
Application Bulletin

Of interest to: General analytical laboratories
 Organic chemistry
 Detergents, surfactants, cosmetics

A 1, 3, 12

Titrimetric methods for the determination of betains

The work described in this bulletin was carried out at Th. Goldschmidt AG, FO/Analytik, D-45127 Essen, Germany

Summary

The two potentiometric titration methods described here allow to determine the content of commercial betain solutions. Neither method is suitable for determining the betain content of formulations. The possibilities and limits of both methods are described and distinctive features and possible sources of interference are mentioned. The bulletin explains the most important theoretical principles and is intended to help users to develop their own product-specific titration methods.

Method A

After protonation at pH = 1, betains show the properties of a cationic surfactant. They can therefore be titrated with sodium tetraphenylborate (= STPB), which forms sparingly soluble precipitates with the betains. The NIO electrode is used for the potentiometric indication of this titration.

Method B

This is a specially developed non-aqueous perchloric acid titration. Indication is also carried out potentiometrically by means of a pH glass electrode and a reference electrode. (This method has nothing to do with the perchloric acid titration that has been known for a long time, in which the total number of basic compounds that can be protonated is determined in a betain solution.)

In the modified perchloric acid titration the sample is first made alkaline with sodium hydroxide. This transforms the compounds contained in the sample to a defined form; these are then present as follows:

- the betain in its internally compensated form (charge-wise),
- the amidamine as free amidamine,
- the acids (e.g. HCl, mono and dichloroacetic acid, formic acid, fatty acids, glycolic acid) as their sodium salts.

During the titration with perchloric acid in a non-aqueous medium:

- the betain is converted to its protonated form,
- the amidamine forms amidamine perchlorate, and
- the excess sodium hydroxide and the sodium salts of the different acids react to form the less-dissociated sodium perchlorate.

A solvent mixture that yields a clear distinction between the different pK values allows to determine the betain in the presence of the above-mentioned components.

Both titration methods are suitable for checking the betain content of the following betain solutions:

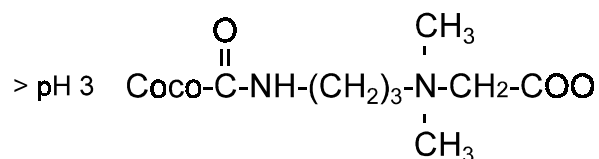
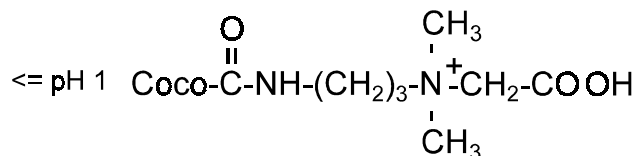
- alkylamidopropyl betains, including cocoamidopropyl betain, as well as
- alkyl betains.

Theoretical principles

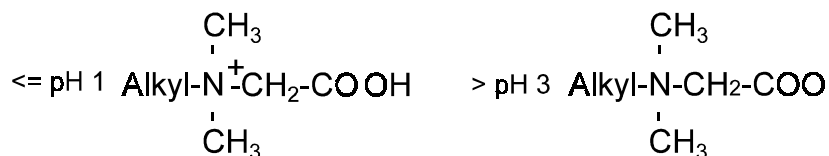
Betains are amphoteric surfactants with very interesting properties for technical applications. They are therefore used in many cosmetic products, but also in washing and cleaning agents. In «rinse-off» formulations betains are the most important co-surfactants.

At pH values > 3 a betain is present in its internally compensated betain-like form. Between pH = 1 and pH = 3 a partially protonated form is present in which the degree of protonation increases as the pH decreases. At pH values < 1 the betain is completely protonated and shows the properties of a cationic surfactant.

Structural formula of cocoamidopropyl betain in the protonated and neutral forms:



Structural formula of an alkyl betain in the protonated and neutral forms:



Instruments and general accessories

- 702 SET/MET Titrino, 716 DMS Titrino, 736 GP Titrino or 751 GPD Titrino or 726 Titroprocessor
- Possibly 2.730.0XXX or 2.717.0XXX Sample Changer
- 2.722.0010 Propeller Rod Stirrer
- 6.3031.223 Exchange Unit(s) 20 mL (with flat ceramic stopcock)
- The required electrodes are listed under the individual titration methods.

