UNIT 4 SURFACE TENSION

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4.1 INTRODUCTION

You already know that matter can exist in three possible states–solid, liquid or gas. In gases, the kinetic energy of the particles is sufficiently high to overcome the intermolecular forces of attraction. As a result of this, the gaseous molecules are free to move randomly in straight lines. In solids, the forces of attraction exceed the net kinetic energy of the molecules. The result is that the molecules become strongly packed together, giving them a shape rather fixed and restricted.

The properties of **liquids** are **in between** those of the gases and solids. In liquids, relatively short range forces of attraction are at work which hold their molecules at moderate distances. Though, the speed of the molecules in liquids is relatively slower than molecules in gases, their motion is still rapid enough to prevent them from being confined in definite positions. Hence, liquids have no specific shape and their molecules easily slide pass each other permitting them to take any possible shape allowed by the container.

Thus, not only the particular state of the substances but also their subsequent physical properties can be regarded as a result of the net balance between the kinetic energy of the molecules, which tend to keep them apart, and the intermolecular forces of attraction which tend to keep the molecules together. Here, in this unit you are going to study about the measurement of one such important property of liquids, namely, the **Surface Tension**.

Objectives

After going through this unit and performing Experiment 1, you should be able to:

- define surface tension and surface free energy, and give their units,
- express clearly the correlation between the molecular forces of attraction and the phenomenon of surface tension in liquids,
- explain interfacial tension and capillary action,
- comment on various methods of measuring surface tension and the principle involved therein,
- discuss how the surface tension varies with temperature and provide possible reasons for this variation, and
- explain why the surface tension of an aqueous solution should decrease in the presence of surface active agents.

4.2 SURFACE TENSION

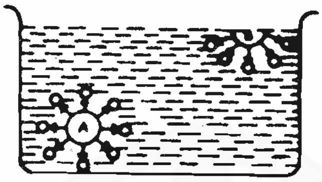


Fig. 4.1 : Forces of attraction at the surface and in the interior of a liquid.

Fig. 4.1 shows that a molecule **in the interior** of a liquid is completely surrounded by the other molecules, and experiences the force of attraction equally in all directions. On the other hand, a molecule **at the surface** experiences the attractive forces *only from downward direction*, and this results in a net inward pull. Thus, under the influence of the molecular forces of attraction from within, a liquid develops a tendency to contract its surface such that it acquires the smallest possible area for a given volume. That is why drops of a liquid and bubbles of a gas in a liquid tend to acquire a spherical shape. As a result of this contraction, a liquid surface eventually comes under the **state of stretch or tension**, and the force (stretching) acting equally at every point in all directions along the surface, is known as the **Surface Tension.**

Quantitatively, the surface tension denoted as γ, may be defined in SI units as the force in newtons (N) acting at right angle to any line of one metre length along the surface of the liquid. Since, the force in newtons acts along a distance of one metre, the unit of surface tension is expressed as N m^{-1}.

The surface tension may also be defined in c.g.s. system as the force in dynes acting at right angle to any line of one centimetre length along the liquid surface. In this case, the force in dynes acts along a distances of one centimetre, so the surface tension is expressed in dynes cm^{-1}.

In other words, we can also say that dynes $\mathrm{cm}^{-1} \times 10^{-3}$ = N m^{-1}

Related to the surface tension is the property of surface free energy. Let us now understand what do we mean by this term.

4.2.1 Surface Free Energy

The **surface free energy**, as such, is a characteristic property of the surface and arises due to surface tension. The surface tension acts inwards allowing a minimum surface area for a given volume of liquid. Therefore, extension of a surface against the force of surface tension requires some work to be done which results in an increase in the energy of the surface by the same amount. The work required to increase the surface area by one unit by moving the molecules from interior of the liquid to surface, is called the surface free energy. The SI units of surface free energy are joule metre^{-2}. The two quantities, the surface free energy (J m^{-2}) and the surface tension (N m^{-1}) and are mathematically equivalent. The surface tension for some substances is given in Table 4.1.

