B.Sc. (Honours) Part-I
Paper-IA

Topic: Liquid State- Characteristics of Liquids

UG
Subject-Chemistry

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4.11 THE LIQUID STATE

Liquid state is intermediate between gaseous and solid states. The liquids possess fluidity like gases but incompressibility like solids.

The behaviour of liquids explained above gives some characteristic properties to the liquids such as definite volume but no definite shape, incompressibility, diffusion, fluidity (or viscosity), evaporation (or vapour pressure), surface tension, etc.

Properties of liquids can be explained on the basis of kinetic molecular theory which has the following postulates:

(i) A liquid is made up of molecules; atoms in rare cases, *e.g.*, Hg (mercury).

(ii) The molecules of the liquid are quite close together.

(iii) The intermolecular forces of attraction in a liquid are quite large.

(iv) The molecules of liquids are in a state of constant rapid motion.

(v) The average kinetic energy of the molecules of a liquid is directly proportional to their absolute temperature.

A liquid state is regarded as a condensed gas or a molten solid. Liquid state, however, has much more in common with solid state than with gaseous state. The following general characteristics are exhibited by liquids:

(i) Shape

Liquids have no shape of their own but assume the shape of the container in which they are kept. No doubt, liquids are mobile but they do not expand like gases as to fill up all the space offered to them but remain confined to the lower part of the container.

(ii) Volume

Liquids have definite volume as the molecules of a liquid are closely packed and the cohesive forces are strong. The molecules are not quite free to occupy any space.

(iii) Density

As the molecules in liquids are closely packed, the densities of liquids are much higher than in gaseous state. For example, density of water at 100°C and 1 atmospheric pressure is 0.958 g mL^{-1} while that of water vapour under similar conditions as calculated from ideal gas law $\left(d = \frac{MP}{RT}\right)$ is 0.000588 g mL^{-1}.

(iv) Compressibility

The molecules in a liquid are held in such close contact by their mutual attractive forces (cohesive forces) that the volume of any liquid decreases very little with increased pressure. Thus, liquids are relatively incompressible compared to gases.

(v) Diffusion

When two miscible liquids are put together, there is slow mixing as the molecules of one liquid move into the other liquid. As the space available for movement of molecules in liquids is much less and their velocities are small, liquids diffuse slowly in comparison to gases.

(vi) Evaporation

The process of change of liquid into vapour state on standing is termed **evaporation.** Evaporation may be explained in terms of motion of molecules. At any given temperature, all the molecules do not possess the same kinetic energy (average kinetic energy is, however, same). Some molecules move slowly, some at intermediate rates and some move very fast. A rapidly moving molecule near the surface of the liquid may possess sufficient kinetic energy to overcome the attraction of its neighbours and escape. Evaporation is accompanied by cooling as average kinetic energy of remaining molecules decreases.

Evaporation depends on the following factors:

(a) Nature of the liquid: The evaporation depends on the strength of intermolecular forces (cohesive forces). The liquids having low intermolecular forces evaporate faster in comparison to the liquids having high intermolecular forces. For example, ether evaporates more quickly than alcohol, and alcohol evaporates more quickly than water, as the intermolecular forces in these liquids are in the order:

$$\begin{array}{c}\text{Ether} < \text{Alcohol} < \text{Water} \\ \text{Alcohol} < \text{Glycol} < \text{Glycerol} \\ \xrightarrow[\text{Increasing extent of hydrogen bonding}]{\hspace{6cm}}\end{array}$$

(b) Surface area: Evaporation is a surface phenomenon. Larger the surface area, greater is the opportunity of the molecules to escape. Thus, rate of evaporation increases with increase of surface area.

$$\text{Rate of evaporation} \propto \text{Surface area}$$

(c) Temperature: Rate of evaporation increases with the increase of temperature as the kinetic energy of the molecules increases with the rise of temperature.

$$\text{Rate of evaporation} \propto \text{Temperature}$$

(d) Flow of air current over the surface: Flow of air helps the molecules to go away from the surface of liquid and, therefore, increases the evaporation.

