

Application Bulletin 233/4 e

Potentiometric determination of anionic and cationic surfactants with surfactant electrodes

Branch

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

Keywords

Anionic and cationic surfactants; titration; 6.0507.120; 6.0507.150; branch 1; branch 3; branch 4; branch 10; branch 12

Summary

Anionic surfactants can be titrated with cationic surfactants and vice versa. This Bulletin describes a wide range of substances that can be determined and lists the relevant working conditions and parameters. In contrast to the classical «two-phase titration» according to Epton, the titration with the anionic and cationic surfactants electrodes can be performed without chloroform. Further, in some cases the titration equivalence point with the Epton method is difficult to detect and the titration cannot be automated.

The surfactant ISE provides help here in many cases and also benefits the environment. It has been specially developed for surfactant determinations using potentiometric indication.

Instruments

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

Electrode

Ionic Surfactant electrode	6.0507.120
Cationic Surfactant electrode	6.0507.150
Ag/AgCl Reference Electrode	6.0726.100

Reagents

Buffers and solvents

- Buffer solution pH = 2.0 citrate/HCl Buffer solution pH = 3.0 citrate/HCl
- Buffer solution pH = 6.0 citrate/NaOH
- Buffer solution pH = 7.0 phosphate, e.g. Metrohm no. 6.2305.020
- Buffer solution pH = 10.0 boric acid /KCl/NaOH
- Hydrochloric acid c(HCl) = 2 mol/L
- Hydrochloric acid c(HCl) = 0.1 mol/L
- Sodium hydroxide c(NaOH) = 2 mol/L
- Methanol puriss p.a.
- Formaldehyde 35%

Titants for anionic surfactants

TEGO®trant A 100	1,3-didecyl-2-methylimidazolium chloride (DDMICl) Metrohm no.: 6.2317.000 (6 g) or 6.2317.010 (60 g)
HDPCI	Hexadecylpyridinium chloride (HDPCI · H ₂ O), also called cetylpyridinium chloride (CPCI) Fluka no.: 52349
Hyamine® 1622	Benzethonium chloride Merck no.: 112058

Titants for cationic surfactants

Sodium dodecylsulfate SDS	Sodium lauryl sulfate LAS Merck no.: 112533 or Sigma no.: 71725; stabilized against bacterial growth by 0.5% formaldehyde.
Diocylsodium sulfosuccinate DOSS	Bis(2-ethylhexyl)-sodium sulfosuccinate Fluka no.: 86139 Note: May saponify at higher pH values

Preparation of Titrants

General

The right selection of the titrant is very important. The lower the solubility of the formed compounds (the greater their oleophilic properties), the larger and steeper the potential jump of the titration curve. Advantage should be taken of this effect when formulations are titrated. (Additives can lead to considerable flattening of the potential jumps.)

Work is preferably performed with titrants of concentration 0.005 mol/L; only in exceptional cases a concentration of 0.02 mol/L is used.

The weight of reagents required for one liter is given by:

$$\text{Weight [in g]} = \frac{M_t \times c_t \times 100}{p_t}$$

M_t : Molar mass of titrant

c_t : titrant concentration, here 0.005 or 0.02 mol/L

100: conversion factor [L]

p_t : Purity of the titrant in %

Weigh in the required amount of titrant (plus slight excess) exactly and dissolve in dist. water, warming gently if necessary. By their nature, the substances do not contain 100% active substance. The major by-product is usually water. The water mass fraction can amount up to 8% and is very difficult to remove. It is essential to take these circumstances into account when weighing in the titrant. Make up to 1 liter with dist. water at 20 °C. The titer is determined against an anionic or cationic surfactant. As long as the solution in the reagent bottle and the buret has not stabilized, the titer is also not stable (surfactants tend to adhere to surfaces; this is characteristic particularly to cationic surfactants). Consequently, use always the same reagent bottles and other equipment (e.g. buret) and allow the solution to stand for one day before determining the titer.

Preparation of $c(\text{TEGO}^{\text{®}}\text{trant A100}) = 0.005 \text{ mol/L}$

Approx. 2.12 g of TEGO[®]trant A100 is weighed into a glass beaker with an accuracy of 0.1 mg and dissolved in approx. 150 mL water. This solution is transferred quantitatively with dist. water to a 1 L volumetric flask and filled up to the mark. Detailed information can be found on the leaflet which is delivered with the TEGO[®]trant.

Preparation of the comparison standard solutions from sodium dodecyl sulfate (SDS)

The raw substances contain some impurities e.g. water. Therefore it is recommended to take the purity of the raw material into the calculation of the weigh in.