The c.g.s. units of surface free energy are ergs cm^{-2}.

$$1\ \mathrm{J} = 1\ \mathrm{N\,m}$$

$$1\ \mathrm{J\,m^{-2}} = 1\ \mathrm{N\,m\,m^{-2}} = 1\ \mathrm{N\,m^{-1}}$$

Table 4.1: Surface Tension of Some Substances

Substance	Temperature/°C	$(10^3 \gamma / \mathrm{N\,m^{-1}})$
Platinum	2273	1900
Copper	1404	1100
Aluminium	700	840
Lead	350	453
Mercury	20	472
Acetone	20	23.7
Benzene	20	28.88
Chloroform	20	27.14
Ethanol	20	22.8
Methanol	20	22.6
Water	20	72.88
Oxygen	–203	18.3
Nitrogen	–203	10.5

Surface tension is measured for liquids. You can see high temperatures being used for the first four entries mentioned in Table 4.1 which are required for reaching their melting point.

4.2.2 Interfacial Tension

When a system contains more than one phase, the region where the phases meet, is called the **interface** or **interfacial region**. The common example of the interface being the surface of separation between two immiscible or partially miscible liquids.

The surface of a liquid is, infact, a surface of separation or an *interface* between the liquid and its vapour phase, and the value of the surface tension is the force acting per unit length along this liquid/vapour interface.

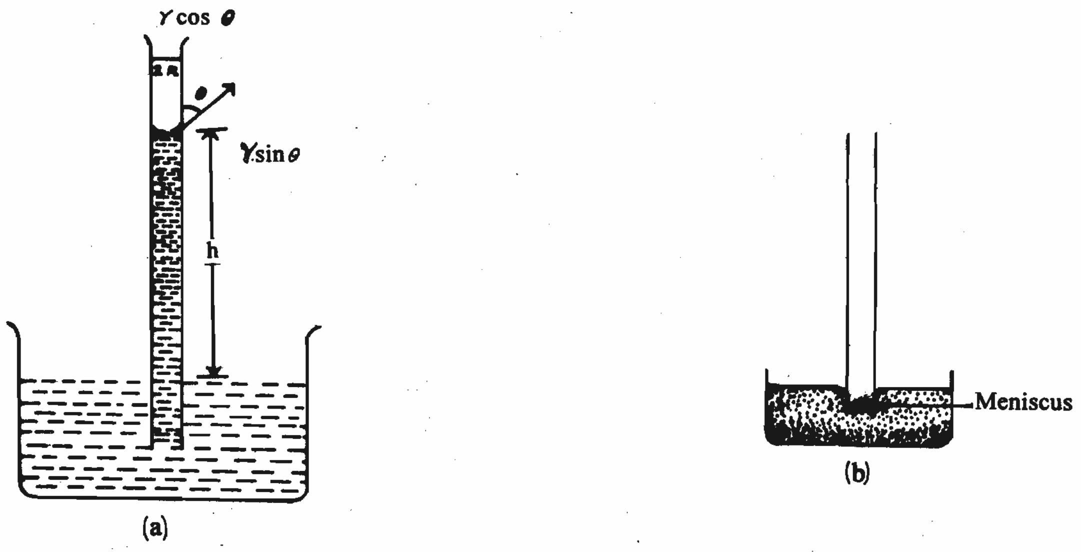
In general, the force acting per unit length along the surface of separation or interface is known as the **interfacial tension**. This is also expressed in Newton metre^{-1} (N m^{-1}) units.

Having understood the term interfacial tension, let us turn to the phenomenon of *capillary action.* You must be familiar with the fact that water rises in a capillary tube. Also you must have seen that mercury shows a depression of level in a capillary tube. The rise or fall (depression) of liquid level in a capillary tube is known as **capillary action.** Can you guess what is responsible for this phenomenon? It is the **surface tension** which is responsible for rise (or fall) of a liquid in the capillary. Let us now study it in more detail.