(vii) Heat of vaporisation

The quantity of heat required to evaporate a unit mass of a given liquid at constant temperature is known as heat of vaporisation or heat of evaporation. The heat of vaporisation depends on the strength of the intermolecular forces within the liquid. The value of heat of vaporisation generally decreases with increase in temperature. It becomes zero at the critical temperature. When the vapour is condensed into a liquid, heat is evolved. This is called **heat of condensation.** It is numerically equal to the heat of vaporisation at the same temperature.

(viii) Vapour pressure

When the space above the liquid is closed, the molecules cannot escape into open but strike the walls of the container, rebound and may strike the surface of the liquid, where they are

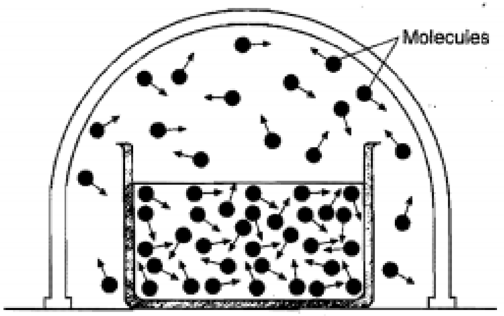

Fig. 4.13 (a) Evaporation in a closed vessel

trapped. The return of the molecules from the vapour state to the liquid state is known as **condensation.** As evaporation proceeds, the number of molecules in the vapour state increases and, in turn, the rate of condensation increases.

The rate of condensation soon becomes equal to the rate of the evaporation, *i.e.*, the vapour in the closed container is in equilibrium with the liquid.

$$\text{Liquid} \underset{\text{Condensation}}{\overset{\text{Evaporation}}{\rightleftharpoons}} \text{Vapour}$$

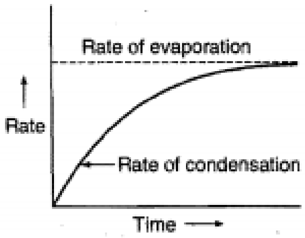

Fig. 4.13 (b)

At equilibrium, the concentration of molecules in the vapour phase remains unchanged. The pressure exerted by the vapour in equilibrium with liquid, at a given temperature, is called the **vapour pressure.** Mathematically, it is given by the gas equation:

$$P = \frac{n}{V}RT = CRT$$

where, C is the concentration of vapour, in mol/litre.

In closed vessel,

Rate of evaporation $\propto e^{-E/RT}$ (Boltzmann factor)

Thus, rate of evaporation remains constant at constant temperature.

Since, the rate of evaporation increases and rate of condensation decreases with increasing temperature, vapour pressure of liquids always increases as temperature increases. At any given temperature, the vapour pressures of different liquids are different because their cohesive forces are different. Easily vaporised liquids are called **volatile liquids** and they have relatively high vapour pressures. Vapour pressure values (in mm of Hg) for water, alcohol and ether at different temperatures are given in the following table:

Substance	Temperatures				
	0°C	**20°C**	**40°C**	**80°C**	**100°C**
Water	4.6	17.5	55.0	355.5	760.3
Ethyl alcohol	12.2	43.9	135.3	812.6	1693.3
Diethyl ether	185.3	442.2	921.1	2993.6	4859.4

It is observed that non-polar or less polar liquids such as diethyl ether and ethyl alcohol possess fairly high vapour pressures on account of weak intermolecular forces (cohesive forces) whereas polar molecules such as water which have stronger intermolecular forces possess relatively lower vapour pressures.

The simplest method for measuring vapour pressure is the **barometric method.** It consists of two barometer tubes as shown in Fig. 4.14. A small quantity of the liquid is introduced into one of the tubes. It changes into vapour and rises into vacuum above the mercury. Some more of the liquid is introduced and the process is continued till a small amount of the liquid is visible on the surface of mercury. The difference in the levels of mercury in the two tubes is noted and this measures the vapour pressure of the liquid at atmospheric temperature. The measurement can also be made at any desired temperature by surrounding the tubes with a jacket maintained at that temperature.

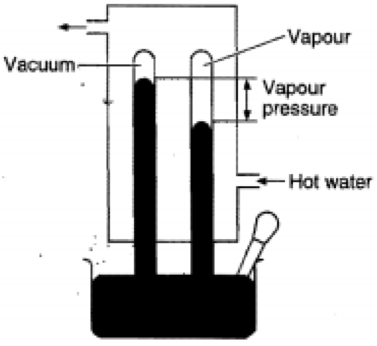

Fig. 4.14 The barometric method for measurement of vapour pressure

The vapour pressure of a given liquid at two different temperatures can be compared with the help of **Clausius-Clapeyron equation.**

$$\log\frac{P_2}{P_1} = \frac{\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where, ΔH is the latent heat of vaporisation and R is the molar gas constant.

