



E-Content

Topic: Properties of liquids (part 2)

Chapter: Liquid State

Physical Chemistry

B. Sc. Chemistry (H) 1st Year

By


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METHODS FOR DETERMINATION OF SURFACE TENSION

(A) Capillary rise method:

In the absence of external forces, liquids form spherical drops spontaneously. This is facilitated by the fact that for a given volume, a sphere has a smaller surface area than any other shape.

Intermolecular forces in liquid give rise to *capillary action*. It is the rise of liquids through a capillary (narrow glass) tube. Two types of forces-cohesive and adhesive-are responsible for this property. The cohesive forces are the intermolecular forces among the molecules of a liquid. Adhesive forces exist between the liquid molecules and the molecules in the capillary walls. For example, glass contains many oxygen atoms; each oxygen atom (with partial negative charge) attracts (the positive end of) -a polar molecule, such as water.

The adhesive forces enable water to "wet" the glass. The adhesive forces acting upward pull up a water column inside a capillary tube when the latter is in contact with water (Fig. 1a). The height of the water column inside the capillary tube is such that the adhesive forces acting upwards balance the cohesive forces acting downwards. The height of the water column inside the capillary tube has been found to be inversely proportional to the radius of the tube. Hence only in tubes of small radius, the capillary rise is meaningful. The concave shape of the meniscus of water in a glass tube indicates that the adhesive forces of water towards the glass are stronger than its cohesive forces. A metallic liquid such as mercury (Fig. 1b) shows a lower level in a capillary tube and a convex meniscus. This behaviour is characteristic of a liquid in which the cohesive forces between its molecules are stronger than the adhesive forces between the molecules and glass.

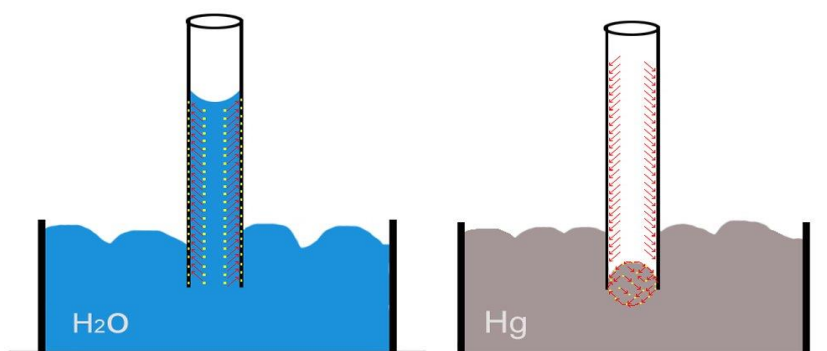


Fig.1 Capillary action in (a) water, (b) mercury

In this method a capillary tube of radius r is vertically inserted into the liquid (Fig. 2). The liquid rises to a height h and form a concave meniscus. The surface tension γ acting in the inner circumference of the tube exactly supports the weight of the liquid column. By definition, surface tension is force per 1 cm acting at a tangent to the meniscus surface. If the angle between the tangent and the tube wall is θ , the vertical component of surface tension is $\gamma \cos\theta$.