4.2.3 Capillary Action

Water in a capillary tube is pulled upwards due to the force of surface tension and is pulled downwards due to the force of gravity. Water continues to rise in the capillary till a balance between the two forces is reached. Such a rise is depicted in Fig. 4.2 (a).

This can be more clearly understood if we take into account the forces operating at the molecular level. Two types of forces operate when a glass capillary is dipped in water viz. **cohesive** and **adhesive** forces. **Cohesive forces** are the **intermolecular forces** among the molecules of water whereas **adhesive forces** operate between the molecules of water and the molecules of the glass which constitutes the capillary walls. The adhesive forces pull water upwards and lead to the **wetting** of glass (capillary walls). On the other hand, cohesive forces act downwards. The height of the resulting column of water in the capillary is determined by the balance of adhesive and cohesive forces.



(a) (b)

**Fig. 4.2: Capillary action: (a) Rise of water in a capillary.
(b) Depression of mercury level in a capillary.**

You must have also noticed the shape of the meniscus when water rises in a glass capillary. The shape is **concave** indicating that the adhesive forces between water and glass are **stronger than** the cohesive forces between water molecules. In some cases, e.g., in case of mercury, the shape of the meniscus is **convex** and there is a depression in the level of mercury inside the capillary, see Fig. 4.2 (b). This is due to stronger cohesive forces as compared to adhesive forces.

Let us now derive an expression which relates the above forces with the surface tension.

A force vector (e.g. γ) can be resolved into two rectangular components : $\gamma\cos\theta$ and $\gamma\sin\theta$ as shown below :

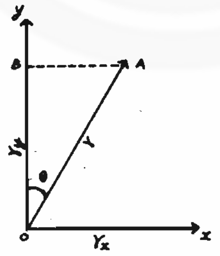


Fig. 4.3 : Resolution of a Vector into components.

The force in the downward direction, F_d, i.e. cohesive force is given by mass of the liquid column (m) above the flat surface of liquid multiplied by the acceleration due to gravity (g). Again mass of the liquid is equal to the product of volume (V) and density (d) of the liquid. Considering the particular bit of liquid portion as cylindrical, the volume can be given by the formula $\pi r^2 h$.

$$F_d = mg = V.d.g = \pi r^2 hdg \qquad \text{... (4.1)}$$

where r is the radius of the capillary and h is the height of the liquid column.

The upward force, F_u i.e. the adhesive force is equal to the vertical component (See Fig. 4.3) of the surface tension ($= \gamma\cos\theta$) multiplied by the circumference of the capillary ($2\pi r$). Therefore F_u, can be represented as given below

$$F_u = 2\pi r\gamma\cos\theta \qquad \text{...(4.2)}$$

where θ is the contact angle as shown in Fig 4.2. At equilibrium, $F_d = F_u$. Hence, we can write from Eqs. 4.1 and 4.2 that

$$\pi r^2 hdg = 2\pi r\gamma\cos\theta$$

$$\text{or} \qquad \gamma = \frac{rhdg}{2\cos\theta} \qquad \text{... (4.3)}$$

We can use Eq. 4.3 for the determination of surface tension (γ).

Having understood the above discussion, answer the following SAQ.

SAQ 1

i) Why do the tiny drops of a liquid look spherical in shape?

....

....

ii) Surface tension of a liquid is .... in newton at right angles to a line of one meter length along the .... of the liquid.

iii) What is the surface free energy?

....

....

iv) The unit of interfacial tension is .... and that of surface free energy is ....

4.3 FACTORS AFFECTING SURFACE TENSION

We will now focus our attention on some of the factors affecting the surface tension. We will first explain the effect of surfactants and then discuss the effect of temperature.

