Title: Properties of Liquid

Course:B.Sc part 1 Chemistry (Hons.)

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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.

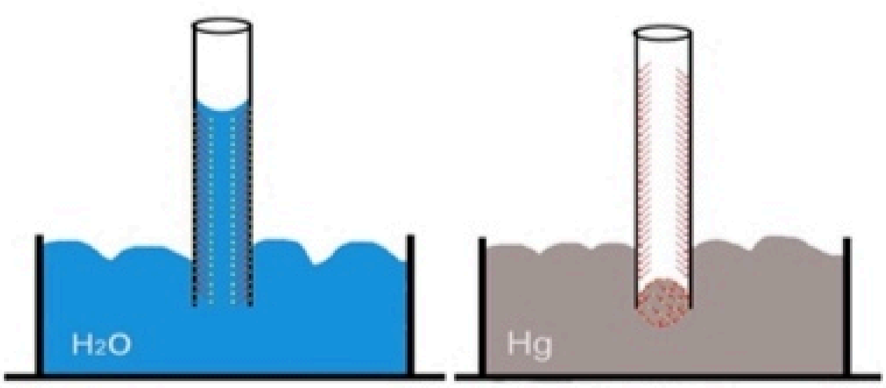


Fig.1 Capillary action in (a) water, (b) mercury

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 $\gamma \cos\theta$.

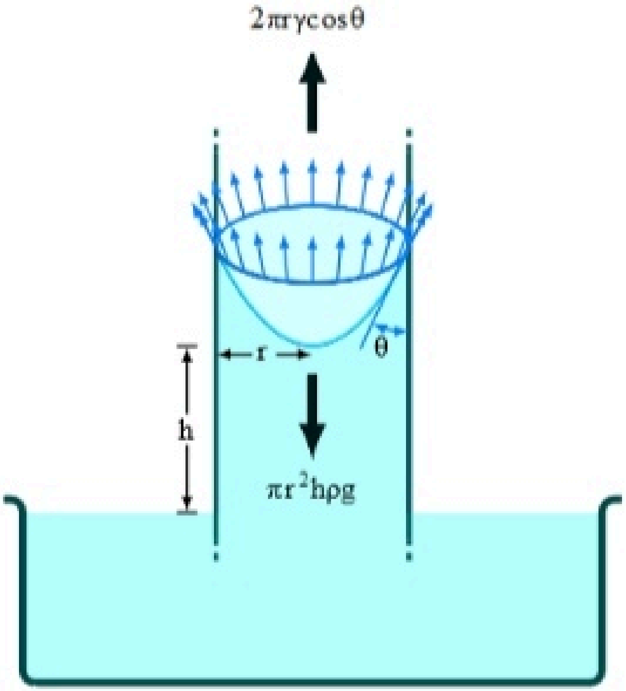


Fig. 2 Capillary rise method for determination of surface tension

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 x g, thus downward force is $h\pi r2\rho g$, where ρ is density of the liquid

Now upward force = downward force

$$2\pi r\gamma = h\pi r2\rho g$$

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

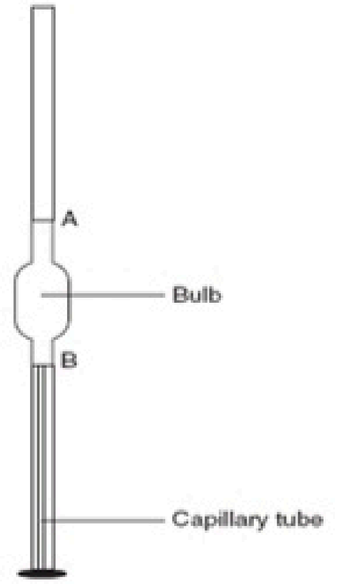
once r, h and ρ are known γ can be calculated.

(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.



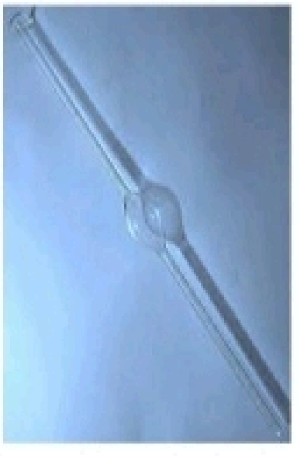


Fig. 3. Stalagmometer for determination of surface tension

(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.

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.

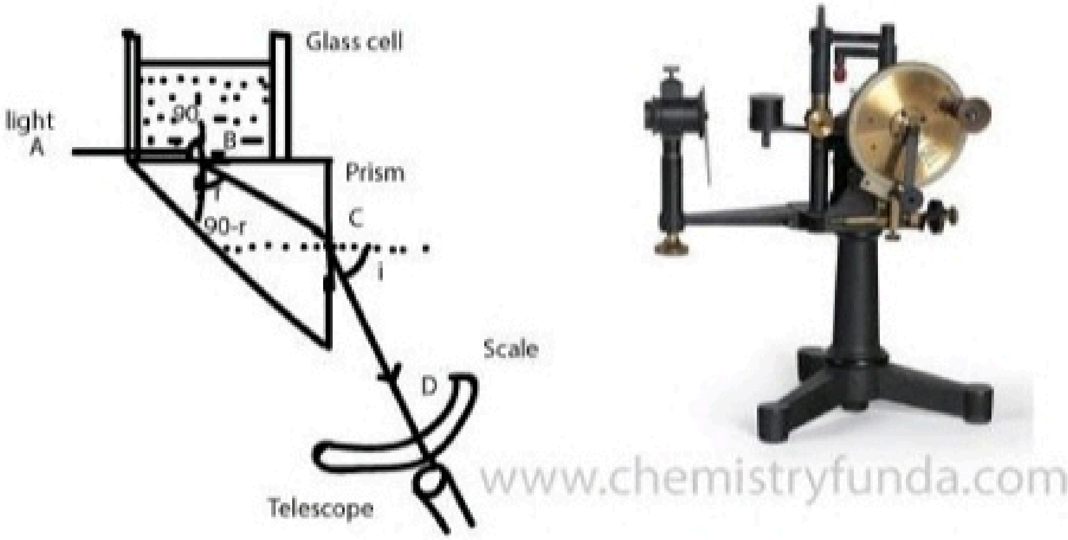


Fig. 5. The optical system of Pulfrich refractometer

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 900 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 900 we have already stated that

$$\sin r = n_1 / n_2 \text{.........}(1)$$

Where n1 is the refractive index of the liquid and n2 is that of glass prism. It is also clear to you from the fig 5 that

$$\sin i/\sin (90\text{-}r) = n_2 \text{...........}(2)$$

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

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

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

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

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

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 n1 the refractive index n1 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

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

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).

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

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		