International
Standard

ISO 1628-1

Plastics — Determination of the viscosity of polymers in dilute solution using capillary viscometers —

Part 1:
General principles

Plastiques — Détermination de la viscosité des polymères en solution diluée à l'aide de viscosimètres à capillaires —

Partie 1: Principes généraux

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 61, *Plastics*, Subcommittee SC 5, *Physical-chemical properties*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 249, *Plastics*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This fifth edition cancels and replaces the fourth edition (ISO 1628-1:2021), which has been technically revised.

The main changes are as follows:

- an introduction section has been added in relation to the new procedure;
- the calculation of K-value was moved to 9.2;
- an alternative procedure has been incorporated, the differential pressure method (see 4.3), based on comparing the differential pressure in capillary tubing due to the flow of polymer solution and neat solvent simultaneously.

A list of all parts in the ISO 1628 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Two methods are described in this document to determine the viscosity of polymer solutions, the efflux time method and the differential pressure method. The results of both methods are equivalent. Differences may be found due to different conditions for the determination, such as concentration, solvent or shear rate.

The differential pressure method which has been incorporated in this document has the important advantage for industry that it is more easily adapted to automation, leading to improved efficiency, higher throughput, and enhanced safety for the operator. The new added method can help in the reduction of solvents use due to the lower requirement for washing of the capillaries.

Another advantage of the new alternative differential pressure method is that it can be integrated within existing polymer characterization workflows, as part of existing or new polymer analysis instrumental setups.

Plastics — Determination of the viscosity of polymers in dilute solution using capillary viscometers —

Part 1:
General principles

1 Scope

This document specifies the general conditions for the determination of the reduced viscosity, intrinsic viscosity and *K*-value of organic polymers in dilute solution. It specifies the standard parameters that are applied to viscosity measurement.

This document is applicable to develop standards for measuring the viscosities in solution of individual types of polymer. It is also applicable to measure and report the viscosities of polymers in solution for which no separate standards exist.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 80000-1, *Quantities and units — Part 1: General*

ISO 80000-4, *Quantities and units — Part 4: Mechanics*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 80000-1, ISO 80000-4 and the following apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

3.1 Terms related to any liquid

3.1.1
viscosity
property of a fluid sheared between two parallel plates, one of which moves relative to the other in uniform rectilinear motion in its own plane, defined by the Newton formula

$$\tau = \eta \dot{\gamma}$$

where

τ is the shear stress;

η is the viscosity;

$\dot{\gamma}$ is the velocity gradient or rate of shear, given by $\frac{dv}{dz}$ where v is the velocity of one plane relative to the other and z the coordinate perpendicular to the two planes

Note 1 to entry: The units of viscosity are Pa·s.

Note 2 to entry: Viscosity is usually taken to mean “Newtonian viscosity”, in which case the ratio of shearing stress to velocity gradient is constant. In non-Newtonian behaviour, which is the usual case with solutions of polymers with high molar masses, the ratio varies with the shear rate. Such ratios are often called “apparent viscosities” at the corresponding shear rate.

3.1.2
viscosity/density ratio
kinematic viscosity
v
ratio defined by the formula

$$v = \frac{\eta}{\rho}$$

where ρ is the density of the fluid at the temperature at which the viscosity is measured

Note 1 to entry: The units of kinematic viscosity are $m^2 \cdot s^{-1}$.

3.2 Terms related to polymer solutions

3.2.1
relative viscosity
viscosity ratio
η_r
ratio of the viscosity of the polymer solution (of stated concentration) η and the viscosity of the solvent η_0, at the same temperature

$$\eta_r = \frac{\eta}{\eta_0}$$

Note 1 to entry: The ratio has no dimensions.

3.2.2
relative viscosity increment
viscosity ratio increment and specific viscosity
η_{sp}
viscosity ratio minus one

$$\eta_{sp} = \left(\frac{\eta}{\eta_0}\right) - 1 = \frac{\eta - \eta_0}{\eta_0}$$

Note 1 to entry: The increment has no dimensions.

3.2.3
reduced viscosity
viscosity number
I

ratio of the relative viscosity increment to the polymer concentration c in the solution

$$I = \frac{\eta - \eta_0}{\eta_0 c}$$

Note 1 to entry: The units of reduced viscosity are m^3/kg.

Note 2 to entry: The reduced viscosity is usually determined at low concentration (less than 5 kg/m^3, i.e. 0,005 g/cm^3), except in the case of polymers of low molar mass, for which higher concentrations can be necessary.

3.2.4

inherent viscosity

logarithmic viscosity number

η_{inh}

ratio of the natural logarithm of the viscosity ratio to the polymer concentration in the solution

$$\eta_{inh} = \frac{\ln\left(\frac{\eta}{\eta_0}\right)}{c}$$

Note 1 to entry: The dimensions and units are the same as those given in 3.2.3.

Note 2 to entry: The inherent viscosity is usually determined at low concentration (less than 5 kg/m^3, i.e. 0,005 g/cm^3), except in the case of polymers of low molar mass, for which higher concentrations can be necessary.