Method A: titration with sodium tetraphenylborate**Electrodes**

- 6.0507.010 NIO Surfactant Electrode with 6.2104.020 electrode cable
- 6.0726.100 Ag/AgCl reference electrode [inner electrolyte $c(\text{KCl}) = 3 \text{ mol/L}$, Metrohm no. 6.2308.020; bridge electrolyte $c(\text{NaCl}) = 3 \text{ mol/L}$] with 6.2106.020 electrode cable

Reagents

- Hydrochloric acid $c(\text{HCl}) = 0.1 \text{ mol/L}$
- Sodium hydroxide $c(\text{NaOH}) = 0.1 \text{ mol/L}$
- Titrant $c(\text{STPB}) = 0.1 \text{ mol/L}$:
In a beaker 34.223 g sodium tetraphenylborate are dissolved in approx. 200 mL distilled water. This solution is then rinsed into a 1000 mL volumetric flask (into which 20 mL $c(\text{NaOH}) = 0.1 \text{ mol/L}$ have been given beforehand) with distilled water, made up to the mark and mixed.
- Gum arabic solution:
In a beaker 1000 mL distilled water are heated almost to boiling. 50 g gum arabic powder (e.g. Sigma no. G 9752) are added with thorough stirring and the stirring process is continued until everything has dissolved. After cooling, 10 mL formaldehyde solution $w(\text{HCOOH}) = 30\%$ are added to the solution to preserve it. The mixture is allowed to cool overnight and then any deposit that may have been formed is removed by decanting it off. The solution is now ready for use (the added formaldehyde does not interfere with the titration).

Preparation, maintenance and storage of the NIO electrode

- The electrode is conditioned by carrying out two or three titrations whose results are not used. It is also advisable to observe a waiting time of 30 s before each titration so that the electrode can adjust to the sample matrix present.
- After every three or four titrations the electrode is rinsed with methanol or wiped with a tissue moistened with methanol.
- On completion of the titrations, the electrode is wiped with a tissue moistened with methanol and then stored dry.

Analysis

Sample weight

The sample weight should be chosen such that a titrant consumption of 5 ... 8 mL is obtained. If the consumption is outside this range then the titration has to be repeated with a correspondingly corrected sample weight. A preliminary titration should be carried out for samples whose betain content is unknown.

Analytical procedure

A suitable amount of the homogeneous sample solution is weighed into the titration beaker to the nearest 0.1 mg. This is dissolved in 90 mL $c(\text{HCl}) = 0.1 \text{ mol/L}$, 10 mL gum arabic solution are added and titration is performed with thorough stirring using $c(\text{STPB}) = 0.1 \text{ mol/L}$ and, e.g., the following parameters:

```
DET U
>titration parameters
  meas.pt.density  4
  min.incr.        10 µL
  titr.rate        30 mL/min
  signal drift     OFF
  equilibr.time    30 s
  pause           30 s
>stop conditions
  stop V:          abs.
  stop V          15 mL
>evaluation
  EP recognition:  all
```

Care must be taken that the stirring process is optimal during the titration. The solution should be well mixed without, however, air bubbles becoming entrained. Foam formation should be avoided as much as possible.

Calculation

The mean molar mass of the betain to be determined is used to calculate the betain content. $M = 350 \text{ g/mol}$ can be assumed for cocoamidopropyl betain. If the mean molar mass of the betain is not known then a typical molar mass should be used.

The betain content is calculated as the mass fraction to one decimal place. The assumed molar mass used for the calculation must be mentioned when the results are presented. If Metrohm titrators are used this information is automatically contained in the printout of the result report (calculation constant).