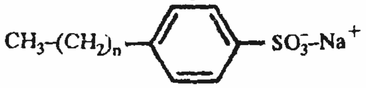
4.3.1 Effect of Surfactants

Surfactants are surface active materials and they generally consist of molecules containing polar and nonpolar parts. These parts have a strong tendency to orient themselves at the interfaces of two immiscible or partially miscible liquids. The tendency of the surfactant molecules to align at an interface favours its expansion. This expansion must be balanced against the tendency of the interface to contract under surface tension forces. Hence, the presence of a surfactant in aqueous solutions lowers the surface tension.

$$\gamma = \gamma_o - \pi \qquad \text{.... (4.4)}$$

where, π is the expanding pressure or **surface pressure** due to absorbed layer of surfactant and γ_o is the surface tension of the liquid in the absence of the surfactant.

The common examples of surfactants are soaps and detergents. Soaps are salts of long-chain fatty acids. The detergents are of two types — anionic and cationic. The anionic detergents are sodium salts of linear alkylbenzene (LAB) sulphonic acids. Their general structure can be represented as,



The cationic detergents are generally the quaternary ammonium salts of the following type

$$(CH_3)_3RN^+Cl^-$$

where R is alkyl chain having 12-18 carbon atoms.

By lowering the surface tension, the surfactants help the grease or dirt (non-polar in nature) to dissolve in water. This solubilised grease is then washed away with water. This forms the basis for the **cleansing action** of soaps and detergents.

4.3.2 Effect of Temperature

As the temperature increases, the kinetic energy of the molecules increases. This causes a decrease in their intermolecular forces of attraction. This results in a decrease in the surface tension of the liquid. For the majority of compounds the temperature dependence of the surface tension can be given as,

$$\gamma = A - B\,T \qquad \text{.... (4.5)}$$

where, A and B are the constants and T is the temperature in degree celsius. The values of A and B for various compounds are available due to the research work done so far. After studying this section, answer the following SAQ.

SAQ 2

i) Addition of a detergent to water will .... its surface tension.

ii) At higher temperature, the surface tension of a liquid .... because .... decreases.

4.4 MEASUREMENT OF SURFACE TENSION

There are various methods for determining the surface tension of a liquid. The names of such methods are given below:

i) Capillary rise method

ii) Torsion balance method

iii) Maximum bubble pressure method

iv) Stalagmometer method

Here, we will be discussing the stalagmometer method only because this method you will be using in the determination of the surface tension in Experiment 1.

4.5 EXPERIMENT 1 : I) DETERMINATION OF SURFACE TENSION OF AN AQUEOUS SOLUTION OF A DETERGENT
II) THE STUDY OF VARIATION OF SURFACE TENSION WITH THE CONCENTRATION OF A DETERGENT (OPTIONAL)

Here, in this experiment you are going to use a stalagmometer. This is shown in Fig. 4.4 and is called Traube's Stalagmometer. It is a simple apparatus and is frequently employed when the values of surface tension of two or more different liquids are to be compared.

Fig. 4.4 : Traube's Stalagmometer.

It consists of a bulbed capillary tube, the end of which is flattened and grounded carefully so that there is a large dropping surface. There are two marks, A and B, on it which are arbitrarily etched; one of them is above the bulb and the other is below the bulb. A liquid is sucked up to the level A and then allowed to flow at a slower rate drop by drop until it reaches the level B. The speed of the drop formation can be adjusted by attaching a piece of rubber tube with a screw pinch cock at the upper end of the tube. Before going to the actual details of the procedure, you should understand the principle involved in this method, which is explained below.

4.5.1 Principle

When a liquid is allowed to flow through a capillary tube, a drop begins to form at its lower end, and increases in size to a certain extent, and then falls off. The size of the drop will depend on the radius of the capillary and the surface tension of the liquid. The total surface tension supporting the drop is $2\pi r.\ \gamma$, where r is the outer radius of the capillary tube, see Fig. 4.5. The drop will fall when its weight w, just exceeds the force of surface tension acting along the circumference. Therefore,

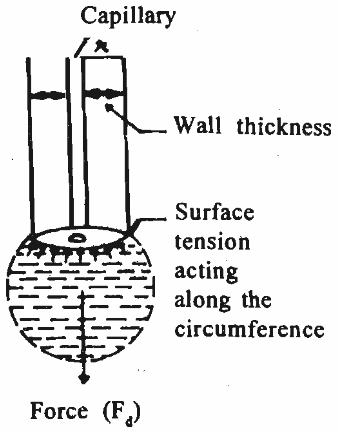


Fig. 4.5 : Formation of a drop at the end of the capillary.

$$w = 2\pi r \gamma \qquad \text{..... (4.6)}$$

where w, is the weight of the drop and $2\pi r$ is the outer circumference of the capillary tube.