Approx. 1.44 g of sodium dodecyl sulfate is weighed into a glass beaker with an accuracy of 0.1 mg and dissolved in approx. 200 mL water. This solution is transferred quantitatively with water to a 1 L volumetric flask, the flask is filled to the mark and its contents are carefully mixed.

The exact sample weight must be noted as it is needed for the subsequent titer calculation.

Titer determination of the TEGO[®]trant A100

10.0 mL of the corresponding sodium dodecyl sulfate standard solution is pipetted into a glass beaker. Followed by adding of 5 mL methanol, 75 mL water and 10 mL buffer solution pH = 3.0. The sample solution is efficiently stirred and then titrated using the corresponding TEGO[®]trant A100 solution as titrant with the following instrument settings:

Pause	30 s
Signal drift	50 mV/min
Measuring point density	4
Min. increment	10.0 µL
Stop volume	20 mL
EP recognition	all

The results may be used only if just one equivalence point is recognized. If this is not the case, additional titrations must be performed.

Calculation of the titer

A threefold determination is always performed. The resulting mean value is calculated to four decimal places.

$$f = \frac{m_s \times V_s \times C_s}{V_{EP1} \times M_s \times 100 \times c_{\text{TEGO}^{\text{®}}\text{trant}}}$$

f : Titer of the titrant

V_{EP1} : Titrant consumption in mL

m_s : Sample weight of SDS standard in g

V_s : Added volume of SDS solution in mL, here 10.0

C_s : Active substance content of the SDS used in %, here 99.2

M_s : Molecular weight of reference substance; here 288.4 g/mol

100: Conversion factor due to %

$c_{\text{TEGO}^{\text{®}}\text{trant}}$: Theoretical concentration of the titrant in mol/L; here 0.005

Preparation of $c(\text{sodium dodecyl sulfate}) = 0.005 \text{ mol/L}$

A titer determination in the usual manner cannot be performed for anionic titrants as there are no suitable primary standards. Cationic surfactants are normally quaternary ammonium compounds that usually cannot be prepared with the purity required for a primary standard. The degree of quaternization of these compounds would have to be 100%, but this is never the case. In addition, most of these compounds are highly hygroscopic. As a result, owing to water uptake, the active substance content changes each time the container is opened.

As a titer determination in the normal sense is not possible, the standard solutions are prepared by very exact weighing in of sodium dodecyl sulfate.

1.44 g of SDS is weighed exactly into a glass beaker and dissolved in approx. 250 mL dist. water. This solution is rinsed quantitatively into a 1 L volumetric flask with dist. water, 10 mL $w(\text{HCHO}) = 35\%$ is added and the flask is filled to the mark with dist. water. The addition of formaldehyde prevents bacterial decomposition of the titrant without having an adverse effect on the surfactant titration. The disinfecting action of the quantity specified is sufficient to keep the titer stable for at least three months. To guarantee thorough mixing, a magnetic stirring bar is added to the flask and the solution is stirred on a magnetic stirrer ensuring that foam formation is kept to a minimum. The titrant can then be transferred to the buret.

Preparation of $c(\text{DOSS}) = 0.02 \text{ mol/L}$ or 0.005 mol/L

As a titer determination in the normal sense is not possible, the standard solutions are prepared by very exact weighing in of dioctylsodium sulfosuccinate.

8.89 g for 0.02 mol/L or 2.22 g for 0.005 mol/L DOSS is weighed exactly into a glass beaker and dissolved in approx. 250 mL dist. water. This solution is rinsed quantitatively into a 1 L volumetric flask with dist. water, 10 mL $w(\text{HCHO}) = 35\%$ is added and the flask is filled to the mark with dist. water.

pH ranges for some detergents

Anionic surfactants

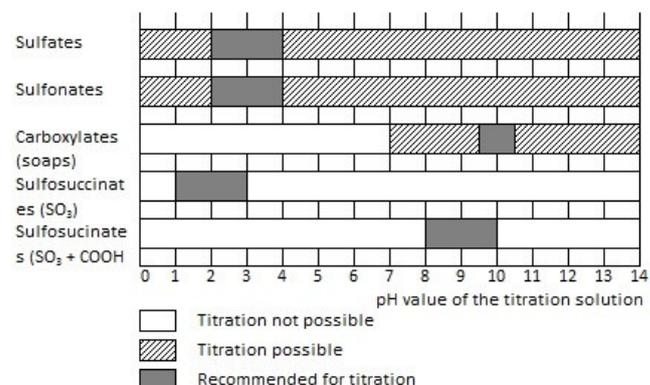


Fig. 1 Titration recommendations for anionic surfactants

- In the case of samples that contain both sulfosuccinates and betaines, the sulfosuccinates are titrated at $\text{pH} = 3.0$.
- For the determination of sulfosuccinates, the following pH values are adjusted for titration
 - sulfonate group at $\text{pH} = 2.0$
 - sulfonate and carboxylate group at $\text{pH} = 10.0$