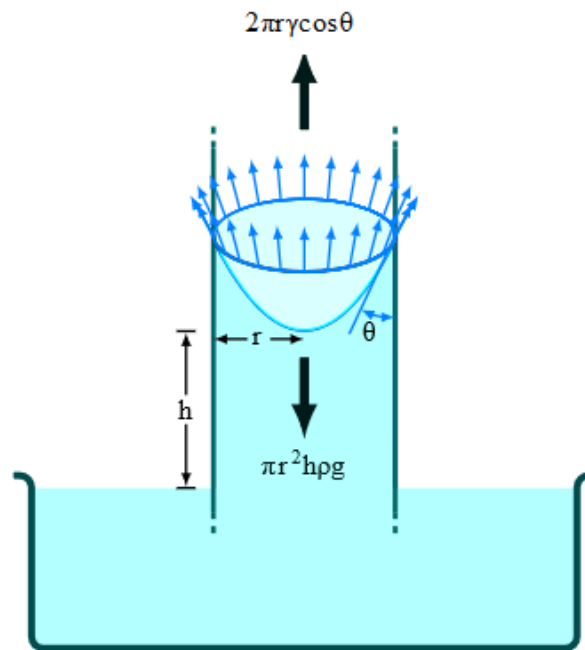


Fig. 2 Capillary rise method for determination of surface tension

The total surface tension along the circular contact line of meniscus is $2\pi r$ times.

Therefore upward force = $2\pi r \gamma \cos\theta$

Where r is radius of capillary. For most liquids, θ is essentially zero, and $\cos\theta=1$ then the upward force reduces to $2\pi r \gamma$.

The downward force on the liquid column is due to its weight which is mass \times g , thus downward force is $h\pi r^2 \rho g$, where ρ is density of the liquid

Now upward force = downward force

$$2\pi r \gamma = h\pi r^2 \rho g$$

$$\gamma = \frac{hr\rho g}{2} \text{ dynes/cm}$$

once r , h and ρ are known γ can be calculated.

(B) Drop weight/ number method:

The apparatus used in this method is called *stalagmometer* which is a glass pipette with a capillary at the lower part. When a liquid is allowed to flow very slowly through the capillary tube a drop will form which will increase upto a certain point and then fall. If the radius of the end of the tube be r , the total surface tension supporting the drop will be $\gamma 2\pi r$. The drop falls down when its weight W is just equal to this force. Hence we have

$$\gamma 2\pi r = W = mg$$

The apparatus is cleaned, dried and filled with the experimental liquid upto the mark A. (Fig 3). Then the surface tension is determined by any of the following two methods.

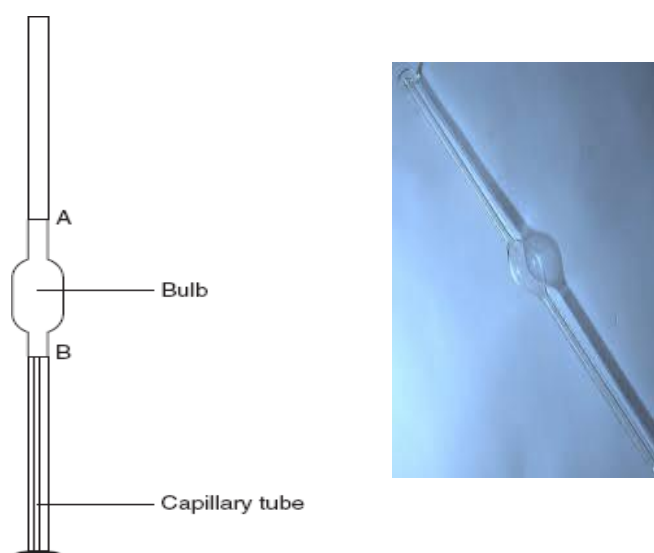


Fig. 3. Stalagmometer for determination of surface tension

(a) Drop number method:

First, stalagmometer is filled up to the mark A with the liquid whose surface tension is to be determined. The numbers of drops are counted as the meniscus passes from A to B. Similarly the pipette is filled with the reference liquid as the meniscus passes from A to B.

Let n_1 and n_2 be the number of drops produced by the same volume V of the two liquids.

Thus, the volume of drop of the experimental liquids = V/n_1

mass of one drop of this liquid = $V/n_1 \times d_1$, where d_1 is its density.

Similarly the mass of one drop of reference liquid = $V/n_2 \times d_2$

Then we have,

$$\gamma_1/\gamma_2 = \frac{(V/n_1)d_1}{(V/n_2)d_2} = \frac{n_2 d_1}{n_1 d_2}$$

The density d_1 can be determined by density bottle, once γ_2 and d_2 are known γ_1 can be calculated.

