Metrohm

Application Bulletin 275/2 e

Potentiometric two-phase titration of anionic surfactants in washing powders and liquid washing agents

Branch

General analytical chemistry, private laboratories; organic chemistry, chemistry; pharmaceutical industry; metals, electroplating; detergents, surfactants cosmetics

Keywords

Two-phase titration, anionic surfactants, Epton titration, washing agents, Surfactrode Resistant, Surfactrode Refill, 6.0507.130, 6.0507.140; branch 1; branch 3; branch 4; branch 10; branch 12

Summary

The two-phase titration with potentiometric indication is a universal method for the determination of ionic surfactants in washing agents. The obtained results are comparable to those of the classical two-phase titration according to Epton (mixed indicator system disulfine blue / dimidium bromide).

In this bulletin special attention is paid to various parameters that can affect the potentiometric surfactant titration. The information provided enables the user to precisely determine the content of anionic surfactants in almost any formulation.

Instruments

- Titrator with DET mode
- 20 mL buret
- Rod Stirrer

Electrode

Surfactrode Resistant	6.0507.130
Surfactrode Refill	6.0507.140
Ag/AgCl Reference Electrode	6.0726.100

Reagents

- Hyamine® 1622
- Hydrochloric acid c(HCl) = 0.5 mol/L
- TEGO add (6.2317.110 or 6.2317.100)
- Buffer solutions pH = 4.00 (6.2307.100),
- pH = 7.00 (6.2307.110)
- pH = 9.00 (6.2307.120)
- Sodium dodecyl sulfate (Sodium lauryl sulfate; SDS)

Solutions

Titrant Hyamine® 1622.	Aprox. 2.24 g Hyamine® 1622 are weighed into a 1000 mL volumetric flask, dissolved in dist. water and filled up to the mark.
Sodium dodecylsulfate SDS	1.4565 ± 0.0005 g sodium dodecyl sulfate (99%) are weighed into a 1000 mL volumetric flask, dissolved in dist. water and filled up to the mark. The molar concentration of this solution is exactly 0.005 mol/L.
Solvent mixture	methyl isobutyl ketone (MIBK) : ethanol = 1 : 1 (volume ratio)

General

Effect of additional detergent components on the surfactant titration

Apart from anionic surfactants, washing powders contain the following main components:

- non-ionic surfactants (NIO surfactants)
- builders
- bleaching agents
- suspension agents

Whereas NIO surfactants do not affect the potentiometric two-phase titration of the anionic surfactants, the other components mentioned above lead to a more or less marked reduction of the overall voltage difference and a flattening of the titration curve. Insoluble builders of the zeolite type strongly affect the surfactant titration. The effect of bleaching and suspension agents, on the other hand, is considerably smaller. Figure 1 illustrates how different builders affect the titration curve obtained for the titration of a linear alkylbenzene sulfonate (LAS) with Hyamine® 1622.

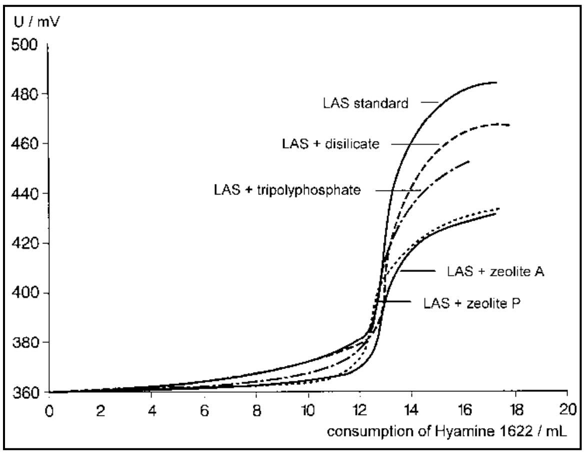

Fig. 1 Titration of SDS with Hyamine 1622 in the presence of different builders.

Effect of the pH value

As with all surfactant titrations the pH value also plays a decisive role in the titrimetric determination of anionic surfactants in washing agents. The pH value of the classical two-phase titration according to the Standard method of the German Association for Fat Sciences (DFG method) is set at pH = 2. In the case of the two-phase titration with potentiometric indication pH values of either 2 or 3 are used, depending on the applied indicator electrode. For further details, please see below under *Analysis*.

Analysis of washing powders

Anionic surfactants can generally be determined according to a universal method in all the following product classes

- universal washing agents
- washing agents for colored fabrics
- washing agents for delicate fabrics
- washing agents for woolen fabrics

Depending on the type and amount of contained surfactants, builders and bleaching agents, the resulting titration curves will be steeper or flatter. They can, however, always be easily evaluated. Figure 2 shows the titration curves of four washing agents strongly differing in their composition.

