INTERNATIONAL STANDARD ISO 304:1985
TECHNICAL CORRIGENDUM 1

Published 1998-07-01

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

Surface active agents — Determination of surface tension by drawing up liquid films

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Agents de surface — Détermination de la tension superficielle par étirement de films liquides

RECTIFICATIF TECHNIQUE 1

Technical Corrigendum 1 to International Standard ISO 304:1985 was prepared by ISO Central Secretariat on behalf of Technical Committee ISO/TC 91, *Surface active agents.*

Page 1

Clause 0

Delete the last sentence.

Page 2

6.1.1

In line 4, replace "see sub-clause 5.2 of ISO 2456" by "complying with the requirements of clause 4 of ISO 2456".

6.2.1

In the last line of the second paragraph, replace "sub-clause 5.2 of ISO 2456" by "clause 5 of ISO 2456".

ICS 71.100.40 **Ref. No. ISO 304:1985/Cor.1:1998(E)**

Descriptors: surfactants, tests, determination, surface tension.

H-13-33

International Standard ISO 304

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Surface active agents — Determination of surface tension by drawing up liquid films

Agents de surface — Détermination de la tension superficielle par étirement de films liquides

Second edition — 1985-12-15

UDC 661.185 : 532.61.08 **Ref. No. ISO 304-1985 (E)**

Descriptors : surfactants, tests, determination, surface tension.

Price based on 10 pages

ISO 304-1985 (E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 304 was prepared by Technical Committee ISO/TC 91, *Surface active agents*.

This second edition cancels and replaces the first edition (ISO 304-1978), of which it constitutes a minor revision.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

Printed in Switzerland

Surface active agents — Determination of surface tension by drawing up liquid films

0 Introduction

Surface tension is a fundamental property of liquids in general and aqueous solutions of surface active agents in particular.

The measurement of this characteristic, however, does not allow, in the case of solutions of surface active agents, any suppositions as to their detergency, wetting, foaming, emulsifying activities, etc. Indeed, no connection can be established between the performance properties of the surface active agents and the surface tension of their solutions.

1 Scope and field of application

This International Standard specifies a test method for the determination, by drawing up liquid films, of the surface tension of aqueous or organic solutions of surface active agents and mixtures containing one or more surface active agents.

It also applies to the measurement of surface tension of pure liquids or solutions other than those mentioned above.

NOTE — Numerous methods have been established to determine surface tension, such as :

a) methods by drawing up liquid films by a plate, stirrup or ring;

b) methods for measuring the rise of liquid in a capillary tube;

c) maximum ball pressure method;

d) drop weight method;

e) drop or sessile ball method;

f) suspended drop method;

g) dynamic methods based on measurements of flow characteristics;

h) methods which study the waves produced in capillary jets.

The methods based on drawing up liquid films have notable advantages in the simplicity of their procedure and the commercial availability of highly automatic appliances.

2 References

ISO 862, *Surface active agents — Vocabulary.*

ISO 2456, *Surface active agents — Water used as a solvent for tests.* *

3 Definition

surface tension : See ISO 862.

NOTE — The SI unit of surface tension is the newton per metre (N/m). In practice, the submultiple millinewton per metre (mN/m)** is used.

4 Principle

Measurement of the maximum force which it is necessary to exert vertically on a stirrup or a ring, in contact with the surface of the liquid being examined placed in a measuring cup, in order to separate it from this surface, or on a plate, with an edge in contact with the surface, in order to draw up the film that has formed.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Tensiometer, which can be fitted with plates, stirrups and rings, and which shall comprise the following items :

a) A **horizontal platform**, which can be moved vertically in both directions by means of a micrometer screw. It shall be fitted with a millimetric scale allowing estimation of vertical movements of 0,1 mm;

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* At present at the stage of draft.

** 1 mN/m = 1 dyn/cm

b) A **dynamometer**, to give a continuous measure of the force applied to the measuring unit with an accuracy of at least 0,1 mN/m.

c) A **device** for indicating or recording the values measured by the dynamometer.

