
Application Bulletin

Of interest to: General analytical laboratories; Waste water; A 1, 2, 3, 10, 12, 13
Organic chemistry; Metals, electroplating;
Detergents, surfactants, cosmetics; Textiles

Titrimetric/potentiometric determination of non-ionic surfactants based on polyoxyethylene adducts using the NIO electrode

Summary

This bulletin treats the titrimetric determination of non-ionic surfactants based on polyoxyethylene adducts (POE adducts). The determination is founded on the conversion of the non-ionic surfactant into a pseudo-cationic compound, which is determined in a precipitation titration using sodium tetraphenylborate (NaTPB). As the indicator electrode, a newly developed surfactant electrode, the NIO electrode, is used. It has been designed taking into account the characteristics of this titration and therefore yields reliable, fast and efficient determinations.

This bulletin treats determinations in raw materials, formulations and waste water. Characteristics, possibilities, limitations and interferences are pointed out.

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 non-ionic 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. An example of this subgroup are the polyethylene glycols.)

The most important subgroup of the non-ionic surfactants – having by far the highest share in production – are 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.

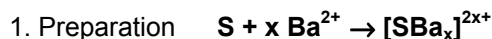
If a NIO (non-ionic) surfactant is designated, e.g., as POE-(20)-stearyl alcohol, this does not mean at all that we have to deal with a uniform compound consisting of a stearyl alcohol with 20 POE units in the molecule. Already the alkyl chains of the starter alcohol show a certain distribution and the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

As a first step, barium ions are added to the NIO surfactant, with which they form a pseudo-ionic compound. This latter may be compared with the compounds formed by crown ethers. Due to the greater mobility of the helix structure formed, the polyether structures are not as specific as those of the crown ethers. Experience has

shown that ca. 11 EO groups form a barium complex carrying a doubly positive charge. To precipitate this complex, 2 NaTPB molecules are needed (accordingly, 1 NaTPB corresponds to ca. 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.

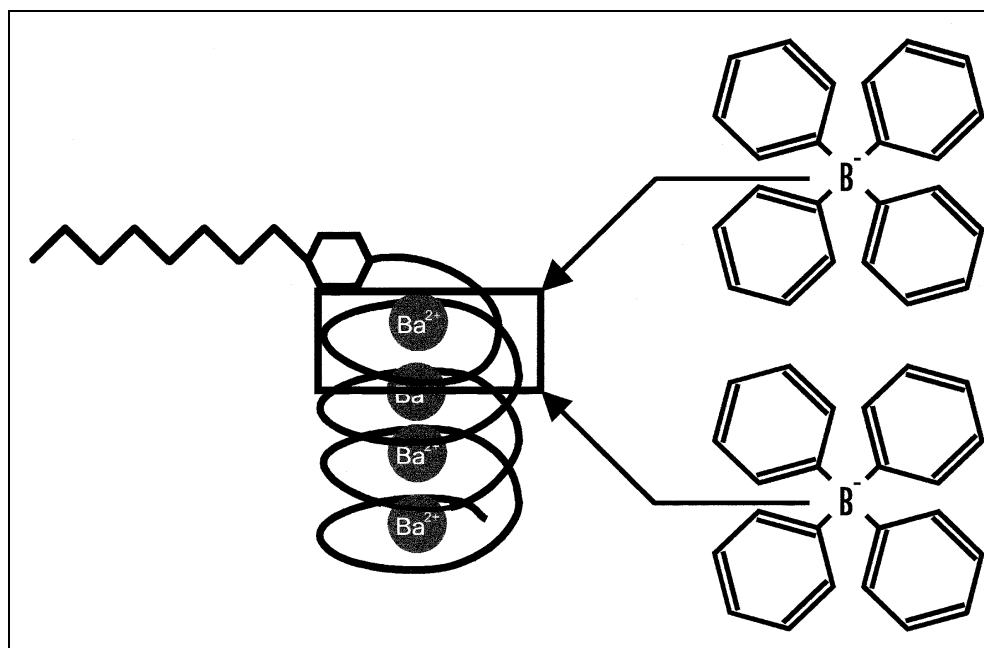
The pseudo-ionic compound can be titrated with sodium tetraphenylborate (NaTPB), whereby hardly soluble precipitates are formed.

