OECD GUIDELINE FOR THE TESTING OF CHEMICALS

Adopted by the Council on 27th July 1995

Surface Tension of Aqueous Solutions

INTRODUCTION

1. This updated version of the original guideline adopted in 1981 is based on the EC Method "Surface Tension"(1). Whereas the original guideline only contained the OECD harmonized ring method, this guideline makes room for the three methods set out in the ISO Standard 304-1985 (2).

INITIAL CONSIDERATIONS

2. The methods described are applicable to aqueous solutions of most substances regardless of their degree of purity. It is useful to have preliminary information on the water solubility, the structure, the hydrolysis properties and the critical concentration for micelle formation before performing the measurement. Substances with a water solubility lower than 1 mg/l need not be tested. The measurement of the surface tension by the ring tensiometer method is restricted to aqueous solutions with a dynamic viscosity of less than 200 mPa s. The fundamental principles are given in reference 3.

DEFINITIONS AND UNITS

3. The free surface enthalpy per unit of surface area is referred to as surface tension. The surface tension is expressed in SI units of N/m or sub-units 10^{-3}N/m. 1N/m equals 10^{3} dynes/cm and 10^{-3}N/m equals 1 dyne/cm in the obsolete cgs system.

REFERENCE SUBSTANCES

4. Reference substances do not need to be employed when investigating a substance. They serve primarily to check the performance of a method from time to time and allow to compare results from different methods. Reference substances which cover a wide range of surface tensions are given in reference 4.

PRINCIPLE OF THE METHODS

5. The methods are based on the measurement of the force which it is necessary to exert vertically on a stirrup or ring, in contact with the surface of the liquid, in order to separate it from the surface, or on a plate, with an edge in contact with the surface, in order to draw up the film that has formed.

DESCRIPTION OF THE METHODS

Plate method

6. This method is fully described in the ISO Standard 304-1985 (2).

Stirrup method

7. This method is fully described in the ISO Standard 304-1985 (2).

Ring method

8. This method is fully described in the ISO Standard 304-1985 (2).

OECD harmonized ring method

9. This method is based upon the standards ISO 304-1985 (2), DIN 53914 (5), ASTM-D-1590 (6) and ASTM-D-1331 (7).

Apparatus

10. Commercially available tensiometers are adequate. They consist of the following elements:

- mobile sample table,
- force measuring system,
- measuring body (ring),
- measurement vessel.

11. The mobile sample table is used as a support for the measurement vessel. Together with the force measuring system, it is mounted on a stand.

12. The force measuring system is located above the sample table. The error of the force measurement shall not exceed ± 10^{-6} N, corresponding to an error limit of ± 0.1 mg in a mass measurement. In most commercial tensiometers, the measuring scale is calibrated in mN/m and the surface tension can be read with an accuracy of 0.1 mN/m.

13. The ring is usually made of a platinum-iridium wire of about 0.4 mm thickness and a mean circumference of approximately 60 mm. The ring is suspended horizontally from a metal pin and a wire mounting bracket to establish the connection to the force measuring system (see figure). If the ring is not kept horizontal erroneous reading will result (8).

14. The measurement vessel holding the test solution is a temperature-controlled glass vessel. It shall be designed so that, during the measurement, the temperature of the test solution and the gas phase above its surface remains constant and that the sample cannot evaporate. Cylindrical glass vessels having an inside diameter of not less than 45 mm are acceptable.

