Calibration and **Calculation of kinematic and Newtonian viscosities of sample fluid:** Proceed as directed in *Method I*.■2S (*USP35*)

Add the following:

■⟨912⟩ ROTATIONAL RHEOMETER METHODS

The principle of the method is to measure the force (torque) acting on a rotor when it rotates at a constant angular velocity (rotational speed) in a liquid. Rotational rheometers/viscometers are used for measuring the viscosity of Newtonian fluids, i.e., a fluid having a viscosity that is independent of the shearing stress or rate of shear, or the apparent viscosity of non-Newtonian fluids, which may exhibit different rheological behavior, depending on shear rate, shear stress, and temperature. The following procedures are used to determine the viscosity of Newtonian fluids or the apparent viscosity of non-Newtonian fluids. The calculated viscosity of Newtonian fluids should be the same (within experimental error), regardless of the rate of shear (or rotational speed). Given the dependence of viscosity on temperature, the temperature of the substance being measured should be controlled to within ±0.1°, unless otherwise specified in the individual monograph. Unless otherwise directed in the individual monograph, use *Method I*.

• **METHOD I. SPINDLE RHEOMETERS (RELATIVE RHEOMETERS—SPINDLE VISCOMETERS)**

Apparatus: In the spindle rheometer, the apparent viscosity is determined by rotating a cylinder- or disc-shaped spindle, as shown in *Figures 1* and *2*, respectively, immersed in a large volume of liquid.

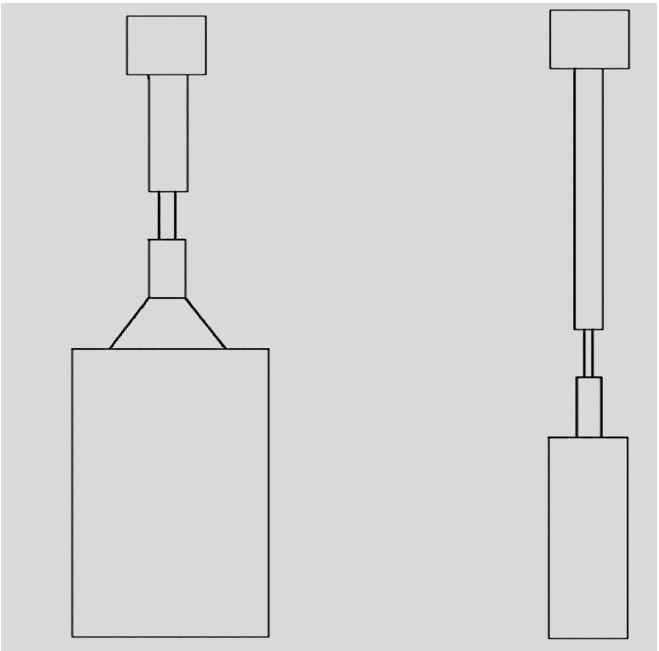

Figure 1. Cylinder-shaped spindles

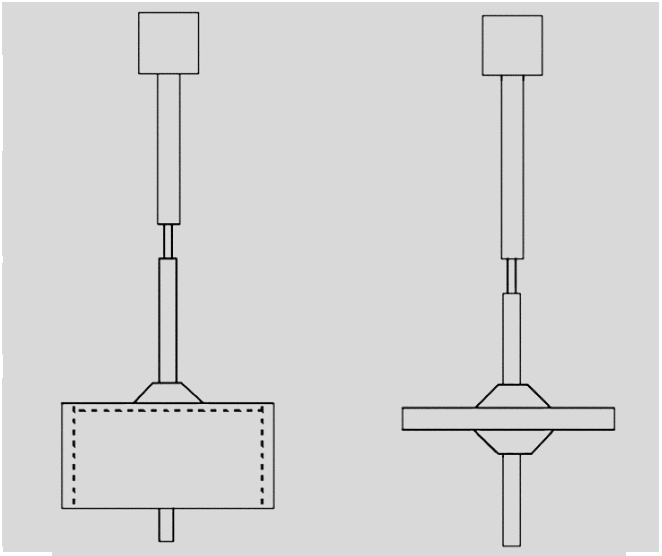

Figure 2. Disc-shaped spindles

Procedure: Under these test conditions the shear rate varies between the outer surface of the spindle and the inner surface of the beaker or cup containing the test substance. As a result, the following additional information must be described along with the measured viscosity:

1. Size and geometry of spindle
2. Angular velocity of the spindle
3. Inner dimensions of the test substance container
4. Temperature of the test substance
5. Use of instrument accessories, such as a spindle guard

The preparation of the test specimen, including its temperature equilibration, is specified in each individual monograph. Follow the instrument manufacturer's recommendations regarding sample loading, spindle selection, and rheometer operation.

Calibration: Select at least two calibration standards whose viscosities differ by an appropriate value within the viscosity range of the test substance under measurement for a particular rheometer configuration. Measure the apparent viscosities of each standard, as described above, at multiple rotational speeds.

A rheometer is deemed to be calibrated if the measured apparent viscosities are within ±5% of the stated values.

Generally, calibration, operation, and cleaning of rheometers should be performed according to the recommendations of the instrument manufacturer.

• **METHOD II. CONCENTRIC CYLINDER RHEOMETERS**

Apparatus: In the concentric cylinder rheometer, the apparent viscosity is determined by placing the liquid in the gap between the inner cylinder and the outer cylinder. Both controlled-stress and controlled-rate rotational rheometers are available commercially in configurations with absolute geometries (e.g., very small annular gaps between concentric cylinders) that can provide consistent meaningful rheological data for non-Newtonian fluids. Controlled-stress rheometers provide controlled-stress input and measurement of the resulting shear rate. Controlled-rate rheometers provide controlled-shear rate input and determination of the resultant shear stress, measured as torque, on the rotor axis. Concen-

tric cylinder rotational rheometers are sometimes referred to as cup-and-bob rheometers. These rheometers involve an additional design consideration depending on whether the outer cylinder (the cup) or the inner cylinder (the bob) rotates. Rotating-cup rheometers are called Couette systems, while rotating-bob rheometers are called Searle systems, as shown in *Figures 3* and *4*, respectively.

