen burner before each experiment. If the contact angle is close to zero, Eq. (2.1.19) simplifies to, $\gamma = F/P$.

- ◆ The Wilhelmy plate method does not need any correction because the weight of the film hanging from the plate is negligibly small.

2.1.5.4 Advantages and disadvantages of du Noüy ring and Wilhelmy plate methods

- ◆ Historically, the ring method has been used widely for measuring surface tension. The ASTM Standard D1331-89 (2001) employs the ring method.
- ◆ The ring method has three main problems associated with it. The first two problems are the need for correction, and tendency to deform during use.
- ◆ The third problem arises in surfactant solutions. The ring is designed for keeping the surface in a non-equilibrium state. When the ring is pulled through the surface, it expands the surface searching for the maximum force in the liquid meniscus. Therefore, the measurement of surface tension is performed on a surface that is in a non-equilibrium state.
- ◆ If the surface tension of a pure liquid is being measured, it does not affect the results. However, for surfactant solutions, the expansion of the surface affects the orientation of the surfactant molecules at the surface, and therefore may be inaccurate. The measured surface tension of surfactant solutions can vary with the speed at which the ring is pulled. This is due to the fact that the surfactant molecules require time to orient properly and adsorb at the surface. This time varies from surfactant to surfactant. This problem can be minimized by applying a very slow speed of pulling the ring. However, the measured surface tension is likely to be different from the equilibrium value.
- ◆ The plate method measures equilibrium surface tension. It does not require the correction for the meniscus. It can be placed right at the surface of the liquid and not moved while the surface tension is measured. Therefore, the surfactants are given sufficiently long time to reach the equilibrium state. For this advantage, the plate method often gives superior accuracy in the measurement.

2.1.5.5 Maximum bubble-pressure method (MBPM)

- ◆ The Wilhelmy plate method gives the equilibrium (static) surface tension.
- ◆ Surfactant solutions require a significantly higher amount of time than the pure liquids to achieve this equilibrium.
- ◆ The surface tension of the surfactant solution decreases with time. An example is shown in Fig. 2.1.6.

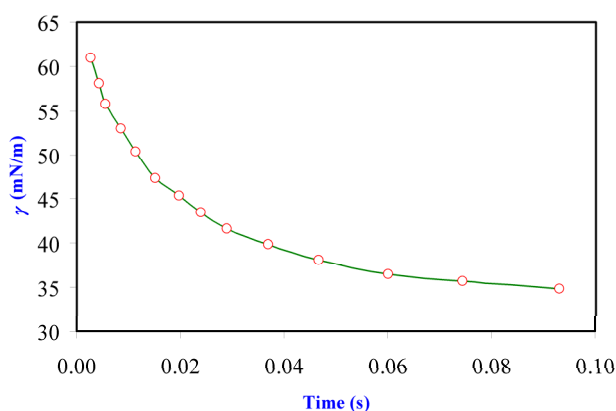


Fig. 2.1.6 Variation of surface tension of 1.6 mol/m³ aqueous Triton X-100 solution with time.

- ◆ In applications such as foaming, cleaning or coating, the interfaces are formed very quickly. For such applications, the dynamics of rapid formation of interface is important, which depends on the mobility of the surfactant molecules.
- ◆ The maximum bubble pressure method (MBPM) is an easy-to-use technique for measuring the dynamic surface tension (DST).
- ◆ In the MBPM method, the gas bubbles are produced in the sample liquid at an exactly-defined rate of generation. The bubble blown at the end of a capillary is stable, and expands with the increasing pressure of the gas in the bubble. The pressure reaches a maximum when the bubble is hemispherical and its radius is equal to the radius of the capillary. The procedure is illustrated in Fig. 2.1.7.

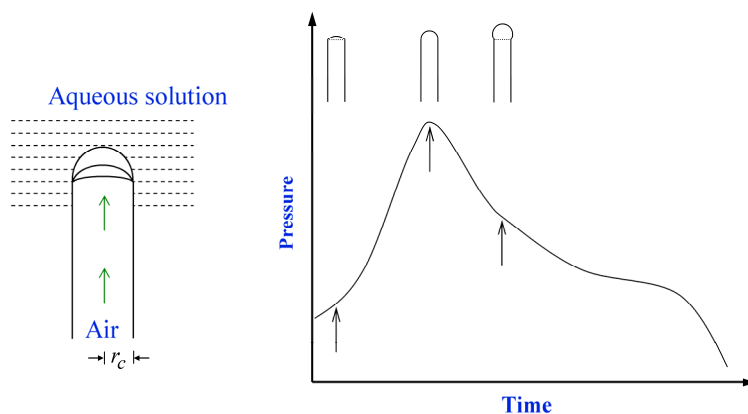


Fig. 2.1.7 Maximum bubble pressure method for measurement of dynamic surface tension.

