International Standard 4311

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

Anionic and non-ionic surface active agents — Determination of the critical micellization concentration — Method by measuring surface tension with a plate, stirrup or ring

Agents de surface anioniques et non ioniques — Détermination de la concentration critique pour la formation de micelles — Méthode par mesurage de la tension superficielle à la lame, à l'étrier ou à l'anneau

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up 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.

International Standard ISO 4311 was developed by Technical Committee ISO/TC 91, *Surface active agents*, and was circulated to the member bodies in October 1975.

It has been approved by the member bodies of the following countries :

Austria
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The member body of the following country expressed disapproval of the document on technical grounds :

United Kingdom

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Anionic and non-ionic surface active agents — Determination of the critical micellization concentration — Method by measuring surface tension with a plate, stirrup or ring

0 INTRODUCTION

Curves showing the variation in the physical properties of aqueous solutions of surface active agents are specifical to individual products; in a certain region of concentration, usually very narrow, these curves show a sharp change of slope. This phenomenon has been attributed to the formation of orientated aggregates of molecules, and the concentration at which this change occurs has been termed the "critical micellization concentration" (c.m.c.)[1].

For a given length of hydrophobic chain, the critical micellization concentration is usually higher in the case of ionic surface active agents than in the case of non-ionic surface active agents. Apart from the structure of the surface active agent, the temperature, and the presence, the nature and the quantity of the metallic salts, organic compounds cause the critical micellization concentration to vary, and hence the operational conditions likely to influence the result must be clearly stated, i.e. the purity of the product and, as far as possible, its impurities, which may greatly alter the value of surface tension measurements (it is very useful to know the organic or mineral nature of these impurities and, if possible, their concentrations). On account of these interactions a definite value cannot be obtained for the critical micellization concentration, but generally its range can be defined by the curve showing the variations in the surface tension, which in practice is deemed satisfactory.

1 SCOPE

This International Standard specifies a method for the determination of the critical micellization concentration of anionic and non-ionic surface active agents in solution in distilled water or other aqueous systems, by measurement of the surface tension with a plate, stirrup or ring.

2 FIELD OF APPLICATION

This method is applicable to purified or unpurified non-ionic surface active agents which are soluble in water and have a cloud temperature at least 5 °C above the testing temperature, and to purified or unpurified anionic surface active agents which are soluble in water and have a Krafft temperature at least 5 °C below the testing temperature.

This method may be used for measurements at temperatures above 35 °C, but very strict precautions shall then be taken to prevent water and other possible solvents from evaporating.

3 REFERENCES

ISO 304, *Surface active agents — Determination of surface tension.*

ISO 607, *Surface active agents and detergents — Methods of sample division.*[2]

ISO/R 862, *Surface active agents — Glossary.*

ISO 2456, *Surface active agents — Water used as a solvent for tests.*[3]

4 DEFINITIONS

4.1 micelle : See ISO/R 862.

4.2 critical micellization concentration (c.m.c.) : See ISO/R 862.

4.3 Krafft temperature : See ISO/R 862.

4.4 surface tension : See ISO/R 862.

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

5 PRINCIPLE

Determination of the surface tension of a series of solutions whose concentrations bracket the critical micellization concentration. Plotting of the graph of surface tension as a function of the logarithm of the concentration : the c.m.c. corresponds to a singular point on this curve.

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[1] Abbreviation for the critical micellization concentration.

[2] At present at the stage of draft. (Revision of ISO/R 607.)

[3] At present at the stage of draft.

* 1 mN/m = 1 dyn/cm

6 REAGENT

Distilled water complying with the specification given in ISO 2456 for water used in special physical tests.

7 APPARATUS

Ordinary laboratory apparatus and :

7.1 Low-form beakers, of capacity 100 ml, complying with the requirements of ISO 3819.

7.2 Watch-glasses.

7.3 Tensiometer, as specified in ISO 304, device with plate, stirrup or ring.

7.4 Water bath, enabling the temperature of the solution to be controlled to within ± 1 °C from 20 to 80 °C.

NOTE – Prior to the tests, allow all the glassware to soak for approximately 12 h in chromic/sulphuric acid mixture prepared by gently adding sulphuric acid, ρ_{20} 1,84 g/ml, to an equal volume of a saturated solution of potassium dichromate. Then rinse with the distilled water specified in clause 6 [the surface tension of the final rinsing water should be equal to that of the initial water; this value is to be measured with the tensiometer (7.3)].