3.2.5

intrinsic viscosity

limiting viscosity number

η

limiting value of the reduced viscosity or of the *inherent viscosity* (3.2.4) at infinite dilution

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta - \eta_0}{\eta_0 c}\right)$$

$$[\eta] = \lim_{c \to 0} \frac{\ln\left(\frac{\eta}{\eta_0}\right)}{c}$$

Note 1 to entry: The dimensions and units are the same as those given in 3.2.3.

Note 2 to entry: The effect of the shear rate on the functions defined in 3.2.1 to 3.2.5 has been neglected, since this effect is usually negligible for values of the reduced viscosity, inherent viscosity and intrinsic viscosity less than 0,5 m^3/kg, i.e. 500 cm^3/g. Strictly speaking, all these functions can be defined at the limiting (preferably infinitely small) value of the shear rate.

3.2.6

***K*-value**

empirical parameter related to the relative viscosity and concentration used to estimate the viscosity average of the molecular mass of polymers

Note 1 to entry: For constant measurement parameters such as type of solvent, concentration and temperature, the K-value depends only on the viscosity average of the molecular mass distribution.

4 Principle

4.1 General

The data needed for the evaluation of the functions defined in 3.2 are obtained comparing viscosity measurements of a polymer solution and the solvent.

4.2 Method A — Efflux time method

The data are obtained by means of a capillary-tube viscometer. The efflux times of a given volume of solvent t_0 and of solution t are measured at fixed temperature and atmospheric-pressure conditions in the same viscometer. The efflux time of a liquid is related to its viscosity by the Poiseuille-Hagenbach-Couette formula as shown in Formula (1):

$$v=\frac{\eta}{\rho}=Ct-\left(\frac{A}{t^2}\right) \tag{1}$$

where

v is the viscosity/density ratio;

C is a constant of the viscometer;

A is a parameter of the kinetic-energy correction;

ρ is the density of the liquid;

η is the viscosity of the liquid;

t is the efflux time.

For the purposes of this document, the kinetic energy correction $\left(\frac{A}{t^2}\right)$ shall be regarded as negligible when it is less than 3 % of the viscosity of the solvent. Hence, Formula (1) can be reduced to Formula (2):

$$v=\frac{\eta}{\rho}=Ct \tag{2}$$

Moreover, if the solution concentrations are limited so that the solvent density ρ_0 and that of the solution ρ differ by less than 0,5 %, the viscosity ratio $\frac{\eta}{\eta_0}$ will be given by the so-called "efflux time ratio" $\frac{t}{t_0}$.

The need for these constraints, and the consequences of not observing them, is described in Annex A.

4.3 Method B — Differential pressure method

The data are obtained by means of a 2-capillary relative viscometer. The differential pressure across each of the 2 capillaries connected in series, one of them receiving the solvent Δp_0, the other receiving the polymer solution Δp, are measured at a fixed temperature while applying a forced flow through them.

The differential pressure across a capillary tubing is related to the viscosity of the flowing liquid under laminar flow regime, by the Poiseuille formula as shown in Formula (3):

$$\Delta p=\frac{8q_v l}{\pi r^4}\eta \tag{3}$$

where

Δp is the differential pressure in a capillary tubing;

q_v is the liquid flow rate;

l is the capillary tubing length;

r is the capillary tubing radius;

η is the viscosity of the liquid;

As in a 2-capillaries serial configuration viscometer (see 5.2) the same flow rate q_v is maintained for the solvent and the polymer solution, the viscosity ratio $\frac{\eta}{\eta_0}$ is proportional to the pressure ratio $\frac{\Delta p}{\Delta p_0}$. By introducing the instrumental constant K_v the viscosity ratio $\frac{\eta}{\eta_0}$ can be calculated from the pressure ratio as seen in Formula (4) and Formula (5):

$$\frac{\eta}{\eta_0} = K_v \cdot \frac{\Delta p}{\Delta p_0} \tag{4}$$

with

$$K_v = \frac{r^4 l_0}{r_0{}^4 l} \tag{5}$$

where

l is the polymer solution capillary tubing length;

r is the polymer solution capillary tubing radius;

l_0 is the solvent capillary tubing length;

r_0 is the solvent capillary tubing radius.

The instrumental constant K_v can easily be measured by flowing solvent through both capillaries given that the viscosity ratio $\frac{\eta}{\eta_0}$ is 1,0 for solvent, and therefore solving in Formula (4):

$$K_v = \frac{\Delta p_0}{\Delta p}$$

Possible sources of errors for this method are described in Annex B.

