2

Physical Properties of Liquids

2.1 INTRODUCTION

Characteristics of Liquid State

In general, liquids can be obtained from gases by cooling the latter below their respective critical temperatures, followed by the treatment of high pressure. The effect of cooling is to decrease the thermal energies of molecules and the effect of high pressure is to decrease the volume of the system so as to allow the molecules to come closer, thereby increasing the forces of attraction amongst them. Alternatively, liquids can be obtained by heating solids up to or beyond their melting points. In solids, molecules do not possess any translational energy but possess only vibrational energy. The forces of attractions amongst them are very strong. The effect of heating solids is to impart sufficient energy to molecules so that they can overcome these strong forces of attractions. Thus, we see that the properties of liquids lie in between those of solids and gases. For example, liquids are less compressible than gases but a little more compressible than solids. They are less dense than solids but more dense than gases. The two important properties of liquids, namely, fixed volume but no fixed shape, arise mainly because of the following two facts:

(i) The energies binding the molecules are larger than their average thermal energy.

(ii) These binding energies are not strong enough to stop the motion of the molecules altogether, as is the case in solids, with the result that molecules can move from one place to another but cannot escape from the liquid unless they are present at the surface.

In this chapter, we will discuss only three properties of liquids, namely, (i) vapour pressure, (ii) viscosity, and (iii) surface tension. The origin of these properties in liquids is basically due to the existence of strong intermolecular attractions. The structural aspect of liquids is discussed in the next chapter as it requires some knowledge about the arrangement of the molecules in solids.

2.2 VAPOUR PRESSURE

Introduction

Suppose a beaker containing a liquid is placed in an evacuated vessel (Fig. 2.2.1). Let the latter be connected to a manometer so that any pressure that is developed in the free space could be measured. After some time, it is found that the manometer records a constant pressure. This pressure is known as the vapour pressure of the liquid.

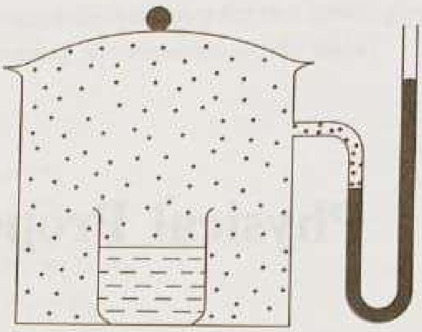

Fig. 2.2.1 Vapour pressure of a liquid

Origin of Vapour Pressure

Before making an attempt to understand how the vapour pressure arises, we will have to consider the following two facts:

(i) The molecules of a liquid, like those of a gas, have different kinetic energies. The distribution of speeds amongst molecules follows the Maxwell-Boltzmann distribution.

Figure 2.2.2 shows such a distribution at two different temperatures. The most important point to be noted in these distribution curves is that the fraction of molecules having higher speeds increases with the increase in temperature (shown by the area marked by tilted lines).

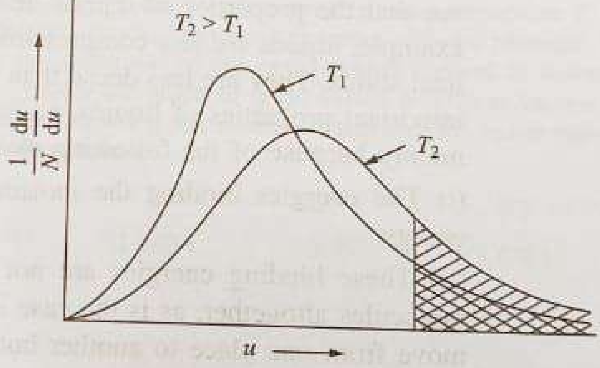

Fig. 2.2.2 Distribution of speeds of molecules

(ii) If we consider a molecule in the bulk of a liquid, it will be surrounded by other molecules in a symmetrical manner. Thus, the forces of attraction on this molecule by the molecules present on one side are completely balanced by the molecules present on the opposite side. Hence, the net force of attraction experienced by this molecule will, on the whole, be zero. It will move as if there exists no force of attraction on it. However, the situation is altogether different at the surface of the liquid (Fig. 2.2.3). There are larger number of molecules towards the liquid side of a molecule than towards the open space above it, with the result that this molecule experiences a net force of attraction in the downward direction.

The forces of attraction between the molecules of a liquid are of a stronger nature and are larger than the average thermal energy of the molecules. However, because of the Maxwell-Boltzmann distribution, some of the molecules can

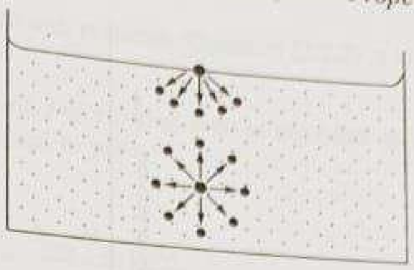

Fig. 2.2.3 Arrangement of molecules within and at the surface of a liquid

have thermal energies equal to or greater than the characteristic energy which is just sufficient to overcome the forces of attraction. If such a molecule happens to be at the surface, it will overcome the net downward forces of attraction and will immediately leave the surface and escape to the empty space above. If the space above the surface is an open one, then the molecules will continue to escape resulting in the phenomenon of evaporation. Since molecules of higher thermal energies are leaving the surface of the liquid, it follows, therefore, that the average thermal energy of molecules in the liquid will decrease. Consequently, the temperature of the liquid is reduced and hence cooling is observed.

