Chapter 2

THEORETICAL ASPECTS

The chapter deals with the theoretical aspects of viscometric technique, different types of viscometers available in the literature are described. The principles and procedures involved in these viscometers have been explained. Principles and theory of open-end capillary tube viscometer developed in the laboratory have been presented in detail.
VISCOMETERS

Various types of viscometers, which are being used for the study of viscometric parameters of many biological and non-biological fluids, have been described.

2.1. DEAD-LOAD VISCOMETERS

A capillary viscometer is basically quite simple device, which is used to study viscous properties of fluids having diverse characteristics. In this viscometer a load mass M is applied as constant load to a specimen placed in the reservoir of the apparatus (Fig. 2.1.)

![Fig. 2.1. Dead-load capillary microviscometer](image)

1. die 2. cylinder (barrel) 3. load
4. displacement gage 5. specimen 6. thermostating device

The load causes the specimen to be forced through a capillary under the cylinder. The shear stress $T_R$ is evaluated as

$$T_R = \frac{Mgr}{2\pi R^2 (L + mr)}$$

Where R and r are the radii of the cylinder and the capillary, respectively m is the end correction, and 'g' is acceleration of free fall. The viscometer allows measurements to be performed within range of shear rates varying from 0.01 to 100 s$^{-1}$, of stresses $T_R$ ranging from 6x10$^2$ to 10$^6$ Pa, and temperatures up to 350°C. The approximate limits with respect to the
viscosity are $10^2$ to $10^3$ Pa.S. From one to two grams of the material are needed for tests. This technique is intended for a comparative technological appraisal of plastics. The volumetric flow rate is measured in this according to the displacement of piston. Knowing the applied load ($M$), flow rate ($Q$) and density ($d$) of the liquid, the coefficient of viscosity can be calculated using the relation.

$$ \eta = \frac{0.5 M d}{Q} $$

Dead load viscometers are often used for the microanalysis of polymers.

2.2. GAS VISCOMETERS OR CONSTANT PRESSURE VISCOMETERS

A constant pressure gas capillary viscometer is shown in Fig. 2.2.

![Fig. 2.2. Pressure gas capillary viscometer](image)

1. replaceable high-pressure cylinder 2. pressure governor 3. distributor
4. cylinder 5. manometric panel 6. manometric panel 7. hydraulic pressure booster
8. pump 9. manometric panel

The energy of compressed gas is used to create a load for forcing a material being studied through a die. This maintains a constant pressure. The rate of mass flow of the fluid is measured according to the mass of the portions of the extrudate emerging from the die in a
definite time. By using dies of various radii and lengths, the rate of the mass flow rising from $1 \times 10^{-5}$ to 10 g/s can be measured. At the lowest rates the error may reach 10%. This viscometer can be used to measure shear rates varying from $10^{-5}$ to $10^{4}$ s$^{-1}$ and shear stress in the range of $10^2 - 10^6$ Pa.

A drawback of this instrument is the need to have a considerable amount of the material for the test. The viscosity ranges from 0.2 to 1.4 Pa.s.

2.3. COUNTER PRESSURE VISCOMETERS

In this viscometer, measurements are to be taken with a counter pressure, when considerable pressure $P_{II}$ is set up at the exit from the die. This method can be used to measure the pressure dependence of the apparent viscosity. In this apparatus (Fig 2.3.)

![Fig. 2.3. Counter-pressure viscometer](image)

- 1. die
- 2. specimen
- 3. piston connected to high-pressure chamber
- 4. piston connected to low-pressure chamber
- 5. heaters

A liquid being studied flows through the die under the action of the load $P_D$, the specimen being under the additional static pressure $P_{II}$. The volumetric rate of flow is determined according to the time needed for motion of the rod connecting the working chamber and gas cylinder between two limit micro switches. One of them triggers a stopwatch and the other stops it. The distance between the micro switches is 2.5 mm.
This apparatus can be used to measure viscous properties of molten polymers and other liquids at a hydrostatic pressure exceeding 2000 kg/cm². This apparatus can also be used to study solutions within a viscosity range from 1 to Pa.s.