5 Apparatus

5.1 Efflux time method

5.1.1 Capillary viscometer, of the suspended-level Ubbelohde type

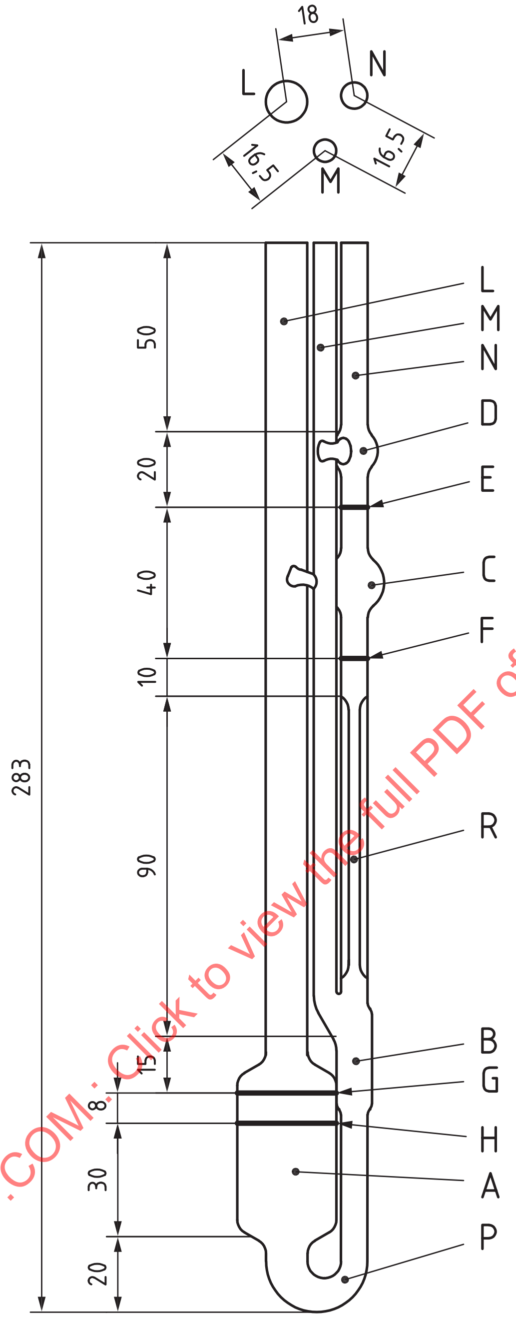
The use of a viscometer having the dimensions given in Figure 1 or Figure 2 is strongly recommended. Furthermore, it is strongly recommended that the size of the viscometer be chosen from among those listed in Table 1. The choice is determined by the viscosity/density ratio of the solvent at the temperature of the measurement, as indicated in Table 1. The next-smaller viscometer may also be used.

Other types of viscometer listed in ISO 3105 may be used, provided they give results equivalent to those given by the particular size of Ubbelohde viscometer chosen on the basis of the criteria specified in the preceding paragraph. In cases of dispute, an Ubbelohde viscometer shall be used.

With automated apparatuses, fitted with special timing devices, equivalent results with larger sizes of capillaries than those listed for the appropriate solvent viscosity/density ratio in Table 1 can be obtained. Some modified viscometer excluding parts P and L can be used, and the measuring part of the viscometer meets the recommendations of the Table 1.

5.1.2 Viscometer holder, suitable to hold the viscometer firmly in the thermostatic bath (5.1.3) in the vertical position.

Dimensions in millimetres



Key

A	lower reservoir 26 mm internal diameter	L	mounting tube 11 mm internal diameter
B	suspended level bulb	M	lower vent tube 6 mm internal diameter
C	timing bulb	N	upper vent tube 7 mm internal diameter
D	upper reservoir	P	connecting tube
E and F	timing marks	R	working capillary
G and H	filling marks		

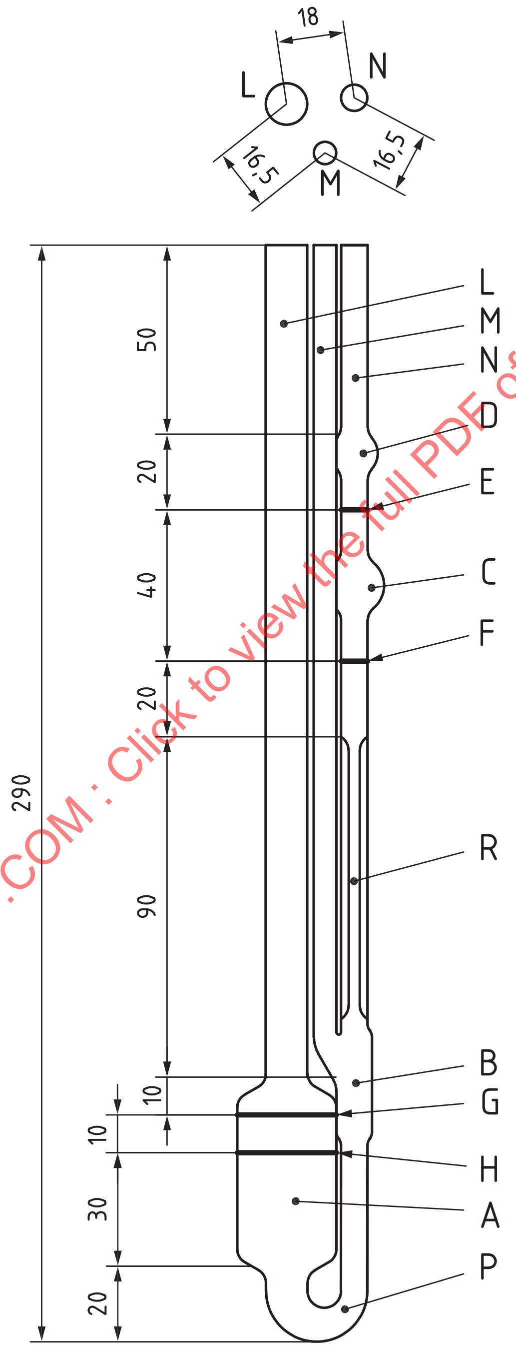
Figure 1 — Ubbelohde viscometer

5.1.3 Thermostatic bath, transparent liquid or vapour bath of a size such that, during the measurement, all sections containing test liquid are at least 20 mm below the surface of the bath medium and at least 20 mm away from all boundaries of the bath tank.