Definition of Vapour Pressure

If the space ‘above the liquid is a closed one, then the molecules escaping from the surface of the liquid (referred to as vapour molecules) will go on collecting in the empty space. After some time it is observed that a constant pressure is registered. This pressure is due to vapour molecules of the liquid and hence it is known as the vapour pressure of the liquid. Since this pressure is constant, it follows that there must be a constant number of molecules in the space above the liquid. This can be true only if the molecules in the space are also returning to the liquid; otherwise, the pressure in the space would continue to increase. In fact, when a vapour molecule with a comparatively smaller thermal energy collides with the surface of the liquid, it sticks to the latter. Thus, there is a two-way process; the molecules are leaving the liquid and are simultaneously coming back to it. We get a state of dynamic equilibrium when the rate of evaporation of liquid molecules is equal to the rate of condensation of the vapour molecules. Thus, the vapour pressure of a liquid may be defined as the *pressure of the vapour in equilibrium with the liquid.* It is the same constant pressure which is required to convert a gas into a liquid when the former is below its critical temperature.

Effect of Temperature on Vapour Pressure

On raising the temperature, more and more molecules of a liquid will have energies equal to or greater than the critical energy which is just sufficient to overcome the forces of attraction between the molecules. As a result, larger number of molecules can leave the surface of the liquid which will consequently have higher vapour pressure. Thus, *the vapour pressure of a liquid increases with the increase in temperature.* The variation of vapour pressure of liquids with temperature is of the type shown in Fig. 2.2.4 with the highest and lowest limits correspond to critical point and triple point, respectively.

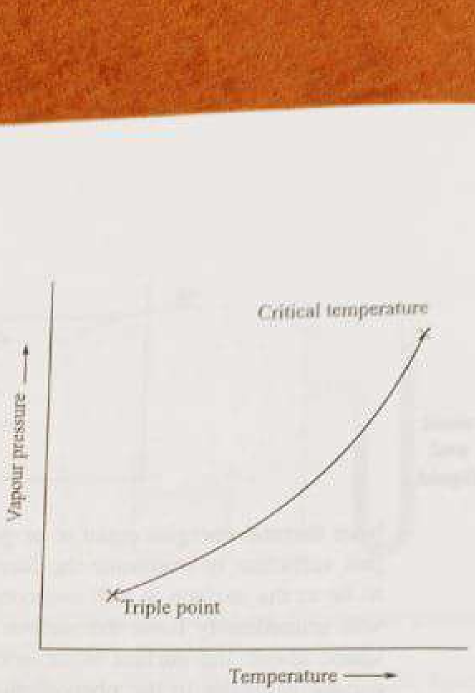

Fig. 2.2.4 Variation of vapour pressure with temperature

Clapeyron Equation The quantitative variation of vapour pressure with temperature is given by *Clapeyron equation,* according to which

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{T(V_{\mathrm{m,v}} - V_{\mathrm{m,l}})} \tag{2.2.1}$$

where $\mathrm{d}p/\mathrm{d}T$ is the rate of change of vapour pressure with temperature, $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ is the molar enthalpy of vaporization of the liquid, and $V_{\mathrm{m,v}}$ and $V_{\mathrm{m,l}}$ are the molar volumes of vapour and liquid, respectively. Equation (2.2.1) represents the slope of the plot of vapour pressure against the absolute temperature. This equation can be used to determine the molar enthalpy of vaporization of a liquid if the rate of change of its vapour pressure with temperature is known. Alternatively, if the value of $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ of the liquid is known, the rate of change of its vapour pressure with temperature can be calculated.

Clausius-Clapeyron Equation Equation (2.2.1) can be simplified under the following approximations as suggested by R. Clausius.

(i) The molar volume $V_{\mathrm{m,l}}$ of a liquid may be considered to be negligible in comparison to the molar volume of its vapour. This will be true provided the temperature is not near the critical temperature.

(ii) The liquid's vapour may be assumed to obey the ideal gas laws so that

$$V_{\mathrm{m,v}} = \frac{RT}{p}$$

With these two approximations, Eq. (2.2.1) modifies to

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{RT^2/p} \quad \text{or} \quad \frac{\mathrm{d}p}{p} = \frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{R}\left(\frac{\mathrm{d}T}{T^2}\right)$$

or

$$\mathrm{d}\ln(p/p^\circ) = \frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{R}\left(\frac{\mathrm{d}T}{T^2}\right) \tag{2.2.2}$$

where p° is the standard unit pressure. Equation (2.2.2) is known as the *Clausius-Clapeyron equation.*

Plot of Vapour Pressure versus Temperature

If the molar enthalpy of vaporization can be regarded as constant, Eq. (2.2.2) may be readily integrated to give

$$\mathrm{d}\,\ln(p/p^\circ) = \frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{R}\int\frac{\mathrm{d}T}{T^2}$$

or
$$\ln(p/p^\circ) = -\frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{RT} + I \tag{2.2.3}$$

where I is the constant of integration. According to this relation a graph between $\ln(p/p^\circ)$ and $1/T$ will give a straight line with a slope of $-\Delta_{\mathrm{vap}}H_{\mathrm{m}}/R$ as shown in Fig. 2.2.5.

