INTERNATIONAL STANDARD

ISO 1065

Second edition
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Non-ionic surface-active agents obtained from ethylene oxide and mixed non-ionic surface-active agents — Determination of cloud point

Agents de surface non ioniques obtenus à partir de l'oxyde d'éthylène et mixtes — Détermination de la température de trouble (point de trouble)

Reference number
ISO 1065:1991(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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 1065 was prepared by Technical Committee ISO/TC 91, *Surface active agents*.

This second edition cancels and replaces the first edition (ISO 1065:1975), to which two new methods (D and E) have been added in order to extend the scope to cover mixed non-ionic surface-active agents.

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Introduction

Aqueous solutions of non-ionic surface-active agents derived from ethylene oxide become heterogeneous when their temperature is raised, because of the formation of two liquid phases. The temperature above which this phenomenon occurs is referred to as the cloud point.

This phenomenon occurs at a temperature which increases as the number of molecules of ethylene oxide combined in the product increases. The system becomes homogeneous when the temperature falls. The temperature at which the system becomes homogeneous is called the "temperature of clarification" as defined in ISO 862:1984, *Surface active agents — Vocabulary* (definition No.10).

The temperature of clarification is often determined as the "cloud point".

The knowledge of the cloud point is of great importance in all applications, as the surface-active properties vary very rapidly around this temperature.

The determination of the cloud point of a non-ionic product is a rapid and precise method of control. In manufacture, it is the quickest method of assessing the quantity of ethylene oxide bonded to a given base molecule. However, it must be remembered that the curve relating cloud point and the extent of ethoxylation tends towards an asymptote; as a consequence, this method of checking is less precise for products with a long ethoxyl chain.

The cloud temperature is a lower critical temperature of separation; above this critical temperature, the solution separates into two phases, and the appearance of these two phases when the temperature is raised leads to the clouding of the solution. This property is not specific to ethoxylated derivatives and it is possible to determine cloud temperatures for other types of derivative.

Methods A, B and C specified in this International Standard deal primarily with the determination of the cloud point of non-ionic surface-active agents derived from ethylene oxide by condensation with lipophilic base molecules such as fatty alcohols, fatty amines, fatty acids, alkylphenols and esters of fatty acids.

Other non-ionic surface-active agents, e.g. ethylene oxide/propylene oxide block copolymers, are known to have properties which make it difficult to determine their cloud points. Such properties include the appearance of a progressive clouding over a temperature range of several degrees, and the existence of two or three very distinct cloud points.

Two further methods (D and E) are therefore specified for the determination of the cloud point of such materials, for which methods A, B and C are unsuitable.

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Non-ionic surface-active agents obtained from ethylene oxide and mixed non-ionic surface-active agents — Determination of cloud point

1 Scope

This International Standard specifies five methods for the measurement of the cloud point of non-ionic surface-active agents.

Methods A, B and C are applicable to non-ionic surface-active agents derived from ethylene oxide by condensation with a lipophilic compound which has no oxypropylene groups. The selection of the method (A, B or C) depends on the temperature at which the aqueous solution of the product being tested becomes cloudy.

Methods D and E are intended for use, after agreement between the parties concerned, with products for which methods A, B and C prove unsatisfactory. Such products include mixed non-ionic surface-active agents such as those derived from ethylene oxide/propylene oxide block copolymers.

The selection of the method (D or E) depends on the temperature at which the acid aqueous solution of the product being tested becomes cloudy. Method E is not applicable, however, to products derived from fatty acids or fatty-acid esters.

NOTE 1 The cloud point of products derived from fatty acids or fatty-acid esters can only be determined if the repeatability of the determination is verified.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 607:1980, *Surface active agents and detergents — Methods of sample division.*

ISO 1773:1976, *Laboratory glassware — Boiling flasks (narrow-necked).*

ISO 2174:1990, *Surface active agents — Preparation of water with known calcium hardness.*

3 Selection of method

NOTE 2 It may be impossible to measure the cloud temperature of certain very pure derivatives of ethylene oxide if dissolved in distilled water of very low conductivity. In such cases, the solution does not become heterogeneous at a definite temperature; instead, only a slight loss of clarity is observed.

However, replacement of the distilled water by an aqueous solution of sodium chloride (234 mg/l) enables the cloud temperature to be measured.

3.1 Method A

If the aqueous solution of the non-ionic surface-active agent becomes cloudy at a temperature between 10 °C and 90 °C, carry out the measurement in distilled water (see 8.1).