The temperature control shall be such that, within the range 25 °C to 100 °C, the temperature of the bath does not vary from the specified temperature by more than 0,05 K over the length of the viscometer, or between the viscometers if several determinations are carried out simultaneously.

At temperatures higher than 100 °C, the tolerance shall be ±0,2 K.

Dimensions in millimetres



NOTE For key, see Figure 1.

Figure 2 — DIN Ubbelohde viscometer

5.1.4 Temperature-measuring device, thermometer, reading to 0,02 °C in the range in which it will be used and in a known state of calibration, is suitable.

5.1.5 Timing device. Any timing device may be used providing that it can be read to 0,1 s and that its speed is constant to 0,1 % over 15 min.

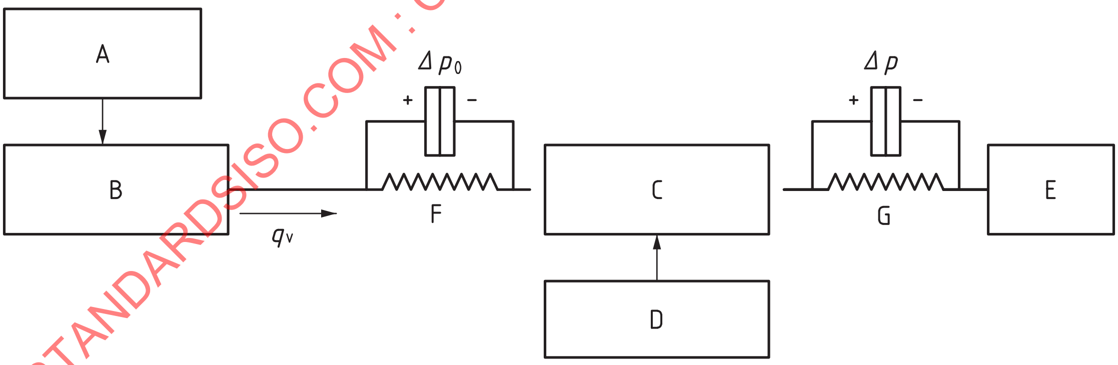
Table 1 — Ubbelohde viscometers recommended for the determination of the dilute-solution viscosity of polymers

Viscosity/density ratio of solvent at temperature of measurement	Nominal viscometer constant	Ubbelohde conforming to ISO 3105		DIN Ubbelohde conforming to ISO 3105	
$mm^2 \cdot s^{-1}$	$mm^2 \cdot s^{-2}$	Size No.	Inside diameter of tube R[a] mm	Size No.	Inside diameter of tube R[a] mm
0,15 to 0,30	0,001	0	0,24	0	0,36
0,31 to 0,50	0,003	0C	0,36	0c	0,47
0,51 to 0,75	0,005	0B	0,46	0a	0,53
0,76 to 1,50	0,01	1	0,58	I	0,63
1,51 to 2,50	0,03	1C	0,77	Ic	0,84
2,51 to 5,00	0,05	1B	0,88	Ia	0,95
5,01 to 15,00	0,1	2	1,03	II	1,13

[a] The tolerance of the inside diameter of tube R is ±2 %.

5.2 Differential pressure method

A schematic diagram of a relative viscometer used in this method is depicted in Figure 3, indicating the relevant components. It is strongly recommended to use automated instruments capable of injecting polymer solutions into the measurement/polymer solution capillary while maintaining a constant flow of solvent (q_v) through the system.



Key

A solvent reservoir

B solvent delivery system

C polymer solution injection system

D polymer solution

E waste reservoir

F reference/solvent capillary

G measurement/polymer solution capillary

q_v liquid flow rate

Δp_0 differential pressure across the reference capillary

Δp differential pressure across the measurement capillary

Figure 3 — 2-capillary relative viscometer

The solvent delivery system (B) may be a positive displacement pump, syringe pump or similar capable of delivering solvent at a consistent flow rate, with maximum permissible error of 5 %. Flow rates from

0,5 cm^3/min to 3,0 cm^3/min may be used. Flow rate will be set to a level to ensure a sufficient differential pressure without reaching the overload limit of the pressure transducer sensors.

NOTE Given the capillary dimensions, the measurement shear rate is controlled by the solvent delivery system flow rate.

A proper polymer solution injection system (C) shall be used that is capable of injecting a definite volume of the polymer solution (D) into the measurement/polymer solution capillary (G).

The reference/solvent capillary (F) and the measurement/polymer solution capillary (G) shall be kept at the same temperature, enclosed in a proper temperature-controlled device with variations from the specified temperature lower than ±0,2 K. The nominal dimensions of the two capillaries are specified by the inside diameter and length. Inside diameter may be 0,25 mm to 0,75 mm, and length 80 mm to 600 mm, depending on the system flow rate and range of solvent and polymer solution viscosity. The dimensions of the capillaries shall ensure that the differential pressure generated upon the flow of solvent or polymer solution lies within the operation range of the used pressure sensor. Capillary specifications, including inner diameter and length, should be used for dilute solution viscosity testing of specific materials.