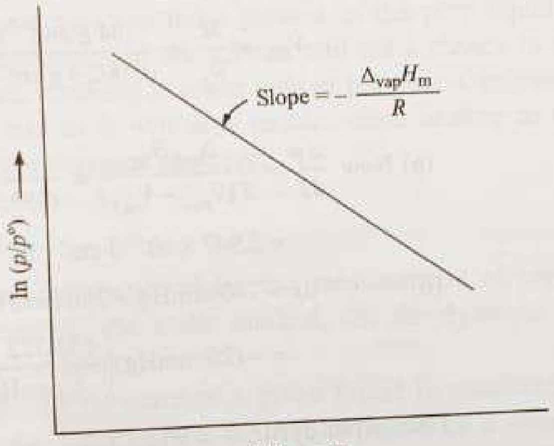

Fig. 2.2.5 Plot of ln (p/p°) versus $1/T$

Correlating Vapour Pressures at two Temperatures

If p_1 and p_2 are the vapour pressures at T_1 and T_2, respectively, then Eq. (2.2.2) can be integrated within the limits to give

$$\int_{p_1}^{p_2}\mathrm{d}\,\ln\left(\frac{p}{p^\circ}\right) = \frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{R}\int_{T_1}^{T_2}\frac{\mathrm{d}T}{T^2}$$

or
$$\ln\frac{p_2}{p_1} = -\frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$\tag{2.2.4}$$

or
$$\log\frac{p_2}{p_1} = -\frac{\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{2.303\,R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

Example 2.2.1

The enthalpy of vaporization of cyclohexane (C_6H_{12}) at its boiling point 80.75 °C is 385.15 J g^{-1}. The densities of the liquid and vapour at this temperature are 0.719 9 g cm^{-3} and 0.002 9 g cm^{-3}, respectively. (a) Calculate the value of dp/dT. (b) Estimate the boiling point at 740 mmHg. (c) If it is to be distilled at 25 °C, to what value must the pressure be reduced?

Solution

Given that
Molar mass of cyclohexane, $M = 84 \text{ g mol}^{-1}$
Enthalpy of vaporization per mole of cyclohexane

$$\Delta_{\text{vap}}H_{\text{m}} = (358.15 \text{ J g}^{-1})(84 \text{ g mol}^{-1}) = 30\,084.6 \text{ J mol}^{-1}$$

Molar volume of liquid,

$$V_{\text{m,l}} = \frac{M}{\rho_{\text{l}}} = \frac{(84 \text{ g mol}^{-1})}{(0.719\,9 \text{ g cm}^{-3})} = 177 \text{ cm}^3 \text{ mol}^{-1}$$

Molar volume of vapour,

$$V_{\text{m,v}} = \frac{M}{\rho_{\text{v}}} = \frac{(84 \text{ g mol}^{-1})}{(0.002\,9 \text{ g cm}^{-3})} = 28\,966 \text{ cm}^3 \text{ mol}^{-1}$$

(a) Now $$\frac{dp}{dT} = \frac{\Delta_{\text{vap}}H_{\text{m}}}{T(V_{\text{m,v}} - V_{\text{m,l}})} = \frac{(30\,084.6 \text{ J mol}^{-1})}{(353.9 \text{ K})(28\,966 - 117) \text{ cm}^3 \text{ mol}^{-1}}$$

$$= 2.947 \times 10^{-3} \text{ J cm}^{-3} \text{ K}^{-1} \equiv 2.947 \times 10^{3} \text{ N m}^{-2} \text{ K}^{-1} \equiv 2\,947 \text{ Pa K}^{-1}$$

(b) $$dp = 740 \text{ mmHg} - 760 \text{ mmHg} = -20 \text{ mmHg}$$

$$= -(20 \text{ mmHg})\left(\frac{133.322 \text{ Pa}}{1 \text{ mmHg}}\right) = -2\,666.44 \text{ Pa}$$

Thus, from $dp/dT = 2\,947 \text{ Pa K}^{-1}$, we get

$$dT = \frac{dp}{2\,947 \text{ Pa K}^{-1}} = \frac{-2\,666.44 \text{ Pa}}{2\,947 \text{ Pa K}^{-1}} = -0.905 \text{ K}$$