The assembly shall be shielded from vibrations and draughts.

5.2 Measuring unit, which shall comprise at least one of the items a), b) and c) and also item d).

a) A **rectangular plate** of sheet platinum, 0,1 mm thick and about 30 mm long by 20 mm wide, roughened using emery paper in such a way that the strokes are perpendicular to the side intended to be submerged. The plate is fixed, preferably by welding but alternatively by any other means, to a suspension rod situated in the axis of symmetry of the plate (see figure 1).

b) A **stirrup** of platinum — iridium wire of diameter not exceeding 0,1 mm; the length of the horizontal arm is 20 to 40 mm and the length of the two vertical branches is 10 mm. The ends of these branches terminate in two small platinum balls which act as counterweights (see figure 2).

c) A **ring** of platinum — iridium wire, 0,3 mm in diameter. The circumference of the ring is generally between 40 and 60 mm. It is fixed to a suspending rod by means of a platinum wire stirrup (see figure 3).

d) A **measuring cup**, to hold the test portion of the liquid to be examined, consisting of a small glass tank capable of containing a sufficient quantity of liquid. Watch-glasses shall not be used.

In the case of the determination of the surface tension of solutions of surface active agents, cylindrical tanks with a diameter of at least 8 cm may be used.

For determinations on pure liquids, the ideal measuring cup is a small tank in the form of a rectangular parallelepiped having sides of at least 8 cm; this shape enables the liquid surface to be cleaned completely by wiping.

NOTE — Generally, in the case of dilute solutions of surface active agents, the surface should only be wiped if the concentration of the surface active agent is close to the critical concentration for micelle formation (c.m.c.).

6 Procedure

6.1 Preparation of solutions of surface active agents

6.1.1 The solutions of surface active agents for the determinations shall be prepared with all necessary care. The water used for preparing them shall be double-distilled water (see sub-clause 5.2 of ISO 2456), checked by measuring its surface tension. Cork stoppers and, more particularly, rubber stoppers, shall on no account be used, either in the construction of the distillation apparatus or for stoppering containers in which the water is kept.

6.1.2 The temperature of the solutions shall be maintained to within 0,5 °C.

NOTE — Determinations carried out in the region of points of critical solubility, such as the Krafft temperature, cloud temperature of ethylene oxide condensates, etc., are seriously marred by errors. It is preferable to proceed at a temperature higher than that of the particular points, or at a temperature lower than the cloud temperature of ethylene oxide condensates.

6.1.3 As the surface tension of solutions varies with time, it is difficult to recommend a standard ageing period for the solution, because the nature and purity of the surface active agent, its concentration and its liability to adsorption all play a particular part in these variations. It is therefore desirable to make several measurements over a period of time, to construct the surface tension curve as a function of time and to determine the position of the level portion, which gives the age at which the solution has reached its equilibrium state. Automatic apparatus is very suitable for carrying out the measurements, the values being recorded as a function of the time.

6.1.4 The surface of the solutions is extremely sensitive to contamination by atmospheric dust or by vapours from solvents handled in the vicinity. Therefore no volatile products shall be handled in the room where the determinations are made and the complete apparatus shall be protected by a bell of the kind used for balances. These precautions also reduce variation in temperature.

6.1.5 The method recommended for taking the test portion of the liquid examined is to suck it, with a pipette, from the centre of the mass of liquid, as the surface may be liable to soiling by insoluble particles and dust.

6.2 Cleaning the measuring unit

6.2.1 Cleaning the measuring cup

In the presence of impurities such as silicones, which are not removed by sulfo-chromic acid mixture, phosphoric acid or a solution of potassium persulfate in sulfuric acid, wash the measuring cup using special products (for example toluene, perchloroethylene or methanolic potassium hydroxide solution).

If these impurities are absent, or after cleaning with these products, wash the measuring cup carefully with hot sulfo-chromic acid mixture and then with concentrated phosphoric acid [83 to 98 % (*m/m*)]. Finally, rinse in double-distilled water until the rinsings are neutral. The double-distilled water shall be freshly prepared according to sub-clause 5.2 of ISO 2456.

