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Surface active agents — Determination of Krafft point and solubility of ionic surface active agents

The European Standard EN 13955:2002 has the status of a
British Standard

ICS 71.100.40

National foreword

This British Standard is the official English language version of EN 13955:2002.

The UK participation in its preparation was entrusted to Technical Committee CII/34, Methods of test for surface active agents, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
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This British Standard, having been prepared under the direction of the Materials and Chemicals Sector Policy and Strategy Committee, was published under the authority of the Standards Policy and Strategy Committee on 20 December 2002

Summary of pages

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EN 13955

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English version

Surface active agents - Determination of Krafft point and solubility of ionic surface active agents

Agents de surface - Détermination du point de Krafft et de la solubilité des agents de surface ioniques

Grenzflächenaktive Stoffe - Bestimmung von Krafft-Punkt und Löslichkeit von ionischen grenzflächenaktiven Stoffen

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Ref. No. EN 13955:2002 E

Contents

Foreword

This document (EN 13955:2002) has been prepared by Technical Committee CEN/TC 276, "Surface active agents", the secretariat of which is held by AFNOR.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by June 2003, and conflicting national standards shall be withdrawn at the latest by June 2003.

Annex A is informative.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European Standard specifies a method for the determination of the solubility of ionic surface active agents in water as a function of concentration and temperature and for the determination of the Krafft point by graphical evaluation of the measurement results.

In the temperature range from 0 °C to 90 °C, the solubility is determined without any limitations if the viscosity of the solution does not exceed about 700 mPas.

At temperatures below 0 °C, determination is only possible if the solvent does not freeze.

The method is applicable both to pure surface active agents and to technical products optically clear and not unduly coloured solutions.

The solubility both of solid and liquid surface active agents and of aqueous solutions of surface active agents is determined by the method specified.

2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN ISO 3696, *Water for analytical laboratory use – Specification and test methods (ISO 3696:1987).*

ISO 383, *Laboratory glassware – Interchangeable conical ground joints*.

3 Terms and definitions

For the purposes of this European Standard, the following terms and definitions apply:

3.1
solubility
concentration at that temperature at which the cloudiness disappears again on heating a cloudy surface active agent solution

NOTE Solutions of ionic surface active agents become cloudy when cooled as soon as the saturation concentration associated with a particular temperature is exceeded. For a given surface active agent concentration, the temperature at which cloudiness appears decreases as the solubility of the surface active agent increases. This cloudiness disappears again if the solution is heated.

3.2
Krafft point
i) temperature at which the solubility of an ionic surface active agent in water changes suddenly or

ii) temperature at which the saturation concentration of the surface active agent reaches its critical micelle concentration (See annex A)

4 Principle

An aqueous solution of the chosen concentration of the sample is cooled while stirring continuously until it is completely cloudy. The solution is then heated slowly at a rate of 0,5 °C/min until it is clear again and the temperature at which this occurs is recorded. To determine the Krafft point, the measurements obtained at various concentrations are plotted in graph form. This yields a solubility curve having the two branches a and b, the Krafft point T_k being indicated by the point at which they intercept.

5 Apparatus

5.1 Test apparatus according to Figure 1, consisting of:

a) the test vessel with ground socket 45/40 in accordance with ISO 383;

b) the heating jacket which shall be connected to a circulating thermostat;

c) the stopper with ground joint 45/40 in accordance with ISO 383, for preventing that air is being stirred into the surface active agent solution;

d) the straight thermometer with a scale division of 0,1 °C, a length of at least 100 mm and a measurement range matched to the temperature to be measured.

NOTE 1 The thermometer can be attached with adhesive tape to the guide for the stirrer spindle (5.1 e)) or to a stand by means of a clamp.