The differential pressure in each of the capillaries is measured by differential pressure sensors as indicated in Figure 3. Any sensor capable of measuring differential pressure with an uncertainty of measurement of 0,5 % of its full range may be used.

6 Solutions

6.1 Preparation

The dissolution of the test sample of polymer in the solvent shall give a true solution, essentially free of microgels and associated macromolecules. Polymer degradation shall also be minimized. For these reasons, the dissolution procedure shall be exactly specified, and the following factors shall be specified:

a) the solvent and its pretreatment, if any;

b) the apparatus and the method of agitation;

c) the temperature range within which the system is maintained during the preparation of the solution;

d) the time interval necessary for the complete dissolution of the polymer without degradation, or at constant degradation;

e) the stabilizer and/or the protective atmosphere used;

f) the conditions of filtration of the solution, if applicable;

g) visual homogeneity of the solution and expected nature/composition of the filter residue.

6.2 Concentration

Where no standard exists, careful consideration shall be given to the choice of solvent and the solution concentration. The solution concentration shall be chosen so that the measured viscosity ratio is at least 1,2 in the case of measuring efflux times, and less than 2,0 in all cases.

NOTE A lower limit of 1,2 ensures sufficient precision of the measured difference in efflux times, while the precision of the measured differential pressures is sufficient even at lower values of viscosity ratio. The upper limit of 2,0 prevents shear effects and non-linearity of the viscosity number in relation to concentration that can occur for polymers with high molecular masses.

More than one concentration may therefore be used for a given polymer/solvent system, depending on the molecular mass of the polymer under test.

The concentration is preferably expressed in kg/m^3 of solution or as the multiple 10^3 kg/m^3, i.e. g/cm^3.

7 Temperature of measurement

The temperature shall be chosen with due regard to sufficient solubility and other technical requirements but kept constant for any particular polymer/solvent system. The temperature tolerance shall be specified. A temperature of 25 °C with a tolerance ±0,05 K for the efflux time method or ±0,2 K for the differential pressure method, shall be chosen whenever possible. If a different temperature is used, as agreed between the parties concerned, this shall be mentioned in the test report.

8 Procedure

8.1 Efflux time method

8.1.1 General

Measure the efflux times for the solution and the solvent successively in the same viscometer, using the procedure described in 8.1.2 and 8.1.3.

8.1.2 Preparing and charging the viscometer

8.1.2.1 Maintain the bath at the specified test temperature.

8.1.2.2 Charge the dry, clean viscometer (the cleaning procedure is specified in Annex C) by tilting it about 30° from the vertical and pouring sufficient liquid through tube L (see Figure 1 or Figure 2) so that, when the viscometer is returned to the vertical, the meniscus is between the filling marks G and H. Avoid trapping air bubbles in the viscometer. The initial filling may be carried out away from the bath.

8.1.2.3 Mount the viscometer in a holder in the bath, ensuring that tube N is vertical. Allow time for the charged viscometer to reach the temperature of the bath. Usually, 15 min will suffice if the measurement is to be made at 25 °C. At higher temperatures, longer times are necessary. Unnecessary delays should be avoided as it is found that the most consistent results are obtained shortly after temperature equilibrium is attained with a freshly charged viscometer.

8.1.2.4 This procedure shall also be followed when a measured amount of solvent is added to a solution, already contained in the viscometer, in order to create a more dilute solution for additional determinations. The additional solvent shall be maintained at the specified test temperature prior to use.

8.1.2.5 In automated equipment, the viscometer is fixed in the vertical position within a temperature-controlled bath and the apparatus is designed to fill the viscometer with liquid in this position. The bath shall be maintained at the specified test temperature and an equilibration time selected in accordance with 8.1.2.3. The charge method of the modified viscometer is according to the requirements of the instrument manufacturer, and the solvent/solution volume charged can make meniscus between the filling marks G and H.

8.1.3 Efflux time measurement

See Figure 1 or Figure 2.

Close tube M and apply suction to tube N, or pressure to tube L, until the liquid reaches a level about 5 mm above mark E. Hold the liquid at this level by closing tube N.

Open tube M so that the liquid drops away from the lower end of capillary tube R.

When the liquid is clear of the end of the capillary and the lower end of tube M, open tube N. Measure the efflux time to the nearest 0,2 s as the time taken for the bottom of the meniscus to pass from the top edge of mark E to the top edge of mark F. For polymer solutions containing small amounts of finely divided pigments, such as carbon black, it shall be necessary to view the top of the meniscus. Where large concentrations of pigments are involved, it shall be necessary to centrifuge the solution before proceeding.

The opening and closing of the tubes may be carried out conveniently by means of taps or clips on clean flexible tubing attached to the ends of the tubes, making sure that no fluff or other contaminant enters the tube.

The first flow shall not be taken into account for measuring the efflux time. Repeat the measurement of efflux time immediately, without emptying or recharging, until two successive efflux times agree to within 0,25 %. Take the mean of these two values as the efflux time.

If two successive determinations of the mean efflux time of the solvent differ by more than 0,4 s, clean the viscometer as specified in Annex C.

The efflux time for any new solution, created by the addition of solvent to an existing solution held in the viscometer, shall be determined as a separate liquid, in accordance with this procedure.

