Metrohm

Application Bulletin 230/2 e

Potentiometric determination of nonionic surfactants based on polyoxyethylene adducts using the NIO electrode

Branch

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

Keywords

titration; washing agents, nonionic surfactants; NIO electrode; 6.0507.010; branch 1; branch 3; branch 4; branch 10; branch 12.

Summary

This bulletin treats the titrimetric determination of nonionic (NIO) surfactants based on polyoxyethylene adducts (POE adducts). The determination is based on the conversion of the nonionic surfactant into a pseudo-cationic compound, which is determined in a precipitation titration using sodium tetraphenylborate (STPB). The NIO electrode is used as indicator electrode. This bulletin shows determinations in raw materials, formulations and waste water. Characteristics, possibilities, limitations and interferences are pointed out.

Instruments

- Titrator with DET and MET mode
- 20 mL burette
- Rod Stirrer

Electrode

NIO electrode	6.0507.010
Ag/AgCl Reference electrode inner electrolyte c(KCl) = 3 mol/L; bridge electrolyte c(NaCl) = 3 mol/L Note: STPB reacts with potassium and ammonium ions and with certain amines.	6.0726.100

Reagents

- Sodium tetraphenylborate, STPB, CAS: 143-66-8
- Polyvinyl alcohol, CAS: 9002-89-5
- Boric acid (H_3BO_3), CAS: 10043-35-3
- Sodium hydroxide 1 mol/L
- Barium chloride $BaCl_2$
- Hydrochloric acid, w(HCl) = 36–38%, p.a.
- Triton X-100 (alkyl phenyl polyethylene glycol)
- Polyethylene glycol 1000

Solutions

Titrant c(STPB) = 0.01 mol/L:	3.4223 g STPB is weighed into a beaker and dissolved in 300 mL dist. water. In another beaker, 10 g polyvinyl alcohol is dissolved in 300 mL dist. water while warming. After cooling down, both solutions are rinsed into a 1000 mL volumetric flask, 10 mL buffer solution pH = 10.0 are added and the volumetric flask is filled up to the mark with dist. water.
Titrant c(STPB) = 0.002 mol/	10 mL buffer solution pH = 10.0 is added to 200 mL c(STPB) = 0.01 mol/L and filled up to 1000 mL with dist. water.
Buffer solution pH = 10.0	1.24 g H_3BO_3 is dissolved in dist. water, 10 mL c(NaOH) = 1 mol/L is added to the solution and filled up to 100 mL with dist. water.
c($BaCl_2$) = ca. 0.1 mol/L (Auxiliary solution)	21 g $BaCl_2$ or 25 g $BaCl_2 \cdot 2H_2O$ is dissolved in dist. water, 1 mL conc. HCl is added and the solution is filled up to 1000 mL with distilled water.

Standard surfactants

These products show a certain molecular weight range; the manufacturer's specifications should be considered as mean values.

It is recommended to purchase a larger amount of the standard raw surfactant (e.g., 1 kg) to have always the

same reference. From this a stock solution containing, e.g., 10.00 g/L is prepared. This is used to prepare the working solutions, which are freshly prepared every day by dilution with dist. water. The following are just two examples for standard surfactants:

- Triton X-100 (alkyl phenyl polyethylene glycol)
- Polyethylene glycol 1000
- The working solutions can be prepared in a way that 1 mL contains 1.00 mg of the standard surfactant.

General

Theoretical considerations

It is primarily the hydrophilic group that determines the surfactant's characteristics regarding application and analysis. Accordingly, the hydrophilic group serves to classify the surfactants into different groups. This bulletin deals with the important group of the NIO surfactants, i.e. substances that exhibit surfactant properties without forming ions. (This group also comprises substances that become active as surfactants only after hydration, i.e. indirect ion formation. Examples for this subgroup are the polyethylene glycols.)

The most important subgroup of the NIO surfactants – having by far the highest share in production – is the alkylene oxide derivatives. These are addition compounds between ethylene oxide (EO) or propylene oxide (PO) and hydrophobic starter molecules, such as fatty alcohols, fatty acids and partially esterified polyhydric alcohols such as glycerol, sorbitol, etc.