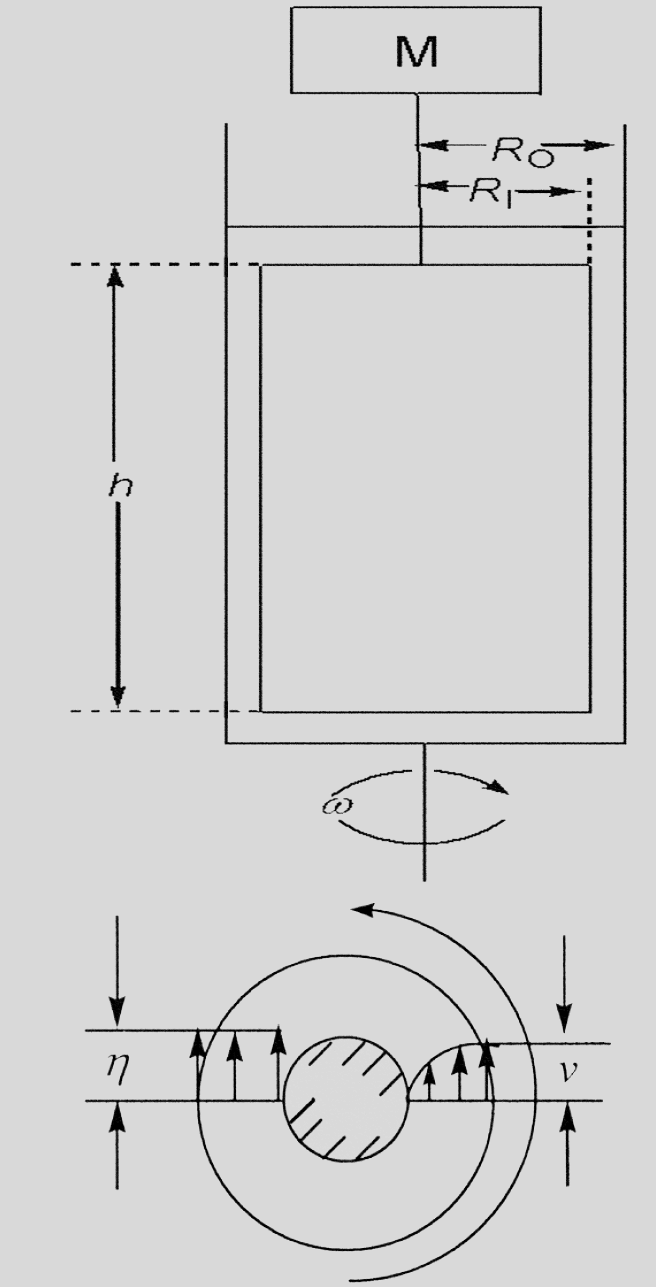

Figure 3. Couette concentric cylinder system for rotational rheometry

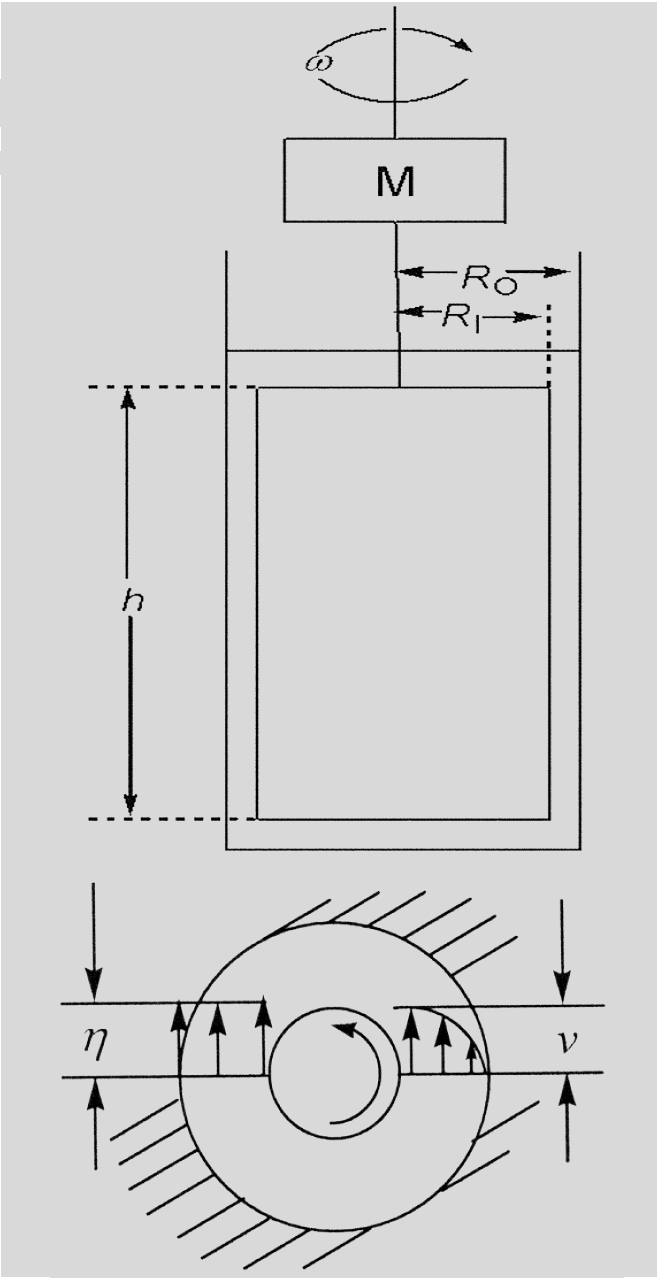

Figure 4. Searle concentric cylinder system for rotational rheometry

Procedure: Place a sufficient quantity of a test solution or fluid in the rheometer, and allow the sample to reach thermal equilibrium, as indicated in the individual monograph. Operate the rheometer following the procedure recommended by the instrument manufacturer. For non-Newtonian systems, the monograph indicates the type of rheometer that should be used and the shear rate(s) at