Before the determination, the measuring cup shall be rinsed several times with the liquid to be examined.

6.2.2 Cleaning the plate, stirrup or ring

If necessary, clean the platinum plate, stirrup or ring (5.2) with special products as specified in 6.2.1. In the absence of impurities requiring cleaning with these products, or after cleaning with these products, wash the platinum measuring unit with hot concentrated sulfuric acid (ϱ_{20} = 1,839 g/ml) and then rinse with double-distilled water until the rinsings are neutral.

Plates shall never be dried by passing through a flame. Do not touch the measuring unit or the inner surface of the measuring cup with the fingers.

6.3 Calibrating the tensiometer

6.3.1 Principle

Calibrate the tensiometer (5.1) by adjusting it so that the indications or recordings of the device [5.1 c)] are expressed directly in millinewtons per metre (mN/m).

6.3.1.1 Using a plate as the measuring unit

During the determination, the roughened platinum plate [5.2 a)], when submerged in the liquid to be examined, is surrounded by a layer of liquid which wets it completely; the system behaves as if the liquid were making tangential contact with a theoretical plate consisting of the plate surrounded by its wetting sheath.

Avoid letting the plate dry completely after cleaning and before submersion in the liquid to be examined.

Because of the system by which the plate is connected to the measuring apparatus, it is easy to drain the plate properly; when the plate is removed from the liquid, one end of its base comes away owing to inevitable lack of symmetry, and leaves one corner immersed. If withdrawal is continued very slowly, the required drainage conditions are obtained, and the plate is removed without bringing away any droplets.

To set the apparatus to zero, it is necessary to proceed with the plate completely withdrawn, the plate being drained as indicated above. Correction for wetting is thus included in the calibration and is not involved in the determinations.

6.3.1.2 Using a stirrup as the measuring unit

In order to avoid the correction of buoyancy resulting from the volume of the immersed wire and the two platinum balls, first set the apparatus to zero with the stirrup [5.2 b)] immersed in a liquid of the same density as the liquid being examined, until its horizontal arm is level with the surface of the liquid.

6.3.1.3 Using a ring as the measuring unit

When using a ring [5.2 c)], it is not necessary to make buoyancy corrections.

6.3.2 Calibration procedure

Calibration can be carried out by two methods :

a) by means of riders of known mass, placed on the plate, stirrup or ring. The operation is lengthy, but very accurate. The instrument reading, indicating the surface tension γ, in millinewtons per metre, is calculated by the formula

$$\frac{m \times g}{b}$$

where

m is the mass, in grams, of the riders;

b is the perimeter, in metres, of the plate, stirrup or ring;

g is the acceleration due to gravity, in metres per second squared.

b) by means of pure substances whose surface tensions are accurately known. This method is quicker.

Calibrate the tensiometer, if necessary, using the procedure specified in 6.4, until the observed reading agrees with the known value of the calibration liquids.

NOTE — For determinations not requiring very great precision, the tensiometer fitted with the plate, stirrup or ring may be calibrated with pure substances whose surface tension is known exactly and whose density is similar to that of the liquid to be examined. In these conditions, the relation between the surface tension and the force applied to the dynamometer may be treated as linear.

The values of the surface tension of a number of pure organic liquids are given in annex A.

6.4 Determination (see also annex B)

6.4.1 Levelling the tensiometer

Place a liquid level on the platform [5.1 a)], and adjust the screws fixed in the base of the apparatus, until the platform is horizontal.

6.4.2 Using a plate as the measuring unit

When the plate [5.2 a)] has been wetted and the apparatus calibrated with the wetting sheath, check that the shorter edges of the plate are horizontal.

Place the measuring cup [5.2 d)], containing the liquid to be examined, on the platform and bring it under the plate. Raise the platform until the plate is suddenly caught by the liquid. Then gently move the platform, maintaining the equilibrium of the dynamometer, until the base of the plate is at the height of the free surface of the liquid (see figure 4). This process eliminates any error due to buoyancy.