Cationic surfactants

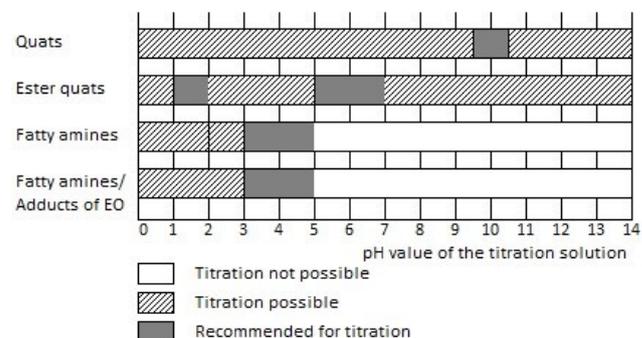


Fig. 2 Titration recommendations for cationic surfactants

- For the determination of the degree of quaternary amines, an additional titration is performed at $\text{pH} = 3.0$ to obtain the sum of the quaternary ammonium compounds and the tertiary starting amine.
- The ester quats contained in softeners are usually titrated at $\text{pH} = 2.0$. However, some ester quats exhibit their greatest stability at $\text{pH} = 5$ or $\text{pH} = 7$ and should thus be determined at these pH values. Here, it should be noted that the pH has to be adjusted immediately following the sample weighing. Slightly alkaline conditions can very quickly lead to ester cleavage

resulting in the ester losing its surfactant properties. This would lead to erroneous results.

- Betaines and amphoteric surfactants cannot be titrated. However, when present in the protonated form (at pH = 0 – 1), they can interfere with the determination of other surfactants.

Theory behind the electrode

The surfactant ISE electrode is a PVC liquid membrane electrode with a membrane composition (ionophore/plasticizer) that has been specially optimized for the determination of ionic surfactants. The electrode potential is due to a specific interaction between the ion carrier incorporated in the PVC membrane and the analyte ions (surfactants) in the analysis solution. This interaction leads in an equilibrium reaction to a potential crossing of the analyte ions from the analysis solution into the membrane and – as a result of this – to the formation of an electrical potential difference at the phase boundary analysis solution/membrane, which can be measured at zero current (potentiometrically) against a reference electrode. The extent of ion transfer from the analysis solution into the membrane depends on the concentration. The relation between the analyte ion concentration and the electrical potential is described by the Nernst equation:

$$E = E_0 + s \times \ln \left(\frac{C_{\text{ox}}}{C_{\text{red}}} \right)$$

In the equation, «s» represents the electrode slope. In the ideal case it is ca. 59 mV per concentration decade for monovalent anions and cations at 25 °C. In practice, lower slopes are frequently observed. Owing to a variety of circumstances (membrane composition, special properties of the surfactants such as boundary activity, substantivity [= tendency to absorb on surfaces], formation of micelles), Nernstian behavior cannot always be assumed for the surfactant electrodes. In practice, this means that

- the electrode is not suitable for direct potentiometric concentration determinations and
- the titration should always be evaluated using the inflection point of the S-shaped titration curve. End point titrations are usually not to be recommended.

Preparation, maintenance and storage of the surfactant electrode

- The electrode is stored dry.
- The electrode is best conditioned by two to three titrations whose results should be ignored.

- Adherent deposits are removed with a soft paper towel, moistened in methanol. In sample changer operation, the electrodes are dipped briefly in methanol, while stirring.
- The electrode (PVC membrane) is not resistant towards almost any organic solvents. Chloroform, hydrocarbons, acetone, MIBK, tetrahydrofuran, etc. destroys the electrode. High proportions of methanol (30 – 40%) or ethanol (20%) in the solvent shorten the lifetime of the electrode.
- Several thousand titrations can be performed with the electrode under normal conditions. Evidence of a decrease in the responding behavior of the electrode is shown in flatter titration curves and a shortened potential range. For a short time, such an electrode can be regenerated by submerging it for 30 min. in a sodium dodecyl sulfate solution (0.005 mol/L). If this does not help, the electrode must be replaced.