The following equations describe these processes:



where S non-ionic surfactant
NaTPB sodium tetraphenylborate

Figure 1 appearing below shows a model of the precipitation compound:



Instruments and accessories

- 2.702.0010 SET/MET Titrino, 2.716.0010 DMS Titrino, 2.736.0010 GP Titrino or another Metrohm titrator
- 2.722.0010 Propeller Rod Stirrer
- 6.3013.223 Exchange Unit
- 6.0507.010 NIO electrode with 6.2104.020 electrode cable
- 6.0726.100 Ag/AgCl reference electrode with 6.2106.020 electrode cable (inner electrolyte $c(KCl) = 3 \text{ mol/L}$; bridge electrolyte $c(NaCl) = 1 \text{ mol/L}$)
- For the automatic determination of sample series:
2.730.0XXX Sample Changer (with 2.722.0020 Rod Stirrer and two 2.741.0010 Magnetic Stirrers)

Reagents

- Titrant $c(\text{NaTPB}) = 0.01 \text{ mol/L}$:
3.4223 g sodium tetrphenylborate (e.g. Fluka no. 72020) are weighed into a beaker and dissolved in 300 mL dist. water. In another beaker, 10 g polyvinyl alcohol (Merck no. 114266) are also dissolved in 300 mL dist. water with warming. After cooling down, both solutions are rinsed into a 1000 mL volumetric flask, 10 mL buffer solution $\text{pH} = 10.0$ are added and the volumetric flask is filled up to the mark.
- Titrant $c(\text{NaTPB}) = 0.002 \text{ mol/L}$ (for waste water samples):
10 mL buffer solution $\text{pH} = 10.0$ are added to 200 mL $c(\text{NaTPB}) = 0.01 \text{ mol/L}$ and filled up to 1000 mL with dist. water.
- Buffer solution $\text{pH} = 10.0$:
1.24 g H_3BO_3 are dissolved in dist. water, 10 mL $c(\text{NaOH}) = 1 \text{ mol/L}$ are added to the solution. Fill up to 100 mL with dist. water.
- Auxiliary solution $c(\text{BaCl}_2) = \text{ca. } 0.1 \text{ mol/L}$:
21 g BaCl_2 or 25 g $\text{BaCl}_2 \cdot 2 \text{ H}_2\text{O}$ are dissolved in dist. water, 1 mL conc. HCl is added and the solution filled up to 1000 mL with distilled water.

Standard surfactant

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

In principle, each user can himself define his standard surfactant. We recommend to purchase a larger amount of your standard surfactant (e.g. 1 ... 5 kg). From this a stock solution containing, e.g., 10.00 g/L is prepared. This is used for 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); Fluka no. 93426, Merck no. 112298
- Polyethylene glycol 1000; Fluka no. 81188, Merck no. 817009

The working solutions can be prepared such, e.g., that 1 mL contains 1.00 mg of the standard surfactant.

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 observe 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.

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. Add 10 mL BaCl₂ solution and fill up to ca. 100 mL with dist. water if necessary. Titrate using 0.01 mol/L or, for waste water, 0.002 mol/L NaTPB titrant.

After 3 to 4 titrations, rinse the electrode with methanol or wipe it with a methanol-moistened tissue (when using, e.g., a 730 Sample Changer, dip the electrode into a beaker filled with methanol and subsequently into a beaker containing dist. water).

Titration parameters

Examples for the 716 or 736 Titrino

Raw materials		Formulations		Waste water	
DET U		DET U		MET U	
mpd	2	mpd	4	V step	0.2 mL
min.incr.	50 ... 200 µL	min.incr.	100 ... 200 µL	signal/drift	5 mV/s
signal/drift	off	signal/drift	10 mV/s	equ.time	360 s
equ.time	20 s	equ.time	60 s	stop EP	1
ERC	10	ERC	10	ERC	10 ... 20 mV
EP recogn.	greatest	EP recogn.	greatest	EP recogn.	greatest
Stop V	20 mL	Stop V	20 mL	Stop V	10 mL

Calculation

The calculation of the content cannot be done directly because the NIO surfactants are non-uniform substances and the precipitation with NaTPB 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 follows:

$$f = E * 1000 / V$$

where f calibration factor (mg/mL)

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

V consumption of NaTPB solution in mL

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

$$\text{NIO surfactant content in \%} = V * f / 10 / E$$

where V consumption of NaTPB solution in mL

f calibration factor in mg/mL

E sample mass in g

Remarks

- The dynamic control 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 722 Propeller Stirrer is adjusted such that no air bubbles are drawn in and only a small vortex is formed.
- This bulletin has been produced in cooperation with the company Th. Goldschmidt AG, ZBF/Analytical dept., Mr. Reiner Schulz, Essen, Germany.