which the measurements should be made. [NOTE—If there is evidence of time-dependent (e.g., thixotropic or rheopectic) rheological behavior, this should be noted as well.] As noted above, apparent viscosity should be determined preferably over a range of shear rates appropriate to the material under test. The procedure employed to measure the apparent viscosity of the liquid is repeated, using a series of different rotational speeds or torques. From a series of such viscosity measurements, the relationship between the shear rate and the shear stress of a non-Newtonian liquid—that is, the flow characteristics of the non-Newtonian liquid—can be obtained.

Calculation of shear rate, shear stress, and viscosity: For non-Newtonian liquids, it is essential to specify the shear stress, σ, or the shear rate $\dot{\gamma}$, at which the viscosity is measured. Under narrow gap conditions (conditions satisfied in absolute rheometers), the shear rate $\dot{\gamma}$ in s^{-1}, and the shear stress σ, in Pa ($N \cdot m^{-2}$ or $kg \cdot m^{-1} \cdot s^{-2}$), are calculated using Equations *(1)* and *(2)* below:

$$\dot{\gamma} = \left(\frac{R_O^2 + R_I^2}{R_O^2 - R_I^2} \right) \omega \qquad (1)$$

$$\sigma = \left(\frac{1}{4\pi h R_O^2} + \frac{1}{4\pi h R_I^2} \right) M \qquad (2)$$

R_O = radius of the outer cylinder (m)
R_I = radius of the inner cylinder (m)
ω = angular velocity (radians/s)
M = torque acting on the cylinder surface ($N \cdot m$)
h = height of immersion of the inner cylinder in the liquid medium (m)

Generally, the angular velocity can be calculated using Equation *(3)*:

$$\omega = \left(\frac{2\pi}{60} \right) n \qquad (3)$$

n = rotational speed, in revolutions/min (rpm)

For laminar flow, the viscosity η (or apparent viscosity η_{App}), in $Pa \cdot s$, is given by the following equation: [NOTE—1 $Pa \cdot s = 1000\ mPa \cdot s$.]

$$\eta \text{ or } \eta_{App} = \frac{1}{4\pi h} \left(\frac{1}{R_I^2} - \frac{1}{R_O^2} \right) \frac{M}{\omega} = k \frac{M}{\omega} \qquad (4)$$

k = the constant of the apparatus (radians/m^3)

Calibration: Rotational rheometers require calibration with rheological standards appropriate for the shear rate or shear stress ranges and the nature of the fluid or material under evaluation. To determine or confirm the apparatus constant, perform the necessary tests beforehand, using fluids of known viscosities of appropriate viscosity standards at the required temperature.

- **METHOD III. CONE-AND-PLATE RHEOMETERS**

Apparatus: In the cone-and-plate rheometer, the liquid is introduced into the gap between a flat disc or plate and a cone forming a defined angle. Viscosity measurement can be performed by rotating the cone or the plate, as shown in *Figures 5* and *6*, respectively. [NOTE—Because the volume of sample is small, even a small absolute loss of solvents can cause a large percentage change in viscosity. Such a loss is particularly relevant for volatile solvents but could be significant even for nonvolatile solvents such as water.]