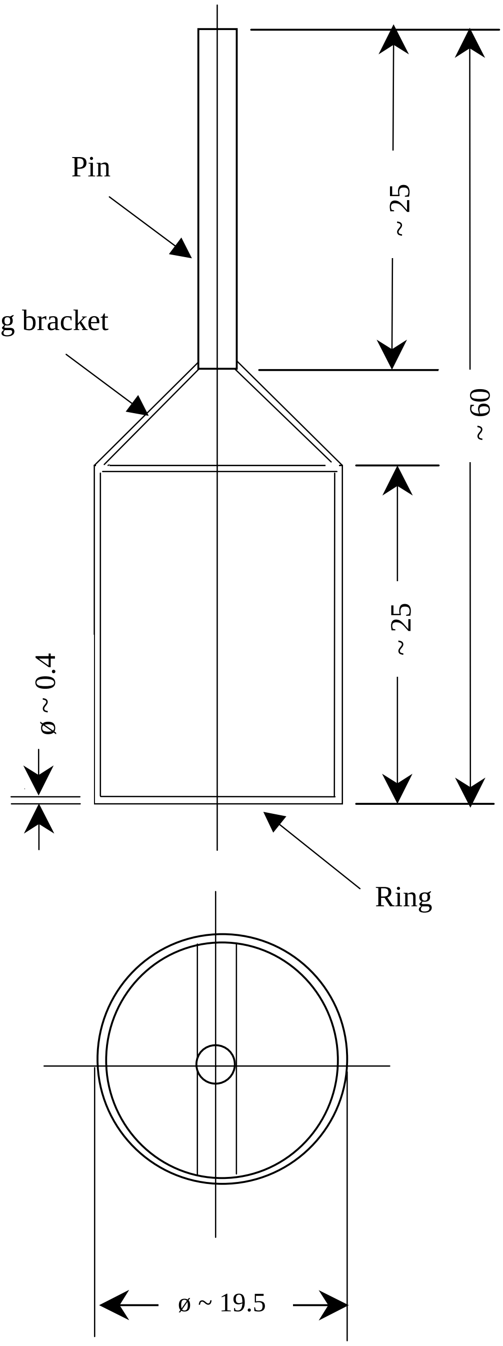
Preparation of the apparatus

Cleaning

15. The measurement vessel shall be cleaned carefully. If necessary, it shall be washed with hot chromo-sulfuric acid and subsequently with syrupy phosphoric acid (83 to 98% by weight of H_3PO_4), thoroughly rinsed in tap water and finally washed with double distilled water until a neutral reaction is obtained and subsequently dried or rinsed with the liquid to be measured.

Figure 1

Force measuring system (all dimensions expressed in millimeters)



16. The ring shall first be rinsed thoroughly with water to remove any substances which are soluble in water, briefly immersed in chromo-sulfuric acid, washed in double-distilled water until a neutral reaction is obtained and finally briefly heated over a methanol flame.

17. Contaminating substances which are not dissolved or destroyed by chromo-sulfuric or phosphoric acid, e.g. silicones, shall be removed by means of a suitable organic solvent.

Zero point adjustment

18. The apparatus shall be levelled, for instance by means of a spirit level on the tensiometer base, by adjusting the levelling screws. The ring is mounted on the apparatus and checked for parallelism to the liquid surface. For this purpose, the liquid surface can be used as a mirror. Prior to immersion of the ring in the liquid, the tensiometer indication is adjusted to zero. The calibration can be accomplished by using a mass or water.

Calibration using a mass

19. A rider of known mass, between 0.1 and 1.0 g, is placed on the ring. The calibration factor, Φ_a, by which all the instrument readings must be multiplied is given by

$$\Phi_a = \frac{\sigma_r}{\sigma_a}$$

where

$$\sigma_r = \frac{mg}{2b}\,(mN/m)$$

with m = mass of rider (g)
g = gravity acceleration (981 cm s^{-2} at sea level)
b = mean circumference of the ring (cm), and

σ_a = reading of the tensiometer after placing the rider on the ring (mN/m).

Calibration using water

20. The procedure using pure water is faster than the weight calibration, but there is the danger that the surface tension of the water (e.g. 72.3 mN/m at 23 °C) is altered by traces of impurities, surfactants for instance. The calibration factor, Φ_b, is given by

$$\Phi_b = \frac{\sigma_o}{\sigma_g}$$

where

σ_o = value cited in the literature for the surface tension of water (mN/m), and
σ_g = measured value of the surface tension of water (mN/m),

both at the same temperature.

Preparation and handling of samples

21. A solution of the substance is prepared in distilled water. The concentration should be 90% of the saturation solubility, but, when this concentration exceeds 1g/l, a concentration of 1g/l is used in the test.

22. Dust and gaseous contamination by other substances interfere with the measurement. This shall therefore be carried out under a protective cover.