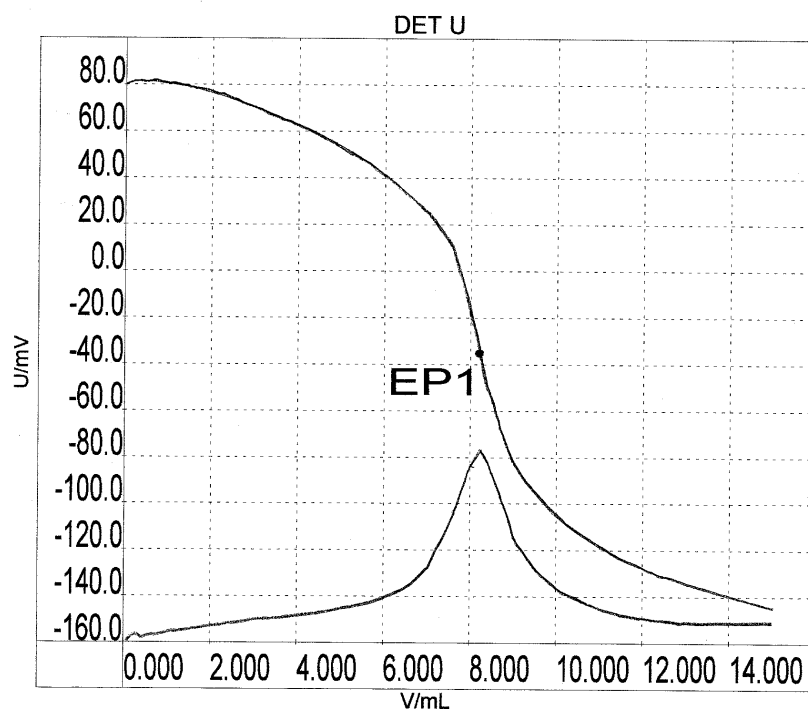
Scope of the method and limitations

- Only NIO surfactants based on POE addition products to oleophilic starter molecules or polyethylene glycols can be titrated.
- This method does not allow to distinguish between different NIO surfactants. Only the total content is determined.
- Mixed POE/POP 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 $c(\text{NaTPB}) = 0.01 \text{ mol/L}$ are consumed.
- POE addition products to monohydric starter molecules (e.g. fatty alcohols, fatty acids, fatty amines, alkyl phenols) show standard deviations of ca. 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: 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.
- Whenever possible one should restrain from adding alcohols to the titration 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, we recommend to work in the range $\text{pH} = 3 \dots 9$.

- Potassium, ammonium and certain organic compounds also form insoluble precipitates with NaTPB. Contrary to expectations, potassium and ammonium hardly interfere.
 - Cationic surfactants are determined during the NIO titration, because they also form hardly soluble precipitates with NaTPB. To differentiate between the cationic and the non-ionic surfactants, two titrations have to be performed:
 - A) without BaCl₂ addition → only cationic surfactants
 - B) with BaCl₂ addition → sum of cationic and non-ionic surfactants
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Literature

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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.



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`fr
date 06/12/1995      time 11:08:26          No. 2
Method   Factor NIO titration
Id1      Triton X-100
Id2      1
Sample size          0.0291 g
Endpoints:
DET U.EP1           8.222 ml          -35 mV
Results:
EP1:NIO factor      3.54 mg/ml
    
```

Fig. 2: Determination of the calibration factor using Triton X-100.

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`cu
736 GP Titrino      OP1/103  736.0010
date 95-10-10      time 11:27    9
start V           0.000 ml  DET U  Tenside
2.0 ml/div        dU=50.0 mV/div
    
```