As immersing the plate in the liquid disturbs the arrangement of the surface layer, wait a few minutes and then determine the force exerted on the dynamometer [5.1 b)]. Several successive measurements should be made in the same conditions.

If the measuring instrument is capable of recording the movement/force curve, plot this by gently lowering the platform, the plate at first being immersed for about 15 mm in the liquid. In this way, a curve is obtained which has a slightly sloping straight portion, the slope corresponding to the buoyancy.

This curve may provide important information concerning small variations in the surface tension.

6.4.3 Using a stirrup as the measuring unit

With the apparatus calibrated in accordance with 6.3.1.2, check that the arm of the stirrup [5.2 b)] is horizontal. Place the measuring cup, containing the liquid to be examined, on the platform and bring it under the stirrup. Raise the platform until the horizontal arm of the stirrup is suddenly caught by the liquid.

Continue raising the platform until the dynamometer is in equilibrium once more.

Lower the platform gently until the dynamometer is slightly out of equilibrium. Then, adjusting the force applied to the dynamometer as well as the position of the platform, restore equilibrium of the dynamometer with the horizontal arm of the stirrup located at the height of the free surface of the liquid. The aim of this operation is to ensure the complete wetting of the arm of the stirrup.

NOTE — Certain commercially available appliances allow the stirrup to be moved vertically while maintaining the position of the platform, as well as the equilibrium position of the balance.

As the contact between the platinum of the stirrup and the surface of the liquid disturbs the arrangement of the surface layer, wait a few minutes before beginning the determination.

Lower the platform using the micrometer screw, maintaining the equilibrium of the dynamometer, either until the "film" linking the horizontal arm of the stirrup and the surface of the liquid breaks or until the lower meniscus of the "film" separates from the horizontal arm of the stirrup. Carefully note the force applied at the moment of breaking.

6.4.4 Using a ring as the measuring unit

Check that the circumference of the ring [5.2 c)] is horizontal. Use the surface of the liquid as a mirror, observing the image of the ring almost in contact with the surface of the liquid.

NOTE — If the surface of the liquid does not give a sufficiently clear image, use a mirror placed on the platform, the mirror having been made horizontal with the help of a liquid level.

Follow the same procedure as that specified in 6.4.3 for the stirrup.

7 Expression of results

7.1 Method of calculation

7.1.1 Using a plate as the measuring unit

The surface tension γ, expressed in millinewtons per metre, is given by the formula

$$\frac{F}{b}$$

where

F is the force, in millinewtons, applied to the dynamometer [5.1 b)] when the base of the plate [5.2 a)] is level with the free surface of the liquid;

b is the perimeter, in metres, of the plate.

7.1.2 Using a stirrup as the measuring unit

The surface tension γ, expressed in millinewtons per metre, is given by the formula

$$\frac{F'}{b'}$$

where

F' is the force, in millinewtons, applied to the dynamometer at the moment of breaking of the "film" linking the arm of the stirrup [5.2 b)] and the surface of the liquid, or of separation of the lower meniscus of the "film";

b' is the perimeter, in metres, of the horizontal arm of the stirrup [5.2 b)].

7.1.3 Using a ring as the measuring unit

The surface tension γ, expressed in millinewtons per metre, is given by the formula

$$\frac{f \times F''}{4 \pi r}$$

where

F'' is the force, in millinewtons, applied to the dynamometer at the moment of breaking of the "film" linking the ring [5.2 c)] and the surface of the liquid, or of separation of the lower meniscus of the "film";

r is the radius, in metres, of the ring [5.2 c)];

f is a correction factor taking into account the directions in which the surface forces act on the ring at the moment immediately preceding breaking of the "film" or separation of the lower meniscus of the "film", as there is not perfect symmetry between the menisci of the inner and outer parts of the ring [5.2 c)] (see figure 5).

NOTE — The value of f depends on the radius of the ring, the thickness of the platinum wire of which it is made, the density of the liquid to be examined and the volume of the liquid raised above the free surface at the moment immediately preceding breaking of the "film" or separation of the lower meniscus of the "film". Bibliographical references on this subject are included in annex C.