8.2 Differential pressure method

8.2.1 General

When an automated instrument is used, follow the instrument manufacturer instructions to proceed with the measurement of the pressure ratio for the polymer solution under test and the viscometer instrumental constant K_v. The viscosity ratio is then calculated applying Formula (4).

The temperature in the capillaries enclosure shall be stabilized before proceeding with the injection of the polymer solution.

8.2.2 Collection of viscosity ratio increment signal

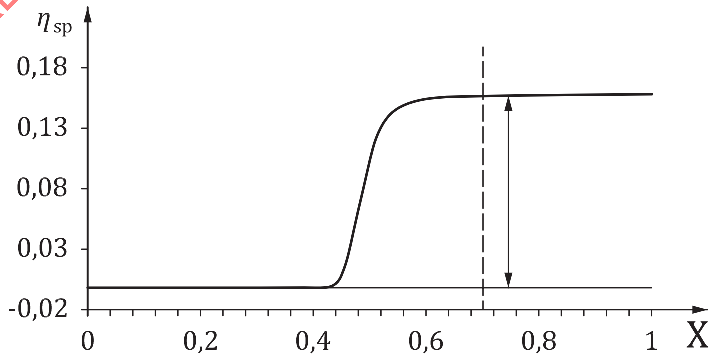
8.2.2.1 General

Typically, in automated instruments the Δp and Δp_0 signals are collected continuously from the differential pressure sensors and a pressure ratio is also continuously calculated directly from them. The pressure ratio allows online or offline calculation of the viscosity ratio signal applying Formula (4), as well as viscosity ratio increment signal according to 3.2.2.

Two alternative procedures may be used to obtain the polymer solution viscosity ratio increment from the collected signals: plateau height and peak area, as described in following paragraphs. The two procedures provide equivalent results.

8.2.2.2 Plateau height

When a large enough volume of polymer solution is injected to the measurement capillary, a steady reading of viscosity ratio increment signal is obtained as illustrated in Figure 4.



Key

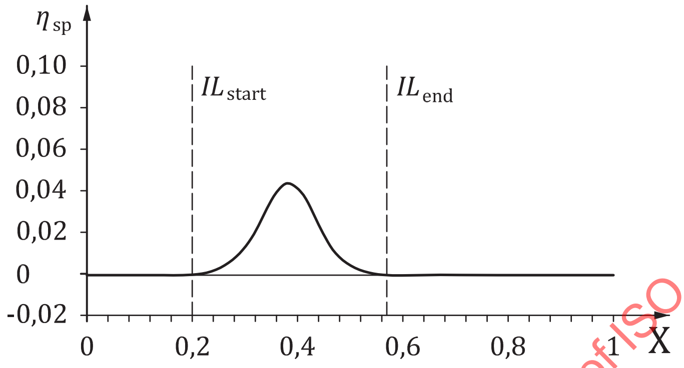
X volume, in ml

Figure 4 — Plateau height — Viscosity ratio increment signal profile

The polymer solution viscosity ratio increment is read as the height of the plateau in the polymer solution viscosity ratio increment signal, as indicated by the double arrow in Figure 4. The height of the plateau shall be taken as the average of the values within a volume range, for which the fluctuation of data is below 0,5 %.

8.2.2.3 Peak area

Alternatively, an accurately specified and relatively small volume (0,2 ml to 0,5 ml) of polymer solution may be injected to the measurement capillary, in which case instead of a steady reading of viscosity ratio increment a chromatographic-like peak as a function of elution volume is obtained. This is illustrated in Figure 5.



Key

X volume, in ml

Figure 5 — Peak area: viscosity ratio increment signal profile

The area under the peak (A) is quantified and used in calculations of the polymer solution viscosity ratio increment using Formula (6):

$$\eta_{sp} = \frac{A\left(\eta_{sp}(V)\right)}{V_{inj}} \tag{6}$$

where

$\eta_{sp}(V)$ is the continuous viscosity ratio increment signal as a function of elution volume, V;

V_{inj} is the volume of polymer solution injected into the measurement capillary.

The area, A, in Formula (6) is calculated as a definite integral according to Formula (7) within the elution volumes range specified by integration limits set before the peak start (IL_{start}) and after the peak end (IL_{end}) as indicated in Figure 5.

$$A\left(\eta_{sp}(V)\right) = \int_{IL_{start}}^{IL_{end}} \eta_{sp}(V)\,dV \tag{7}$$

9 Expression of results

9.1 Reduced viscosity and intrinsic viscosity

Results are preferably expressed as a reduced viscosity.

In the efflux time method, the reduced viscosity I, in the units 10^{-3} m^3/kg, i.e. cm^3/g, is calculated using Formula (8):

$$I = \frac{t - t_0}{t_0 c} \tag{8}$$

where

t is the efflux time of the solution, in seconds;

t_0 is the efflux time of the solvent, in seconds, through the same viscometer;

c is the concentration, expressed as 10^3 kg/m^3, i.e. g/cm^3.