Hence, boiling point at this pressure = 80.75 °C − 0.905 °C ≈ 79.85 °C

(c) Making use of Clausius-Clapeyron equation,

$$\log \frac{p_2}{p_1} = \frac{\Delta_{\text{vap}}H_{\text{m}}}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

we get $$\log\left(\frac{p_2}{\text{mmHg}}\right) - \log(760) = \frac{(30\,084.6 \text{ J mol}^{-1})}{2.303(8.314 \text{ J K}^{-1} \text{ mol}^{-1})}\left(\frac{1}{353.9 \text{ K}} - \frac{1}{298.15 \text{ K}}\right)$$

$$\log(p_2/\text{mmHg}) = 2.880\,8 - 0.830\,4 = 2.050\,4$$

or $$p_2 = 112.3 \text{ mmHg}$$

Vapour Pressure and Boiling Point

If the pressure above a liquid is adjusted to a definite value, it is possible to raise the temperature so that the vapour pressure becomes equal to the external pressure. At this stage, bubbles of vapour are formed within the liquid which rise upwards and escape from the surface. We then say that the liquid has started boiling and the corresponding temperature is known as the *boiling point* of the liquid. Thus, the boiling point of a liquid can be defined as the *temperature at which its vapour pressure is equal to the external pressure.* If the latter is 1.013 25 bar (=1 atm), the boiling point is known as the normal boiling point. Obviously, the boiling point of a liquid can be varied by varying the external pressure. Increase in the external pressure will increase the boiling point of a liquid and decrease in external pressure will decrease its boiling point. It is evident from this that a plot of the variation of vapour pressure with temperature also represents the variation of boiling point of a liquid with the external pressure.

The Effect of Impurities on Boiling Point

The vapour pressure of a liquid invariably decreases with nonvolatile impurities. This is because of the fact that the surface will now be occupied by the molecules of both solute and solvent. Thus, there will be lesser number of molecules of the solvent as compared to those present in the pure liquid. Consequently, lesser number of molecules of the solvent will get a chance to escape from the surface of the liquid, resulting in lower vapour pressure. Obviously, boiling point of the liquid will rise as it will now require more heating to make its vapour pressure equal to the external pressure.

Measurement of Vapour Pressure

The methods generally employed for the measurement of vapour pressure fall into three categories: (i) the static method, (ii) the dynamic method, and (iii) the gas saturation method.

The Static Method

In this method, vapour pressure of a given liquid is measured by a manometer attached to the open space above the liquid placed in a closed vessel. One of the simplest procedures is to employ two barometric tubes. A small amount of the liquid is introduced in one of the tubes until the space above the mercury is saturated with vapour as shown by a small quantity of liquid remaining on the surface of mercury. The difference in the levels of mercury in the two tubes gives the vapour pressure of the liquid. An alternative form of the above method is due to A. Smith and A.W.C. Menzies and is known as the *isoteniscope method.* In this method, the liquid is introduced in the bulb A and in the attached U-tube as shown in Fig. 2.2.6. This system, which is known as the isoteniscope, is connected to a manometer M and to a vessel B which has a large volume in order to smooth out minor pressure fluctuations. The isoteniscope is put in a thermostat to keep the temperature constant. First of all, the apparatus is evacuated until the liquid begins to boil and the air between the liquid in the bulb and the U-tube is removed and contains only the vapour of the liquid. Now air is introduced slowly until the levels of liquid are same in both the limbs of the U-tube. At this stage, the pressure above the liquid in A (vapour pressure) is equal to pressure in B. The latter can be read with the help of a manometer (Fig. 2.2.6).

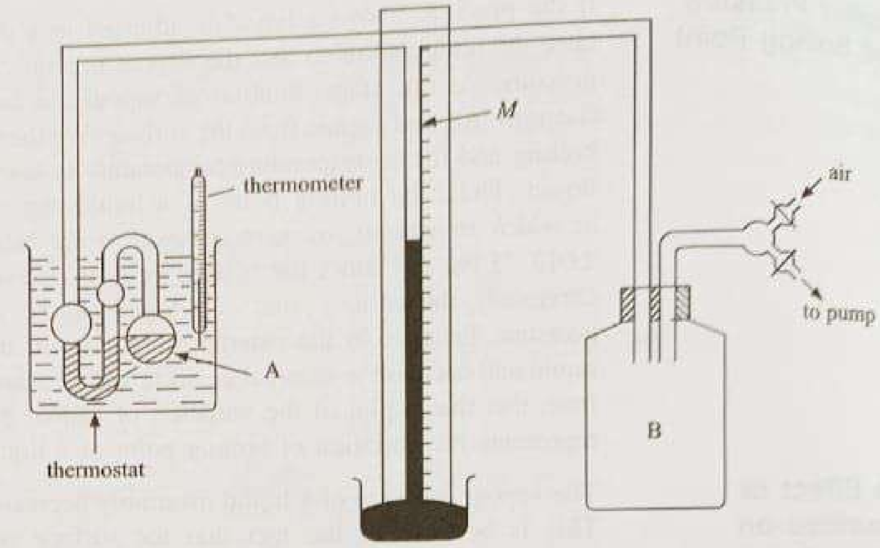

Fig. 2.2.6 The isoteniscope method for the measurement of vapour pressure

The Dynamic Method In this method, the external pressure is kept constant and temperature of the liquid is raised till it starts boiling. By definition, the vapour pressure of the liquid at this temperature will be equal to the external pressure. In recording the temperature, the thermometer should be placed in the vapour phase and not in the liquid so as to avoid the superfluous temperature recording, which may be caused due to the superheating of the liquid.