7.2 Precision

The precision of determinations of surface tension varies considerably according to the nature of the liquid examined and its wetting power towards platinum.

In the case of a *physically pure* liquid capable of wetting platinum completely, the precision is 0,1 mN/m. For the purposes of this International Standard, a *physically pure* liquid is a liquid the surface of which, particularly, is free from any foreign matter capable of affecting the surface properties.

8 Test report

The test report shall include the following information :

a) all information necessary for the complete identification of the product to be examined, including details of sampling and, in the case of solutions of surface active agents, critical solubility temperatures, such as the Krafft temperature, cloud temperature of ethylene oxide condensates, etc.;

b) the reference of the method used (reference to this International Standard), together with an indication of the measuring unit used (plate, stirrup or ring) and the diameter of the measuring cup;

c) the nature of the water used, or the nature of the solvent used, and the concentration of the solutions;

d) the temperature of the determination;

e) the age of the solution at the time of the determination, i.e., the time which has elapsed between the preparation of the solution and the determination;

f) the variation of the surface tension with time, until equilibrium is reached;

g) the results and the method of expression used;

h) any operational details not specified in this International Standard or in the International Standards to which reference is made, or regarded as optional, as well as any incidents liable to have affected the results.

Dimensions in millimetres

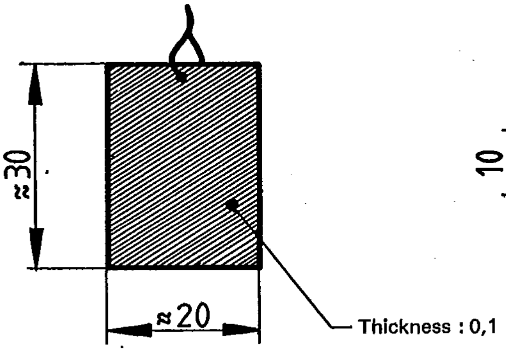

Figure 1 — Plate [5.2 a)]

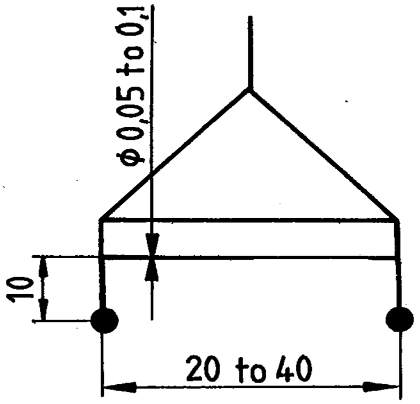

Figure 2 — Stirrup [5.2 b)]

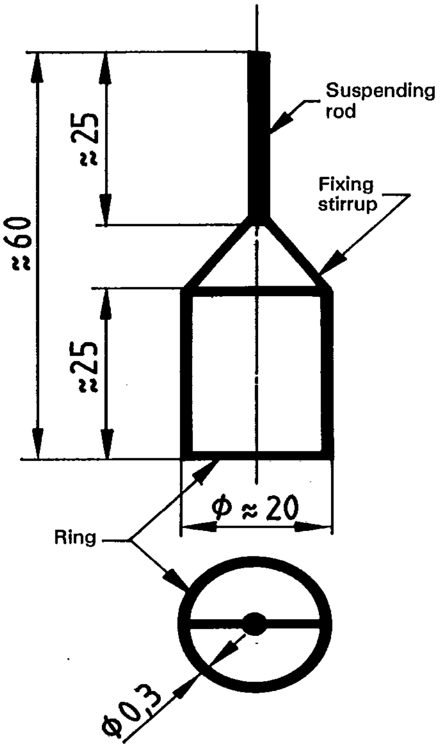

Figure 3 — Ring [5.2 c)]