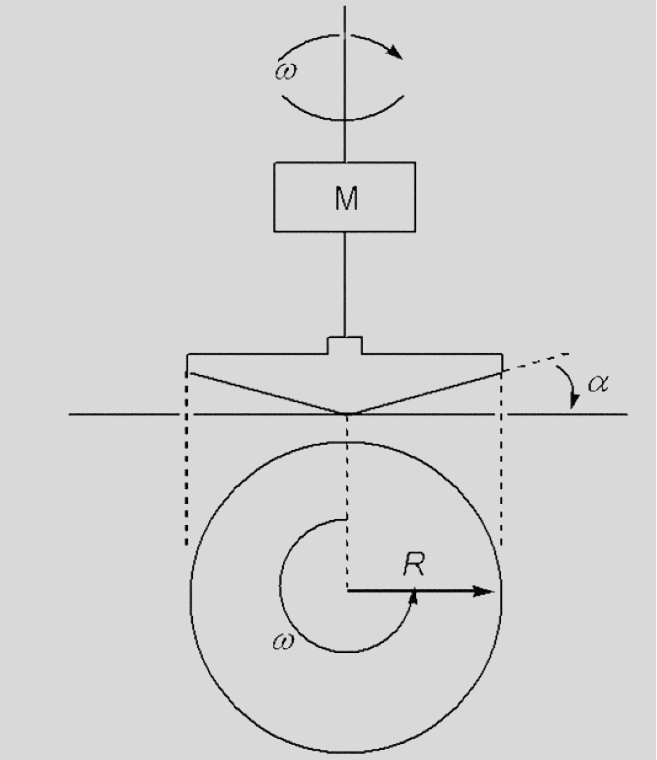

Figure 5. Cone-and-plate rotational rheometer with rotating cone

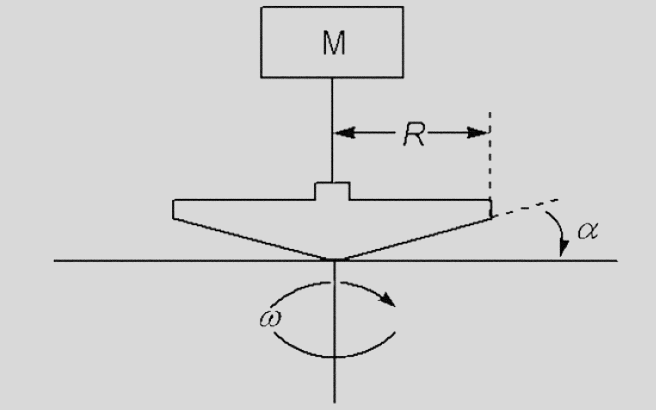

Figure 6. Cone-and-plate rotational rheometer with rotating plate

Procedure: Proceed as directed for *Method II. Concentric Cylinder Rheometers*.

Calculation of shear rate, shear stress, and viscosity: The shear rate $\dot{\gamma}$ in s^{-1}, and the shear stress σ, in Pa, are calculated by Equations *(5)* and *(6)*.

$$\dot{\gamma} = \left(\frac{1}{\alpha}\right)\omega \qquad (5)$$

$$\sigma = \left(\frac{1}{\frac{2}{3}\pi R^3}\right)M \qquad (6)$$

α = angle between the flat plate and the cone (radians)
R = radius of the cone (m)
ω = angular velocity (radians/s)
M = torque acting on the flat plate or cone surface (N · m)

For laminar flow, the viscosity η (or apparent viscosity η_{App}), in Pa · s, is given by the following equation:

$$\eta \text{ or } \eta_{App} = \left(\frac{3\alpha}{2\pi R^3}\right)\left(\frac{M}{\omega}\right) = k\frac{M}{\omega} \qquad (7)$$

k = constant of the apparatus (radians/m^3)

Calibration: Proceed as directed for *Calibration* in *Method II. Concentric Cylinder Rheometers*.■2S *(USP35)*

Add the following:

■⟨913⟩ ROLLING BALL VISCOMETER METHOD

The following procedure is used to determine the viscosity of a Newtonian fluid, i.e., a fluid having a viscosity that is independent of the shearing stress or rate of shear.

Apparatus: See *Figure 1*.

