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Determination of anionactive tensides using cetylpyridinium tetrachlorozincate as titrant

Analytical methods in respect to environmental and economical concern, part 20*

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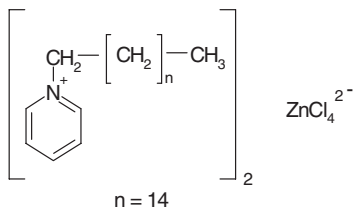
Sodium lauryl sulphate (sodium dodecylsulphate) can be determined in aqueous medium using cetylpyridinium tetrachlorozincate as standard solution and methyl orange resp. bromophenol blue as indicator. However, the determination of cetostearyl sulphate is problematic due to its slight solubility in cold water. Therefore, the titration has to be performed in warm solution. As well with methyl orange as with bromophenol blue the change of the indicator has to be titrated to colour shade. A photometric detection is recommended. The visual indication concerning the determination of the content of the technical solutions of the secondary paraffin sulphonates such as Ateban TH liquid and Marlon® PS 30 is also critical.

1. Introduction

PH. EUR. 2002 determines the anionic active tenside sodium lauryl sulphate (sodium dodecyl sulphate) using a two phase titration and chloroform as solvent and benzethonium chloride as titrant (Hartke et al. 1999a). Furthermore, the method is time consuming, because vigorous shaking and separation of the layers before each addition of titrant is necessary. Benzethonium chloride is hygroscopic and not suitable as primary standard. According to PH. EUR. 2002 the standardisation of the titrant is performed by chloride titration with perchloric acid in anhydrous acetic acid and is obsolete due to the employment of environmentally hazardous mercuric acetate.
For sodium cetostearyl sulphate the assay is performed by a complicated GC-determination (Hartke et al. 1999b).



Cetylpyridinium tetrachlorozincate

As recently published (Hilp and Zembatova 2004), cetylpyridinium tetrachlorozincate can be used as primary standard for the standardisation of dodecyl sulphate solutions using methyl orange resp. bromophenol blue as indicator. Therefore, cetylpyridinium tetrachlorozincate may also be used as standard solution for the titration of anionic active tenside. The titre of this standard solution can be obtained by an accurate weight of the standard or by a simple zinc determination (Hilp Zembatova 2004).

2. Investigations, results, and discussion

No problems arise when titrating sodium lauryl sulphate (sodium dodecylsulphate) in aqueous solutions at a pH-range of 2.6 to 3.0. The change of the indicator is recognised easily, whereby the cetylpyridinium lauryl sulphate ionpair precipitates, when the equivalence point is reached. Using methyl orange the colour changes from red to yellow orange resp. using bromophenol blue from yellow to green.
On the other hand the determination of sodium cetostearyl sulphate is problematic due to its slight solubility. Water has to be heated to dissolve the sample. The hot solution has to be titrated before a part of the substance precipitates. The change of the indicators methyl orange and bromophenol blue is difficult to recognise. It has to be titrated to colour shade. Only a photometric determination for example using a phototrode** removes the subjectivity of the endpoint detection. Then, the determination is independent of the analyst and allows automation of the titration.
The visual indication is also problematic concerning the determination of the technical solution of the sodium salts of secondary paraffin sulphonates such as Ateban TH liquid and Marlon® PS 30.

3. Experimental

3.1. Materials

Ateban TH liquid, 30–31% sodium sec. alkanesulfonate, 1% < C_{13}, 58% C_{13-15}, 39% C_{17}, 2% > C_{17}, Dr. Th. Böhme KG, Chemie und Service, 82527 Geretsried; Marlon® PS 30, 30 ± 0.5% sodium sec. alkanesulfon-

ate, 1% C_{13}, 59%t C_{13-15}, 39% C_{16-17}, 1% C_{17}, Condea Chemie GmbH, 58453 Witten; sodium cetostearyl sulphate [68955-20-4] Lanette E; Cognis GmbH, Düsseldorf; sodium lauryl sulphate (sodium dodecyl sulphate) [151-21-3] for biochemistry and surfactant test ≥ 99.0, Merck art. 1.12533.0050

3.2. Solutions

Bromophenol blue (3 mM): 201 mg (0.3 mmol) of bromophenol blue are dissolved with water to 100 ml; 0.01 M cetylpyridinium tetrachlorozincate: 8.163 mg (10 mmol) of cetylpyridinium tetrachlorozincate (Hilp, Zembatova 2004) are dissolved with water to 1000.0 ml; 3 mM methyl orange: 98.2 mg (0.3 mmol) of methyl orange are dissolved with water to 100 ml. A solution of bromophenol blue and methyl orange is less stable than the separately prepared solution of the indicators.

3.3. Determination of anionic active tenside

3.3.1. Lauryl sulphate (sodium dodecyl sulphate)

$C_{12}H_{25}NaO_4S$, Mr = 228.4; about 57 mg (0.2 mmol) of the sample, accurately weighed, are dissolved in 50 ml of water. After addition of 0.5 ml of 0.1 M HCl to reach a pH-value of about 2.6 and 0.1 ml of 3 mM methyl orange titrate with 0.01 M cetylpyridiniium tetrachlorozincate until the red colour of the solution changes to yellow orange; $n = 7$; $\bar{x}$ =100.1%; $s_{rel} = 0.17\%$

3.3.2. Sodium cetostearyl sulphate

Calcd. as a mixture of 50% $C_{16}H_{33}NaO_4S$ ($M_r = 344.5$) and of 50% $C_{18}H_{35}NaO_4S$, ($M_r = 372.5$); about 71.7 mg (0.1 mmol) accurately weighed are dissolved in 50 ml of water by heating. Cool down in such a manner, that no precipitation is allowed to arise. Add 0.1 ml of 3 mM bromophenol blue and 1.0 ml of 0.1 M HCl (pH 2.8), titrate the still warm solution with 0.01 M cetylpyridinium tetrachlorozincate until the yellow colour changes to green. The indicator change is difficult to recognize. It has to be titrated to colour shade.
$n = 7$; $\bar{x} = 95.8\%$; $s_{rel} = 0.89\%$

3.3.3. Ateban TH flüssig, 30–31% sodium sec. alkanesulfonate

$\sim C_{15}H_{31}NaO_3S$, $\sim M_r = 314.5$, about 209 mg (0.1 mmol), accurately weighed, are dissolved in 50 ml of water. After addition of 1.0 ml of 0.1 M HCl to reach a pH-value of about 2.7 and 0.1 ml of 3 mM methyl orange titrate with 0.01 M cetylpyridiniium tetrachlorozincate until the red colour of the solution changes to yellow orange. The indicator change is difficult to recognize. It has to be titrated to colour shade; $n = 7$; $\bar{x} = 29.7\%$; $s_{rel} = 1.54\%$.

3.3.4. Marlon® PS 30, 30 ± 0.5% sodium sec. alkanesulfonate

See Ateban TH; $n = 7$; $\bar{x} = 30.4\%$; $s_{rel} = 0.45\%$

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* Part 19: Hilp and Zembatova (2004)
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