The actual form of Clausius-Clapeyron equation is:

$$\log_{10} P = \frac{-\Delta H_{\text{vap}}}{2.303RT} + A$$

Note : Vapour and gas: A gas can be liquefied only below critical temperature, by applying pressure. There is no characteristic critical temperature for vapours.

When ΔH_{vap} = Latent heat of vaporisation and 'A' is constant. A graph between $\log_{10} P$ and $\frac{1}{T}$ will be a straight line with negative slope.

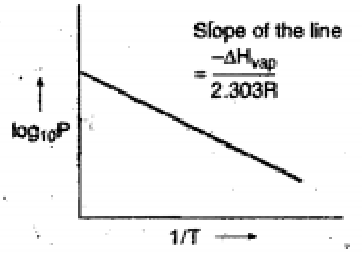

Fig. 4.15 Variation of vapour pressure with temperature

(ix) Boiling point

The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called the **boiling point** of the liquid. When a liquid is heated under a given applied pressure, bubbles of vapour begin to form below the surface of the liquid. They rise to the surface and burst releasing the vapour into the air. This process is called **boiling.** The normal boiling point is the temperature at which the vapour pressure of a liquid is equal to exactly one standard atmospheric pressure (760 mm of Hg). Fig. 4.16 shows that normal boiling points of diethyl ether, ethyl alcohol and water are 34.6°C, 78.5°C and 100°C respectively.

The temperature of the boiling liquid remains constant until all the liquid has been vaporised. Heat must be added to the boiling liquid to maintain the temperature because in the boiling process, the high energy molecules are lost by the liquid. The higher rate at which heat is added to the boiling liquid, the faster it boils.

The boiling point of a liquid changes with the change in external pressure. A liquid may boil at temperature higher than normal under external pressure greater than one atmosphere; conversely, the boiling point of a liquid may be lowered than normal below one atmosphere. Thus, at high altitudes where the atmospheric pressure is less than 760 mm, water boils at temperature below its normal boiling point of 100°C. Food cooks more slowly at higher altitudes because the temperature of boiling water is lower than it would be nearer the sea level. The temperature of boiling water in a pressure cooker is higher than the normal, thus making it possible to cook foods faster than in open vessels.

If a liquid decomposes when heated, it can be made to boil at lower temperature by reducing the pressure. This is the principle of vacuum distillation. Unwanted water is removed from many food products by boiling it away under reduced pressure.

Boiling and evaporation are similar processes (conversion of liquid into vapour) but differ in the following respects:

(a) Evaporation takes place spontaneously at all temperatures but boiling occurs only at a particular temperature at which the vapour pressure is equal to the atmospheric pressure.

(b) Evaporation is a surface phenomenon. It occurs only at the surface of the liquid whereas boiling involves formation of bubbles below the surface of the liquid.

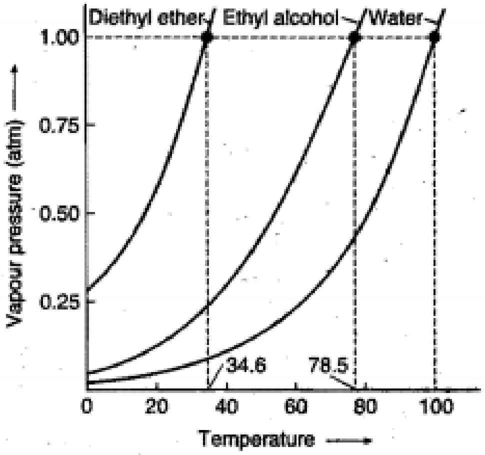

Fig. 4.16 Vapour pressure curves for diethyl ether, ethy alcohol and water

(c) In vaporisation, the vapour molecules diffuse from the liquid into the atmosphere but in boiling, molecules escape with sufficient pressure into the space over the surface of liquid.