3.2 Method B

If the aqueous solution of the non-ionic surface-active agent becomes cloudy at a temperature lower than 10 °C, or if the product is not sufficiently soluble in water, carry out the measurement in an aqueous 25 % (*m*/*m*) solution of *n*-butyldiglycol (see 8.2). However, this method is not applicable to certain products with low ethylene oxide contents and which are insoluble in the aqueous 25 % (*m*/*m*) solution of *n*-butyldiglycol.

3.3 Method C

If the aqueous solution of the non-ionic surface-active agent becomes cloudy at a temperature higher than 90 °C, carry out the measurement in a sealed ampoule (see 8.3), which makes it possible, by operating under pressure, to reach temperatures higher than the boiling point of the solution at atmospheric pressure.

NOTE 3 It is also possible, if agreed between the parties concerned, to determine the cloud point in salt solution, but this technique is not so sensitive and there is no simple correlation between the results obtained in salt solution and those obtained with the sealed-ampoule method.

3.4 Method D

If the acid aqueous solution of the non-ionic surface-active agent tested becomes cloudy at a temperature between 10 °C and 90 °C, carry out the measurement in standard volumetric hydrochloric acid solution, c(HCl) = 1,0 mol/l (see 8.4).

3.5 Method E

If the acid aqueous solution of the non-ionic surface-active agent tested becomes cloudy at a temperature higher than 90 °C, carry out the measurement in water of calcium hardness 40 mg Ca^{2+} ions per litre and containing 5 % (m/m) of butan-1-ol (see 8.5).

4 Principle

The product under test is heated in solution at the required concentration until the liquid is completely opaque. It is then cooled, with constant stirring. The temperature at which the opacity disappears is observed.

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

5.1 *n*-Butyldiglycol [2-(2-butoxyethoxy)-ethanol], 25 % (m/m) solution, for method B.

The *n*-butyldiglycol [$C_4H_9O(CH_2)_2O(CH_2)_2OH$] shall have the following characteristics:

— density, ρ_{20} = 0,954 g/ml ± 0,002 g/ml;

— refractive index, n_D^{20} = 1,432 ± 0,00 1;

— water content less than 0,1 % (m/m).

NOTE 4 Even with the given specification, variable amounts of impurities in the *n*-butyldiglycol will influence the cloud point to a certain extent.

5.2 Hydrochloric acid, standard volumetric solution, c(HCl) = 1,0 mol/l, for method D.

5.3 Butan-1-ol, 5 % (m/m) solution in water of calcium hardness 40 mg Ca^{2+} ions per litre, prepared in accordance with ISO 2174, for method E.

6 Apparatus

Ordinary laboratory apparatus and:

6.1 Conical flask, capacity 250 ml, complying with ISO 1773.

6.2 Thermometer, graduated in 0,1 °C, with a range appropriate to the temperature to be measured.

6.3 Graduated cylinder, capacity 100 ml.

6.4 Beaker, capacity 1 000 ml, containing a transparent heat-transfer fluid (ethylene glycol, for example).

6.5 Test tube, capacity 20 ml.

6.6 Ampoule, made of safety glass covered with wire gauze, outside diameter 14 mm, inside diameter 12 mm, height 120 mm.

6.7 Analytical balance.

6.8 Conventional heating appliance.

6.9 Magnetic stirrer with heater.

7 Sampling

The laboratory sample of surface-active agent shall be prepared and stored in accordance with the instructions given in ISO 607.

8 Procedure

IMPORTANT — The cloud point is related to the number of ethylene oxide units bonded to the base molecule, but it also depends on the concentration of the solution. It is therefore essential to operate the test at a clearly defined concentration.

8.1 Method A (Use when cloudiness appears at a temperature between 10 °C and 90 °C)

8.1.1 Test portion

Weigh out, to the nearest 0,01 g, 0,5 g of the laboratory sample (see clause 7).

8.1.2 Determination

Place the test portion in the conical flask (6.1). Add 100 ml of distilled water, measured with the graduated cylinder (6.3). Stir until the test portion has dissolved or dispersed.

Place 15 ml of this solution in the test tube (6.5). Put the thermometer (6.2) in the tube, place the tube in the beaker (6.4) and heat with the heating appliance (6.8), stirring the solution with the thermometer until it is completely opaque. (The opacity appears in the form of bands which thicken and then coalesce. At no time shall the temperature of the solution exceed by more than 10 °C the temperature at which the opacity appears.) Allow to cool slowly while stirring. Read the temperature at which the opaque bands disappear.