For the potentiometric two-phase titration absolute standard deviations between 0.2 and 0.8 mmol / 100 g sample were found. Recovery was 98 – 102%, compared to the values obtained with the classical two-phase titration. The titration results for various types of products (builders) are summarized in Table 1.

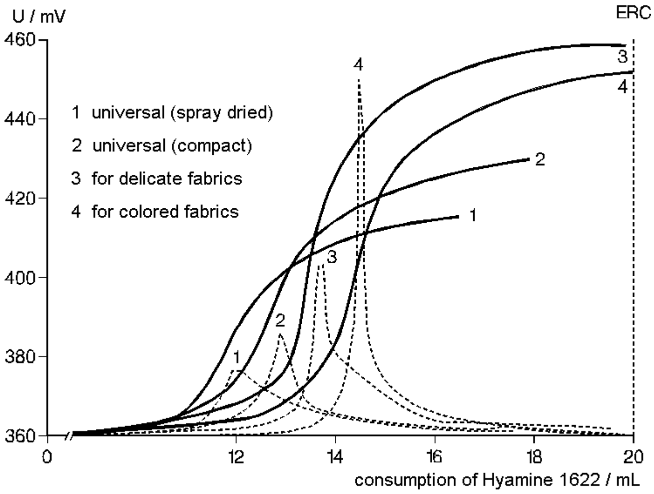

Fig. 2 Titration curves with first derivative obtained for four different washing agents.

Table 1: Determination of anionic surfactants in washing powders. Detailed table can be found in the appendix

	Epton Titration	Potentiometric two-phase titration	
Type of product (builder)	DGF H-III 10* / [mmol/100 g]	Equivalents / [mmol/100 g]	Recovery /[%]
All-purpose detergent (phosphates)	61.8	61.6	99.7
All-purpose detergent (zeolite A)	49.4	48.8	98.8
Detergent for colored fabrics (zeolite A)	51.6	50.6	98.1
All-purpose detergent (zeolite P)	29.3	29.8	101.4
Detergent for delicate fabrics (zeolite P)	33.4	33.3	99.6
All-purpose detergent (disilicate / zeolite A)	32.2	32.2	100.1

* Standard method of the German Association for Fat Sciences (Deutsche Gesellschaft für Fettwissenschaften – DGF); manual two-phase titration according to Epton, ISBN 978-3-8047-3024-3

Determination of soaps in washing powders

Two titrations are necessary for this analysis. In a first titration at pH = 2.0 only the anionic surfactants are determined, whereas during the second titration at pH = 11.5 the sum of the anionic surfactants and the soaps is determined. The sample weight should be at least 200 mg and be chosen to produce a titrant consumption of approx. 10 mL (c(titrant) = 0.005 mol/L).

Due to the high pH value, only the Surfactrode Refill can be used for these titrations!

The well homogenized sample is weighed into a glass beaker and dissolved in approx. 80 mL dist. water, then 0.2 mL TEGO add is added and the pH value of the solution is adjusted to 2.0 with c(HCl) = 0.5 mol/L. After addition of 20 mL solvent mixture the anionic surfactants are determined by titration with c(Hyamine® 1622) = 0.005 mol/L.

For the determination of the sum of the anionic surfactants and the soaps, an appropriate quantity of the well homogenized sample is weighed into a glass beaker and dissolved in approx. 80 mL dist. water. 0.2 mL TEGO add are added and the pH value of the solution is adjusted to 11.5 with c(NaOH) = 0.5 mol/L. After addition of 20 mL solvent mixture the titration is performed with c(Hyamine® 1622) = 0.005 mol/L.

Analysis of liquid washing agents

By means of two-phase titration with potentiometric indication, anionic surfactants can also be easily determined in liquid washing agents. This applies also to products with a high content of non-ionic surfactants or betains, which cannot be titrated in aqueous media. Examples of these are washing agents for woolen and silk fabrics, special shampoos for woolen fabricsand products used for hand washing.

Sample preparation

Using a sample divider, powdered samples must be split down to a representative amount and homogenized in an ultracentrifugal mill.

In the case of pure raw materials it is advisable to first prepare an intermediate dilution in dist. water. When weighing in the product directly, the sample mass to be used would be too small.