If a NIO surfactant is designated, e.g., as POE-(20)-stearyl alcohol, this does not mean at all that it is a uniform compound consisting of a stearyl alcohol with 20 POE units in the molecule. Already the alkyl chains of the starter alcohol show a certain distribution and the 20 POE units must be regarded as a statistical mean. In this particular example, the distribution will at least range from 10 to 30 POE.

As a first step for the titration, barium ions are added to the NIO surfactant, with which they form a pseudo-ionic compound. Experience has shown that approx. 11 EO groups form a barium complex carrying a doubly positive charge. To precipitate this complex, 2 STPB molecules are needed (accordingly, 1 STPB corresponds to approx. 5.5 EO groups). One has to be aware, however, that this complex formation depends strongly on the chain length. Short EO chains are unable to bind the barium ions. For POE addition products to oleophilic starter molecules, at least 4 POE units are required, whereas polyethylene glycols need 11 to 12 POE units.

The pseudo-ionic compound can be titrated with sodium tetraphenylborate (STPB), whereby hardly soluble precipitates are formed.

The following equations describe these processes:

$$S + x\ Ba^{2+} \rightarrow [SBa_x]^{2x+} \quad (1)$$

$$[SBa_x]^{2x+} + 2x\ STPB \rightarrow [SBa_x]\cdot TPB_{2x} + 2x\ Na^{+} \quad (2)$$

S: Surfactant

STBP: Sodium tetraphenylborate

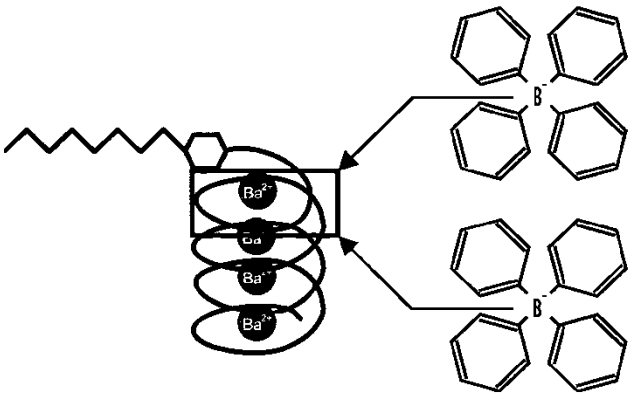

Fig.: 1: A model of the precipitation compound.

Preparation, maintenance and storage of the NIO electrode

- The electrode is preconditioned by performing two to three titrations, whose results are rejected. It is also recommended to maintain a waiting time of 30 s before each titration to allow the electrode to adjust to the sample matrix present.
- After performing 3 to 4 titrations, the electrode is rinsed with methanol or wiped with a tissue that has been moistened with methanol.
- After concluding the titrations, the electrode is wiped with a methanol-moistened tissue and subsequently stored dry.
- If NIO titrations are performed frequently, the electrode can be stored in a 1% solution of polyethylene glycol 1000 (in dist. water). This has the advantage that the electrode is ready for use immediately and the pre-titrations mentioned above are not necessary.
- The electrode should be stored dry.
- The electrode is not resistant against organic solvents.

Analysis

Raw materials and formulations should be diluted before analysis. Waste water samples can be used directly, possibly after passing through a coarse filter.

Samples corresponding to 25–50 mg of NIO surfactant, or alternatively 100 mL waste water samples are given into a beaker. 10 mL of $BaCl_2$ solution is added and fill up to approx. 100 mL with dist. water if necessary. The solution is then titrated using c(STPB) = 0.01 mol/L, or for waste water, c(STPB) = 0.002 mol/L as titrant.

After 3 to 4 titrations, the electrode is rinsed with methanol or wiped with a methanol-moistened tissue.

Parameters

Raw materials

Mode	DET U
Pause	30 s
Measuring point density	2
Min. increment	150 µL
Signal drift	10mL /min
Max. waiting time	52 s
EP criterion	10
EP recognition	greatest
Stop volume	20 mL

Formulations

Mode	DET U
Pause	30 s
Measuring point density	1
Min. increment	150 µL
Signal drift	10 mV/s
Max. waiting time	52 s
EP criterion	10
EP recognition	greatest
Stop volume	20 mL

Waste water

Mode	DET U
Pause	30 s
Measuring point density	4
Min. increment	150 µL
Signal drift	10 mV/s
Max. waiting time	52 s
EP criterion	5
EP recognition	greatest
Stop volume	20 mL