- ◆ If the maximum pressure is $p_{\max}$ (whose value is recorded by the instrument), and the hydrostatic pressure is p_o , then the following equation gives the dynamic surface tension.

$$\gamma = \frac{(p_{\max} - p_o)r_c}{2} \quad (2.1.20)$$

where r_c is the inner radius of the capillary. After reaching the maximum, the pressure decreases, and the size of the bubble increases. As the size of the bubble becomes larger than a hemisphere, it becomes unstable because the equilibrium pressure within it decreases as it grows. Such a bubble expands further, escapes and rises through the liquid. The entire cycle of bubble formation, its growth and release is repeated.

- ◆ The growth of the bubble and its separation can be divided into two time periods. During the first period, the surfactant molecules adsorb on the surface of the bubble and the surface tension varies accordingly. This period is termed *surface lifetime*. The second period is the time in which the bubble grows rapidly and finally separates from the capillary. This period is termed *dead time*.
- ◆ Modern instruments use electronic sensors for measuring the pressure and the frequency of bubble formation. These instruments can record surface lifetime as

small as 0.001 s (which is important when the interface is formed very quickly). Therefore, the bubbles can be formed very rapidly by these instruments.

2.1.5.6 Applications of dynamic surface tension

- ◆ Flow in capillaries and porous media is affected by DST. This finds importance in enhanced oil recovery where aqueous foams are often used to increase the sweep-efficiency in carbon dioxide flooding.
- ◆ In bioprocessing systems, DST affects the rate of water-oxygenation by influencing the mass transfer coefficient.
- ◆ DST is also important in metal and textile processing, pulp and paper production, and pharmaceutical formulations.
- ◆ An important application of dynamic surface tension is for lung surfactants, where the dynamic tension under constant or pulsating area conditions controls the health and stability of the alveoli.
- ◆ In the formulation of pesticides, if the aqueous spray has a low DST, it can be dispersed into smaller droplets, which will spread more easily on the leaves. For these reasons, surfactants are used as pesticide spraying aids known as *adjuvants*.

Exercise

Exercise 2.1.1: Explain the shape of the waves shown in the following figure.



Such waves are created when a drop falls on a quiescent liquid surface (e.g., rain drops on a calm lake).

Exercise 2.1.2: Calculate the surface tensions of methyl alcohol and toluene at 293 K using the Brock–Bird and Sastri–Rao correlations. Collect the necessary data from a suitable source.

Exercise 2.1.3: It is desired to measure the surface tension of carbon tetrachloride by the drop-weight method, using high-purity water as the reference liquid. The weight of 100 water drops released from the stalagmometer is measured to be 85.4 g, and the same for carbon tetrachloride is 31.6 g. What is the surface tension of carbon tetrachloride? State any assumption that you need to make in performing this calculation.

Exercise 2.1.4: The interfacial tension between an aqueous surfactant solution and carbon tetrachloride, measured by a platinum–iridium du Noüy ring, is 32.5 mN/m. The diameter of the ring is 10 mm and the diameter of the wire of the ring is 0.3 mm. Compute the Zuidema–Waters correction factor.

Exercise 2.1.5: Answer the following questions clearly.

- Explain the origin of surface tension from a molecular viewpoint.
- What is the relationship between surface tension and surface energy?

- c. Explain why a drop or a bubble assumes spherical shape.
- d. How does the surface tension of a liquid vary with temperature?
- e. What is parachor?
- f. What is the major drawback of the Brock–Bird correlation?
- g. Explain why a correction factor is required in the drop-weight method.
- h. What precautions will you take to measure surface tension by drop-weight method?
- i. Explain how surface tension of a liquid is measured by the du Noüy ring method.
- j. Explain why a correction factor is required in the du Noüy ring method, but not in the Wilhelmy plate method.
- k. How will you ensure a near-zero contact angle while using the Wilhelmy plate for measuring surface tension?
- l. Discuss the advantages and disadvantages of the du Noüy ring and Wilhelmy plate methods.
- m. Explain the working principle of the maximum bubble pressure method.

Suggested reading

Textbooks

- ◆ A. W. Adamson and A. P. Gast, *Physical Chemistry of Surfaces*, John Wiley, New York, 1997, Chapter 2.
- ◆ J. C. Berg, *An Introduction to Interfaces and Colloids: The Bridge to Nanoscience*, World Scientific, Singapore, 2010, Chapter 2.
- ◆ P. Ghosh, *Colloid and Interface Science*, PHI Learning, New Delhi, 2009, Chapter 4.

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- ◆ J. Lyklema, *Fundamentals of Interface and Colloid Science, Vol. 3*, Academic Press, London, 1991, Chapter 1.
- ◆ L. L. Schramm, *Dictionary of Nanotechnology, Colloid and Interface Science*, Wiley-VCH, Weinheim, 2008 (find the topic by following the alphabetical arrangement in the book).
- ◆ P. -G. de Gennes, F. Brochard-Wyart, and D. Quéré, *Capillarity and Wetting Phenomena*, Springer, New York, 2004, Chapter 1.
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