(x) Freezing point

When a liquid is cooled, the kinetic energy of the molecules goes on decreasing. A stage comes when the intermolecular forces become stronger and the translational motion is reduced to minimum. At this stage, the formation of solid begins and the liquid is seen to freeze out. The point (temperature) at which the vapour pressure of solid and liquid forms of a substance become equal is termed as **freezing point.**

Normal freezing point of a liquid is the temperature at which its liquid and solid forms are in equilibrium with each other under a pressure of one atmosphere. The freezing point of a liquid is the same as the melting point of its solid form. At the freezing point the temperature of the solid-liquid system remains constant until all the liquid is frozen. The amount of heat that must be removed to freeze a unit mass of the liquid at the freezing point is called the **heat of fusion.**

The freezing point of a liquid is affected by the change of external pressure. With increased external pressure, the freezing point of some liquids rises while of others falls.

(xi) Surface tension

It is the property of liquids caused by the intermolecular attractive forces. A molecule within the bulk of the liquid is attracted equally in all the directions by the neighbouring molecules. The resultant force on any one molecule in the centre of the liquid is, therefore, zero. However, the molecules on the surface of the liquid are attracted only inward and sideways. This unbalanced molecular attraction pulls some of the molecules into the bulk of the liquid, *i.e.*, are pulled inward and the surface area is minimized. **Surface tension is a measure of this inward force on the surface of the liquid. It acts downwards perpendicular to the plane of the surface.** The unit of surface tension is dyne cm^{-1} or Newton metre^{-1} (N m^{-1}). It is a scalar quantity. Surface tension is, thus, defined as **the force acting on unit length of a line imagined to be drawn tangentially anywhere on the free surface of a liquid at rest. It acts at right angles on both sides of the line and along the tangent to the liquid surface.** Surface tension depends on the area, not on the length, like elastic properties.

As the intermolecular forces of attraction decrease with the rise of temperature, the surface tension of a liquid, thus, decreases with increase in temperature. Similarly, addition of chemicals to a liquid reduces its surface tension. For example, addition of chemicals like soaps, detergents, alcohol, camphor, etc., lowers the surface tension of water.

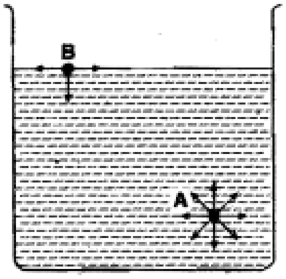

Fig. 4.17 (a) Molecules at the surface are under unequal tension

Many common phenomena can be explained with the help of surface tension. Some are described here:

(a) Small droplets are spherical in shape: The surface tension acting on the surface of the liquid tries to minimise the surface area of a given mass of a liquid. It is known that for a given volume, a sphere has the minimum surface area. On account of this, drops of liquids acquire a spherical shape.

(b) Insects can walk on the surface of water: Many insects can walk on the surface of water without drowning. This is due to the existence of surface tension. The surface tension makes the water surface to behave like an elastic membrane and prevents the insects from drowning.

(c) Cleaning action of soap and detergents: Soap and detergent solutions due to their lower surface tensions penetrate into the fibre and surround the greasy substances and wash them away.

(d) Capillary action: The tendency of a liquid to rise into narrow pores and tiny openings is called capillary action. The liquids rise in the capillary tubes due to the surface tension. The force of adhesion between the molecules of water and the molecules of glass of the capillary tube is greater than the force of cohesion between water molecules. Due to this, surface of water in a glass capillary tube curves upwards in convex shape and then the force of surface tension of water pulls the water up into the tube. The water rises into a capillary tube to such a height that the weight of resulting water column is just balanced by the force of surface tension.

The rise of oil in a lamp wick and flow of water from the roots of a tree to upper parts are also the examples of capillary action. In general, the liquids which wet the material show capillary rise. Those liquids which do not wet the material of a capillary always show depression, *e.g.*, glycerine, honey, mercury, etc.

When a liquid rises in a column, its upper surface becomes concave and when the liquid goes down in a capillary, its upper surface becomes convex.

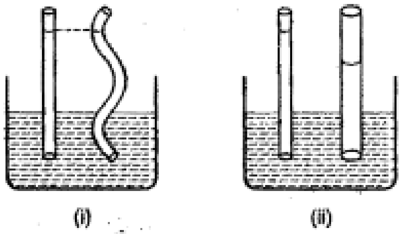
(i) (ii)

Fig. 4.17 (b) Effect of shape and radius on capillary rise

(i) Height of liquid in the column of capillary is independent of shape of capillary if its radius is same.