Test conditions

23. The measurement shall be made at approximately 20°C and shall be controlled to within ± 0.5 °C.

Performance of the test

24. The solution to be measured is transferred to the measurement vessel, taking care to avoid foaming. The time from transferring the solution to the measurement vessel shall be recorded. The measurement vessel is placed on the table of the test apparatus. The measurement vessel is raised until the ring is immersed below the surface of the solution. Subsequently, the table top is lowered gradually and evenly at a rate of approximately 0.5 cm/min to detach the ring from the surface until the maximum force is reached. The force is read on the tensiometer. The liquid layer attached to the ring must not separate from the ring. After completing the first measurement, measurements are repeated until a constant surface tension value is reached.

Table 1

Correction of the Measured Surface Tension

Only for aqueous solutions, $\rho \approx 1 g/cm^3$
R = 9.55 mm (average ring radius)
r = 0.185 mm (ring wire radius)

Experimental value σ'(mN/m)	Corrected value σ(mN/m)	
	Water calibration	Weight calibration
20	18.1	16.9
22	20.1	18.7
24	22.1	20.6
26	24.1	22.4
28	26.1	24.3
30	28.1	26.2
32	30.1	28.1
34	32.1	29.9
36	34.1	31.8
38	36.1	33.7
40	38.2	35.6
42	40.3	37.6
44	42.3	39.5
46	44.4	41.4
48	46.5	43.4
50	48.6	45.3
52	50.7	47.3
54	52.8	49.3
56	54.9	51.2
58	57.0	53.2
60	59.1	55.2
62	61.3	57.2
64	63.4	59.2
66	65.5	61.2
68	67.7	63.2
70	69.9	65.2
72	72.0	67.2
74	-	69.2
76	-	71.2
78	-	73.2

DATA AND REPORTING

Data

25. In order to calculate the surface tension, the value read in mN/m on the apparatus shall first be multiplied by the calibration factor Φ_a or Φ_b, depending on the calibration procedure used. This yields a value which is only approximate and requires a correction. Harkins and Jordan (9) have empirically determined correction factors which are dependent on ring dimensions, the density of the liquid and its surface tension. Since it is laborious to determine the correction factor for each individual measurement from the Harkins-Jordan tables, a simplified procedure applicable to aqueous solutions may be used. It consists in taking the corrected surface tension values from Table 1 below. Interpolation shall be used for readings ranging between the table values. The table has been compiled on the basis of the Harkins-Jordan correction. It is similar to that in the Standard DIN 53914 (5) for water and aqueous solutions (density ρ = 1g/cm^3) and is for a commercially available ring having a mean ring radius of 9.55 mm and a ring wire radius of 0.185 mm. The table provides corrected values for measurements taken after calibration with weights or with water.

26. Alternatively, without preceding calibration, the surface tension can be calculated according to the following formula:

$$\sigma = \frac{f \times F}{4 \pi R}$$

where

F = the force measured on the dynamometer at the breakpoint of the film,
R = the radius of the ring, and
f = the correction factor (9,10).

Test Report

27. The test report must include the following information:

- method used;
- type of water or solution used;
- precise specification of the substance (identity and impurities);
- measurement results: individual readings, their arithmetic mean and the corrected mean; concentration of the solution;
- test temperature;
- age of solution used, in particular the time between the preparation of the solution and the measurement;
- description of the time dependence of the measured surface tension after transferring the solution to the measurement vessel;
- all information and remarks relevant for the interpretation of the results, especially with regard to impurities and physical state of the substance.

LITERATURE

(1) Official Journal of the European Communities L 383 A, 47-53 (1992)

(2) ISO 304 (1985)

(3) Weissberger, R., ed. (1959). Technique of Organic Chemistry, Vol. I, Part I, Physical Methods of Organic Chemistry, Chapter XIV, 3rd ed., Interscience Publ., New York.

(4) Pure Appl. Chem. (1976). 48, 511.

(5) DIN 53914

(6) ASTM D 1590

(7) ASTM D 1331

(8) Gaonkar and Neuman (1984). J. Colloid. Interface Sci. 98, 112.

(9) Harkins, W.D. and Jordan, H.F. (1930). J. Amer. Chem. Soc., 52, 1751.

(10) Fox, H.W., and Chrisman, C.H. (1952). J. Phys. Chem., 56, 284.