The Gas-Saturation Method In this method, a known mass of the liquid, whose vapour pressure is to be determined, is taken in a closed vessel and a known volume of dry air (or any gas which does not interact with the liquid) is passed repeatedly through it, keeping its pressure P constant. This way, the air carries along with it some of the molecules of the liquid and thus there occurs a loss in mass of the liquid. The gas is continuously passed till no further loss in mass occurs. At this stage, the air is saturated with the vapour of the liquid and the partial pressure p of the vapour in the mixture is equal to the vapour pressure of the liquid. If n_1 and n_2 are the amounts of vapour and dry air, respectively, then

$$p = \left(\frac{n_1}{n_1 + n_2}\right)P$$

If m is the loss in mass of the liquid and M is its molar mass, then

$$n_1 = \frac{m}{M}$$

Assuming air to be an ideal gas, we have

$$n_2 = \frac{PV}{RT}$$

Thus $$p = \frac{(m/M)P}{\left(\frac{m}{M} + \frac{PV}{RT}\right)} = \frac{mPRT}{mRT + PVM} \tag{2.2.5}$$

Thus knowing m (the loss in mass of the liquid), V (the volume of air to start with), P (the pressure at which the gas is being passed), M (the molar mass of the liquid), the vapour pressure p of the liquid at the given temperature T can be calculated from Eq. (2.2.5).

Example 2.2.2

A volume of 10.5 dm^3 of nitrogen measured at 30 °C and 102.66 kPa pressure is bubbled through a saturator containing bromobenzene (C_6H_5Br) at 40 °C. The mass of the saturator and its contents is reduced by 0.856 g. Calculate the vapour pressure of bromobenzene at 40 °C.

Solution

Amount of nitrogen, $n_2 = \dfrac{pV}{RT} = \dfrac{(102.66 \text{ kPa})(10.5 \text{ dm}^3)}{(8.314 \text{ kPa dm}^3 \text{ K}^{-1} \text{ mol}^{-1})(303.15 \text{ K})}$

$$= 0.427\,7 \text{ mol}$$

Pressure of nitrogen gas at 40 °C, $p = (102.66 \text{ kPa})\left(\dfrac{313.15 \text{ K}}{303.15 \text{ K}}\right) = 106.05 \text{ kPa}$

Amount of bromobenzene lost, $n_1 = \dfrac{m}{M} = \dfrac{0.856 \text{ g}}{(156.9 \text{ g mol}^{-1})} = 0.005\,5 \text{ mol}$

Total amount in the mixture, $(n_1 + n_2) = 0.005\ 5 \text{ mol} + 0.427\ 7 \text{ mol} = 0.433\ 2 \text{ mol}$

Mole fraction of bromobenzene in the mixture, $x = \dfrac{n_1}{n_1 + n_2} = \dfrac{0.005\,5 \text{ mol}}{0.433\,2 \text{ mol}}$

Vapour pressure of bromobenzene = partial pressure of bromobenzene in the mixture

$$= xp = \frac{(0.005\,5)}{(0.433\,2)} \times 106.05 \text{ kPa} = 1.347 \text{ kPa}$$

Empirical Relations Relating the Normal Boiling Point

It is of interest to mention here some of the empirical relations between the normal boiling point of a liquid and its other physical properties. Two such relations are given below.

For most liquids, the ratio of normal boiling point T_b and the critical temperature T_c is found to be 0.66.

$$\frac{T_b}{T_c} \simeq 0.66$$

Trouton's rule The molar enthalpy of vaporization divided by the normal boiling point has an approximately constant value of $10.5R$, i.e.,

$$\frac{\Delta_{vap}H_m}{T_b} \approx 10.5\,R$$

This relation holds more closely for non-associated substances of molar mass of about 100 g mol^{-1} and having not too high boiling points. For liquids of low boiling points, e.g., H_2 and He, the ratio is much less than $10.5R$ and for the associated liquids, such as water and alcohols, the value is greater.

2.3 VISCOSITY

Origin of Viscosity

It is a common experience of daily life that different liquids flow with different speeds. For example, water flows with greater speed than glycerol. Obviously, some sort of an internal friction is operating which checks the flow of liquids and which varies from liquid to liquid. This internal friction in the case of liquids is primarily due to forces of attraction between the molecules. If we have a laminar flow of a liquid in a tube, then the velocity of the layer just in touch with the side of the tube is zero and it increases as we proceed towards the centre of the tube (Fig. 2.3.1). Thus, there exists what is known as the velocity *gradient* between different layers of the liquid.