(b) Drop weight method:

About 20 drops of the given liquid are taken from the stalagmometer in a weighing bottle and weighed. Thus weight of one drop is found. The apparatus is again cleaned and dried. It is filled with the second reference liquid (say water) and weight of one drop is determined as before.

Then we have, $m_1 g = 2\pi r \gamma_1$ and $m_2 g = 2\pi r \gamma_2$

$$\gamma_1/\gamma_2 = \frac{m_1}{m_2}$$

Thus knowing the surface tension of one liquid, the surface tension of other liquid can be obtained.

DETERMINATION OF VISCOSITY

The apparatus used for determination of viscosity is called *Ostwald's viscometer*. A Ostwald viscometer has right-hand arm which is essentially a pipette with two calibration marks A and B (Fig. 4). A length of capillary tube joins the pipette to the bulb in the left-hand arm.

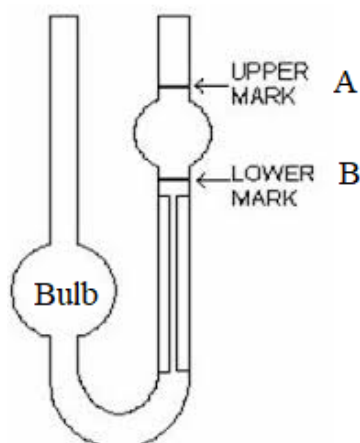


Fig. 4. Ostwald viscometer

A known volume of liquid is poured into the bulb with a pipette. The liquid is sucked up near to the top of the right-hand arm. The liquid is then released to flow back into the bulb. The time t_1 to flow from A to B is noted with a stopwatch. Then the apparatus is cleaned and the experiment is repeated with water taking about the same volume. The time of flow of water t_2 from A to B is recorded. The density of the liquid d and that of water d_w are determined with the help of density bottle. The relative viscosity is calculated from the expression

$$\eta/\eta_w = dt_1/dwt_2$$

where η is coefficient of viscosity of the experimental liquid and η_w is the coefficient of viscosity of water. Knowing the value of coefficient of viscosity of water η_w at the temperature of experiment, the absolute viscosity coefficient η of the given liquid can be found.

Surface tension and chemical constitution

From the study of a large number of liquids, Maclead (1923) showed that

$$\frac{\gamma^{1/4}}{D-d} = C \quad \dots\dots\dots(1)$$

where γ is surface tension of the liquid, D its density and d density of vapour at the same temperature, C is a constant.

Sugden (1924) modified this equation by multiplying both sides by M, the molecular weight of the liquid

$$M \cdot \gamma^{1/4} / D - d = MC = [P] \dots\dots\dots (2)$$

The quantity P, which is a constant for a liquid, was given the name parachor. As d is negligible as compared to D equation (2) reduces to

$$M \gamma^{1/4} / D = [P]$$

$$\text{or } M/D \gamma^{1/4} = [P]$$

$$V \gamma^{1/4} = [P] \dots\dots\dots (3)$$

Where γ is molar volume of the liquid. If surface tension γ is unity then $V = [P]$

Thus parachor may be defined as the molar volume of a liquid at a temperature at which its surface tension is unity.

Use of parachor in elucidating molecular structure:

Sugden examined the experimental parachor values of several organic compounds of known molecular structure. He showed that parachor is both additive and constitutive property. That is parachor of an individual compound can be expressed as sum of

- (i) Atomic parachors: which are the contributions of each of the atoms present in the molecule.
- (ii) Structural parachors: which are the contributions of various bonds, rings and other structural factors present in the molecule.

By correlating the experimental values of parachor with molecular structure, Sugden (1924) calculated the atomic and structural parameters. These values were further revised by Vogel (1948) on the basis of more accurate measurements of surface tension (table 1).