Alternatively, the reduced viscosity may be obtained by the differential pressure method using the determined pressure from differential pressure sensors using Formula (9):

$$I = \frac{\Delta p - \Delta p_0}{\Delta p_0 c} \tag{9}$$

where

Δp is the differential pressure in the measurement capillary tubing;

Δp_0 is the differential pressure in the reference capillary tubing;

c is the concentration, expressed as 10^3 kg/m^3, i.e. g/cm^3.

or using the calculated solution viscosity ratio increment according to Formula (10):

$$I = \frac{\eta_{sp}}{c} \tag{10}$$

where

η_{sp} is the viscosity ratio increment of the tested polymer solution;

c is the concentration, expressed as 10^3 kg/m^3, i.e. g/cm^3.

The results can also be expressed as an intrinsic viscosity $[\eta]$, for example in order to compare copolymers of different average molecular masses for which it has been necessary to use different concentrations (see 6.2).

The intrinsic viscosity should be calculated from the values of inherent viscosity or reduced viscosity obtained for concentrations c1, c2, c3 ..., in the approximate ratio 1:2:3 ..., by a graphical method consisting of plotting the inherent-viscosity values or the reduced-viscosity values (on the ordinate axis) against the concentration (on the abscissa) and extrapolating the curve to zero concentration. The intrinsic viscosity is read off the ordinate axis.

It is recommended that the method of least squares be used for analysing the experimental values.

The intrinsic viscosity $[\eta]$ can also be calculated from one value of the reduced viscosity, for instance by using Formula (11):

$$[\eta] = \frac{I}{1 + k'cI} \tag{11}$$

where k' is an experimental constant, usually between 0,2 and 0,3, which shall be determined previously by measuring the reduced viscosity at two different concentrations and applying Formula (12):

$$k' = \frac{I_2 - I_1}{I_1 I_2 (c_2 - c_1)} \qquad (12)$$

In the calculation of k', it should be preferable to use several concentrations and plot I against c, drawing a straight line through the points and selecting two positions on this line to give values for substitution in the formula for k'.

9.2 *K*-value

The *K*-value can be calculated from the relationship shown as Formula (13):

$$K\text{-value} = 1\,000\, k \qquad (13)$$

where k is calculated as follows, according to H. Fikentscher[1]:

$$\lg \eta_\mathrm{r} = \left(\frac{75k^2}{1+150kc} + k \right) 100c$$

and therefore

$$k = \frac{1{,}5 \lg \eta_r - 1 + \sqrt{1 + \left(\frac{2}{c} + 2 + 1{,}5 \lg \eta_\mathrm{r} \right) 1{,}5 \lg \eta_\mathrm{r}}}{150 + 300c}$$

where

$\eta_\mathrm{r} = \frac{\eta}{\eta_0}$ is the viscosity ratio (see 3.2.1);

c is the concentration, in 10^3 kg/m^3, i.e. g/cm^3.

A limiting viscosity number $[\eta]_\mathrm{k}$ can be calculated from k:

$$[\eta]_k = 230{,}3\left(75k^2 + k\right)$$

10 Test report

The test report shall contain the following particulars:

a) a reference to this document including its year of publication, i.e. ISO 1628-1:2024;

b) the specific method used (efflux time or differential pressure), the procedure used to obtain the polymer solution viscosity ratio increment when the differential pressure method is used, and the particular standard for the polymer tested, if one exists;

c) all details necessary for identification of the material tested, including type, source and manufacturer's code number;

d) the concentration of material in the solution used, a description of the solvent and details of the preparation of the solution;

e) details of the viscometer used;

f) the temperature of the test;

g) the test results;

h) the date of the test;

i) any deviations from the procedure;

j) any unusual features observed.

Annex A
(informative)

Efflux time method — Notes on sources of error

A.1 General

Guidance is given in this document on the determination of the viscometric properties of polymers in dilute solution as defined in Clause 3. The measurement of these properties can usually be carried out with better reproducibility than that attained in absolute measurements of viscosity since many of the instrumental errors are approximately the same for both solvent and solution and are effectively cancelled.

A.2 Principle of measurements

The relative viscosity and the other parameters defined in Clause 3 are calculated from the efflux times of solution and solvent. The liquid flows, under the force of gravity, through the capillary of a suspended-level Ubbelohde viscometer. The efflux times are taken to be proportional to the viscosity/density ratio of the fluids (see Clause 4). This is equivalent to stating that the kinetic energy and other errors are negligible, and that the density of the solvent differs negligibly from the density of the solutions.

A.3 Sources of error

The most important sources of error in capillary viscometry are related to

a) surface tension,

b) capillary end effects,

c) drainage effects,

d) viscous heat effects,

e) deviation of the viscometer from the vertical,

f) hydrostatic head variations,

g) losses by evaporation,

h) errors in the measurement of the concentration and efflux time,

i) shear effects,

j) errors in temperature stability and measurement and

k) kinetic energy.

Fortunately, most of these effects can be considered negligible for the proposed procedures. Errors due to surface tension, end effects and drainage effects are quite small in tests with organic solvents in the Ubbelohde viscometer, when relative measurements of viscosity are concerned[2][3]. Viscous heat effects are negligible when the capillary viscometer is operated by gravity. Errors due to deviation from the vertical and variations in the hydrostatic head are usually very small with this type of viscometer.

Solvent losses by evaporation and concentration errors depend on the particular test procedure and have to be taken into account.

The solvent efflux time should preferably be at least 70 s in order to measure it reproducibly, but it should not be longer than about 200 s in order to avoid long efflux times for the corresponding solutions.