(ii) Thinner is the capillary, greater is the height of liquid in the column.

(e) Surface energy: The work in erg required to be done to increase or extend surface area by 1 sq. cm is called surface energy. The units of surface energy are, therefore, erg per sq. cm (or joule per sq. metre, *i.e.*, J m^{-2} in SI system). Surface tension of liquid is numerically equal to the surface energy.

Surface energy,

$$\gamma = \text{Work done to increase the surface area by one unit}$$

$$= \frac{\text{Work}}{\text{Change in area}}$$

$$= \frac{\text{force} \times \text{displacement in the direction of force}}{\text{area}}$$

$$= \frac{\text{Force}}{\text{Length}}$$

The unit of surface tension is therefore dyne cm^{-1} (force per unit length).

Measurement of surface tension: The surface tension of a liquid is measured by the drop count method using a stalagmometer.

Let γ_1 and d_1 be the surface tension and density of water and γ_2 and d_2 be surface tension and density of the liquid whose surface tension is to be determined. Using a stalagmometer the number of drops formed by the same volume of water and liquid is determined.

$$\frac{\gamma_1}{\gamma_2} = \frac{n_1 d_2}{n_2 d_1}$$

Using the above relation, the surface tension of the liquid, γ_2, can be calculated.

Note: At the critical temperature, surface tension of liquid becomes zero (where the meniscus between the liquid and the vapour disappears). Surface tension is scalar quantity.

Surface tension of the liquid can also be measured by capillary rise method.

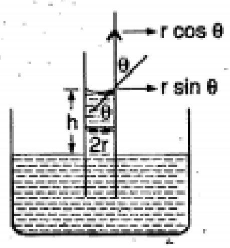

Fig. 4.18 Capillary rise

When liquid rises in a capillary, upward force due to surface tension is balanced by gravitational force.

$\therefore \quad 2\pi r\gamma \cos\theta = mg$

where, m = mass of liquid in column

r = radius of capillary

h = capillary rise

g = gravitational force

Mass of liquid in column $(m) = V \times \rho$

$= \pi r^2 h \times \rho$

$$\therefore \quad 2\pi r\gamma \cos\theta = \pi r^2 h\rho g$$

$$\gamma = \frac{rh\rho g}{2\cos\theta} \qquad (\rho = \text{density of liquid})$$

If angle of contact between glass and liquid is zero, *i.e.*, $\cos\theta = 1$, then

$$\gamma = \frac{rh\rho g}{2}$$

Effect of temperature on surface tension : Surface tension decreases with rise in temperature because the intermolecular force also decreases with rise in temperature. The decrease in surface tension with rise in temperature continues till critical temperature at which the surface tension of liquid becomes zero, *i.e.*, meniscus between liquid and vapour disappears.

According to Eotvos equation,

$$\gamma = \left(\frac{M}{\rho}\right)^{2/3} = K\,(t_c - t)$$

$\therefore$ As t increases, γ decreases linearly, when $t = t_c$, $\gamma = 0$, here t_c is the critical temperature.

(xii) Viscosity

All liquids have a characteristic property of flow. Some liquids like water, alcohol, ether, etc., flow quickly while glycerine, castor oil, molasses, etc., flow very slowly. **The property of the liquids which determines their resistance to flow, is called viscosity.**

When a liquid flows through a pipe, all parts of it do not move at the same rate. The thin layer in immediate contact with the wall of the pipe is almost stationary. The velocity of flow of each successive layer of liquid increases progressively as we proceed inward towards the centre. At the centre, the flow becomes fastest. Each layer of liquid moving with greater velocity over the one having lower velocity will experience a retarding effect due to the internal friction between the two layers. **This internal friction or resistance is called viscosity.**

Imagine a liquid to be made up of a large number of thin cylindrical coaxial layers.

