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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION
R 304

SURFACE ACTIVE AGENTS

DETERMINATION OF SURFACE TENSION AND INTERFACIAL TENSION

1st EDITION
May 1963

For each individual country the only valid standard is the national standard of that country.

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BRIEF HISTORY

The ISO Recommendation R 304, *Surface Active Agents—Determination of Surface Tension and Interfacial Tension*, was drawn up by Technical Committee ISO/TC 91, *Surface Active Agents*, the Secretariat of which is held by the Association Française de Normalisation (AFNOR).

Work on this question by the Technical Committee began in 1960 and led in the same year to the adoption of a Draft ISO Recommendation.

In March 1961, this Draft ISO Recommendation (No. 438) was circulated to all the ISO Member Bodies for enquiry. It was approved by the following Member Bodies:

Australia
Austria
Belgium
Canada
Chile
Colombia
Czechoslovakia
France
Germany
Hungary
Iran
Ireland
Israel
Italy
Mexico
Poland
Portugal
Romania
Spain
United Kingdom
U.S.S.R.
Yugoslavia

No Member Body opposed the approval of the Draft.

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in May 1963, to accept it as an ISO RECOMMENDATION.

ISO Recommendation R 304 May 1963

SURFACE ACTIVE AGENTS

DETERMINATION OF SURFACE TENSION AND INTERFACIAL TENSION

FOREWORD

Surface and interfacial tensions are fundamental properties of solutions of surface active agents.

The measurement of these characteristics, however, does not allow any suppositions as to their detergency, wetting, foaming activities, etc.

Indeed, no connection can be established between the performance properties of the surface active agents and the surface or interfacial tensions of their solutions.

1. SCOPE

The purpose of this ISO Recommendation is to set out a method for the determination of:

(1) the surface tension of aqueous or organic solutions of surface active agents and mixtures containing one or more surface active agents;

(2) the interfacial tension of systems of two immiscible phases containing surface active agents.

These determinations also apply to the measurement of surface tensions of pure liquids or solutions, and to that of the interfacial tension of binary liquid systems other than those mentioned above.

2. PRINCIPLE

The method consists in measuring the force which should be exerted vertically on a plate or a stirrup in contact with the surface of the solution being studied in order to draw up the film that is formed.

3. APPARATUS

3.1 Constitution of apparatus

The apparatus consists of the following:

3.1.1 *Tensiometer*

The tensiometer, which should be capable of being fitted with plates or stirrups, consists essentially of three parts:

(*a*) horizontal platform which can be moved vertically downwards or upwards by means of a micrometer screw;

(*b*) a balance to give a continuous measure of the force applied either to the plate or to the stirrup, and at least capable of a precision of 0.05 dyn/cm;*

(*c*) a device for indicating the force expressed in dynes per centimetre of the perimeter of the plate or the stirrup, transmitted to the balance.

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* Dyne per centimetre (dyn/cm is the unit of the CGS system. The unit of the International System (SI) is the newton per metre (N/m): 1 N/m = 10^3 dyn/cm.

3.1.2 *Plate or stirrup*

PLATE consists of sheets of platinum of about 30 mm × 20 mm × 0.1 mm; it is roughened by sand blasting or emery papering in the direction of the longest dimension; it is fixed to a suspending rod, at a short distance from one of the shorter sides, and in the axis of symmetry.

STIRRUP (see figure) is made of platinum wire of diameter not exceeding 0.5 mm; the length of the horizontal arm is 20 to 30 mm and the length of the two branches is 10 mm; the lower ends of these branches terminate in two small platinum balls which act as counterweights.

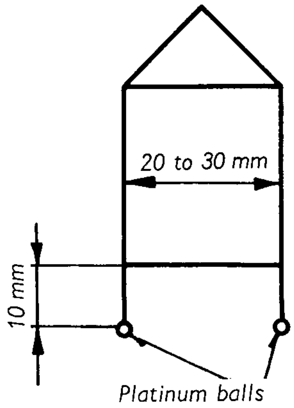

FIGURE. — **Stirrup**

3.1.3 *Sample vessel*

The sample vessel for the solution on which the measurement is to be made is a small glass vessel containing a fairly large quantity of liquid (watch glasses should not be used). The ideal is a small tank with the form of a parallelepiped having sides of at least 8 cm. Only the form of a parallelepiped enables the liquid surface to be cleaned before measuring the surface tensions of pure liquids. In the case of solutions of surface active agents, and especially in the case of dilute solutions, the surface should not be cleaned, and cylindrical containers can be used provided that the diameter is at least 8 cm.

This vessel can be raised or lowered by the screw control, in order to alter its position in a vertical plane.

3.2 Preparation of apparatus

There are two possible cases represented:

3.2.1 If the solution or one of the phases of the binary system wets the plate perfectly, the plate should be preferred to the stirrup.