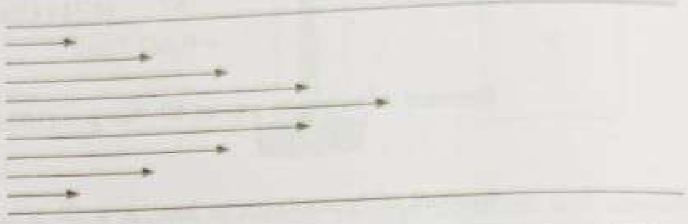

Fig. 2.3.1 Laminar flow of liquid in a tube

Due to greater intermolecular attractions amongst molecules of a liquid, the molecules moving in any one layer will tend to impede the movement of the molecules in the adjacent faster moving layer. As a result, the velocity of molecules in the faster layer decreases. Unless this decrease is prevented by applying a force along the layer in the forward direction, the velocity of the faster moving layer will go on decreasing and ultimately it will become zero. At this stage the liquid will stop flowing.

Definition of Coefficient of Viscosity

The internal friction which resists the flow of a liquid can be measured in terms of the tangential force which is needed to keep the speeds of different layers constant. This force F depends upon the following factors:

(i) It is directly proportional to A, the area of contact of two adjacent layers. Larger the area of contact between the two layers, larger the effect of intermolecular attractions and hence larger the decrease in speeds. Consequently larger force is required to maintain the speeds constant.

(ii) It is directly proportional to du, the velocity difference between two adjacent layes. Larger the velocity difference, larger the force required to maintain the constant velocity difference.

(iii) It is inversely proportional to dx, the distance between the two adjacent layers. Larger the distance, lesser the effect of intermolecular attractions and thus lesser the decrease in speed. Consequently, lesser force will be required to maintain the speeds of different layers.

Taking these factors together, we express F in the form,

$$F \propto A\frac{\mathrm{d}u}{\mathrm{d}x}$$

Removing the proportionality sign, we have

$$F = \eta A\frac{\mathrm{d}u}{\mathrm{d}x} \quad \text{or} \quad \eta = \frac{F}{A(\mathrm{d}u/\mathrm{d}x)} \qquad (2.3.1)$$

The constant η is known as the *coefficient of viscosity* of a liquid or simply *viscosity* of a liquid. It may be defined as *the force per unit area required to maintain a velocity difference of unity between two parallel layers of liquid unit distance apart*. The unit of viscosity in CGS units is dyn cm^{-2} s and is known as the poise unit. The unit of viscosity in SI units is N m^{-2} s (= Pa s). The unit viscosity in this case is equal to a unit force (1 N) required to maintain a velocity difference of unity (1 m s^{-1}) between two adjacent layers having unit area of contact (1 m^2) and being unit distance (1 m) apart. The viscosities of most of liquids are small in magnitude. Therefore, these are usually expressed in the units of centipoise (10^{-2} poise) and millipoise (10^{-3} poise). The SI equivalent of the poise unit may be derived as follows.

Unit of viscosity in CGS units = dyn cm^{-2} s
Unit of viscosity in SI units = N m^{-2} s = Pa s

$$1 \text{ poise} = 1 \text{ dyn cm}^{-2}\text{ s} = 1\,(10^{-5}\text{ N})\,(10^{-2}\text{ m})^{-2}\text{ s} = 10^{-1}\text{ N m}^{-2}\text{ s}$$

Dimension of η The dimension of viscosity η can be worked out as follows:

$$\eta = \frac{F}{A\dfrac{\mathrm{d}u}{\mathrm{d}x}} = \frac{\text{mass} \times \text{acceleration}}{\text{Area} \times \dfrac{\text{velocity difference}}{\text{distance}}} = \frac{m(lt^{-2})}{l^2\left(\dfrac{(lt^{-1})}{l}\right)} = ml^{-1}t^{-1} \quad (2.3.2)$$

Measurement of Viscosity

The following two methods are commonly employed for the determination of viscosity of a liquid.

Ostwald's Viscometer Method

This method is based on the Poiseuille's equation. If the volume v of a liquid requires the time t to flow through a capillary tube of radius r and length l under pressure head p, then its coefficient of viscosity as given by Poiseuille's equation is

$$\eta = \frac{\pi r^4 pt}{8\,lv} \quad (2.3.3)$$

The apparatus used, known as Ostwald's viscometer, is shown in Fig. 2.3.2. It consists of two bulbs A and B connected through a fine capillary tube. The bulb A is of bigger size whereas the bulb B is of smaller size. A known volume of liquid is taken in the bulb A and the liquid is sucked into the bulb B. The time taken in seconds for the liquid to flow from the mark a to mark b is noted down.

In order to avoid measurements of l, v and other factors in Eq. (2.3.3), one employs the relative method. Here, using the same viscometer, the experiment is repeated by taking same volume of a liquid whose viscosity is known. Water is usually employed for this purpose. If t_l and t_w are the times taken by the liquid and water to flow from mark a to mark b, respectively, we have

$$\eta_l = \frac{\pi r^4 p_l t_l}{8lv} \quad \text{and} \quad \eta_w = \frac{\pi r^4 p_w t_w}{8lv}$$