2.4. CONSTANT RATE CAPILLARY VISCOMETERS

The capillary viscometers in which a constant piston speed is set and the forces are measured are known as constant-rate viscometers. The measuring cell is installed between the piston and the drive. Using a set of interchangeable capillaries of diameter ranging from 0.25 to 2.5 mm and length ranging from 12 to 100 mm, the viscometers can measure the viscosity at rates of shear from $1.71 \times 10^{-2}$ to $7.4 \times 10^{5}$ s⁻¹ at a preset temperature from room to 340°C.

2.5. DEAD-LOAD VISCOMETERS WITH VARIABLE LOADS

In this apparatus (Fig. 2.4)

![Diagram of a two-capillary dead-load scanning viscometer]


the material being studied is simultaneously extruded through two dies of the same diameter, but of different lengths. The forces acting in each cylinder are changed separately, which makes it possible to calculate shear rate using the relation
A variable load in a capillary viscometer can be produced by lowering column of the liquid, whose viscosity is to be measured. Such a viscometer with varying conditions of extrusion is a cylindrical vessel terminating in a die. The height \( h(t) \) of the liquid column diminishes with the time \( t \). The pressure determined by the varying height of the liquid column, the volumetric rate of flow and rate of change of the level \( dh/dt \). Therefore, the parameter \( h(t) \) gives information of pressure and volumetric rate of flow. Hence, directly follows the formula for the viscosity.

\[
\eta = \frac{A}{dh/dt} \left( 1 + \frac{B}{h} \right)
\]

Where \( A = \rho g r^2/8 \) and \( B = 1 R^4/r^4 \) are constants of the apparatus expressed in terms of its geometric dimensions; the radius of the cylinder \( R \), the radius of the die \( r \), its length \( l \), and also the density of the liquid being studied and the acceleration of free fall. This method can be used for measuring the viscosity of conventional liquids.

2.6. GLASS VISCOMETERS

The glass viscometers, widely used for determining the viscosity of dilute solutions of polymers and low-molecular liquids, are a variety of dead-lead capillary viscometers intended for measurements at low pressures. Scores of designs and arrangements of glass viscometers are known that are, intended for determining the viscous properties in such special cases as measurement of the viscosity of opaque, highly volatile, poisonous etc. liquids.

In general, glass viscometers include Ostwald viscometer and Ubbelohde viscometer. The common elements of the Ostwald - Fenske (Fig. 2.5.a) and Ubbelohde (Fig. 2.5.b) glass viscometers, which have been found the greatest favour for studying polymers solutions, consist of a calibrated capillary and a measuring reservoir. A test consists in measuring the time needed to empty a reservoir of a definite volume.
In these viscometers, the liquid flows out through the capillary under the action of a liquid column of varying height and, consequently, with the application of a varying pressure. A formula is proposed for calculating the mean pressure $P$ as (Back & Meissner, 1967).

$$p = \frac{(h_1 - h_2) \rho g}{\ln h_1 - \ln h_2}$$

where $h_1$ and $h_2$ are the initial and final heights of the liquid column, $\rho$ is its density, and ‘$g$’ is the acceleration due to gravity.

The viscosity can be considered to be proportional to ‘$\eta$’ and $t_0$ the time $t_0$ needed for the outflow of a calibrated volume, i.e.,

$$\eta = C \rho t_0$$
where C is constant of the apparatus automatically taking into account the way of averaging the height of the column. Since the constant C is not known before hand, it can be determined in calibration of the apparatus. It is possible, however, to compare the viscosities $\eta$ and $\eta'$ of two liquids directly, knowing their densities $\rho$ and $\rho'$ and measuring the durations of out flow $t_0$ and $t_0'$. Using the above formula, $\eta/\eta' = \rho_0 / \rho't_0'$. This measuring arrangement is commonly used for $t_0 > 100$ s.