3.2.2 If the solution does not wet the plate perfectly or, in case of a measurement of interfacial tension, if one of the two phases does not wet the plate preferentially, a stirrup should be used.

Wash the glassware carefully with hot sulphochromic mixture, rinse in double-distilled water until neutral and then dry. (The double-distilled water should be prepared in an apparatus fitted throughout with ground-glass joints and kept in a container with ground-glass stopper, the ground-glass joints being not greased; rubber should not be used in any circumstances).

Clean the platinum plate or stirrup with hot sulphuric acid (mass density at 20 °C $\rho =$ 1.83 g/ml), and then rinse with double-distilled water until neutral.

3.3 Calibration of apparatus

3.3.1 *Principle*

The calibration of the apparatus consists principally in adjusting it so that the readings, such as the displacement of the spot of light from an optical device, are expressed directly in dynes per centimetre.

(*a*) WHEN USING A PLATE. When making the measurement, the roughened platinum plate is surrounded by an adsorption layer, and everything happens as if the liquid were making tangential contact with a theoretical plate consisting of the plate surrounded by its wetting sheath. It is thus easy to dry the plate properly because, thanks to inevitable lack of symmetry, when the plate is removed from the liquid, one end of its base comes away and leaves one corner immersed. If withdrawal is continued very slowly, the plate comes out in required drainage conditions, without bringing away any droplets. In practice, in order to make the measurement, a certain depth of the plate is wetted, it is drained as indicated above, and only then, with the plate completely withdrawn, is the apparatus set to zero; correction for wetting is thus included in the calibration and is no longer involved in the measurements.

(*b*) WHEN USING A STIRRUP. In order to avoid the correction of buoyancy resulting from the volume of the immersed wire and the two platinum balls, the apparatus should be calibrated with the stirrup immersed in a liquid of the same density as the solution being investigated.

3.3.2 *Level of the apparatus*

The apparatus is set horizontally by means of a liquid level placed on the support for the sample vessel, adjustment being made by means of screws fixed in the seat of the apparatus.

3.3.3 *Calibration*

Actual calibration can be done by two methods:

(1) **Method by means of riders of known mass,** placed on the plate or stirrup. The operation is lengthy, but very accurate.

If M is the mass of the riders, in grammes,

b is the breadth of the plate or stirrup, in centimetres,

g is the acceleration due to gravity, in centimetres per second square,

the expected instrument reading, indicating the superficial tension in dynes per centimetre, should be:

$$\gamma = \frac{Mg}{2b}$$

(2) **Method by means of pure substances** whose surface tensions are accurately known. This method is quicker.

Adjust the tensiometer, if necessary, until the observed reading agrees with the expected value.

4. PREPARATION OF SOLUTIONS

4.1 The solutions to be measured should be prepared with all necessary care. The water used for preparing them should be double-distilled water. Cork stoppers and, more particularly, rubber stoppers, should on no account be used, either in the construction of the distillation apparatus or for stoppering containers in which the water is kept.

4.2 Solutions should be kept at 20 ± 0.5 °C. However, as measurements made in the region at or below the Krafft point have no value, the measurements should necessarily be made at a temperature higher than this particular point. Any measurements made in the region of any other point of critical solubility are seriously marred by errors (above the cloud point of ethylene oxide condensates, for example).

4.3 As the surface and interfacial tensions of solutions vary with time, it is difficult to recommend an age for the solution, because the influence of the chemical nature of the surface active agent, its concentration, its liability to adsorption and its speed of adsorption all play a particular part in these variations. It is therefore desirable to make several measurements at different ages so as to construct the surface-tension curve as a function of time and to determine the position of the level portion, which gives the age from which the solution has reached its equilibrium state.

4.4 The surface of these solutions is extremely sensitive to contamination by atmospheric dust or by vapours from solvent handled in the vicinity; therefore no volatile products should be handled in the room where the measurements are made, and the complete apparatus should be protected by a bell of the kind used for balances. This precaution also makes it possible to keep the apparatus at constant temperature.

5. PROCEDURE

5.1 Measurement of surface tension

There are two possible cases:

5.1.1 *If the liquid wets the plate perfectly*

When the plate has been wetted and the apparatus calibrated with the wetting sheath, check that the platform is horizontal.

Place the sample vessel containing the solution on its support and bring it under the plate. Raise it until the plate is suddenly caught by the liquid. Then gently lower the platform until the base of the plate is at the height of the free surface of the liquid (this process eliminates any error due to buoyancy).

As immersing the plate in the solution disturbs the arrangement of the surface layer, wait a few minutes and then measure the force exerted on the balance per centimetre of the plate perimeter.

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 stand, the plate at first being immersed in the solution; in this way, a curve is obtained which has a slightly sloping straight portion, the slope corresponding to the buoyancy. It is thus possible to make a precise measurement of the surface tension in equilibrium.