Dividing, we get

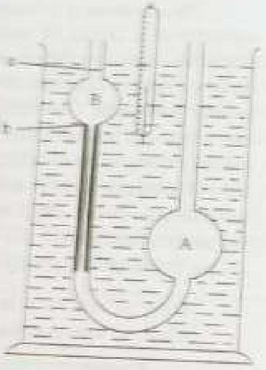

Fig. 2.3.2 Ostwald viscometer

$$\frac{\eta_l}{\eta_w} = \frac{\rho_l t_l}{\rho_w t_w} \tag{2.3.4}$$

The pressure head because of which the liquid flows through the capillary tube is numerically equal to the weight of the liquid in the bulb B. Though this pressure head changes during the flow of the liquid, yet at any instant it may be considered to be proportional to the density of the liquid. Thus Eq. (2.3.4) modifies to

$$\eta_l = \left(\frac{\rho_l t_l}{\rho_w t_w}\right)\eta_w \tag{2.3.5}$$

Hence if the factors on the right side of Eq. (2.3.5) are known, the value of η_l can be calculated.

Stokes Falling Sphere Method

If a steel ball is allowed to fall through a liquid, after some time it acquires a constant velocity. This happens when the force responsible for its downward motion (i.e. weight of the ball in the liquid) becomes equal to the frictional forces (due to the viscosity of the liquid) acting in the opposite direction. The uniform rate of streamlined fall of a sphere of radius r in a liquid is related to its viscosity through the Stokes relation:

$$u = \frac{F}{6\pi\eta r} \tag{2.3.6}$$

where F is the force acting downwards and is equal to the weight of the ball in air minus the weight of the displaced liquid, i.e.

$$F = \left(\frac{4}{3}\pi r^3\right)\rho_s g - \left(\frac{4}{3}\pi r^3\right)\rho_l g = \frac{4}{3}\pi r^3(\rho_s - \rho_l)g$$

Substituting this in Eq. (2.3.6) and rearranging, we have

$$\eta = \frac{F}{6\pi ur} = \frac{\frac{4}{3}\pi r^3(\rho_s - \rho_l)g}{6\pi ur} = \frac{2r^2(\rho_s - \rho_l)g}{9u} \tag{2.3.7}$$

The apparatus used in this method is shown in Fig. 2.3.3.

Fig. 2.3.3 Stokes falling sphere method

A General Comment on the Viscosity of Liquids

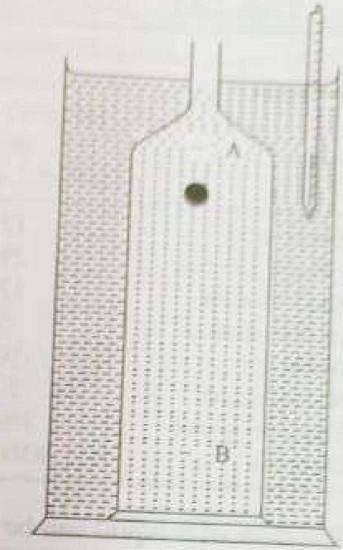

Fig. 2.3.3 Stokes falling sphere method

The given liquid is taken in a tall cylindrical vessel and its temperature is kept constant by surrounding the vessel with a thermostat. A small stainless steel ball is introduced from the top of the liquid and the time taken by it to travel between two marks A and B on the cylinder with a uniform velocity is noted down.

Thus in Eq. (2.3.7), $u = l/t$, where l is the distance between the two marks A and B. If we know the radius of the ball and densities of the ball and the liquid, the coefficient of viscosity of the liquid as given by Eq. (2.3.7) becomes

$$\eta = \frac{2r^2(\rho_s - \rho_l)g}{9(l/t)} \qquad (2.3.8)$$

If the experiment is repeated with a liquid (known as the reference liquid) of known viscosity then r and l in Eq. (2.3.8) can be eliminated. Thus

$$\frac{\eta_1}{\eta_2} = \frac{(\rho_s - \rho_1)t_1}{(\rho_s - \rho_2)t_2} \qquad (2.3.9)$$

where η_1 and η_2 are the viscosities, ρ_1 and ρ_2 are the densities, and t_1 and t_2 are the times required for the steel ball to travel through the given liquid and the reference liquid, respectively. Thus by knowing η_2 and determining values of t_1 and t_2 experimentally, the value of η_1 can be calculated by using Eq. (2.3.9.)

A General Comment on the Viscosity of Liquids

The coefficients of viscosity at 20 °C of some of the common liquids are given in Table 2.3.1.

It can be concluded from these values, that, in general, the coefficients of viscosity of associated liquids are larger than those of non-associated liquids. For example, $\eta(C_2H_5OH) > \eta(C_2H_5OC_2H_5)$. This is largely due to the hydrogen bonding between the molecules of a liquid. Glycerol and ethylene glycol have comparatively larger values of coefficients of viscosity since they have more than one hydroxyl group. Because of these hydroxyl groups, a network of hydrogen bonds is formed between the molecules which extends throughout the liquid, thus offering greater resistance to flow.