2.7. ROTATIONAL VISCOMETERS

The use of rotational apparatus is for studying the mechanical properties of liquids. The rotational viscometers involve the relation between the torque (M) and the angular speed (w) of rotation of the measuring surfaces. The rotational viscometers commonly used are described below:

2.7.1. Concentric cylinder viscometry

Let the radii of the inner and outer concentric (coaxial) cylinders be $R_1$, and $R_0$ ($\varepsilon = R_0/R_1$), the radial distance from the axis of rotation be $r$ and the depth of the gap filled with medium being studied be $h$ (Fig. 2.6.).

![Fig. 2.6. Concentric cylinder viscometer](image)

The torque $M = 2 \pi r^2 nT$

For the Surfaces of the outer and inner cylinders we have $M = 2\pi R_2 T_0 = 2\pi R_1^2 h T_0 =$ Constant; where $T_0$ and $T_1$ are the shear stresses on the surface of the outer and inner cylinders, respectively. It thus follows that
\[ \frac{T_r}{T_0} = \frac{R_o}{R_r} = \varepsilon^2 \] The degree of homogeneity of the stress field is \((1-\varepsilon^2)\).

Rate of shear

Let \(w\) be the angular and \(u\) the linear speed at a point with radius \(r\).

\[ \frac{du}{dr} = \frac{d}{dr} (wr) = w + \frac{rdw}{dr} \]

If the outer cylinder is stationary and the inner one rotates, i.e., \(w = 0\) at \(r = R_0\), and \(w = \Omega\) at \(r = R\)

\[ \Omega = 1/2 \int_{r_i}^{r_o} f(T) \, dT \]

When measuring the viscosity \(\eta_0\) of a Newtonian liquid, the rate of shear depends linearly on the stress

Therefore, \[ \eta_n = \frac{KM}{\Omega} \]

Where \(K = (\varepsilon^2 - 1)/4\pi\eta R_i^2 \varepsilon^2\) is the form factor or apparatus constant.

2.7.2. Conical Surface Viscometers

An important way of measuring the viscosity, especially of highly viscous liquids, is the finding of the rotational speeds and torques in the isothermal flow of a specimen in the gap between two coaxial cones with a common apex or between a conical surface and plate (Fig. 2.7.).

![Fig. 2.7. (a) Cone and cone (b) Cone and plate viscometers](image-url)
The theory of operation of such viscometers is based on analysing the flow of the liquid with the use of a spherical coordinate system, where the angle $\theta$ is measured from the vertical axis.

Shear stress $T = C / \sin^2 \theta$

The integration constant $C$ is related to the torque $M$ acting on the surface of a cone. If the altitude of the inner cone is $H$ and the stress on its surface are $T$, we have

$$M = 2\pi \int_0^H T \cdot h^2 \frac{\sin^2 \alpha}{\cos^2 \alpha} \, dh = 2\pi H^3 \frac{\sin^2 \alpha}{\cos^3 \alpha} T$$

$$T_{\alpha} = \frac{3M}{2\pi H^3} \frac{\cos^3 \alpha}{\sin^3 \alpha}$$

$$T(\theta) = T_{\alpha} \frac{\sin^2 \alpha}{\sin^2 \theta}$$

For cone and plate apparatus, as a general rule, the angle $\delta$ is small. Hence degree of homogeneity of the stressed as $T \beta / T \alpha = \cos^2 \delta$ is least 99%, and we may consider that $T =$ constant. Since $\sin \alpha = \cos \delta = 1 - \delta^2 / 2$ we have

$$T = \frac{3M}{2\pi R^3} \frac{\cos^3 \delta}{1 - \delta^2 / 2} = \frac{3M}{2\pi R^3}$$

The main source of errors in viscometers with conical surfaces are the end effects i.e., the perturbations appearing near the edge of the cone.