8 SAMPLING

The laboratory sample of anionic or non-ionic surface active agent shall be prepared and stored according to the instructions given in ISO 607.

9 PROCEDURE

9.1 Test solutions

Prepare, in the previously weighed beakers (7.1), a series of ten solutions with different concentrations so that these bracket the expected critical concentration. These solutions, each weighing exactly 50 g, are prepared either by dilution of a 200 mg/l stock solution, for concentrations lower than 200 mg/l, or by dissolution of a portion of the laboratory sample, for higher concentrations. In the latter case the appropriate amount of laboratory sample is weighed to the nearest 0,1 mg.

9.2 Measurements

9.2.1 *Approximate determination of the c.m.c. region*

Set the temperature of the water bath (7.4) at the measuring temperature. If the Krafft temperature is sufficiently low (lower than or equal to 15 °C), operate at 20 ± 1 °C; if this is not the case, select a temperature at least 5 °C above the Krafft temperature for anionic surface active agents. For non-ionic surface active agents, operate at 20 ± 1 °C.

NOTE – The tests may be carried out at a temperature other than 20 °C, provided that the temperature used is stated in the test report.

Cover each of the beakers, containing the test solutions (9.1), with one of the watch-glasses (7.2) and place them in the temperature-controlled water bath (7.4). Measure the surface tension of each solution in accordance with the procedure specified in ISO 304. Using the results, plot a primary curve (9.3) of surface tension as a function of concentration, which will include the region in which the c.m.c. is located.

9.2.2 *Determination of c.m.c.*

According to the result obtained, prepare, either by weighing or by dilution of the stock solution, six new solutions with closely related concentrations bracketing the c.m.c. Cover the beakers containing these solutions with the watch-glasses (7.2) and place in the temperature-controlled water bath (7.4). Agitate the solutions without using a stirrer; in order to do this, agitate the beaker itself by hand, using a rotating motion. (Take care not to cause the formation of foam when testing strongly foaming products.)

Note the time, introduce the measuring unit of the tensiometer (7.3) into the solution and do not commence taking measurements in accordance with the procedure specified in ISO 304 until 3 h after the dissolution or dilution, whichever is the case, and until the desired temperature is attained. [If necessary, this time may be increased until the surface tension values become stable (see paragraph 3) or the measurement may be commenced as soon as stability is reached.] In the case of concentrations higher than the c.m.c., the time for attaining equilibrium may be reduced to 15 min.

Carry out at intervals of 15 min three successive measurements at each concentration without rinsing the plate, the stirrup or the ring between each measurement; the pause before the measurement is adequate if the three successive measurements do not show any progressive systematic variation. Each time the concentration is changed, rinse the plate, the stirrup or the ring in ethanol and then in distilled water. Do not dry by passing it through a flame.

9.3 Plotting the curve

Plot a curve taking the surface tension values as ordinates and the logarithms of the concentrations, expressed in grams per litre, as abscissae. Use the average of the three values determined for each concentration.

The six values determined as in 9.2.2 and the ten values determined as in 9.2.1 should appear on the curve, making a total of sixteen values.

The c.m.c. may be determined using this curve.

It is advisable to confirm the result by a measurement carried out on a solution of the concentration previously determined as being that of the c.m.c.

For plotting the graph, use the scale that is most appropriate to the values determined (for example 1 cm = 2,5 mN/m).

10 EXPRESSION OF RESULTS

10.1 Graph of surface tension

The c.m.c of anionic or non-ionic surface active agents, expressed in grams per litre1), may be determined by plotting the graph of surface tension as a function of the logarithm of concentration and comparing it with one of the three graphs below : A, B and C shown in the figure.

Graph A : The c.m.c. corresponds to the point on the curve at which a sharp charge of slope occurs.