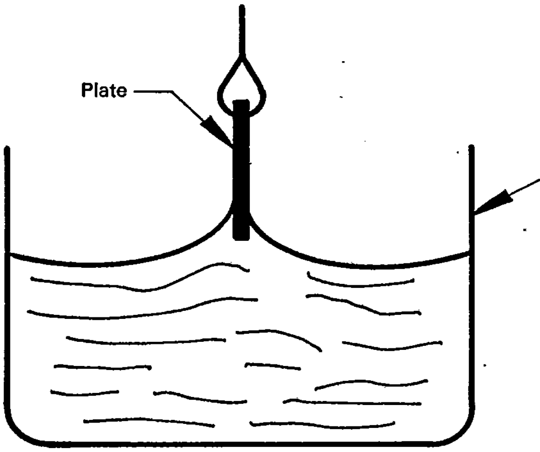

Figure 4 — Measurement using a plate

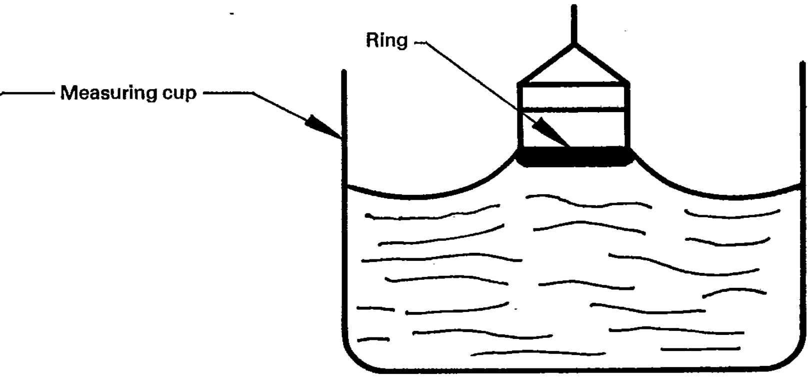

Figure 5 — Measurement using a ring

Annex A

Values of surface tension of some pure organic liquids with respect to air, at 20 °C

(This annex forms an integral part of the Standard.)

Liquid	Surface tension	Density at 20 °C	Boiling point
	mN/m	g/ml	°C
Glycerol	63,4	1,260	290
Methylene diiodide (diiodomethane)	50,76	3,325	180
Quinoline	45,0	1,095	237
Benzaldehyde	40,04	1,050	179
Bromobenzene	36,5	1,499	155
Ethyl acetoacetate	32,51	1,025	180
o-Xylene	30,10	0,880	144
Octan-1-ol [*n*-Octyl alcohol]	27,53	0,825	195
Butan-1-ol [*n*-Butyl alcohol]	24,6	0,810	117
Propan-2-ol	21,7	0,785	82,3

Annex B

Illustration of the measurement procedure — Case of the ring

(This annex forms an integral part of the Standard.)