**Rate of shear**

The quantity $r$ in spherical coordinates is given by

$$r = f(r') = \sin \theta \frac{dw}{dw}$$
Substituting the quantity $T$ from formula $T = T_a \frac{\sin^2 \alpha}{\sin^2 \theta}$ for the variable $\theta$ loads to the following equation for the function $f(T)$

$$d\omega = -\left[ \frac{f(T)}{2} \sqrt{T(T - T_a \sin^2 \alpha)} \right] dT$$

With a high degree of accuracy, and $\hat{r}$ is evaluated as follows:

$$\hat{r} = \frac{\Omega}{\delta(1 - \delta^2/6)} = \frac{\Omega}{\delta}$$

$$= \frac{KM}{\Omega}$$

$K = 3\delta / 2\pi R^3$ is the constant of apparatus.

### 2.7.3. Coni-Cylindrical and Bioconical Viscometers

A combination of a cylindrical measuring surface with a conical one is one of the ways to eliminate end effects. Designs of apparatus are possible in which both edge surfaces of the outer cylinder make small angles with the conical surfaces of the inner part of an apparatus (Fig. 2.8).

The shear stress $T$ and the torque $M$ is related by

$$T = \frac{M}{2R^3 \left[ 2 + \left( \frac{H}{R} \right) - \left( \frac{R_e}{R_i} \right)^2 \right]}$$
2.7.4. Disk Viscometers

If both conical surface degenerate into a plane between which a gap is height ‘h’ is left, the apparatus obtained can be called a disk viscometer. For Newtonian liquids, the viscosity $\eta_0$ can be determined according to the ratio of the torque $M$ to the angular speed $\Omega$

$$\eta = K \frac{M}{\Omega}$$

Where $K = \frac{2h}{\pi R^4}$ for non-Newtonian liquids

$$\eta(\tau_m) = \bar{\eta}\left(1 + 0.25 \frac{d \log \bar{\eta}}{d \log \tau_m}\right)$$

Where $\bar{\eta}$ stands for the quantity $2hM/\pi R_4\Omega$, ‘h’ is the distance between the disks, $M$ is the torque $R$ is the radius of the disks, $\Omega$ is the speed of rotation, and

$$\tau_m = \Omega R/L$$

2.7.5. Sphere-Sphere Viscometers

In this, the liquid to be studied is poured between the spheres of a common center. The inner sphere is rotated at a constant speed $\Omega$, and the torque $M$ appearing as a result is measured. The viscosity then is

$$\eta_0 = \frac{M \left(R_i^{-1} - R_o^{-1}\right)}{8\pi\Omega}$$

Where $R_i$ and $R_o$ are the radii of the inner and outer spheres respectively.
2.7.6. Monospherical Viscometer

The torque $M$ produced upon the rotation of a sphere of radius $R$ about its axis is measured. The viscosity then is

$$\eta = \frac{M}{8 \pi R \cdot \Omega}$$

2.8. FALLING BALL METHOD

The resistance to motion of a body in a viscous liquid depends on the viscosity of the latter. Hence, one can appraise the viscosity of a liquid by measuring the speed of a body in it. This method of measuring the viscosity is realized in the most obvious way in devices in which a ball falls vertically in vessel filled with the test liquid (Fig. 2.9).

Fig. 2.9. falling ball viscometer

1. Cylindrical tube  2. ball  3. liquid

This method of measuring the viscosity is in great favour for low-molecular liquids.

When a ball of radius $R$ made from a material of density $\rho_1$ moves in a liquid whose density is $\rho_2$ and whose viscosity is $\eta$, the driving force $F$ is given by

$$F = \frac{4}{3} \pi R^3 (\rho_1 - \rho_2)g$$
This formula is valid for Reynolds number less than 0.1.