NOTE 2 The thermometer and the basket stirrer (5.1 f)) do not completely seal the test apparatus so as to enable any air bubbles introduced into the test solution to escape. The stopper (5.1 c)), however, adequately separates the liquid above it from the liquid in the measurement chamber so that the liquid above the stopper remains stationary even during vigorous stirring and no air can penetrate into the measuring chamber;

e) the stirrer spindle of stainless steel;

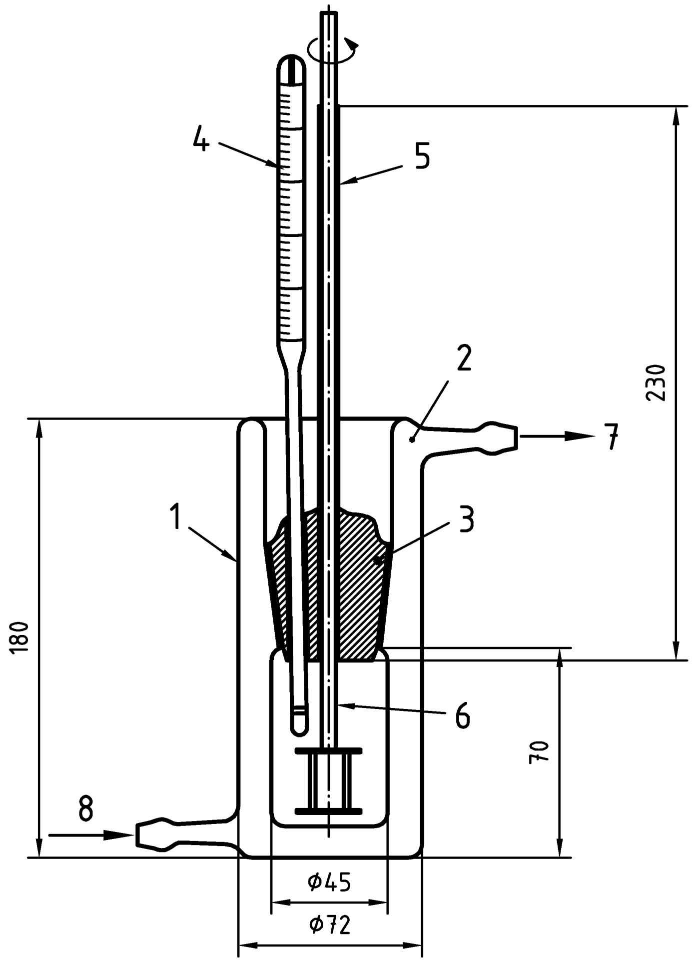
f) the basket stirrer of stainless steel.

5.2 **Analytical balance.**, accurate to 0,1 mg .

5.3 **One-mark pipettes** with nominal capacities of 20 ml and 100 ml.

5.4 **Conical flask**, wide neck, with a nominal capacity of 250 ml.

Dimensions in millimetres



Key

1 Test vessel
2 Heating jacket
3 Stopper
4 Thermometer
5 Stirrer shaft
6 Basket stirrer
7 To thermostat
8 From thermostat

Figure 1 — Test apparatus

6 Procedure

Solutions which are cloudy due to dispersed contaminants shall be filtered, but steps shall be taken to ensure that the temperature is above the solubility limit and no change occurs in the surface active agent concentrations.

Weigh the sample ,to the nearest 0,01 g, into the conical flask (5.4), use the one-mark pipettes (5.3) to add 120 ml of water grade 3, W_A, in accordance with EN ISO 3696 and stir in the closed flask, heating if necessary, until the sample is completely dissolved. Then transfer the solution to the test vessel (5.1 a)) and fit the stopper (5.1 c)), thermometer (5.1 d)) and basket stirrer (5.1 f)) and stirrer spindle (5.1 e)). Ensure that the temperature of the test vessel is about the same as that of the test solution. The quantity of solution shall be such that the stopper is covered by a layer of solution above 1 cm deep. Remove any air bubbles in the solution introduced when the surface active agent is dissolved or while transferring it by slowly stirring and heating the solution. Then lower the temperature using the thermostat until the solution is completely cloudy. When this point is reached, heat the solution at a rate of 0,5 °C/min while stirring until it is completely clear again.

When heating the cloudy surface active agent solution, always ensure that equilibrium is established, particularly if the rate at which the surface active agent dissolves is low.