From the above expression, it is clear that the surface tension of a liquid can be determined if the weight of a single drop w and the outer radius of the dropping tube, r are known.

If, we have two liquids, such that

$$w_1 = 2\pi r \gamma_1,$$

and $$w_2 = 2\pi r \gamma_2,$$

then, we can say that

$$\frac{w_1}{w_2} = \frac{\gamma_1}{\gamma_2} \qquad \text{... (4.7)}$$

If γ_1 for one of the liquids is known, γ_2 for other liquid can be determined without needing a measurement of r, the outer radius of the dropping end of the capillary, provided the weights of the individual drops of two liquids are known. This method of determination is also known as **Drop Weight Method**. Alternatively, the surface tension can also be determined using the **Drop Number** method as given below.

Drop Number Method

Instead of finding the weights of individual drops, it is easier to count the number of drops formed by equal volumes of two liquids. With two different liquids, the weights of equal volumes are proportional to their densities. If n_1 and n_2 are the number of drops formed by the same volume V of the two liquids, then; v_1, the volume of a single drop of first liquid (i.e., liquid one) = V/n_1.

Thus,

weight of the single drop of the first liquid = $w_1 = V/n_1 \times d_1 \times g$ for first liquid, where d_1 is the density of the first liquid.

and

weight of the single drop of the second liquid = $w_2 = V/n_2 \times d_2 \times g$ for second liquid, where d_2 is the density of the second liquid.

Substituting the above values of w_1 and w_2 in Eq. 4.7, we get

Weight of an object is the force experienced by it due to gravitation when it is freely suspended (as in spring balance). Therefore,

weight = mass × acceleration due to gravity

or $w = m \times g$

$w_1 = m_1 \times g$

and $w_2 = m_2 \times g$

Thus, $\dfrac{w_1}{w_2} = \dfrac{m_1 \times g}{m_2 \times g} = \dfrac{m_1}{m_2}$

We get,

$$\frac{\gamma_1}{\gamma_2} = \frac{(V/n_1) \times d_1 \times g}{(V/n_2) \times d_2 \times g} = \frac{d_1/n_1}{d_2/n_2} = \frac{n_2 d_1}{n_1 d_2} \qquad \ldots (4.8)$$

where, γ_1 and γ_2 are the surface tensions of two individual liquids, and d_1 and d_2 are their densities, respectively. Thus, for the determination of surface tension of any liquid, the number of drops produced from equal volume of two liquids and their densities must be known, in addition to the surface tension of the reference liquid (e.g. water).

You can also check your understanding about the Eq. 4.8 involved in the determination of surface tension by answering the following SAQ.

SAQ 3

Calculate the ratio of number of drops of water to those of mercury if the values of density for mercury and water are 13.6 kg dm^{-3} and 1.00 kg dm^{-3}, respectively. Use the values of surface tension of the two liquids as given in Table 4.1.

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Let us now focus our attention on the actual procedure and requirements for the experiment.

4.5.2 Requirements

Traube's Stalagmometer	1
Weighing bottle/conical flask (50 ml)/ Outer jacket of transition temperature of C.S.T. apparatus	1
Rubber stopper	1
Rubber tube (small piece)	1
Pinch cock	1
Clamp stand	1
Specific gravity bottle	1
Thermometer (110°)– $\frac{1}{10}$ degree	1
Large beaker or glass trough	1

In addition, you will be provided with different solutions (upto 3 or 4 in numbers) of household detergents (with varying concentrations) and also a bottle of distilled water.

Chromic acid is prepared by dissolving potassium dichromate ($K_2Cr_2O_7$) in conc. H_2SO_4.