Calculation

The calculation of the content cannot be done directly because the NIO surfactants are non-uniform substances and the precipitation with STPB is not strictly stoichiometric. As with other analytical methods (e.g., HPLC) a calibration factor (f) has to be determined first. This is done either using the NIO surfactant to be determined or a NIO surfactant that has been defined as a standard. The NIO surfactant is titrated as described under *Analysis* and the calibration factor f calculated as following:

$$f = \frac{m_S \times 1000}{V_{EP1}}$$

f: calibration factor (mg/mL)

m_S: sample mass in g (calculated as 100% NIO surfactant)

V_{EP1}: consumption of STPB solution in mL

1000: Correction factor due to g to mg

Accordingly, the NIO surfactant content of the samples is calculated using the following formula:

$$\text{NIO surfactant content in \%} = \frac{V_{EP1} \times f \times 100}{1000 \times m_S}$$

V_{EP1}: consumption of STPB solution in mL

f: calibration factor in mg/mL

100: Correction factor because of %

1000: Correction factor due to g to mg

m_S: sample mass in g

Comments

- The parameters should be adjusted in such a way that there are sufficient measuring points for the evaluation and that the titration curve is smooth, without significant spikes (check with derivative curve).
- There must be optimum stirring during the titration. To achieve this, the propeller stirrer is adjusted such that no air bubbles are drawn in and only a small vortex is formed.

Scope of the method and limitations

- Only NIO surfactants based on POE addition products to oleophilic starter molecules or polyethylene glycols can be titrated.
- This method does not allow distinguishing between different NIO surfactants. Only the total content is determined.
- Mixed POE/POP (Polyoxypropylene) polymers can be titrated as well. However, only the POE content will react, the POP compounds are not determined. The POE content should be at least 25%.
- The titration of polyether siloxanes is also possible. However, here as well, the POE content should be at least 25%.
- POE addition compounds to monohydric alcohols are easier to titrate than those to polyhydric alcohols or their partial esters. With the partial esters the titration curves become worse with increasing sample weight. The sample weight should therefore be chosen such that not more than 4 mL titrant c(STPB) = 0.01 mol/L are consumed.
- POE addition products to monohydric starter molecules (e.g., fatty alcohols, fatty acids, fatty amines, alkyl phenols) show a standard deviation of approx. 0.5%. The standard deviations for POE addition products to polyhydric starter molecules (e.g., monoesters of glycerol or sorbitan) are in the region of 4%.
- The following NIO surfactants cannot be titrated with this method: non-ethoxylated glycerol and sorbitan esters, alkyl polyglucosides (APGs) and sugar esters.
- Anionic surfactants based on POE addition compounds (e.g., fatty alcohol ether sulfates or fatty alcohol ether mono sulfo succinates) are determined to the extent that they fulfil the conditions for the titrimetric determination of NIO surfactants (from 4 POE per molecule upwards). Lauryl ether-(2,5)-sulfate or lauryl ether-(3)-monosulfosuccinate may contain more highly ethoxylated compounds. These will be determined during the NIO titration and produce high results.
- Complexing agents such as EDTA and NTA do not interfere.
- No alcohol should be added to the sample solution. These additions increase the solubility of the precipitates formed during the titration and therefore have a detrimental influence on the titration curve. As a rule, alcohol contents up to 2–3% will not affect the results. If titrations have to be performed in the presence of higher alcohol concentrations, one has to use the same alcohol concentration for the calibration titration.
- For the NIO titration, it is not necessary to adjust a given pH. However, it is recommended to working in the range between pH = 3–9.
- Potassium, ammonium, and certain organic compounds form also insoluble precipitates with STPB, but they do hardly interfere.
- Cationic surfactants are determined together with the NIO surfactants, because they also form hardly soluble precipitates with STPB. To differentiate between the cationic and the nonionic surfactants, two titrations have to be performed:
    1. without $BaCl_2$ addition
       only cationic surfactants
    2. with $BaCl_2$ addition
       sum of cationic and nonionic surfactants

Literature

- Thomas 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.
- DGF Einheitsmethoden
  Deutsche Einheitsmethoden zur Bestimmung von Fetten, Fettprodukten, Tensiden und verwandten Stoffen. H-I 2
  Wissenschaftliche Verlagsgesellschaft, Stuttgart, 1993.

Author

Competence Center Titration

Metrohm International Headquarters