Analysis

The dynamic equivalence titration (DET) is the most suitable as it allows the fastest titrations and offers the best reproducibility. An amount of sample that corresponds to a titrant consumption of at least 10 mL is weighed into a beaker and approx. 50 mL dist. water are added. Following addition of 10 mL buffer solution and 5 mL methanol, the titration is started (examples in the Practical examples). In the case of concentrates and raw materials, for reasons of accuracy a dilution should first be made. In order to prevent formation of micelles, about 5 – 20 % vol. methanol are added. An aliquot of the initial dilution is then used for the titration (take into account the methanol fraction of the initial dilution).

Anionic surfactants

- Anionic surfactants are normally titrated with a cationic surfactant at pH = 3.0. For special cases, see Fig. 1.
- Soaps (sodium or potassium salts of higher fatty acids) must be titrated with TEGO®trant A 100 at pH values >10. Other cationic titrants produce poor titration curves that are often impossible to evaluate. In mixtures, anionic surfactants and soaps are determined as a sum. With decreasing pH value, the fraction of the soaps determined by titration becomes increasingly smaller. Complete separation is achieved by acidifying the sample to pH = 2.0 (allow the sample to stand 13 – 30 min for the reaction to run to completion). In the titration with TEGO®trant A 100 only the anionic surfactants are then determined. The pH value for the sum titration depends on the sample used and must be

determined by preliminary titrations (pH = 10 – 13). Two potential jumps result with the second being used to determine the sum of the soaps and anionic surfactants content together.

Cationic surfactants

- Cationic surfactants are normally titrated with an anionic surfactant at pH = 10.0. For special cases see Fig. 2.
- Samples that contain amine hydrochlorides are titrated at pH = 3.0. If the content without amine hydrochlorides is required, the titration is performed at pH = 10.0.

Calculation

For raw materials or known formulations:

$$W_{\text{Surfactant}} = \frac{V_{\text{EP1}} \times M_{\text{S}} \times c_{\text{t}} \times f \times 100}{m_{\text{S}}}$$

- $W_{\text{surfactant}}$: Content of surfactant in %
 V_{EP1} : mL titrant consumed to reach the first EP
 M_{S} : Molar mass of Surfactant in g/mol
 c_{t} : concentration of the titrant in mol/L
 f : Titer of the titrant
 100: Conversion factor due to %
 m_{S} : Sample weight in mg

If the molar mass of the surfactant under investigation is unknown or if the total surfactant content needs to be determined (without using an average molar mass), the analysis result can also be specified in mmol surfactant / 100 g sample or as sulphur equivalent:

$$\frac{\text{mmol}}{100 \text{ g}} = \frac{V_{\text{EP1}} \times 1000 \times c_{\text{t}} \times f \times 100}{m_{\text{S}}}$$

mmol/100g: Content in mmol surfactant per 100 g sample

- V_{EP1} : mL titrant consumed to reach the first EP
 1000: Conversion factor mol to mmol
 c_{t} : concentration of the titrant in mol/L
 f : Titer of the titrant
 100: Conversion factor due to 100 g
 m_{S} : Sample weight in mg

$$W_{\text{surfactant-S}} = \frac{V_{\text{EP1}} \times 100 \times M_{\text{Sulphur}} \times c_{\text{t}} \times f}{m_{\text{S}}}$$

- $W_{\text{surfactant-S}}$: Content of surfactant as sulphur equivalent in %
 V_{EP1} : mL titrant consumed to reach the first EP
 M_{Sulphur} : Molecular weight of sulphur, 32.064 g/mol
 100: Conversion factor due to %
 c_{t} : concentration of the titrant in mol/L
 f : Titer of the titrant
 m_{S} : Sample weight in mg

Calculation for cationic surfactants in formulations (3.2):

$$\frac{\text{meq}}{\text{g}} \text{ ester quats} = \frac{V_{\text{EP1}} \times c_{\text{t}}}{m_{\text{S}}}$$

- meq/g ester quats : Molar equivalence ester quats per 1 g of sample
 V_{EP1} : mL titrant consumed to reach the first EP
 m_{S} : sample weight in g
 c_{t} : concentration of the titrant, here 0.02 mol/L or 0.005 mol/L

Calculation for cetylpyridinium chloride (3.2.6):

$$\frac{\text{mg}}{\text{L}} \text{ CPCI} = \frac{V_{\text{EP1}} \times CF_1 \times 1000}{V_{\text{S}}}$$

- V_{EP1} : mL c(SDS) = 0.005 mol/L consumed to reach the first equivalence point
 V_{S} : sample volume in mL
 CF_1 : 1.79005 (conversion factor: 1 mL c(SDS) = 0.005 mol/L \triangleq 1.79005 mg CPCI)
 1000: Conversion factor due to g to mg