NOTE 1 To check that the solution is saturated at the clear point, it can be kept for a few minutes while still cloudy at a temperature just below the clear point measured. If the solution becomes clear at this temperature, equilibrium had not yet been established.

If the equilibrium has not been established, repeat the determination of the clear point at a lower heating rate.

Note the temperature at which the test solution is clear again.

To plot the solubility curve, determine the measured points for at least six different surface active agent concentrations, ensuring that the curve branches a and b in the phase diagram shown in Figure A.1 each contain three measurements. If both curves a and b are not straight lines, which is generally the case, determine the number of measurements necessary for the solubility curve by carrying out preliminary experiments. Carry out two determinations which are independent of each other for every measured value.

NOTE 2 A plot of the solubility curve can be obtained much more quickly if the determinations are carried out simultaneously in several test vessels which contain different surface active agent concentrations. It is advisable to choose the concentrations so that the measured values are about 5 °C to 10 °C apart.

7 Expression of results

Record the concentrations chosen and the measured values obtained as shown in Table 1.

Table 1

Serial number of test	Sample		Mass of solvent	Sample concentration		Measured temperature
	Type and identification	Initial sample mass		Mass of substance in 100 g of solvent	Mass of substance in 100 g of solution	
		g	g	g/100 g	g/100 g	°C

The value of the Krafft point in degrees Celsius is given by the intercept of the two branches a and b of the phase diagram shown in Figure A.1 obtained by plotting the measured values with the temperature, T, in degrees Celsius as horizontal axis and the concentration in g/100 g of solvent or as mass fraction in percent as vertical axis.

8 Precision

The results of duplicate and multiple determinations shall not differ from one another by more than 0,5 °C. If this is not the case, the determinations shall be repeated.

9 Test report

The test report shall include the following information:

a) a reference to this European Standard;

b) the values and information contained in Table 1;

c) the Krafft point, in degrees Celsius;

d) any deviations from this European Standard;

e) the date of testing.

Annex A
(informative)

Graphical representation of the Krafft point

Expressed in the form of a graph (Figure A.1), the Krafft point is the temperature T_{k} at the triple point in the phase diagram of the surface active agent/water system in which the concentration and temperature are the variables. In the simplest case, this phase diagram is divided into three regions as follows.

¾ region I:

this is a region of low concentration in which all the surface active agent is dissolved in monomolecular form;

¾ region II:

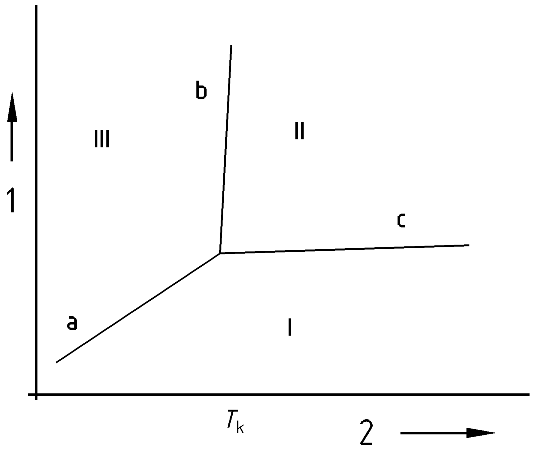
this is a region of high concentration which is above the Krafft point and in which the solution contains not only true dissolved molecules but also micelles;

¾ region III:

this is a region of fairly high concentration which is below the Krafft point and in which the surface active agent assumes either the form of crystals or of a gel.

The absolute values at which the concentration is described as "low", "high" and "fairly high" always depend in a given system on the nature of the surface active agent and no figures can therefore be specified here;

The branches a and b of the curve in Figure A.1 are the solubility curve of the surface active agent above and below the Krafft point, whereas the branch c shows the micelle formation concentration as a function of temperature.



Key

1 Concentration
2 Temperature

Figure A.1 — Typical phase diagram of a surface active agent/water system

The Krafft point of homologous surface active agents increases with the length of the hydrocarbon chain.

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