Atom	Parachor	Bonder ring	parachor
C	8.6	single bond	0
H	15.7	double bond	19.9
O	20.0	coordinate bond	0
N	12.5	3-member ring	12.3
Cl	55.2	6- member ring	1.4
S	48.2	= CO	44.4

Rheochor:

Newton Friend (1943) showed that if molecular volume (M/d) be multiplied by the eighth root of the coefficient of viscosity it gives a constant value [R], it is termed as Rheochor

$$M/d \times \eta^{1/8} = R$$

Like parachor, rheochor is both additive and constitutive property.

REFRACTIVE INDEX

Definition

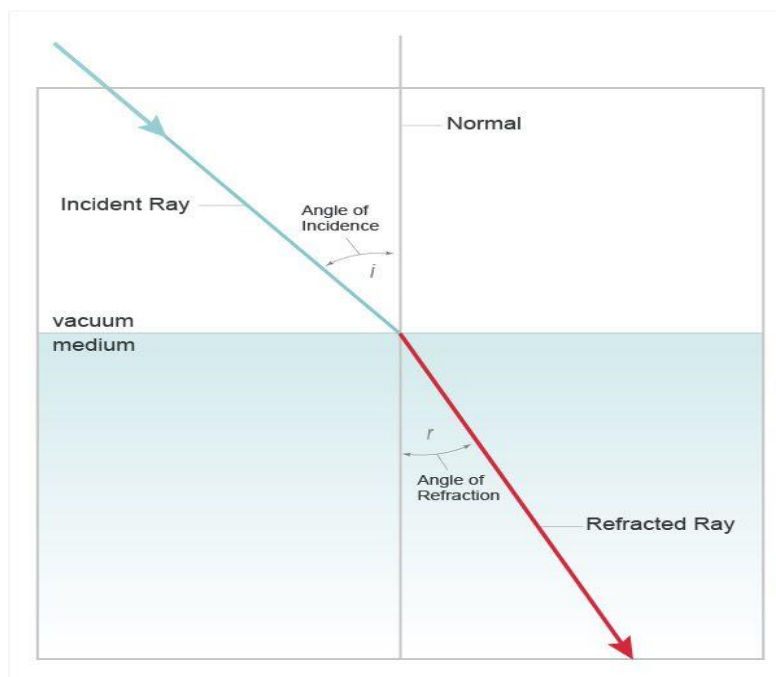
When a ray of light passes from air into denser medium say a liquid, it is bent or refracted towards the normal. The ratio of the sine of angle of incidence and the sine of angle of refraction is constant and characteristic of that liquid. This is known as Snell's law. **The constant ratio n is called refractive index of the liquid** and may be written as

$$\sin i / \sin r = n$$

The ratio of sines of the angles of incidence and refraction is identical with the ratio of the velocity of light in two media. Thus $n = \sin i / \sin r = \text{velocity in air} / \text{velocity in liquid}$ when a ray of light passes from a rarer to denser medium it can be shown from law of refraction that

$$\frac{\sin i}{\sin r} = \frac{n_2}{n_1}$$

n_1 is refractive index of rarer medium and n_2 is refractive index of denser medium



Determination of refractive index

The instruments used for determining refractive index are known as refractometers.

Pulfrich-refractometer:

This refractometer is very accurate and simple in principle. It is indicated diagrammatically in fig 5.