Equivalence calculation

- 1 mL anionic surfactant 0.005 mol/L
 = 1.9985 mg Tego@trant
 = 1.7901 mg HDPCI
 = 2.2405 mg Hyamine® 1622
 1 mL cationic surfactant 0.005 mol/L
 = 1.4419 mg sodium dodecylsulfate
 = 2.2229 mg DOSS

Practical examples

1. Titration parameters

Table 1: different settings for different sample types

Curve shape	Steep titration curve	Intermediate titration curve	Flat titration curve
Mode	DET U	DET U	DET U
Pause	30 s *	30 s *	30 s *
Signal drift	30 mV/min	50 mV/min	50 mV/min
Max. waiting time	38 s	26 s	26 s
MPD	5	3	2
Stop volume	20 mL	20 mL	20 mL
EP criterion	5	5	5
EP recognition	greatest	greatest	greatest

*) The waiting time of 30 s is necessary to allow the electrode to adapt to the titration solution.

2. Analysis of raw materials

2.1 Determination of anionic surfactants

2.1.1 Fatty alcohol ether sulfates

5 mL methanol, 10 mL buffer solution pH = 3.0, approx. 40 mL of dist. Water; minimum consumption of c(TEGO®trant) = 0.005 mol/L: 10 mL; Titration parameters «intermediate titration curve».

2.1.2 Fatty alcohol sulfates

5 mL methanol, 10 mL buffer solution pH = 3.0, approx. 40 mL of dist. Water; minimum consumption of c(TEGO®trant) = 0.005 mol/L: 10 mL (if sample is based on coconut fat: 12 mL); Titration parameters «intermediate titration curve».

2.1.3 Sulfosuccinate monoesters

5 mL methanol, 10 mL buffer solution pH = 1.0 or pH = 2.0 if only the sulfonate group needs to be determined. 10 mL buffer solution pH = 10 if the sulfonate and carboxylate groups need to be determined, approx. 40 mL of dist. Water; minimum consumption of c(TEGO®trant) = 0.005 mol/L: 10 mL; Titration parameters «intermediate» or «flat titration curve» (depending on the number of Polyoxyethylene units (POE)); take into consideration the hydrolysis stability of the ester group!

2.1.4 Sulfosuccinate diesters

5 mL methanol, 10 mL buffer solution pH = 3.0, approx. 40 mL of dist. Water; minimum consumption of

c(TEGO®trant) = 0.005 mol/L: 10 mL; parameters «steep titration curve»; take into account the hydrolysis stability of the ester group!

2.1.5 α -olefin sulfonates

5 mL methanol, 10 mL buffer solution pH = 3.0, approx. 40 mL of dist. Water; minimum consumption of c(TEGO®trant) = 0.005 mol/L: 8 mL; parameters «intermediate titration curve»; values may be too high in comparison with the two-phase titration*.

2.1.6 Secondary alkanesulfonates

5 mL methanol, 10 mL buffer solution pH = 3.0, approx. 40 mL of dist. Water; minimum consumption of c(TEGO®trant) = 0.005 mol/L: 10 mL; parameters «intermediate titration curve»; values may be too high in comparison with the two-phase titration*.

2.1.7 Linear alkylbenzene sulfonates

5 mL methanol, 10 mL buffer solution pH = 3.0, approx. 40 mL of dist. Water; minimum consumption of c(TEGO®trant) = 0.005 mol/L: 10 mL; parameters «steep titration curve».

2.1.8 Isethionates

10 mL methanol, 10 mL buffer solution pH = 3.0, approx. 40 mL of dist. Water; minimum consumption of c(TEGO®trant) = 0.005 mol/L: 10 mL; parameters «intermediate titration curve».

Dissolve coconut fat isethionates in 5 mL methanol and 5 mL dist. water with gentle warming (allow to stand 3 – 5 min); then add 90 mL dist. water and 2 mL c(HCl) = 0.1 mol/L and titrate immediately.

*) With the potentiometric titration, it is easily recognized that titration is performed according to decreasing oleophilic character. In particular, the differentiated titration curve indicates different inflection points with several products (e.g. C-12 – C-10 – C-8). This could be one of the reasons why somewhat higher values (up to 3%) are found in comparison with the two-phase titration.