Analysis

Titer of the Hyamine® 1622 solution

Approx. 70 mL dist. water, 0.2 mL TEGO add as well as 10.00 mL sodium dodecyl sulfate solution are placed in a glass beaker. The pH value of the solution is adjusted to 2.0 (Surfactrode Refill) or 3.0 (Surfactrode Resistant) with c(HCl) = 0.5 mol/L. 20 mL solvent mixture are added and the titration is performed with c(Hyamine® 1622) = 0.005 mol/L.

Sample

Approx. 200 mg of the washing powder, divided and homogenized as described above, are weighed into a glass beaker. After addition of ca. 80 mL dist. water as well as 0.2 mL TEGO add the pH value of the solution is adjusted to 2.0 (Surfactrode Refill) or 3.0 (Surfactrode Resistant) with c(HCl) = 0.5 mol/L. 20 mL solvent mixture are added, then the titration is performed with c(Hyamine® 1622) = 0.005 mol/L under thorough stirring. It is extremely important that the two phases are well mixed and an emulsion is formed without the incorporation of air bubbles through stirring or the formation of a stirring vortex.

Parameter settings (DET mode)

1. Surfactrode Refill (pH = 2.0)

Table 2: Measuring parameters for raw materials, washing and cleaning agents for the Surfactrode Refill. Parameters should be adapted according to sample.

Measuring point density	2
Min. increment	50 µL
Dosing rate	Maximum
Signal drift	10 mV /min
Max. waiting time	120 s
pause (before titration)	30 s

2. Surfactrode Resistant (pH = 3.0)

Table 3: Measuring parameters for raw materials, washing and cleaning agents for the Surfactrode Resistant. Parameters should be adapted according to sample.

	Raw materials:	Washing and cleaning agents:
Measuring point density	0	0
Min. increment	50 µL	50 µL
Dosing rate	Maximum	Maximum
Signal drift	10 mV/min	5 mV/min
Max. waiting time	120 s	300 s
pause (before titration)	60 s	300 s

Calculation

Titer

$$f = \frac{10}{V_{EP1}}$$

f: Titer of the titrant

10: Used volume of sodium dodecyl sulfate solution

V_{EP1}: Titrant consumption until the first equivalence point in mL

Sample

$$\frac{\text{mmol anionic surfactants}}{\text{100 g sample}} = \frac{V_{EP1} \times f \times c_t \times 100}{m_S}$$

V_{EP1}: Titrant consumption until the first equivalence point in mL

f: Titer of the titrant

c_t: Concentration of the titrant, here 0.005 mol/L

100: Conversion factor due to 100 g

m_S: Sample weight in g

Comments

- The service life of the Surfactrodes can be prolonged if they are stored dry when not in use (overnight, over the weekend).
- It is always advisable to place the electrodes in the sample solution shortly before each titration to assure their adaptation to the sample matrix.
- If sufficient sample is available, the sample weight should be chosen to produce a titrant consumption of at least 10 mL for the equivalence point. This is the only way to ensure that the total amount of surfactants is determined. Although lower sample weights produce better titration curves, they sometimes lead to results that are too low.
- For anionic surfactants, TEGO®trant A100 provides steeper and larger potential jumps than Hyamine® 1622. With TEGO®trant A100, more hydrophilic surfactants (surfactants with shorter alkyl chains or those with hydrophilic groups such as esters, amides, POE compounds) can thus still be titrated.

Author

Competence Center Titration

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Appendix

Table 4: Comparison of the Epton titration and the potentiometric two-phase titration of anionic surfactants in washing powders.

	Epton titration	Potentiometric two-phase titration			
Type of product (builder)	Equivalents DGF H-III 10* / [mmol/100 g]	Equivalents / [mmol/100 g]	Standard deviation / [mmol/100 g]	Variation coefficient / [%]	Recovery / [%]
All-purpose detergent (phosphates)	61.8	61.6	0.2	0.38	99.7
All-purpose detergent (zeolite A)	49.4	48.8	0.2	0.39	98.8
Detergent for colored fabrics (zeolite A)	51.6	50.6	0.4	0.87	98.1
All-purpose detergent (zeolite P)	29.3	29.8	0.2	0.51	101.4
Detergent for delicate fabrics (zeolite P)	33.4	33.3	0.8	2.31	99.6
All-purpose detergent (disilicate / zeolite A)	32.2	32.2	0.3	0.96	100.1

* Standard method of the German Association for Fat Sciences (Deutsche Gesellschaft für Fettwissenschaften – DGF); manual two-phase titration according to Epton, ISBN 978-3-8047-3024-3