The effect of shear rate can be serious, since polymer solutions are often non-Newtonian[4][5]. Strictly speaking, the measurements should be carried out at very low shear rates, but in the usual procedures the shear rate is as high as 1 000 s^{-1} or more. Fortunately, it can be shown[6][7][8] that shear rate effects are very small unless the molar mass of the polymer is higher than 10^6 g/mol, which seldom happens with commercial polymers. Furthermore, it is impractical to take account of shear rate effects for the purposes of international standardization, and a better approach is to specify the tolerance of the viscometer dimensions in such a way that the shear rate is closely reproducible in different laboratories testing the same polymer sample.

It can be concluded that the most important source of error in the measurements is the kinetic-energy term. Its value may be considerable. For example, using Formula (A.1) to calculate the error with different standard Ubbelohde viscometers when the solvent is dichloromethane, the error is approximately 0,28 % when the inner diameter is 0,36 mm, and increases to 15 % with 0,58 mm. The increased resultant error in the reduced viscosity will be of the order of 30 % and, for special work outside the scope of this document, it might be appropriate to include a kinetic-energy correction.

A.4 Choice of viscometers

Since it is impractical to introduce a kinetic-energy correction into international standardization, it is necessary to choose the viscometer in such a way that

a) either the kinetic-energy term is negligible, or

b) it is constant and reproducible in different laboratories.

It can be shown that the second condition cannot be realized easily. In fact, the maximum fractional hydrostatic pressure *X* spent in kinetic energy is given approximately by Formula (A.4).

The efflux time of a liquid is related to its viscosity by the Poiseuille-Hagenbach-Couette formula as shown in Formula (A.1)[9].

$$v = \frac{\eta}{\rho} = \frac{\pi g h R^4}{8LV} \cdot t - \frac{mV}{8\pi L t} \tag{A.1}$$

v is the viscosity/density ratio;

η is the viscosity of the liquid;

ρ is the density of solvent or solution;

R is the capillary inner diameter;

L is the length of the capillary;

V is the volume of timing bulb;

t is the efflux time;

m is the coefficient.

Coefficient m is related to the capillary structure and solvent/solution viscosity at a certain temperature. To approximate the calibration of hydrostatic pressure spent in kinetic energy, let *m* be equal to 1,0. In Formula (A.2), A is the kinematic viscosity and B is the kinetic energy correction. Calculate the approximate efflux time t of the liquid using the kinematic viscosity with Formula (A.3).

$$v \cong \frac{\pi g h R^4}{8LV} \cdot t - \frac{V}{8\pi L t} = A - B \tag{A.2}$$

$$t \cong \frac{\nu \cdot 8LV}{\pi g h R^4} \tag{A.3}$$

$$X = \frac{B}{A} \cong \frac{V^2}{\pi^2 g h R^4} \cdot \frac{1}{t^2} = \frac{R^4 g h}{64 L^2 \nu^2} \tag{A.4}$$

It is important to note in Formula (A.4) that the efflux time and the reservoir volume by themselves do not influence the value of X.

For standard glass capillaries with diameters between 0,3 mm and 1,0 mm, the tolerance limits for the diameter[10][11] are usually ±0,02 mm, corresponding to approximately ±30 % and ±8 %, respectively, of the value of X, whereas the mean hydrostatic head h is 120 mm ± 10 mm and the capillary length L is 90 mm ± 9 mm, corresponding to approximately ±30 % of the value of X. The conclusion is that, unless the normal tolerances on standard capillaries are severely restricted, the kinetic-energy term cannot be made reproducible. It is therefore necessary to choose viscometers which minimize it.

In this document, the maximum permitted value of the kinetic energy correction X is fixed at 3 % corresponding to approximately 4 % to 6 % of the reduced viscosity. Under these conditions the kinetic energy correction may be regarded negligible as specified in 4.2.

From Formula (A.4), it can be seen that, at fixed values of h and L, the critical parameter which determines the magnitude of X is the ratio R^2/ν.

By inserting

$h = 120$ mm,

$L = 90$ mm

and

$X < 0{,}03$

in Formula (A.4), a relationship between the maximum capillary radius to be used and the value of ν is obtained as shown in Formula (A.5):

$$R^2 < 0{,}111\nu \tag{A.5}$$

or, for the diameter,

$$D^2 < 0{,}444\nu \tag{A.6}$$

where R and D are in mm and ν is in mm²·s⁻¹.

It will be noted that Formula (A.6) is dependent on the particular values ascribed to the mean hydrostatic head and the capillary length. These will vary between various designs of viscometer and, in particular, are slightly different for the Ubbelohde and DIN Ubbelohde versions.

Formula (A.6) permits calculation of the maximum theoretical diameter that could be used for a solvent whose viscosity/density ratio ν is known at the temperature of measurement. It follows that, in order to determine the properties of polymers described in this document, the viscosity/density ratio for the solvent chosen shall be known. Table A.1 gives values at 25 °C for several of the established solvents for polymers, together with the calculated theoretical maximum capillary diameter for the Ubbelohde viscometer.

Formula (A.6) has also been used to select the recommended sizes of Ubbelohde and DIN Ubbelohde viscometers given in Table 1. Other appropriate series of viscometers and sizes can be identified by substituting the relevant values into Formula (A.3).