4.5.3 Procedure

Before starting the experiment, the stalagmometer should be cleaned by chromic acid solution to remove oil, grease etc. sticking on the inner capillary surface and then washed with distilled water and finally with acetone or alcohol, and dried by passing air. Now take a weighing bottle, tightly fitted with a rubber stopper having two holes. Insert the stalagmometer through one of the holes. Through the other hole, pass a glass tube for air ventillation (see Fig. 4.6). Attach a small rubber tubing with a screw pinch cock to the upper end of the stalagmometer. Take out the stalagmometer from the bottle, and fill it with distilled water by sucking it up to the mark A. Close the pinch cock and insert the stalagmometer into the weighing bottle. Now, clamp the stalagmometer in a thermostat and allow it to acquire the temperature of the bath. Now, open the pinch cock gently such that the liquid flows out slowly. Adjust the air inflow so that the number of drops formed should not exceed 15 drops per minute. Count the number of drops obtained when a fixed volume of water flows between the marks A and B, i.e., count the number of drops when the water level changes from A to B.

Refill the stalagmometer and repeat the counting of drops thrice, and record it in the observation table, shown as Table 4.2.

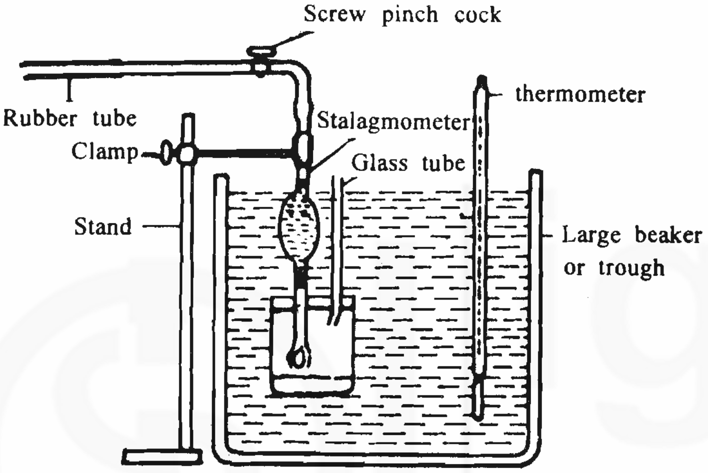

Fig. 4.6 : Apparatus for the determination of surface tension.

Now remove the stalagmometer from the weighing bottle, wash it thoroughly and dry it. Fill it with the given detergent solution and reset the stalagmometer in the weighing bottle. Count the number of drops fallen for the same volume of the detergent solution between the marks A and B. Repeat the counting process thrice and record in the observation table.

While doing the experiment, the following precautions should be taken.

Precautions

- The stalagmometer should be cleaned and dried before use.
- While sucking the liquid into the stalagmometer, no air bubble should be formed.
- Stalagmometer should be held in a vertical position throughout the drop counting process.
- Drop formation should be adjusted at a slower rate and should not exceed fifteen drops per minute.

You can record your observations in the space given below·

4.5.4 Observations

Temperature, t = ... °C
Density of water at t°C = d_w = ... kg dm^{-3}
Surface tension of water at t°C = γ_w = ... N m^{-1}
(use from Table 4.3)

Table 4.2

Number of drops formed from equal volume of liquids (between marks A and B)					
Sl. No.	Water	Detergent Solutions			
		s_1	s_2	s_3	s_4
i	.....	.....	.....	.....	.....
ii	.....	.....	.....	.....	.....
iii	.....	.....	.....	.....	.....
Average	..... n_w	..... n_{s_1}	..... n_{s_2}	..... n_{s_3}	..... n_{s_4}

mass of empty specific gravity bottle $= w_1 = ... g$
mass of specific gravity bottle + detergent solution $= w_2 = ... g$
mass of specific gravity bottle + Water $= w_3 = ... g$

The calculations to be done are also explained below:

4.5.5 Calculations

Density of the detergent solution 1 =

$$d_{s_1} = \frac{\text{Mass of the detergent solution}}{\text{Mass of water}} \times \text{density of water}$$

$$= \frac{w_2 - w_1}{w_3 - w_1} \times d_w$$

Relative surface tension of the detergent solution (s_1) =

$$\frac{\gamma_s}{\gamma_w} = \frac{d_{s_1} \times n_w}{d_w \times n_{s_1}}$$

Absolute surface tension of the detergent solution (s_1) =

$$\gamma_{s_1} = \gamma_w \times \frac{d_{s_1} \times n_w}{d_w \times n_s} = \text{..........} \ \mathrm{N\,m^{-1}}$$

Likewise repeat the determination of density and calculations of surface tension for other solutions and get $\gamma_{s_2}, \gamma_{s_3}$ etc.

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Specific gravity is a term sometimes used in place of density. Specific Gravity is the ratio of density of a substance to that of water. Since it is a ratio of two densities, it is expressed without units.

Specific Gravity =

$$\frac{\text{density of solution (in kg dm}^{-3})}{\text{density of water (in kg dm}^{-3})}$$

The density of water is 1 kg dm^{-3}; therefore, specific gravity of a liquid or solution is its density expressed without units.

From the following steps, you can verify the relationship between the density of a solution and density of water as given by specific gravity measurement.

Specific gravity of a solution =

$$\frac{\text{Density of a solution}}{\text{Density of water}} = \frac{\text{Mass of solution/Volume of solution}}{\text{Mass of water/(same) Volume of water}}$$

= Mass of solution/Mass of water

Since we use same specific gravity bottle for measuring the masses of water and solution, volume is same in both the cases.

Hence Density of a solution =

$$\frac{\text{Mass of solution}}{\text{Mass of water}} \times \text{Density of water}$$

This relationship holds only if masses of water and solution are measured using same specific gravity bottle.

The surface tension of water γ_w at different temperatures is given in Table 4.3 for your reference.

Table 4.3 : Surface Tension of water at different temperatures

Temperature/°C	Surface Tension ($10^3\gamma$ /N m^{-1})
0	75.83
5	75.09
10	74.36
15	73.62
20	72.88
21	72.73
22	72.58
23	72.43
24	72.29
25	72.14
26	71.99
27	71.84
28	71.69
29	71.55
30	71.70
35	70.66
40	69.92
45	69.18
50	68.45
55	67.71
60	66.97
100	61.80

The result obtained can be reported as shown below:

4.5.6 Result

i) The absolute surface tension of the detergent solutions (s_1, s_2, s_3, s_4) at temperature .....°C are as follows:

γ_{s_1} = ... N m^{-1}
γ_{s_2} = ... N m^{-1}
γ_{s_3} = ... N m^{-1}
γ_{s_4} = ... N m^{-1}

ii) Similarly, you can determine the surface tension values for solutions of the same detergent having different concentrations and plot a graph of surface tension Vs concentration values (c_1, c_2, c_3 etc.). Discuss this graph with your counsellor and find the possible reasons for the variation of surface tension with concentration of the detergent solution.

4.6 ANSWERS

Self Assessment Questions

1 i) Because of surface tension, a liquid develops a tendency to acquire smallest possible area for a given volume. A sphere has the smallest surface area for a given volume.

ii) force, surface

iii) Work required to be done in order to expand the surface area by one unit.

iv) N m^{-1}, J m^{-2}

2 i) reduce

ii) decreases, intermolecular forces

3 Let subscript 2 represent water and subscript 1 represent mercury. Then Eq. 4.8 becomes,

$$\frac{\gamma_{Hg}}{\gamma_w} = \frac{n_w d_{Hg}}{n_{Hg} d_w}$$

or

$$\frac{n_w}{n_{Hg}} = \frac{\gamma_{Hg}}{\gamma_w} \times \frac{d_w}{d_{Hg}}$$

$$= \frac{0.472}{0.07288} \times \frac{13.6}{1.00} = 88.1$$

(rounded to three significant figures)