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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION

R 1628

PLASTICS

DIRECTIVES FOR THE STANDARDIZATION OF METHODS FOR THE DETERMINATION OF THE DILUTE SOLUTION VISCOSITY OF POLYMERS

1st EDITION

June 1970

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BRIEF HISTORY

The ISO Recommendation R 1628, *Plastics – Directives for the standardization of methods for the determination of the dilute solution viscosity of polymers*, was drawn up by Technical Committee ISO/TC 61, *Plastics*, the Secretariat of which is held by the American National Standards Institute (ANSI).

Work on this question led to the adoption of Draft ISO Recommendation No. 1628, which was circulated to all the ISO Member Bodies for enquiry in May 1968. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

Austria
Belgium
Brazil
Czechoslovakia
France
Germany
Hungary
India
Iran
Israel
Italy
Japan
Netherlands
Poland
Portugal
Romania
South Africa, Rep. of
Spain
Sweden
Switzerland
U.A.R.
United Kingdom
U.S.A.
U.S.S.R.

No Member Body opposed the approval of the Draft.

This Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in June 1970, to accept it as an ISO RECOMMENDATION.

ISO Recommendation R 1628 June 1970

PLASTICS

DIRECTIVES FOR THE STANDARDIZATION OF METHODS FOR THE DETERMINATION OF THE DILUTE SOLUTION VISCOSITY OF POLYMERS

INTRODUCTION

This ISO Recommendation is composed of two parts :

Part I : Recommendations for the preparation of "standard methods of test" for the determination of the dilute solution viscosity of polymers;

Part II : Significance and justifications of these recommendations.

PART I

RECOMMENDATIONS

1. DEFINITIONS AND UNITS

1.1 Definitions applicable to any liquid

1.1.1 *Viscosity* (or *dynamic viscosity*) (symbol η) (see ISO Recommendation R 31 – Part III, *Quantities and units of mechanics*).

The viscosity of a fluid sheared between two parallel planes, one of which moves relative to the other in rectilinear and uniform motion in its own plane, is defined by the Newton equation :

$$\tau = \eta . \dot{\gamma} \qquad \ldots (1)$$

where

τ is the shear stress;

η is the viscosity;

$\dot{\gamma} = \frac{dv}{dz}$ the velocity gradient (v is the velocity of one plane relative to the other and z the coordinate perpendicular to the two planes).

NOTE. – Viscosity is usually taken to mean "Newtonian viscosity", in which case the ratio of shearing stress to the velocity gradient is constant. In non-Newtonian behaviour, which is the usual case with high polymer solutions, the ratio varies with the shearing stress. Such ratios are often called the "apparent viscosities" at the corresponding shearing stresses.

The dimensions of viscosity are

$$ML^{-1}T^{-1}$$

and its units are

- *c.g.s. system* : poise (P) = 1 g.cm^{-1}.s^{-1}
- *international system* : N.s.m^{-2} = 10 P

1.1.2 *Viscosity/density ratio* (kinematic viscosity)* (symbol ν)

This ratio is defined by the equation :

$$\nu = \frac{\eta}{\rho} \qquad \ldots (2)$$

where ρ is the density of the fluid.

Its dimensions are

$$L^2 T^{-1}$$

and its units are

- *c.g.s. system* : stokes (St) = 1 $cm^2.s^{-1}$
- *international system* : $m^2.s^{-1}$ = 10^4 St

1.2 Definitions applicable to polymer solutions

1.2.1 *Viscosity ratio* (formerly called relative viscosity). The ratio of the viscosities of the polymer solution (of stated concentration) η and of the pure solvent η_0 at the same temperature :

$$\frac{\eta}{\eta_0} \qquad \ldots (3)$$

This ratio being a number, it is dimensionless.

1.2.2 *Viscosity relative increment* (formerly called specific viscosity). Viscosity ratio minus one :

$$\left(\frac{\eta}{\eta_0}\right) - 1 = \frac{\eta - \eta_0}{\eta_0} \qquad \ldots (4)$$

Being a number, it is dimensionless.

1.2.3 *Viscosity number* (formerly called reduced viscosity). Ratio of the viscosity relative increment to the polymer concentration c in the solution :

$$\frac{\eta - \eta_0}{\eta_0 c} \qquad \ldots (5)$$

Its dimensions are

$$M^{-1} L^3$$

and its units in the c.g.s. system : ml/g.