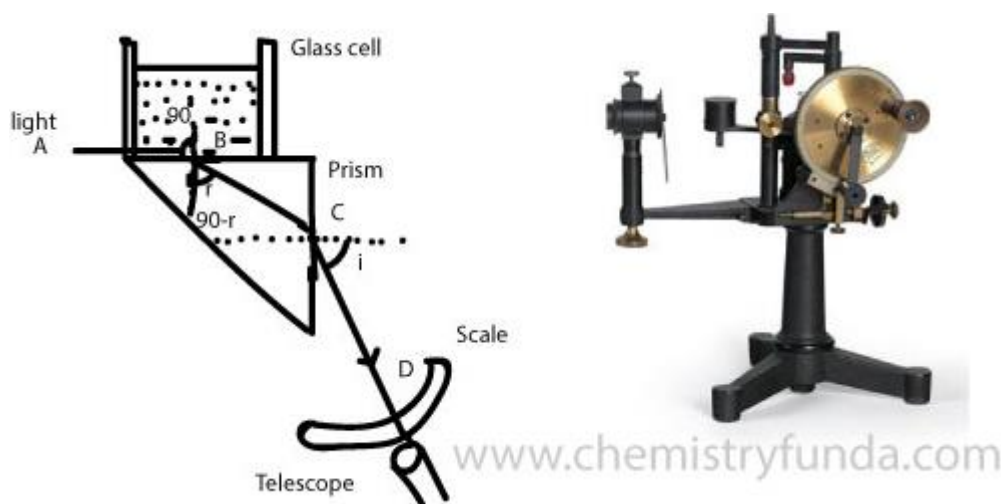


Fig. 5. The optical system of Pulfrich refractometer

The main part of the instrument is a right angled glass prism with a small glass cell connected to its top. The liquid under examination is placed in the cell and a beam of monochromatic light is made to enter the liquid at an angle of 90° along the surface between the liquid and the prism. If the telescope is moved to make an angle with the horizontal which is less than i no light can reach it. At this angle i a sharp boundary between a dark and a bright field can be seen through the telescope.

For a ray of light passing from the liquid into the prism, if r be the angle of refraction when the angle of incidence is 90° we have already stated that

$$\sin r = n_1 / n_2 \dots\dots\dots(1)$$

Where n_1 is the refractive index of the liquid and n_2 is that of glass prism. It is also clear to you from the fig 5 that

$$\sin i / \sin (90-r) = n_2 \dots\dots\dots(2)$$

$$\text{or } \sin i / \cos r = n_2 \dots\dots\dots(3)$$

$$\text{or } \cos r = \sin i / n_2 \dots\dots\dots(4)$$

$$\text{But } \sin r = \sqrt{(1-\cos^2 r)}$$

substituting the value of $\cos r$ in equation (4) we get

$$\sin r = \sqrt{(1-\sin^2 i / n_2^2)} \dots\dots\dots 5$$

From equation (1) we get

$$n_1 = n_2 \sin r = \sqrt{n_2^2 - \sin^2 i}$$

If the refractive index n_2 of the glass is known and angle i is measured n_1 the refractive index n_1 of liquid can be calculated.

Refractive index and chemical constitution

Lorenz and Lozentz (1880) purely from theoretical considerations derived the following relation for refracting power of substance

$$R = \frac{n^2 - 1}{n^2 + 2} \times \frac{1}{d} \quad \dots\dots(1)$$

where R is specific refraction, d the density and n the refractive index. The value of R was constant at all temperatures.

Molar refraction:

It is defined as the product of specific refraction and molecular mass. Thus molar refraction is obtained by multiplying equation (1) by molecular mass (M).

$$R_M = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d} \quad \dots\dots\dots(2)$$

The value of molar refraction is characteristic of a substance and is independent of temperature. Since it depends on wavelength of light, the values of molar refraction are generally reported for D-line of sodium. Molar refraction R_M is an additive and constitutive property. The molar refraction of a molecule is thus a sum of the contributions of the atoms (atomic refraction) and bonds (bond refraction). From the observed value of R_M of appropriate known compounds, the atomic refractions of different elements and bonds are obtained.

Table. 2. Some atomic and bond refractions

Carbon C	2.418	3-membered ring	0.710
Hydrogen H	1.100	4- membered ring	0.480
Chlorine Cl	5.967	6- membered ring	0.15
Bromine Br	8.861	O in OH group	1.525
Iodine I	13.900	O in C=O group	2.211
Double bond	1.733	O in ethers	1.64
Triple bond	2.398		