It has been found that force of friction 'f' between two cylindrical layers each having area 'A' sq. cm separated by a distance 'x' cm and having a velocity difference v cm/sec is given by:

$$f \propto A\,\frac{v}{x}$$

$$f = \eta\,A\,\frac{v}{x}$$

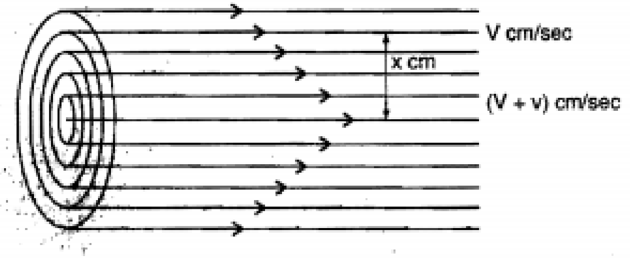

Fig. 4.19

Here, η is a constant known as coefficient of viscosity. If $x = 1$ cm, $A = 1\,\text{cm}^2$ and $v = 1$ cm/sec., then $f = \eta$.

Thus, coefficient of viscosity can be defined as **the force per unit area needed to maintain unit difference of velocity between two consecutive parallel layers of the liquid which are one centimetre apart.**

Coefficient of viscosity is expressed in dyne cm^{-2} sec. It is more commonly expressed as poise, centipoise (10^{-2} poise) and millipoise (10^{-3} poise), after the name of **Poiseuille** who derived the formula and gave the method for its determination. 1 poise is equal to a force of 1 dyne per unit area which maintains a velocity difference of 1 cm per second between two parallel consecutive layers of the liquid 1 cm apart.

The reciprocal of the coefficient of viscosity is called **Fluidity** (ϕ).

$$\phi = \text{Fluidity} = \frac{1}{\eta}$$

Liquids with low viscosity are termed mobile and others with high viscosity are called viscous.

Viscosity depends on the following factors:

(a) *Intermolecular forces*: The liquids with high intermolecular attractive forces offer greater resistance to the flow of molecules and thus possess high viscosity.

(b) *Molecular mass*: The flow of molecules is inversely proportional to its mass. Liquids having high molecular mass possess greater viscosity.

(c) *The structure and shape of molecules*: Viscosity generally increases as the branching in the chain increases. Symmetrical molecules have low viscosity.

(d) *Temperature*: Intermolecular forces decrease with rise in temperature. Thus, viscosity decreases with the increase of temperature. This property is used to select the lubricant for a machine and engine. The variation of viscosity with temperature can be expressed by the following relationship:

$$\eta = Ae^{-Ea/RT} \quad \ldots(i)$$

where, A = Pre-exponential factor (constant)

E_a = Activation energy

Taking logarithm of equation (i) we get :

$$\log_{10}\eta = \log_{10}A - \frac{E_a}{2.303R} \times \frac{1}{T} \quad \ldots(ii)$$

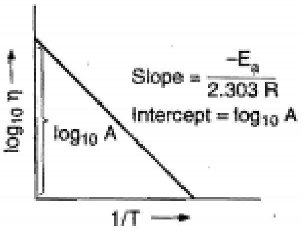

Fig. 4.20

This equation represents straight line with formula $y = mx + C$

Equation (ii) may also be given as

$$\log_{10}\frac{\eta_2}{\eta_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

where η_2 is the coefficient of viscosity at temperature T_2 and η_1 is the coefficient of viscosity at temperature T_1.

(e) *Pressure*: The increase of pressure increases the intermolecular forces. Thus, the viscosity of a given liquid increases with increase of pressure.

(f) *Density* : Viscosity of a liquid increases with increase in density while that of gas decreases.

Measurement of viscosity: Viscosity is generally determined by Ostwald's method. It involves the comparison of time of flow of equal volumes of two liquids through the same capillary using an apparatus called **viscometer.**

$$\frac{\eta}{\eta_w} = \frac{d \times t}{d_w \times t_w}$$

where, η_w, η = coefficients of viscosity of water and liquid respectively; d = density of liquid; d_w = density of water; t = time of flow of liquid; t_w = time of flow of water.

Note: Viscosity of gases increases with increase in temperature.

Comparison between viscous force and solid friction

Points of differences :

Viscous force	Solid friction
1. It is directly proportional to the area of layers in contact.	It is independent of the area of the surfaces in contact.
2. It is directly proportional to the relative velocity between the two liquid layers.	It is independent of the relative velocity between two solid surfaces.

Point of similarities:

(i) Both viscous force and solid friction come into action where ever there is relative motion.

(ii) Both these forces oppose the motion.

(iii) Both are due to molecular attraction.