2.2 Determination of cationic surfactants

2.2.1 Benzalkonium halides

10 mL methanol, 10 mL buffer solution pH = 3.0 or pH = 10.0, approx. 40 mL of dist. Water; minimum consumption of c(SDS) = 0.005 mol/L: 6 mL, with bis(2-ethylhexyl)-sodium sulfosuccinate c(DOSS) = 0.005 mol/L: 4 mL; parameters «intermediate titration curve»;

2.2.2 Quaternary ammonium compounds

10 mL methanol, 10 mL buffer solution pH = 10.0, approx. 40 mL of dist. Water; minimum consumption of c(SDS) =

0.005 mol/L; 10 mL; parameters «intermediate titration curve»;

3. Analysis of formulations

3.1. Determination of anionic surfactants in formulations

3.1.1 Rinse-off formulations without sulfosuccinates

Weigh in 100 – 300 mg sample, add 10 mL buffer solution pH = 5.0, 40 mL dist. water and dissolve sample. Add 5 mL methanol and titrate with $c(\text{TEGO@trant}) = 0.005 \text{ mol/L}$; minimum consumption of titrant: 10 mL; parameters for «intermediate» or «flat titration curve» depending on the formulation,; perform at least three determinations (turbidities caused by pearl lustre concentrates do not interfere).

3.1.2 Rinse-off formulations with sulfosuccinates

Weigh in 100 – 300 mg sample, add 10 mL buffer solution pH = 3.0, 40 mL dist. water and dissolve sample. Add 5 mL methanol and titrate with $c(\text{TEGO@trant}) = 0.005 \text{ mol/L}$; minimum consumption of titrant: 10 mL; depending on the formulation, parameters for «intermediate» or «flat titration curve»; perform at least three determinations (turbidities caused by pearl lustre concentrates do not interfere).

3.1.3 Mouth wash solutions on a dodecyl sulfate basis

To 5 – 10 g sample add 10 mL buffer solution pH = 3.0 and 40 mL dist. water, then add 5 mL methanol and titrate with $c(\text{TEGO@trant}) = 0.005 \text{ mol/L}$; minimum consumption of titrant: 10 mL; parameters «intermediate titration curve».

3.1.4 Toothpastes on a dodecyl sulfate basis

To 1 – 2 g sample add 10 mL buffer solution pH = 3.0 and 40 mL dist. water, then homogenize with Polytron high frequency mixer; rinse the Polytron with 10 mL methanol and titrate sample solution with $c(\text{TEGO@trant}) = 0.005 \text{ mol/L}$; minimum consumption of titrant: 10 mL; parameters «intermediate titration curve».

3.1.5 Anionic surfactants (dioctyl sulfosuccinates) in glass/window cleaning agent

To 6 – 7 g sample add 10 mL buffer solution pH = 3.0 and 40 mL dist. water, then add 5 mL methanol and titrate with $c(\text{TEGO@trant}) = 0.005 \text{ mol/L}$; parameters «intermediate titration curve».

3.1.6 Anionic surfactants in toilet cleaning agent

To 2.5 – 3.5 g sample add 10 mL buffer solution pH = 3.0 and 40 mL dist. water, then add 10 mL methanol and titrate with $c(\text{TEGO@trant}) = 0.005 \text{ mol/L}$; minimum consumption of titrant: 10 mL; parameters «steep titration curve».

3.1.7 Anionic surfactants in dishwashing concentrate

To ca. 3 g sample add 10 mL buffer solution pH = 5.0 and 40 mL dist. water, then add 10 mL methanol and titrate with $c(\text{TEGO@trant}) = 0.005 \text{ mol/L}$; minimum consumption of titrant: 10 mL; parameters «steep titration curve».

3.1.8 Anionic surfactants and soaps in all-purpose cleaning agents

To ca. 3 g sample add 10 mL buffer solution pH = 5.0 (for the determination of the anionic surfactants) or 10 mL buffer solution pH = 10.0 (for the determination of the anionic surfactants and soaps) and 40 mL dist. water; then add 10 mL methanol and titrate with $c(\text{TEGO@trant}) = 0.005 \text{ mol/L}$; minimum consumption of titrant: 8 mL; parameters «intermediate» to «flat titration curve».

3.1.9 Sum of the anionic surfactants in a shampoo and shower gel (non oil, fat free)

Weigh ca. 200 mg sample exactly into a beaker and dissolve in 45 mL dist. water and 3 mL methanol; add 5 mL buffer solution pH = 3.0 and titrate with $c(\text{TEGO@trant}) = 0.005 \text{ mol/L}$; parameters «intermediate» (shower gel) to «steep titration curve» (shampoo).