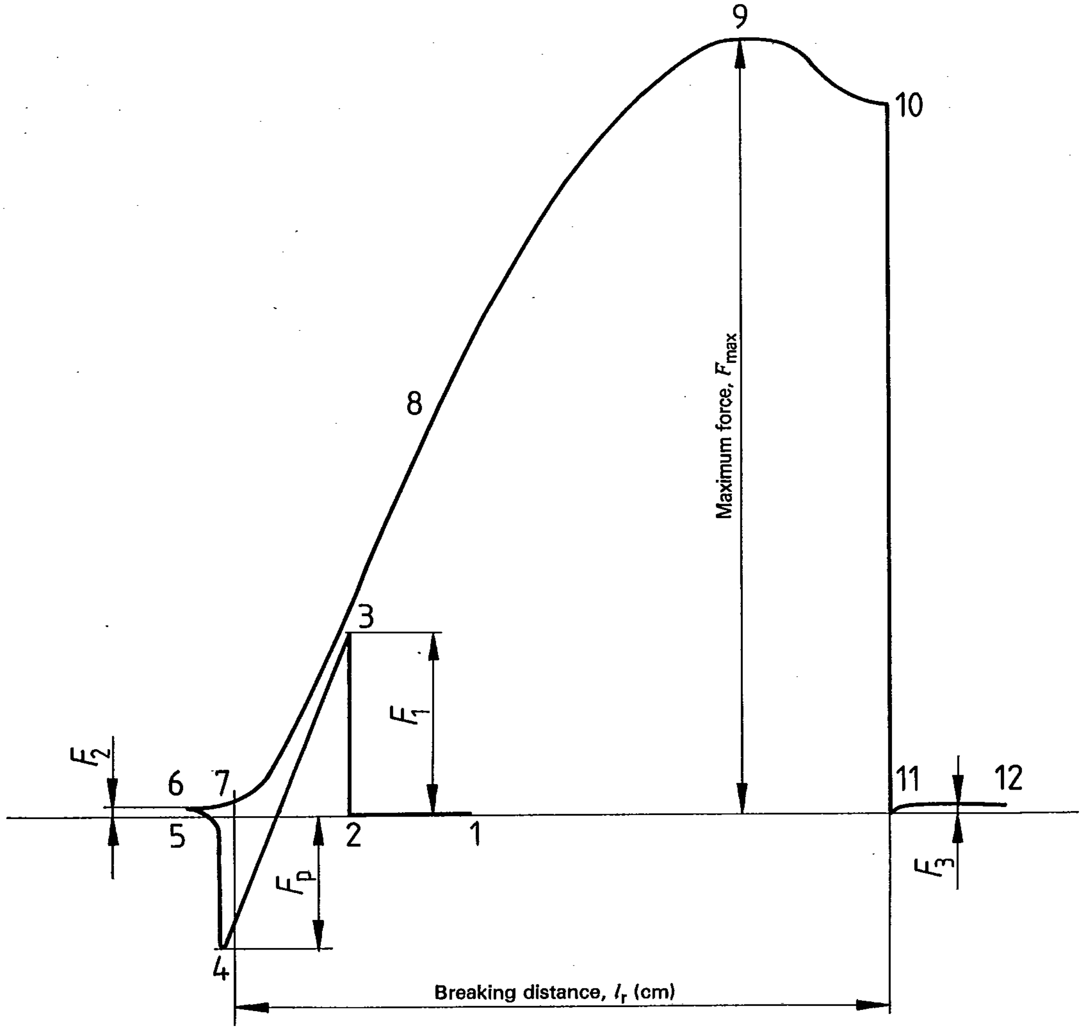

Figure 6 — Graph of force F as a function of displacement l of the measuring unit — Case of the ring