Shear stress \( T_w = \frac{R(\rho_1 - \rho_2)g}{3} \)

2.8.1. Correction for Non-Newtonian effect

If the viscosity of a liquid being studied depends on the rate of shear the results of the viscosity obtained by the falling ball method depend on falling speed. By varying the material with which the falling balls are made from, and can vary the stresses within the range from 1 to 100 pa. For this, the method of extrapolation of the results is obtained to a zero shear stress. The viscosity of the non-Newton liquids.

\[
\eta = \frac{\eta_0}{1 + C T^2}
\]

Where \( C \) is an empirical constant, and \( \eta_0 \) is the initial Newtonian viscosity that must be determined. \( \eta_0 \) is obtained by plotting \( \eta^1 \), versus \( T^2 \) with \( T = 0 \)

2.8.2. Rolling Ball Method

The cylindrical tube can be arranged at a certain angle \( \theta \) to the vertical axis so that the driving force is expressed by the formula

\[
F = 4 \pi R \left( \rho_1 - \rho_2 \right) g \cos \theta
\]

A ball in an inclined tube rolls down along a wall over its entire length. The resistance to motion of the ball

\[
\eta = \frac{C_1 P}{U}
\]

Where \( p \) is the pressure produced by the weight of the ball or by an external force, \( u \) is the speed, and \( C \) is the apparatus.
2.9. FALLING CYLINDER VISCOMETER

In the laminar flow of a body of any shape in a viscous Newtonian liquid, the force of resistance $F$ is proportional to the viscosity of the liquid $\eta$. This allows one to replace a ball with a different geometrical shape.

The longitudinal motion of a cylinder of radius $R_i$ in a coaxial cylindrical tube of radius $R_o$ is attended by the appearance of a velocity profile described by

$$U(r) = u_i \frac{\ln (r / R_o)}{\ln (R_o / R_i)}$$

Where $u_i$, is the speed of the inner cylinder, and $r$ is the radial position in the gap.

This gives the following expression for the force $F$ per unit cylinder length

$$F = 2\pi R_i \eta \frac{du}{dr} \Big|_{r = R_i} = \frac{2\pi \eta u_i}{\ln (R_o / R_i)}$$

The above equation allows to find only the component of the total force of resistance to motion of the cylinder associated with friction, when the liquid flows between the cylinder and the tube. The complete expression for the speed $u_i$, of a body falling under the action of a density difference $(\rho_i - \rho_\gamma)$ has the form

$$u_i = \eta \frac{\rho_i - \rho_\gamma}{2} R_i^2 \ln k^{-1} + \frac{k^2 - 1}{k^2 + 1} \theta$$

Where $k = R_i / R_o$ and $\theta$ is a correction factor, taking into account, the boundary effects appear owing to the features of the velocity field near the cylinder ends.

Calculation of the viscosity using formula with account of the factor $\theta$ makes these viscometers as absolute ones.
Although there exists a strict theory of falling cylinder viscometers, they are commonly treated as relative instruments and viscosity is calculated from the values of $u_1$, with the aid of the formula

$$\eta = \frac{Bu_1}{\rho_1 - \rho_2}$$

Where $B$ is a constant determined in calibration of the instrument according to reference liquids with a known viscosity.

2.10. THEORETICAL CONSIDERATIONS OF THE PRESENT TECHNIQUE

Capillary viscosity is the most traditional method for measuring the viscosity of the viscous media. The development of capillary viscometer is associated with the transition from qualitative to quantitative procedures, improvement of the experimental equipment and the theoretical fundamentals of the method.

In the present investigation a theory is developed for the dynamics of a liquid column in an open capillary tube. No external pressure is applied on the liquid column. The pressure at the two ends of the capillary tube is the atmosphere pressure.

Assume that a liquid column of length $L$ flows through a capillary tube of radius $R$. The forces acting on the liquid column are:

1. Gravitational force ($F_g$)
2. Viscous force ($F_v$)
3. Force due to surface tension ($F_s$)
4. Inertial force ($F_a$)

From Poiseuille's equation, viscous force ($F_v$) acting on the fluid column can be obtained as

$$F_v = 8 \pi \eta L v$$
Where $\eta$ = coefficient of viscosity of the fluid.