Table 2.3.1 Coefficients of Viscosity of Some Common Liquids at 20 °C

Substance	*Coefficient of viscosity* $(\eta/\text{poise}) \times 10^3$ or $(\eta/\text{N m}^{-2}\text{ s}) \times 10^4$	*Substance*	*Coefficient of viscosity* $(\eta/\text{poise}) \times 10^3$ or $(\eta/\text{N m}^{-2}\text{ s}) \times 10^4$
Acetic acid	12.29	Ethyl ether	2.33
n-Butyl alcohol	29.5	Acetone	3.29
Ethyl alcohol	12.0	Carbon tetrachloride	9.68
Methyl alcohol	5.92	Chloroform	5.63
Water	10.02	Benzene	6.47
Nitrobenzene	20.10	Toluene	5.90
Ethylene glycol	199		
Glycerol	8500		

Fluidity of Liquids

The flow of a liquid can be expressed in terms of fluidity ϕ, which is reciprocal of the viscosity, i.e.

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

The fluidity (or the viscosity) of a liquid depends on various factors, some of which are:

(i) Heavier and larger molecules flow less easily than the lighter and smaller molecules.

(ii) Spherical molecules offer less resistance to flow than the plate-like molecules. Molecules with flexible chains offer a very high resistance to flow because of entangling of side chains.

(iii) Impurities invariably increase the viscosity of a liquid. The presence of lyophilic colloids, in particular, enhance the viscosity of a liquid to a large extent.

Effect of Temperature on Viscosity

The viscosity of a liquid decreases with increase in temperature and this decrease is roughly of the order of 2 per cent per Celsius degree. This is due to the fact that on raising the temperature of a liquid, the average thermal energy of its molecules is increased and thus the effect of intermolecular attractions is decreased. Before a molecule can take part in liquid flow, it is expected that it should have sufficient energy to overcome the forces of intermolecular attraction due to the surrounding molecules. This energy is known as the *activation energy for viscous flow*. It is known that the number of molecules having this minimum energy or greater than this, increases in proportion to the Boltzmann factor $\exp(-E/RT)$ and hence the resistance to flow of the viscosity may be expected to decrease in a reciprocal manner, i.e.,

$$\eta \propto \exp(E/RT) \quad \text{or} \quad \eta = A\exp(E/RT)$$

or

$$\ln(\eta/\eta^\circ) = \ln(A/\eta^\circ) + \frac{E}{RT}$$

where η° is the standard unit viscosity. Thus, $\ln(\eta/\eta^{\circ})$ varies linearly with $(1/T)$ as shown in Fig. 2.3.4. From the slope, the activation energy for viscous flow can be calculated.

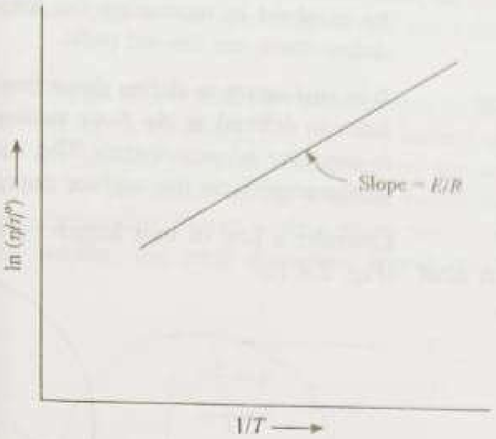

Fig. 2.3.4 Plot of ln (η/η°) versus $1/T$

Viscosities of Mixtures

The fluidity of an ideal mixture which involves similar types of liquids, such as a mixture of benzene and toluene, is best represented by the following equations:

$$\phi = x_{\mathrm{A}}\phi_{\mathrm{A}} + x_{\mathrm{B}}\phi_{\mathrm{B}} \qquad \text{(Bingham's equation)}$$

$$\log(\phi/\phi^{\circ}) = x_{\mathrm{A}}\log(\phi_{\mathrm{A}}/\phi^{\circ}) + x_{\mathrm{B}}\log(\phi_{\mathrm{B}}/\phi^{\circ}) \qquad \text{(Kendall's equation)}$$

where ϕ° is the standard unit fluidity. These equations are not applicable to non-ideal solutions which involve dissimilar type of liquids. If the constituents of a solution strongly interact with each other then the observed fluidity is less than the calculated value, i.e., a considerable increase in viscosity occurs in such a case. One of the examples is the water and ethanol mixture. In this mixture, a strong interaction between the molecules of water and ethanol takes place due to the hydrogen bondings. If the mixture involves a polar and a nonpolar liquid such as alcohol and benzene then the observed fluidities are higher than the predicted fluidities as obtained by the use of either Bingham or Kendall equation.

2.4 SURFACE TENSION

Introduction

It was seen during the study of vapour pressure that the molecules at the surface of a liquid experience a net inward pull because of the larger number of molecules towards the liquid side than towards the vapour side. There is a tendency on the part of surface molecules to go in the bulk of the liquid. The surface of liquid is therefore in some sort of tension and it tends to contract to the smallest possible area in order to have the minimum number of molecules at the surface. It is for this reason that the surface of a liquid is spherically curved, since the surface area is minimum for a given volume in the case of a sphere.

Surface Energy

If the area of the surface is to be extended then one has to bring more molecules from the bulk of a liquid to its surface. This will require expenditure of some energy because work has to be done in bringing molecules from the bulk against