3.2 Determination of cationic surfactants in formulations

3.2.1 Hair conditioner

To 0.5 – 2 g sample add 10 mL buffer solution pH = 2.0 to pH = 10.0 (test and match to the particular formulation) and 40 mL dist. water and homogenize with a Polytron; rinse the Polytron with 10 mL methanol and titrate sample solution with $c(\text{SDS}) = 0.005 \text{ mol/L}$; minimum consumption of titrant: 10 mL; parameters «flat titration curve»;

3.2.2 Mouth wash solution on a benzalkonium basis

To 100 – 300 mg sample add 10 mL buffer solution pH = 3.0 or pH = 10.0 (test and match to the particular formulation) and 40 mL dist. water, then add 10 mL methanol and titrate with $c(\text{DOSS}) = 0.005 \text{ mol/L}$; minimum consumption of titrant: 10 mL; parameters «intermediate titration curve»;

3.2.3 Mouth/dental wash solutions on an amino fluoride basis

To 5 – 10 g sample add 10 mL buffer solution pH = 3.0 and 30 mL dist. water, then add 10 mL methanol and titrate with $c(\text{DOSS}) = 0.005 \text{ mol/L}$; minimum consumption of titrant: 10 mL; parameters «flat titration curve»;

3.2.4 Toothpastes on an amino fluoride basis

To 1 – 2 g sample add 10 mL buffer solution pH = 3.0 and 40 mL dist. water and homogenize with a Polytron; rinse the Polytron with 10 mL methanol and titrate sample solution

with $c(\text{SDS}) = 0.005 \text{ mol/L}$; minimum consumption of titrant: 10 mL; parameters «flat titration curve».

3.2.5 Cationic surfactants (ester quats) in a fabric softener

Dissolve ca. 1 g sample in 90 mL dist. water and 5 mL methanol; add 5 mL buffer solution $\text{pH} = 3.0$ and 1 mL $c(\text{HCl}) = 2 \text{ mol/L}$ and titrate with $c(\text{DOSS}) = 0.02 \text{ mol/L}$; parameters «flat titration curve».

3.2.6 Cetylpyridinium chloride (CPCI) in a mouth/dental wash solution

Pipet 10.0 mL sample into a beaker, add 40 mL dist. water and 5 mL buffer solution $\text{pH} = 3.0$ and titrate with $c(\text{SDS}) = 0.005 \text{ mol/L}$.

Example determination

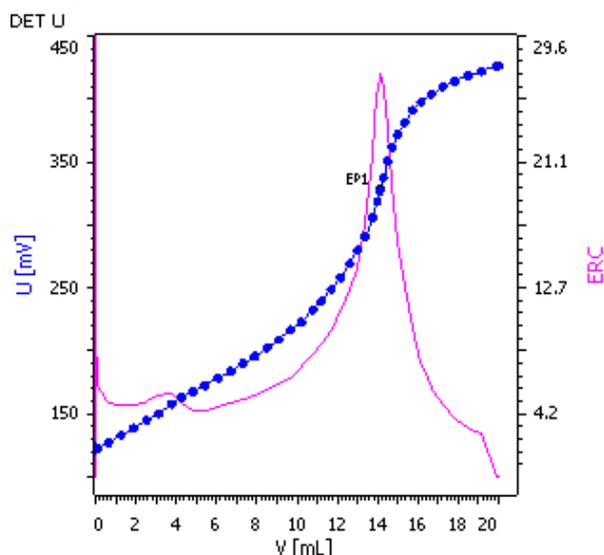


Fig. 3 Titration curve (steep) for the determination of the anionic surfactants in a shampoo. (blue = titration curve, pink = ERC)

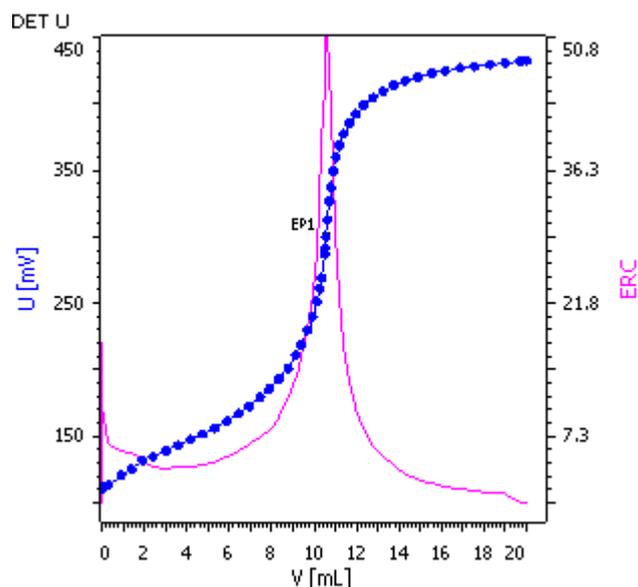


Fig. 3 Titration curve (Intermediate) for the determination of the anionic surfactants in a shower gel. (blue = titration curve, pink = ERC)