The basic design of a rolling ball viscometer consists of a tube (or capillary) that contains the sample liquid under test and a ball chosen so that it will require a minimum rolling time of 20 s at the measuring angle in the sample liquid.

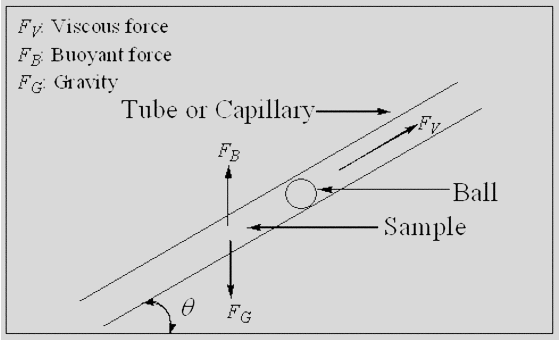

Figure 1. Basic design for rolling ball viscometer.

Measuring Principle: The rolling ball measurement is based on Stokes's Law, as influenced by the angle of inclination of the tube (or capillary). The Newtonian viscosity, η, in mPa · s, is calculated using the following equation:

$$\eta = [(\rho_1 - \rho_2) \times g \times r^2 \times \sin\theta] / v_\infty$$

ρ_1 = density of the ball used (g/mL)
ρ_2 = density of the sample liquid (g/mL)
g = gravitational constant (mm/s²)
r = radius of the ball (mm)
θ = angle of inclination of the tube (or capillary)
v_∞ = terminal velocity of the ball (mm/s)

Determine the viscosity of a liquid by observing the rolling time of a solid sphere (ball) under the influence of gravity in an inclined cylindrical tube filled with the sample liquid. Measure the time taken by the ball to travel the fixed distance between two ring marks or measuring sensors. For each single measured rolling time, the resulting viscosity can be expressed as dynamic viscosity (mPa · s) as well as kinematic viscosity (mm²/s) for a sample of known density.

Procedure: Select a measuring system [tube (or capillary) and ball combination] within the anticipated range of viscosity of the sample liquid. As necessary, heat the clean and dry tube and ball of the viscometer to the temperature specified in the individual monograph, and control the temperature to ±0.1°, unless otherwise specified in the individual monograph. Select a measuring angle to obtain a minimum rolling time of 20 s. Fill the tube with the sample liquid, being careful to avoid bubble formation. Close the tube, and insert it in the instrument. Allow to equilibrate at the specified temperature for NLT 15 min for a rolling ball viscometer with a tube of large diameter. For a micro rolling ball viscometer, follow the instrument manufacturer's instructions regarding temperature equilibration. Release the ball, and record the time required for the ball to roll from the upper to the lower ring mark (or measuring sensor). Repeat the test run at least four times.

The rolling time in the fluid under examination is the mean of NLT four consecutive determinations. The result is valid if the percent relative standard deviation (%RSD) for the four readings is NMT 2.0%.

Calculation and Calibration: Calculate the Newtonian viscosity, η, in mPa · s, using the formula:

$$\eta = k \times (\rho_1 - \rho_2) \times t$$

k = calibration constant of the instrument (mm²/s²) at a specified measuring angle and temperature
ρ_1 = density of the ball used (g/mL)
ρ_2 = density of the sample liquid (g/mL)
t = rolling time of the ball (s).

Calibrate each tube (or capillary) and ball combination at the test temperature and test angle using fluids of known viscosities and densities (viscosity standards) to determine the measuring system constant, k. [NOTE—Some automated viscometers use a polynomial function to determine the calibration for different angles and temperatures.] The viscosity values of the calibration standards should bracket the expected viscosity value of the sample liquid.

Calibrations are specific to the ball radius, ball density, temperature, and test angle. Recalibration is necessary when any of these parameters is changed.

Where no reference values at the required test temperature are available, follow the manufacturer's instructions for mathematical corrections to the calibration function. When the materials of the ball and tube are dissimilar, apply corrections calculated using the linear thermal expansion coefficients of the materials.■2S (*USP35*)