NOTE 5 The liquid may stay clear or opalescent, depending on the nature of the non-ionic products and the purity of the raw materials used for their preparation (see clause 3, note 2, on purity of materials).

Carry out several temperature measurements on different test portions until at least two results differing by not more than 0,5 °C are obtained.

8.2 Method B (Use when cloudiness appears at a temperature below 10 °C, or when the product is insoluble in water)

8.2.1 Test portion

Weigh out, to the nearest 0,01 g, 5 g of the laboratory sample (see clause 7).

8.2.2 Determination

Place the test portion in the conical flask (6.1). Add 45 g of the *n*-butyldiglycol solution (5.1). Stir until the test portion is dissolved.

Proceed as in method A (see 8.1.2, beginning at the second paragraph).

8.3 Method C (Use when cloudiness appears at a temperature higher than 90 °C)

8.3.1 Test portion

Weigh out, to the nearest 0,01 g, 0,5 g of the laboratory sample (see clause 7).

8.3.2 Determination

Place the test portion in the conical flask (6.1). Add 100 ml of distilled water, measured with the graduated cylinder (6.3). Stir until the test portion has completely dissolved.

Transfer a quantity of this solution to the glass ampoule (6.6), to a depth of approximately 40 mm. Seal the ampoule by means of a flame and cover it with coarse wire gauze. Put it in the beaker (6.4) containing the heat-transfer fluid. The upper end of the ampoule shall project slightly from the beaker.

As a precaution against flying glass, place a protective screen of safety glass or transparent plastic in front of the apparatus since the ampoule may burst if it has not been well sealed (see figure 1).

Place the thermometer (6.2) in the heating fluid next to the sealed ampoule. Set the heater and the magnetic stirrer (6.9) in operation; stop the heating when the liquid contained in the ampoule becomes cloudy. Allow to cool while stirring the heat-transfer fluid and note the temperature at which the cloudiness disappears, as indicated for method A (see 8.1.2).

Carry out several temperature measurements on different test portions until at least two results differing by not more than 0,5 °C are obtained.

NOTE 6 If agreed between the parties concerned, the cloud point can be determined in salt solution rather than in a sealed ampoule.

The technique is analogous to that of method A (see 8.1), the surface-active agent being dissolved in 100 ml of an aqueous 50 g/l solution of sodium chloride instead of in 100 ml of distilled water.