The viscosity number is usually determined at low concentration (under 0.01 g/ml).

1.2.4 *Logarithmic viscosity number* (formerly called inherent viscosity). Ratio of the natural logarithm of the viscosity ratio to the polymer concentration in the solution :

$$\frac{\ln\left(\frac{\eta}{\eta_0}\right)}{c} \qquad \ldots (6)$$

Dimensions and units are the same as those given in clause 1.2.3. The logarithmic viscosity number is usually determined at low concentration (under 0.01 g/ml).

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* This name and several of the following names are the result of I.U.P.A.C. decisions (6).

1.2.5 *Limiting viscosity number* (formerly called intrinsic viscosity) (symbol $[\eta]$). Limiting value of the viscosity number, or of the logarithmic viscosity number at infinite dilution :

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta - \eta_0}{\eta_0 c}\right) \quad \ldots (7)$$

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

Dimensions and units are the same as those given in clause 1.2.3.

NOTE. – The effect of the shear rate of the functions defined in clauses 1.2.1 to 1.2.5 has been disregarded since this effect is usually negligible for values of these functions less than 500 ml/g. Strictly speaking, all these functions should be defined at the limiting (preferably infinitely small) value of the shear rate.

2. MEASUREMENTS

The data needed for the evaluation of the functions defined in clause 1.2 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. The efflux time of a liquid is related to its viscosity by the Poiseuille-Hagenbach-Couette equation :

$$\eta = kt - \frac{A}{t} \quad \ldots (8)$$

where

k is a constant of the viscometer;

A is a parameter of the kinetic energy correction.

This equation can be reduced to

$$\eta = kt \quad \ldots (9)$$

if the kinetic energy correction $\frac{A}{t}$ can be disregarded.

In this ISO Recommendation, the term $\frac{A}{t}$ is considered to be negligible when it is smaller than 3 % of the viscosity of the solvent (see Part II). If this condition is accepted (i.e. unless other agreements have been made) the viscosity ratio $\frac{\eta}{\eta_0}$ will be given therefore by the "efflux time ratio" $\frac{t}{t_0}$.

3. APPARATUS

Capillary viscometer, suspended-level, Ubbelohde type (see Figure, page 10).

It is strongly recommended that its dimensions be chosen from among those indicated in Table 1. The choice is determined by the viscosity/density ratio of the solvent at the temperature of measurement, as indicated in Table 1.

TABLE 1 – **Ubbelohde viscometers recommended for the determination of the dilute solution viscosity of polymers**

Viscosity/density ratio of the solvent at temperature of measurement	Viscometer model	Capillary diameter	Reservoir volume
cSt		mm	ml
0.30 to 0.55	A	0.36 ± 0.02	1.5 to 2.0
0.56 to 0.85	B	0.46 ± 0.02	2.0 to 3.0
0.86 to 1.50	C	0.59 ± 0.02	3.0 to 4.0
1.51 to 3.0	D	0.78 ± 0.02	5.0 to 6.0

For all models the capillary length L is 90 ± 5 mm and the mean hydrostatic head h is 130 ± 5 mm (see Figure, page 10).

The next smaller viscometer can also be used. The average diameter of the capillary is determined by a suitable method.

4. SOLUTIONS

4.1 Preparation of solutions

The dissolution of the polymer sample in the solvent should give "true" solutions, free of microgels and of associated macromolecules. Also, the polymer degradation should be minimized. For these reasons, the dissolution procedure has to be exactly defined and it is recommended that the following items be mentioned :

(*a*) the solvent used and its pretreatment, if any;

(*b*) the apparatus and the method of agitation used;

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

(*d*) the time interval necessary for completely dissolving the polymer without degradation, or at constant degradation;

(*e*) the stabilizer and/or the protecting atmosphere used;

(*f*) the conditions of filtration of the solution, if applied.

4.2 Concentration

The solution concentration is such that the ratio of the efflux time of the solution t to the efflux time of the solvent t_0 is at least 1.2 and less than 2.

More than one concentration can therefore be used for a given resin-solvent system, depending on the resin molecular weight.

In this case, however, a clear definition of the efflux time limits, which determine the choice of the concentration, has to be given.