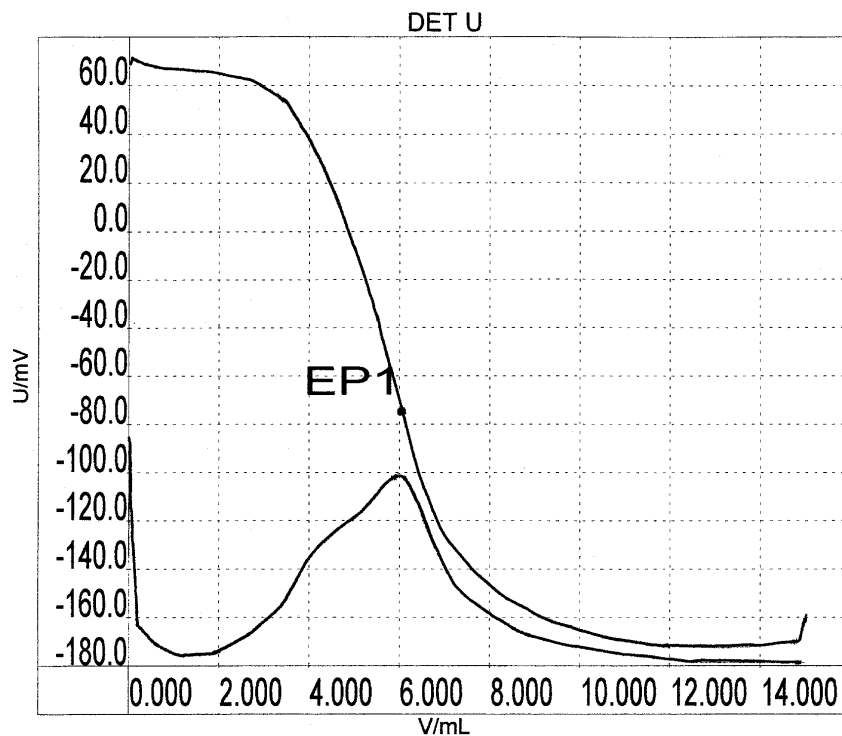
$$\% \text{ betain} = V * c * M / (10 * E)$$

V = titrant consumption in mL to reach the equivalence point

c = 0.1 (concentration of the titrant in mol/L)

M = mean molar mass of the betain to be determined in g/mol

E = sample weight in g



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'fr
Date 07.05.1996 Time 11:26:28           Nr.      7
User      R.Unthan                       TiNet  2.00
Method    Betain with STPB
Id1       Betain
Id2       3
SmplSize                0.6343 g
Endpoints:
DET U.EP1                6.036 ml      -75 mV
Results:
EP1:Betain MG=349              33.21 %
EP2:Betain MG=349              not valid %
    
```

Fig. 1: Titration curve with first derivative and result report of a typical betain titration with sodium tetraphenylborate (716 DMS Titrino with Metrodata TiNet 2.0).

Remarks

- As potassium and ammonium ions also form precipitates with STPB, auxiliary solutions containing these ions should not be used. For the same reason the double junction reference electrode should be filled with $c(\text{NaCl}) = 3 \text{ mol/L}$.
- The NIO electrode should be used only for this titration and not for the titration of non-ionic surfactants.
- Cationic surfactants are also determined because they also form insoluble precipitates with STPB.
- Anionic surfactants react with the protonated betains (cationic surfactants) and also form sparingly soluble ion associates. Their presence therefore leads to results that are too low.

Method B: non-aqueous perchloric acid titration

Electrodes

- 6.0133.100 pH glass electrode with 6.2104.020 electrode cable
- 6.0726.100 Ag/AgCl reference electrode [inner electrolyte $c(\text{KCl}) = 3 \text{ mol/L}$, Metrohm no. 6.2308.020; bridge electrolyte LiCl sat. in ethanol, Metrohm no. 6.2312.000] with 6.2106.020 electrode cable

Reagents

- Titrant: $c(\text{HClO}_4) = 0.1 \text{ mol/L}$ in dioxan
- Methyl glycol, p.a.
- Methanol, p.a.
- Sodium hydroxide/sodium acetate solution:
In a beaker 8 g $\text{NaCH}_3\text{COO} \cdot 3 \text{ H}_2\text{O}$ are dissolved in approx. 30 mL distilled water. In a second beaker 4 g NaOH are also dissolved in approx. 30 mL distilled water. After cooling, the contents of both beakers are transferred to a 100 mL volumetric flask and the solution is made up to the mark.

Analysis

For raw materials with a betain content larger than 20%:

Depending on the betain content, 0.8 ... 1.3 g sample are weighed into the titration beaker to the nearest 0.1 mg and then dissolved in 20 mL methanol. 0.5 mL NaOH/NaCH₃COO solution are added and the mixture is allowed to react at room temperature for 5 ... 10 min. [One or two drops of an ethanolic phenolphthalein solution (0.1%) can be added in order to check whether the mixture is alkaline.] When the reaction time has elapsed a further 20 mL methanol as well as 60 mL methyl glycol are added. After addition of a start volume of 6 mL titrant*, titration is performed with $c(\text{HClO}_4) = 0.1 \text{ mol/L}$ in dioxan using, e.g., the following parameters:

```

DET U
>titration parameters
  meas.pt.density    4
  min.incr.         10 µL
  titr.rate          max.
  signal drift      50 mV/min
  equilibr.time     26 s
  start V:          abs.
  start V           6 mL
  pause             10 s
>stop conditions
  stop V:           abs.
  stop V           30 mL
>evaluation
  EPC              20
  EP recognition:  all
  
```

*) If no start volume is added, a titration curve with three inflection points (EPs) is obtained. The first equivalence point, which is caused by interfering substances, is suppressed by dosing a start volume.

Calculation

The mean molar mass of the betain to be determined is used to calculate the betain content. $M = 350$ g/mol can be assumed for cocoamidopropyl betain. If the mean molar mass of the betain is not known then a typical molar mass should be used. The betain content is calculated as the mass fraction to one decimal place.

$$\% \text{ betain} = (EP2 - EP1) * c * M / (10 * E)$$

EP1 = titrant consumption in mL to reach the first equivalence point

EP2 = titrant consumption in mL to reach the second equivalence point

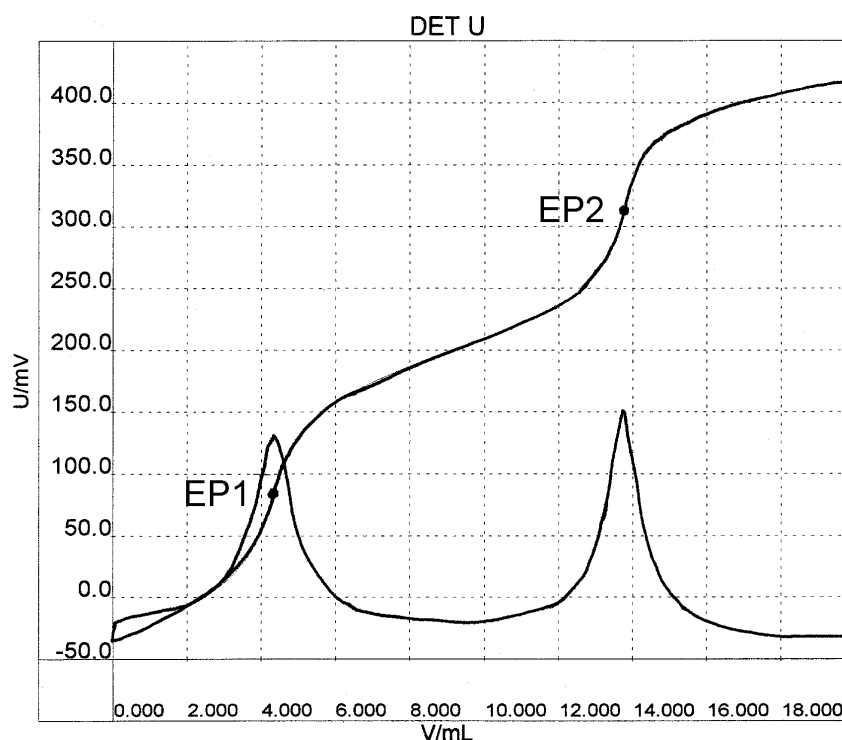
c = 0.1 (concentration of the titrant in mol/L)

M = mean molar mass of the betain to be determined in g/mol

E = sample weight in g

Remarks

- In the perchloric acid titration all compounds that have a betain structure are determined, including trimethylaminoacetic acid as the lowest molecular representative of this group. The presence of this compound in the sample leads to results that are too high.
- It must be assumed that basic compounds with pK values > 10 will also cause interferences. However, such compounds are not expected to be present in betains.



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Date 29.02.1996 Time 13:41:42                               Nr.      4
User      R.Unthan                                           TiNet  2.00
Method    Betain with HClO4
Id1       Betain
Id2       1
SmplSize                               0.9407 g
Endpoints:
DET U.EP1                               4.326 ml      84 mV
DET U.EP2                               13.734 ml    312 mV
Results:
Betain MG=349                           34.90 %
EP3-EP2                                 not valid %
EP3-EP1                                 not valid %
    
```