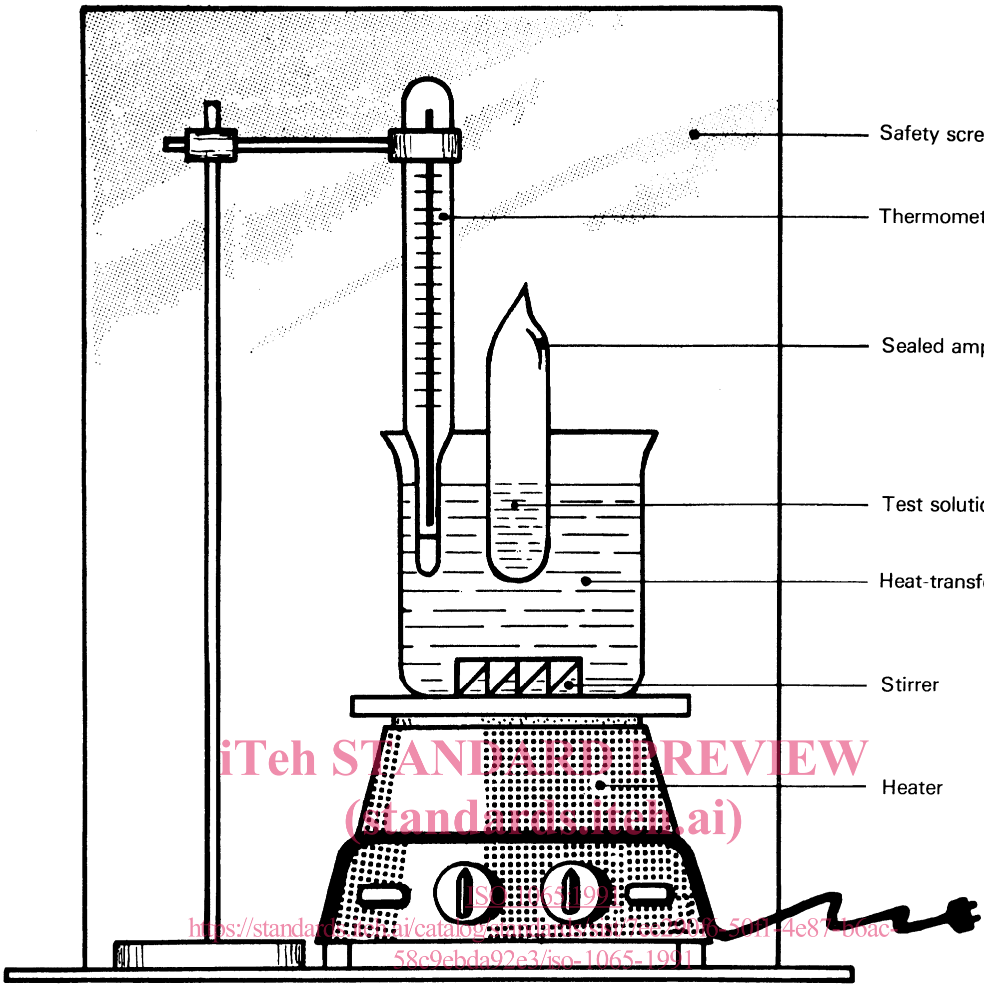

Figure 1 — Apparatus for method C

8.4 Method D (Use when cloudiness appears at a temperature between 10 °C and 90 °C)

8.4.1 Test portion

Weigh out, to the nearest 0,01 g, 1 g of the laboratory sample (see clause 7).

8.4.2 Determination

Place the test portion in the conical flask (6.1). Add 50 ml of the hydrochloric acid solution (5.2), measured with the graduated cylinder (6.3). Stir until the test portion has dissolved or dispersed, then add hydrochloric acid solution (5.2) to give a final volume of 100 ml.

Place 15 ml of this solution in the test tube (6.5). Put the thermometer (6.2) in the tube, place the tube in the beaker (6.4) and heat with the heating appliance (6.8), stirring the solution with the thermometer until it is completely opaque. (The opacity appears in the form of bands which thicken and then coalesce. At no time shall the temperature of the solution exceed by more than 10 °C the temperature at which the opacity appears.) Allow to cool slowly while stirring. Read the temperature at which the opaque bands disappear.

NOTE 7 The liquid may stay clear or opalescent, depending on the nature of the non-ionic products and the purity of the raw materials used for their preparation (see clause 3, note 2).

Carry out several temperature measurements on different test portions until at least two results differing by not more than 0,5 °C are obtained.

8.5 Method E (Use when cloudiness appears in method D at a temperature higher than 90 °C)

8.5.1 Test portion

Weigh out, to the nearest 0,01 g, 1 g of the laboratory sample (see clause 7).

8.5.2 Determination

Place the test portion in the conical flask (6.1). Add 100 ml of the calcium/butan-1-ol solution (5.3), measured with the graduated cylinder (6.3). Stir until the test portion has completely dissolved or dispersed.

Proceed as in method D (see 8.4.2, beginning at the second paragraph).

9 Expression of results

Take as the result the arithmetic mean of at least two results which do not differ by more than 0,5 °C.

Indicate, to the first decimal place, the mean temperature at which the solution of the non-ionic surface-active agent became either clear or opalescent again and the medium in which the measurement was made.

EXAMPLES

Cloud point at 5 g/l in distilled water: ...

Cloud point at 100 g/kg in the presence of *n*-butyldiglycol: ...

Cloud point at 5 g/l in sealed ampoule: ...

Cloud point at 10 g/l in 1,0 mol/l hydrochloric acid solution: ...

Cloud point at 10 g/l, in water of calcium hardness 40 mg of Ca^{2+} ions per litre in the presence of butan-1-ol: ...

10 Precision

10.1 Repeatability

The difference between the results of two determinations carried out simultaneously, or in rapid succession, on the same sample and by the same operator, shall not exceed 0,5 °C.

10.2 Reproducibility

The difference between results obtained by two different laboratories on the same sample shall not exceed 1 °C.

11 Test report

The test report shall include the following particulars:

a) all details required for complete identification of the sample;

b) a reference to this International Standard and the method used, e.g. "ISO 1065, method A";

c) the medium in which the measurement was carried out;

d) the results and the units in which they have been expressed;

e) any unusual features noted during the determination;

f) any operation not included in this International Standard, or regarded as optional.