The concentration is expressed preferably in grammes of resin per millilitre of solution (g/ml).

5. TEMPERATURE OF MEASUREMENT

The temperature should be chosen with respect to sufficient solubility and other technical requirements but kept uniform for one particular resin-solvent system, and the temperature tolerance is to be specified. A temperature of 25 ± 0.05 °C should be chosen whenever possible.

6. EXPRESSION OF RESULTS

The result should preferably be expressed as a *viscosity number* (V.N. in ml/g).

However, the result can be expressed as a *limiting viscosity number* (L.V.N. in ml/g) for polymers whose different commercial grades require that different concentrations be used. (See clause 4.2.)

The limiting viscosity number (L.V.N.) can be calculated from the viscosity number by means of suitable approximate equations, for example by the equation :

$$\text{L.V.N.} = \frac{(\text{V.N.})}{1 + k\,(\text{V.N.})\,c}$$

where k is an empirical constant between 0.2 and 0.3.

This constant must be experimentally determined for each resin-solvent system, that is for each particular ISO Recommendation.

PART II

SIGNIFICANCE AND JUSTIFICATIONS

Recommendations are given for the determination of the dilute solution viscometric properties of polymers as defined in clause 1.2. The measurement of these properties (viscosity ratio, etc.) can usually be carried out with greater accuracy than that attained in absolute measurements of viscosity since many instrumental errors are approximately the same for both solvent and solution, and effectively cancelled.

7. PRINCIPLE OF MEASUREMENTS

The viscosity ratio and the other functions defined in clause 1.2 are calculated from the efflux times of solution and solvent. The liquids flow, under the force of gravity, through the capillary of a suspended-level Ubbelohde viscometer. The efflux times are taken to be proportional to the ratio "viscosity/density" of the fluids (see section 2). This is equivalent to stating that the kinetic energy and other errors are negligible and that the density of solvent differs negligibly from the density of the solutions. The importance of several possible errors must therefore be discussed.

8. SOURCES OF ERROR

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

(*a*) surface tension;

(*b*) capillary end effect;

(*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 concentration and efflux time;

(*i*) shear effect;

(*j*) errors in temperature stability and measurement;

(*k*) kinetic energy.

Fortunately, most of these effects can be considered negligible in the proposed procedure. Errors due to surface tension, end effects and drainage are quite small in tests with organic solvents in the Ubbelohde viscometer, when relative measurements of viscosity are concerned(1). Viscous heat effects are negligible when the capillary viscometer is operated by gravity. The errors due to deviation from the vertical and variation of the hydrostatic head are usually very small with suspended-level viscometers.

The solvent losses by evaporation and the concentration errors depend on the particular test procedure and have to be taken into account in the method of test (see section 4).

The solvent efflux time should be of the order of 70 to 80 seconds at least, in order to measure it with good reproducibility. It should not, however, be larger than about 200 seconds, in order to avoid long efflux times of the solutions.

The effect of shear rate can be serious, since polymer solutions are often non-Newtonian(2). Strictly speaking, it should be necessary to carry out the measurements at very low shear rates, whereas in the usual procedures the shear rate is as high as 1000 s^{-1} or more. Fortunately, it can be shown(3) that the shear rate effects are very low unless the molecular weight of the polymer is higher than 10^6, which seldom happens with commercial polymers. Furthermore, it would be very unpractical to take into account shear rate effects for purposes of international standardization and a better approach to the problem is to define the tolerance of the viscometer dimensions in such a way that the shear rate is closely reproducible in different laboratories testing the same polymer. It may be concluded that the most important source of error in measurements carried out with the Ubbelohde viscometer is the kinetic energy term. Its value can be considerable : for example, it is approximately 15 % for chloroform in a standard Ubbelohde viscometer having the capillary diameter of 0.56 mm. The resultant error in viscosity number can be of the order of 30 %.

9. CHOICE OF THE VISCOMETERS

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

(*a*) the kinetic energy term is negligible, or

(*b*) it is constant and well reproducible in different laboratories.

It can be shown that the second condition cannot be realized easily. In fact the fractional hydrostatic pressure X spent in kinetic energy is given approximately by the equation :

$$X = \frac{R^4\, hg}{64 L^2 \nu^2} \qquad \ldots (10)$$

where

R is the capillary radius;

h is the hydrostatic head;

g is the acceleration of free fall;

L is the capillary length;

ν is the viscosity/density ratio.