Comments

- If the surfactant electrode is left in the titrated sample solution for too long, it will either not respond at all or wrongly during the next titration. In such cases, rinse it with methanol and place it in $c(\text{SDS}) = 0.005 \text{ mol/L}$ for a few minutes.
- It is always advisable to immerse the electrode in the sample solution for 20 – 40 s before each titration to allow adaptation to the sample matrix.
- You can extend the lifetime of the electrode by storing it dry.
- The titrant TEGO®trant A 100 provides much steeper titration curves and larger potential jumps than other titrants. These advantages are particularly apparent with surfactants and soaps that produce only very weak potential jumps when using Hyamine® 1622. With TEGO®trant A 100 lower detergent concentrations can thus be determined.
- If sufficient sample is available, the sample weight should be chosen to produce a titrant consumption of at least 10 mL. Only this guarantees determination of the total amount of surfactants. While lower sample weights give better titration curves, they sometimes lead to values that are too low.
- Addition of methanol is absolutely necessary, particularly in finished formulations (e.g. shampoos, shower gels, softeners). In some cases it may even be necessary to increase the methanol content drastically in order to obtain precise results. Possible micelle and

foam formation can be prevented in this way (see also examples in the Practical determinations).

- The determination limit for ionic surfactants in waste waters lies at approx. 3 – 5 mg/L. For this purpose the titrant must be diluted to 0.002 mol/L. Measure 100 mL of the sample solution and adjust its optimum pH value with NaOH or HCl. Do not add methanol!
- These surfactant electrodes are not suitable for fatty or oily products (e.g. drilling and cutting oils, cooling lubricants, cleaning baths, special household cleaning agents and furniture polishes, shower gels and bath salts). Here a Surfactrode must be used. See Application Bulletin No. 269.
- The surfactant concentration is considerable higher in the foam phase than in the aqueous solution beneath it. Surfactant solution with a head of foam on top should only be used for analysis after the foam has collapsed.

References

- R. Schulz, R. Gerhards, Optimization of the potentiometric titration of ionic detergents, American Laboratory 26/11, (1994) 40-44 and International Laboratory 24/10, (1994) 10-14.
- Schulz, R. Gerhards, H.-D. Käseborn, Die potentiometrische Bestimmung von Anionentensiden in Rinse-off-Produkten, SÖFW-Journal 120/13, (1994) 776-783.
- R. Schulz, R. Gerhards, A new titrant for the potentiometric titration of anionic detergents, Tenside/Detergents, issue 1, 1995.
- S. Selig, The potentiometric titration of surfactants and soaps using ionselective electrodes, Fresenius J. Anal. Chem. 300, (1980) 183-188.
- G. C. Dilley, Determination of anionactive matter in detergents by potentiometric titration, Analyst 105, (1980) 713-719.
- K. Kosswig, H. Stache, Die Tenside, Carl Hanser Verlag, München/Wien, 1993, ISBN 3-446-16201-1.
- Stache, K. Kosswig, Tensid-Taschenbuch, 3. Auflage, Carl Hanser Verlag, München/Wien, 1990, ISBN 3-446-15704-2.
- M. Schmitt, Analysis of Surfactants, Surfactant Science Series Vol. 40, Marcel Dekker Inc., New York, 1992, ISBN 0-8247-8580-0.
- D. C. Cullum, Introduction to Surfactant Analysis, Blackie Academic & Professional, London, 1994, ISBN 0-7514-0025-4.
- ASTM D 4251-89, Standard Test Method for Active Matter in Anionic Surfactants by Potentiometric Titration.
- ASTM D 5070-90, Standard Test Method for Synthetic Quaternary Ammonium Salt in Fabric Softeners by Potentiometric Titration.
- R. Schulz, Th. Goldschmidt AG, Zentralbereich Forschung/Analytik, Goldschmidtstrasse 100, D-45127 Essen, Fax +49 201 173 19 97, Numerous personal communications regarding his work and lecture material.
- R. Schulz, P. Bruttel Bestimmung ionischer Tenside in Mundpflegeprodukten SÖFW-Journal 124/3, (1998) 138-146.
- R. Schulz, P. Bruttel Analytik ionischer Tenside in Haarpflegeprodukten SÖFW-Journal 125/2, (1999).

Author

Competence Center Titration
Metrohm International Headquarters