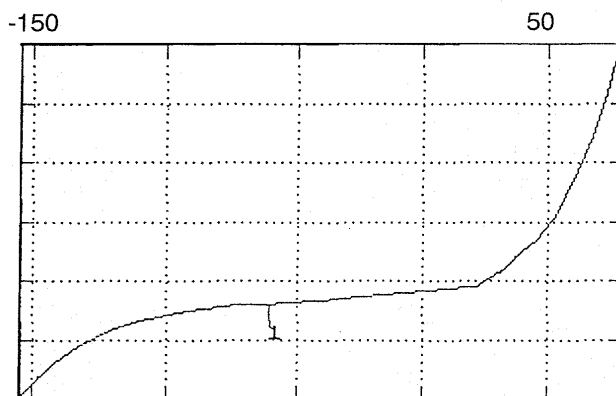


Fig. 3: Titration curve of polyoxyethylene-(10)-fatty alcohol.

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'pa
716 DMS Titrimo      0E2/237  716.0020
date 95-11-15      time 10:02      8
DET U              Tenside
Parameters
>titration parameters
  meas.pt.density      4
  min.incr.           100 ul
  titr.rate            max. ml/min
  signal drift        10 mV/min
  equilibr.time       60 s
  start V:            OFF
  pause               0 s
  meas.input:         1
  temperature         25.0 °C
>stop conditions
  stop V:             abs.
  stop V              18 ml
  stop U              OFF mV
  stop EP             9
  filling rate        max. ml/min
>statistics
  status:             OFF
>evaluation
  EPC                 10
  EP recognition:    greatest
  fix EP1 at U      OFF mV
  pK/HNP:           OFF
>preselections
  req.ident:         OFF
  req.smpl size:    value
  activate pulse:   OFF
  
```

```

'fr
716 DMS Titrimo      0E2/237  716.0020
date 95-11-15      time 08:51      3
U(init)            243 mV DET U Tenside
smpl size          4.844 g id 1 Softlan
EP1                7.521 ml      145 mV
Nonionic           0.1553 meq/g
stop V reached
  
```

```

'cu
716 DMS Titrimo      0E2/237  716.0020
date 95-11-15      time 08:51      3
start V            0.0000 ml DET U Tenside
2.0 ml/div        dU=50.0 mV/div
  
```

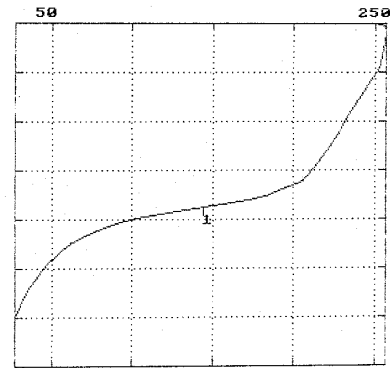


Fig. 4: NIO surfactants in a fabric softener.

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'pa
716 DMS Titrimo      0E2/237  716.0020
date 95-12-06      time 10:11      6
MET U              TensideA
Parameters
>titration parameters
  V step              0.2 ml
  titr.rate            max. ml/min
  signal drift        5 mV/min
  equilibr.time       360 s
  start V:            OFF
  pause               0 s
  meas.input:         1
  temperature         25.0 °C
>stop conditions
  stop V:             abs.
  stop V              6 ml
  stop U              OFF mV
  stop EP             9
  filling rate        max. ml/min
>statistics
  status:             OFF
>evaluation
  EPC                 5 mV
  EP recognition:    greatest
  fix EP1 at U      OFF mV
  pK/HNP:           OFF
>preselections
  req.ident:         OFF
  req.smpl size:    OFF
  activate pulse:   OFF
  
```

```

'fr
716 DMS Titrimo      0E2/237  716.0020
date 95-12-05      time 15:36      1c
U(init)            149 mV MET U TensideA
smpl size          100 ml id 1 WasteH2C
EP1                3.248 ml      116 mV
Nonionic           3.2483 ml
stop V reached
  
```

```

'cu
716 DMS Titrimo      0E2/237  716.0020
date 95-12-05      time 15:36      1c
start V            0.0000 ml MET U TensideA
2.0 ml/div        dU=20.0 mV/div
  
```

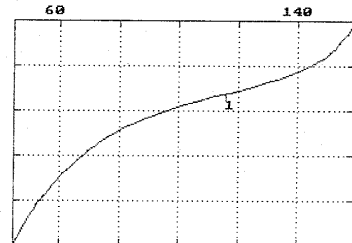


Fig. 5: NIO surfactants in a waste water of the textile industry.