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Cationic surface active agents (hydrochlorides and hydrobromides) — Determination of critical micellization concentration — Method by measurement of counter ion activity

Agents de surface cationiques (chlorhydrates et bromhydrates) — Détermination de la concentration critique pour la formation de micelles — Méthode par mesurage de l'activité de l'ion contraire

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Foreword

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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 6840 was developed by Technical Committee ISO/TC 91, *Surface active agents*, and was circulated to the member bodies in November 1981.

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

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China
France
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No member body expressed disapproval of the document.

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INTERNATIONAL STANDARD **ISO 6840-1982 (E)**

Cationic surface active agents (hydrochlorides and hydrobromides) — Determination of critical micellization concentration — Method by measurement of counter ion activity

0 Introduction

Curves showing the variations in the physical properties of aqueous solutions of surface active agents are specific to these products; over a certain concentration range, which is usually very narrow, these curves show a singularity. This phenomenon has been attributed to the formation of oriented aggregates of molecules, and the concentration at which this change occurs has been termed the "critical micellization concentration" (c.m.c.).

For a given hydrophobic chain length, 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, nature and quantity of 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 measurements of potential (it is very useful to know the organic or mineral nature of these impurities and, if possible, their concentrations).

1 Scope and field of application

This International Standard specifies a method for the determination of the critical micellization concentration of cationic surface active agents (hydrochlorides and hydrobromides) in solution in distilled water or other aqueous systems, by measurement of the counter ion activity using a membrane electrode.

The method is applicable to purified or unpurified cationic surface active agents (hydrochlorides and/or hydrobromides), which are soluble in water and which have a Krafft temperature below 60 °C.

2 References

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

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

3 Definitions

3.1 micelle : See ISO/R 862.

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

3.3 Krafft temperature : See ISO/R 862.

4 Principle

Potentiometric determination of the chloride or bromide ion activity of a series of solutions of cationic surface active agents the concentrations of which cover the expected critical micellization concentration. Plotting the graph of potential as a function of the logarithm of the concentration; the c.m.c. corresponds to the singularity on this curve.

5 Reagents

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

5.1 Sodium chloride and sodium bromide, standard solutions of concentration approximately 10^{-4} to 10^{-2} mol/l.

6 Apparatus

Ordinary laboratory apparatus and :

6.1 Polycrystalline membrane electrode (sensitive to chlorides (Ag_2S + AgCl) or to bromides (Ag_2S + AgBr).

NOTE — It is very important to clean the electrodes according to the manufacturer's instructions.

6.2 Reference electrode : mercury-mercury(I) sulphate with a bridge containing saturated potassium sulphate solution, or a **calomel electrode** with a double bridge. In the latter case, the outer bridge shall be filled with saturated potassium nitrate solution.

NOTE — If the bridge contains sulphate ions, the most concentrated and most dilute surface active agent solutions should be tested with a

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portion of this bridge solution and no precipitation should be observed. If a precipitate does form, another type of bridge should be used.

6.3 Potentiometer, sensitivity 2 mV (potential of − 500 to + 500 mV) with a multi-range scale facility.

6.4 Thermostatically controlled water-bath, enabling the temperature of the solution to be controlled to within ± 0,5 °C.

6.5 Jacketed glass vessel, with an opening suitable for introducing the electrodes.

6.6 Magnetic stirrer.

7 Sampling

The laboratory sample of cationic surface active agent shall be prepared and stored according to the instructions given in ISO 607.

8 Procedure

8.1 Test portion and preparation of solutions

Weigh, to the nearest 0,1 mg, a quantity of the laboratory sample such that 500 ml of a solution about ten times more concentrated than the c.m.c. is obtained, dissolve in hot water and dilute to 500 ml in a one-mark volumetric flask. Let the concentration of this solution be *c*. Then, prepare by dilution 200 ml each of solutions of concentration $c/2$ — $c/4$ — $c/8$ — $c/16$ — $c/32$ — $c/64$ and $c/128$.

Keep these solutions in the thermostatically controlled bath (6.4) at the measurement temperature for at least 1 h, but not more than 3 h, before the measurements.

8.2 Measurement temperature

In order to reduce the effects of thermal and electrical hysteresis, take care that the temperatures of the electrodes, of the water used for washing, of the standard solutions and of the test solution are as close to each other as possible. The temperatures of the standard solutions and the test solution shall not differ by more than 0,5 °C. The measurement temperature should be 20 °C whenever possible.

8.3 Calibration and controls of the potentiometer

Calibrate the potentiometer (6.3) fitted with the membrane electrode (6.1) and the reference electrode (6.2) with standard reference halide solutions, the halide ion concentrations of which shall include the lowest and highest concentrations of halide ion which will be found in the surface active agent solutions on which measurements are performed.

Assemble the potentiometer (6.3) as required, and switch on. Allow the potentiometer to operate, according to the manufacturer's instructions, for a sufficient time to obtain good electric stabilization before beginning the measurements. Take care that the internal liquid of the reference electrode (6.2) is in equilibrium with atmospheric pressure, so that there is no inhibition to its movement across the bridge. Note the temperature of the standard reference solutions, make the appropriate adjustments to the temperature-correction circuit, and check the zero of the potentiometer. These settings shall not be modified during the measurements.

Introduce, in turn, each of the standard halide solutions (5.1) into the jacketed glass vessel (6.5), stir using the magnetic stirrer (6.6) and immerse the electrodes at the same time. Continue stirring until the reading has become constant, i.e. for at least 60 s. Stop the stirrer before taking the final reading. Plot a calibration graph with the values of potential, in millivolts, as ordinates and the logarithms of the halide ion concentrations as abscissae.

Verify that the halide ion concentration is a strictly linear function of the measured potential.

NOTE — The comparison with the calibration graph permits the calculation of the purity of the tested cationic surface active agent.

8.4 Determination of c.m.c.

Proceed in the same manner as 8.3 using the solutions of concentrations $c/2$ — ... and $c/128$ (see 8.1), starting with the most dilute and finishing with the most concentrated solution.

8.5 Plotting the graph

Plot a graph having the values of potential, in millivolts, as ordinates and the logarithms of the surface active agent concentrations, in grams per litre, as abscissae. The graph corresponds approximately to two straight lines.

NOTE — If the assumed c.m.c. was correct, four measured values of potential should be above and below the c.m.c.

If this is not the case, prepare a new series of solutions based on the new estimate of the c.m.c. and measure the halide ion concentration, i.e. the potential. It is recommended to use smaller concentration steps in this second series.

9 Expression of results

9.1 Graph of potential

From the graph (8.5) of potential as a function of the logarithm of concentration, determine the c.m.c. of the cationic surface active agents, expressed in grams per litre,1) as the abscissa corresponding to the intersection of the two straight lines.

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

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9.2 Reproducibility

The difference between the results obtained on the same sample in two different laboratories should not differ by more than 5 % from the mean value found.

10 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 and the relative molecular mass;

b) the temperature of dissolution or dilution and the temperature at which the potential was measured;

c) the range of concentrations used;

d) the value of potential, as a function of the halide ion concentration;

e) the types of electrodes used;

f) the graph showing the values of potential as a function of the logarithms of the concentrations;

g) the numerical value of the c.m.c.;

h) any operations not included in this International Standard, or regarded as optional, as well as any incidents which may have affected the results.

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