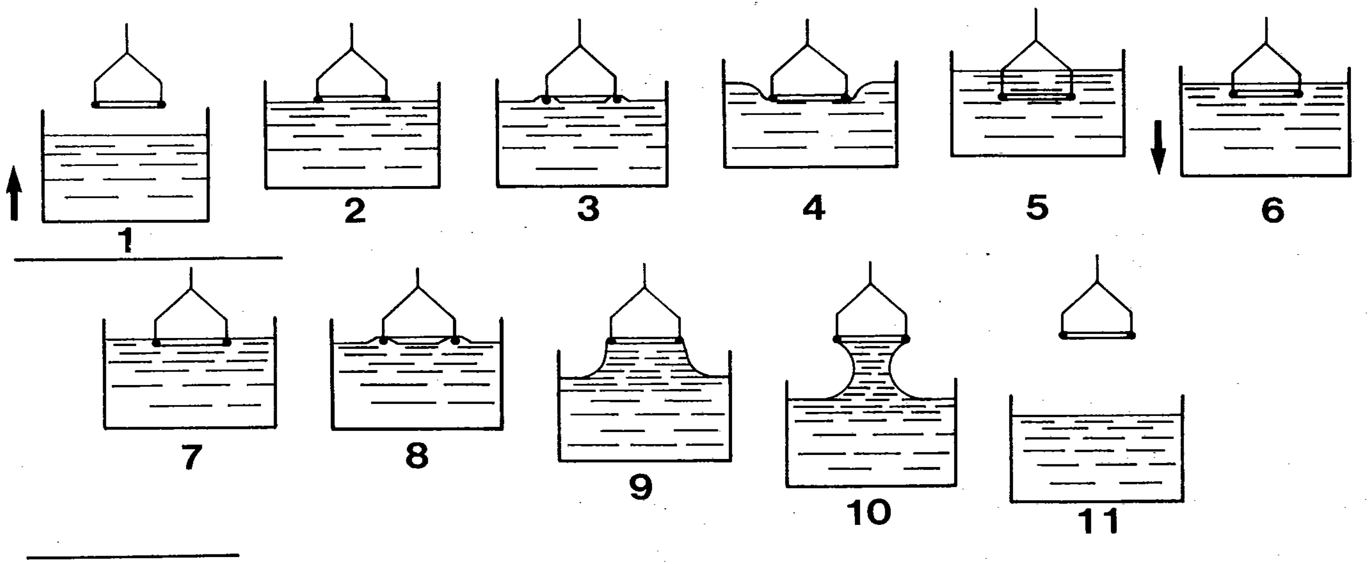

Figure 7 — Illustration of the measurement of surface tension — Case of the ring

On figure 6, stages 1 to 5 correspond to upward displacement of the measuring cup, containing the liquid to be examined, and at the moment when the ring is immersed in the liquid.

From stage 1 to stage 2, the ring is above the liquid surface (see illustration 1 of figure 7).

At stage 2, the lower part of the ring touches the liquid surface (see illustration 2 of figure 7).

From stage 2 to stage 3, the liquid wets the ring. The liquid exerts a traction force F_1 on the ring (see illustration 3 of figure 7).

From stage 3 to stage 4, the ring compresses the liquid surface, the traction force F_1 decreases, the pressure force F_p increases (see illustration 4 of figure 7).

At stage 4, the ring goes through the liquid surface.

From stage 4 to stage 5, the pressure force F_p decreases, the traction force F_2 exerted is due to wetting of the upper part of the ring.

From stage 5 to stage 6 the ring is in the liquid (see illustration 5 of figure 7).

On figure 6, stages 6 to 12 correspond to downward displacement of the measuring cup, containing the liquid to be examined, and at the moment when the ring emerges from the liquid.

From stage 6 to stage 7, the ring is still immersed in the liquid (see illustration 6 of figure 7).

At stage 7, the upper part of the ring touches the liquid surface (see illustration 7 of figure 7).

From stage 7 to stage 10, the ring draws up a liquid film out of the liquid. The liquid exerts a traction force F on the film (see illustration 8 of figure 7).

From stage 7 to stage 8, the force F varies linearly.

From stage 7 to stage 10, the shape of the liquid film varies continuously.

At stage 9, the liquid exerts the maximal traction force F_{max} on the ring (see illustration 9 of figure 7).

At stage 10, the liquid film separates from the ring (see illustration 10 of figure 7).

From stage 10 to stage 11, the traction force F decreases after rupture of the film.

The remaining force F_3 results from the liquid film which remains attached to the ring (see illustration 11 of figure 7).

From stage 11 to stage 12, the ring is out the liquid (see illustration 11 of figure 7).

Annex C

Bibliography

(This annex does not form an integral part of the Standard.)

For information concerning the correction factor, *f*, in the formula for the calculation of surface tension in the case where the ring is used (see 7.1.3), the following works may be consulted :

[1] HARKINS, W. D., and JORDAN, H. F., "A method for the determination of surface and interfacial tension from the maximum pull on a ring", *J. Am. Chem. Soc.* **52** (1930),pp. 1751-1772.

[2] FOX, H. W., et CHRISMAN, C. H., Jr., "The ring method of measuring surface tension for liquids of high density and low surface tension", *J. Phys. Chem.* **56** (1952), p. 284.

Apparatus using a plate :

[3] DOGNON, A., and ABRIBAT, M., *Compt. Rend. Acad. Sc.* Paris **208** (1939), p. 1881.

[4] SCHWUGER, M. J., and ROSTEK, H. M., *Chemie-Ing. Techn.* **43** (1971), p. 1075.