It is important to notice in equation (10) that the efflux time and the reservoir volume by themselves do not influence the kinetic energy term.

For standard glass capillaries (diameters between 1.0 and 0.3 mm) the tolerances are usually ± 0.02 mm(4), corresponding to approximately ± 8 % and ± 30 % in the value of X, whereas the hydrostatic head h is 130 ± 5 mm and the capillary length L is 90 ± 5 mm, corresponding to approximately ± 15 % in the value of X. *The conclusion is that, unless the normal tolerances of standard capillaries are severely restricted, the kinetic energy term cannot be made reproducible.* It is therefore necessary to choose viscometers which minimize it.

In the present ISO Recommendation it was decided *to fix the maximum permitted value of X at 0.03* (approximately 4 to 6 % of the viscosity number).

From equation (10) it is seen that, at fixed values of h and L, the critical parameter which defines the magnitude of X is the ratio $\frac{R^2}{\nu}$.

Inserting in equation (10) the following conditions :

$$h = 13.0 \text{ cm}$$
$$L = 9.0 \text{ cm}$$
$$X \leqslant 0.03$$

one obtains the relation between the maximum capillary radius to be used and the value of ν :

$$R^2 \leqslant 0.111\, \nu \qquad \ldots (11)$$

or, for the diameter :

$$D^2 \leqslant 0.444\, \nu \qquad \ldots (12)$$

where R and D are in millimetres and ν in centistokes (or R and D in centimetres and ν in stokes).

Equation (12) permits calculation of the maximum diameter to be used for a solvent whose viscosity and density are known at the temperature of measurement.

As can be seen from Table 2, the values of ν for most common organic solvents vary between 0.3 and 2 centistokes (5), at 20 °C*.

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* Most organic solvents have, at 25 °C a viscosity/density ratio only 5 % smaller than at 20 °C.

TABLE 2 – **Viscosity/density ratios and maximum capillary diameters**

Solvent	**Viscosity/density ratio at 20 °C**	**Maximum diameter in accordance with equation (12)**
	cSt	mm
Carbon disulphide	0.25	0.33
Diethyl ether	0.34	0.38
Pentane	0.37	0.40
Chloroform	0.38	0.41
Acetone	0.41	0.42
Hexane	0.50	0.46
Carbon tetrachloride	0.61	0.52
Methanol	0.735	0.57
Benzene	0.74	0.57
Water	1.004	0.66
Ethanol (100 %)	1.51	0.81
Cyclohexanone	2.20	0.97
Propanol	2.74	1.10
Orthochlorophenol	3.40	1.23
Metacresol	16.30	2.7

Equation (12) has been used to calculate the values in Table 1 in Part I of this ISO Recommendation. Of course, any convenient series of viscometers could be used, provided that D is given by equation (12).

The four viscometers recommended in Table 1 have been chosen so that

(*a*) it is possible for precision-bore tubing to be made easily (the tolerance of 0.02 mm cannot be reduced);

(*b*) the viscometer is available commercially;

NOTE. – Viscometers A, B, C and D correspond respectively to size numbers OC, OB, 1 and 1C of ASTM D. 2515 – 66.

(*c*) they have convenient efflux times (they will be approximately 90 to 200 seconds for viscometer A and 70 to 150 seconds for viscometers B, C and D, in the viscosity ranges indicated in Table 1).

10. DISSOLUTION OF POLYMERS

It is necessary to specify the agitation used, the temperature and time of dissolution, because this process can give sometimes “untrue” solutions or solutions containing microgels. Moreover, too high a temperature or too long a time can produce degradation of the polymer. Also, polymer solutions can have a tendency to oxidize easily.

11. CONCENTRATION OF THE SOLUTION

The value of the “viscosity ratio” $\frac{\eta}{\eta_0}$ is determined, for a given system, by the molecular weight and the concentration of the polymer in the solution. It is necessary to fix the lower limit of the viscosity ratio at 1.2 in order to have sufficient precision on the measured difference of efflux times.

The upper limit of 2.0 for $\frac{\eta}{\eta_0}$ is recommended because at high molecular weight there can be, at the usual concentrations, shear effects and non-linearity of the concentration in relation to the viscosity number.