Fig. 2: Titration curve with first derivative and result report of a typical betain titration with perchloric acid (716 DMS Titrimo with Metrodata TiNet 2.0).

General hints

- It shall be mentioned again that both titration methods are suitable for determining the following compounds:
 - alkylamidopropyl betains, including cocoamidopropyl betain, as well as
 - alkyl betains.
- The methods clearly differ from each other in their possibilities and limitations. Which of the two methods is more suitable depends on the betain that is to be analysed. It may therefore be a good idea to carry out both titration methods in parallel. Interferences can be taken from the table below.

Substance	Method	
	HClO ₄	STPB
TEGO Betain L7	yes	yes
TEGO Betain F	yes	yes
TEGO Betain F50	yes	yes
TEGO Betain CK	yes	yes
TEGO Betain HS	yes	yes
Betain C8	yes	yes
Betain C10	yes	yes
Betain C12 and higher	yes	yes
Alkyl betains	yes	yes
Amidamine	no	yes
Fatty acids	no	no
Glycerol	no	no
Hydrochloric acid	no	no
Glycolic acid	no	no
Monochloroacetic acid	no	no
Dichloroacetic acid	no	no
Trichloroacetic acid	no	no
Acetic acid	no	no
Sodium acetate	no	no
Potassium sorbate	no	no
Formaldehyde	no	no
Sodium chloride	no	no
EDTA	interferes	no
NTA	interferes	no
Aminoacetic acid	interferes	no
Dimethylaminoacetic acid	interferes	no
Trimethylaminoacetic acid	interferes	no
Quaternary surfactants	no	interfere

Assessment of the two methods

The optimised perchloric acid titration is the simpler and more accurate of the two methods. It can be carried out without any problems, has already proved itself in several laboratories and is therefore the method of choice. It is also highly suitable for routine analyses and determinations with sample changers. Approximately 10 ... 15 min are required for a double determination.

A standard deviation of 0.19% can be achieved with this method (n = 10).

The STPB method requires a certain experience in surfactant titrations. It should therefore only be used by specialists who are familiar with the titration of surfactants (effect of the dynamic titration parameters). The precipitated product formed by the protonated betain and STPB can cause problems as it is very substantive and sticky. The electrodes can therefore become coated and measuring errors can occur (frequently cleaning the electrodes with a tissue moistened with methanol helps). Automated determination using a sample changer is only possible with the 730 and 717 Sample Changer models. In this case the electrodes must be rinsed with methanol in a separate beaker. The advantage of this method is that it only determines surfactant-like substances. Low-molecular compounds such as trimethylaminoacetic acid (so-called beet root betain) are not determined.

A standard deviation of 1.04% can be achieved with this method (n = 10).

Literature

- R. Gerhards, I. Jussofie, D. Käseborn, S. Keune, R. Schulz
Modern methods for the analysis of cocoamidopropyl betains
Tenside Surfactants Detergents 33/1 (1996) 8–14.
- R. Schulz,
Titration von Tensiden und Pharmaka – Moderne Methoden für den Praktiker
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