Graph B : The range of c.m.c. corresponds to the point on the curve at which the surface tension is considerably lower than that at higher concentrations. The abscissa of this "minimum" specifies, by definition, the range of c.m.c.

Graph C : Experimentally no value for the range of c.m.c. can be defined. It is advisable to repeat the measurements, since a procedural error or a particular phenomenon may be involved which has made the results unusable; if, in spite of repetition of measurements, a curve without a minimum is still obtained, this unfortunately does not allow the range of c.m.c. to be determined.

10.2 Reproducibility

The difference between the results obtained on the same sample in two different laboratories should not differ by more than 10 % from the average value found.

11 TEST REPORT

The test report shall include the following particulars :

a) the characteristics of the products, giving the fullest possible details relating to appearance , purity, content of active material, relative molecular mass;

b) the temperature of dissolution or dilution, and the temperature of the surface tension measurement;

c) the method used : dilution of a stock solution or direct weighing;

d) the time between the preparation of the solution and the taking of the measurements;

e) the range of concentration used;

f) the nature and quality of the distilled water used;

g) the value of the surface tension for each concentration;

h) the calculation of surface tensions, determined where appropriate by a formula;

j) the curve giving the value of the surface tension as a function of the logarithm of the concentration;

k) the method used and results obtained, i.e. the numerical value of c.m.c. or the region of the c.m.c.;

m) the apparatus used;

n) any operation not included in this International Standard or in the International Standards to which reference is made, or regarded as optional, as well as any incidents which may have affected the results.

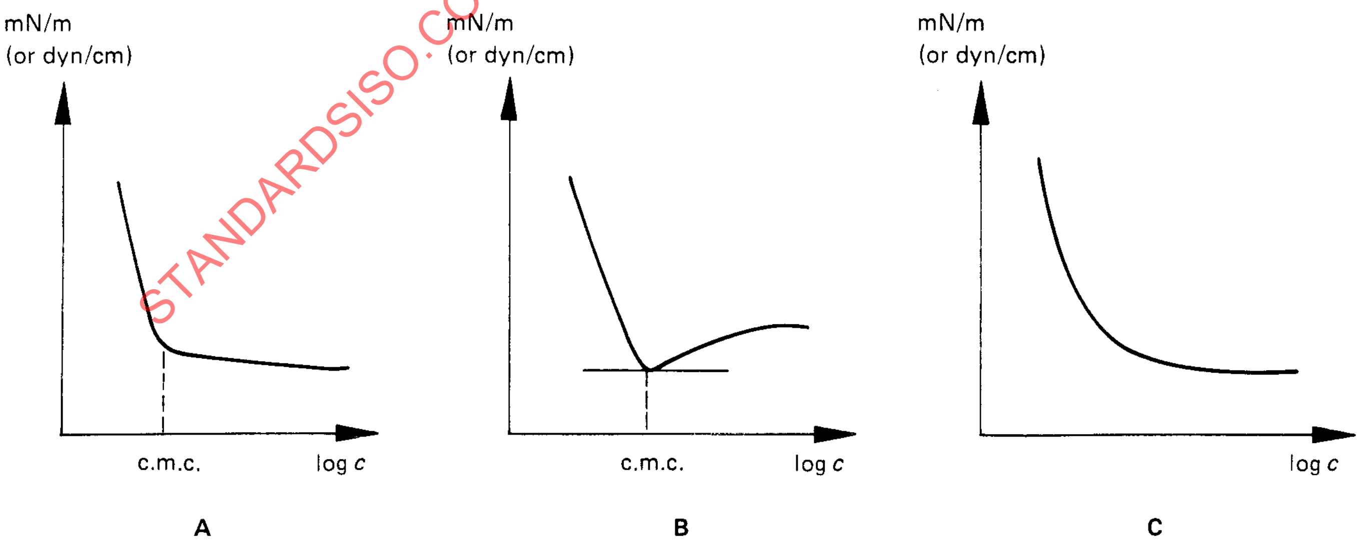

FIGURE — **Examples of graphs of surface tension**

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1) In the case of chemically pure products, the c.m.c. may be expressed in moles per litre.