$v$ = velocity of the fluid column

$L$ = length of the fluid column.

The gravitational force $(F_g)$, acting on the fluid column $L$ is

$$F_g = \pi R^2 L \rho g$$

Where $L$ = length of the fluid column

$\rho$ = density of the fluid

$R$ = radius of the capillary tube

$g$ = acceleration due to gravity

The liquid column in the vertical capillary tube has two free surfaces (upper and lower) in which the upper surface experiences a force due to surface tension of the liquid, which can be given as

$$F_s = 2\pi RT \cos \theta$$

Where $T$ is surface tension of the liquid, $\theta$ is the angle of contact of the liquid.

Here, it is assumed that the lower surface does not experience the force due to surface tension of the liquid, when the liquid column in the vertical capillary tube is in motion.

The inertial force $(F_a)$ is acting on the liquid column due to the accelerated motion of the liquid when the external pressure is applied on it. This force is given by the equation

$$F_a = \pi R^2 L \rho \frac{d^2 L}{dt^2}$$

Where $\frac{d^2 L}{dt^2}$ is the acceleration of the liquid column.
The free-body diagram of the forces acting on the liquid column in a vertically held capillary tube, when the liquid is flowing is depicted in Fig. 2.10.

![Free-body diagram](image)

\[ \uparrow F_v = 8 \pi \eta L v \]
\[ \uparrow F_s = 2 \pi r T \cos \theta \]
\[ \downarrow F_s = \pi r^2 L \rho \]

*Fig. 2.10. Free-body diagram*

The upward forces are viscous force \( F_v \) and force due to surface tension \( F_s \). The downward forces are gravitational pull \( F_g \) and inertial force \( F_s \) due to the accelerated motion of liquid column.

From free-body diagram,

\[ \sum F_y = F_u \]

\( F_y \) represents the vertical component of the force.
Here, it is observed that flow of the liquid is steady. Hence, \( F_a = 0 \)

Therefore \( \Sigma F_y = F_g - F_v - F_s = 0 \)

Substituting Eqn. 2 to 4 in above Eqn. 5, we get

\[
\pi R^2 \rho g l - 8 \pi \eta L v + (-2 \pi RT \cos \theta) = 0
\]

When divided by \( \pi L \) throughout

\[
R^2 \rho g - 8 \pi \eta v - \frac{2RT \cos \theta}{L} = 0
\]

\[
8 \pi \eta v = -2 RT \frac{l}{L} + R^2 \rho g
\]

\[
v = \frac{-2 RT \cos \theta}{8 \pi} \frac{l}{L} + \frac{R^2 \rho g}{8 \pi \eta}
\]

The above equation fits into the equation of a straight line,

\[
Y = mx + C
\]

Therefore, if the parameters, \( L \) and \( V \) related to the liquid column were plotted as X-axis and Y-axis respectively, the response would be a straight line. The intercept of the straight line on Y-axis gives the characteristic velocity \( V_0 \) the velocity of continuous flow, of the liquid, (Fig. 2.11).
From the Fig 2.11 we get;

\[ v_u = \frac{R^2 \rho g}{8 \eta v} \]

Then the coefficient of viscosity,

\[ \eta = \frac{R^2 \rho g}{8 v_u} \]
The slope of the straight line is given as

\[ \tan \alpha = \frac{2\pi RT \cos \theta}{8\eta} \]

The surface tension of the liquid can be obtained as

\[ \tau = \frac{4\eta \tan \alpha}{R \cos \theta} \]

Thus, coefficient of viscosity and surface tension of the liquid can be obtained by measuring velocity for different lengths of liquid column and plotting a graph between \( L^{-1} \) on X-axis and \( v \) on Y-axis.