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Short communication

Determination of amphoteric surfactants in cosmetic cleansing products by high-performance liquid chromatography on a cation-exchange column

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Abstract

An HPLC method with diode-array detection at 210 nm is described for the routine determination of amphoteric surfactants with a betaine structure in cosmetic cleansing products. In a strongly acidic pH range cocamidopropylbetaine and alkylbetaine are successfully separated from non-ionic and anionic matrix components on a cation-exchange column (Nucleosil 100-5 SA, 5 μm , 250 \times 4 mm I.D.). Chromatographic separation was carried out under isocratic conditions at a flow-rate of 1.0 ml/min. The mobile phase consisted of 70% acetonitrile and 30% 0.05 M lithium hydroxide in water, adjusted to pH 1.6 with phosphoric acid (v/v). As sample preparation the products and standards were simply diluted and subsequently filtered before injection. The method is precise, robust, independent of the shampoo matrix and thus suitable for routine use, such as product quality control.

1. Introduction

Today the use of cosmetic cleansing products, such as shampoos or shower foams and foam baths, has become an important part of our regular habits and, as consumers, it is difficult to imagine life without them. Besides the auxiliary agents, such as thickeners, opacifiers, perfume oils, colourants and preservatives, the detergents are the most important ingredients of such products. From the analytical point of view the present formulations represent extremely complex mixtures on account of their numerous components, of which the surfactants can also exhibit variation in the length of the carbon chain and the degree of ethoxylation.

A typical present-day formula could contain an anionic (e.g. alkyl ether sulfate), a non-ionic (e.g. alkyl polyglucoside) as well as an amphoteric surfactant (e.g. cocamidopropylbetaine) as cleansing agents. As amphoteric surfactants are gentle to the skin and mucous membranes, they particularly influence the quality of a shampoo. For this reason it is absolutely essential to have an efficient but uncomplicated method to quantify them in the appropriate products.

In the past, several papers were published dealing with the solution of this problem using HPLC on different types of columns and with different detection techniques [1–5]. When we repeated these methods in our laboratory we discovered, however, that the determination was highly dependent on the product matrix and was in many cases impossible. Therefore, we de-

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veloped a method on a cation-exchange column in the strongly acidic pH range to enhance the selectivity so that neutral or anionic matrix components show no retention, but the amphoteric surfactants are retarded, as they carry a positive charge under these conditions. Thus, the detection and quantitative determination of the two most important members of this class of compounds in our shampoos, i.e. cocamidopropylbetaine and alkylbetaine, are described in the following.

2. Experimental

2.1. Chemicals

Acetonitrile and HPLC grade water were supplied by Zinsser Analytik (Frankfurt, Germany), orthophosphoric acid (85%, p.a.) and lithium hydroxide (approx. 98%) were supplied by Merck (Darmstadt, Germany). Cocamidopropylbetaine (Fig. 1) was obtained from Goldschmidt (Essen, Germany) as the raw material Tego Betain L7 (approx. 30% active substance in water). Alkylbetaine (Fig. 2) was obtained from Kaprolactam (Dzerzhinsk, Russia) as a 30% aqueous solution.

The alkyl chain-lengths of cocamidopropylbetaine are given by the supplier and correspond to the well-known coconut fatty acid distribution. The chain-length distribution of the alkylbetaine raw material was determined by a GC-MS method, where the betaines are pyrolyzed in the injection port of the GC to the

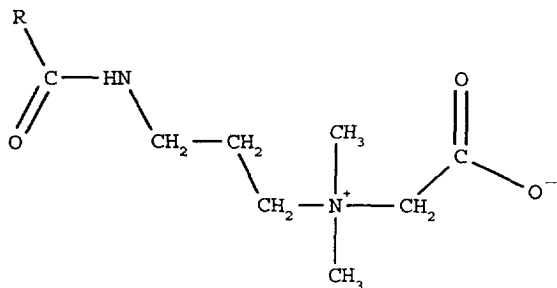


Fig. 1. Structure of cocamidopropylbetaine, R = alkyl chains of coconut fatty acids.

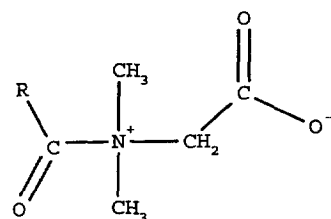


Fig. 2. Structure of alkylbetaine, R = alkyl chains of C₁₂ and C₁₄ fatty acids.

corresponding N,N-dimethylalkylamines which afterwards can be separated and quantified [6].

2.2. Instrumentation

The analyses were carried out on a liquid chromatograph HP 1090 Series M (Hewlett-Packard, Palo Alto, CA, USA) with autosampler, HPLC^{3D} ChemStation (DOS series) and a diode-array detector operated at a wavelength of 210 nm.

2.3. Chromatographic conditions

A cation-exchange column Nucleosil 100-5 SA, 5 μm , 250 \times 4 mm I.D. (Macherey-Nagel, Düren, Germany) was used. The mobile phase consisted of 70% acetonitrile and 30% 0.05 M lithium hydroxide in water, adjusted to pH 1.6 with phosphoric acid (v/v). Separation was carried out under isocratic conditions at a flow-rate of 1.0 ml/min and a constant temperature of 40°C. The injected sample volumes were 10 μl in each case.

2.4. Sample preparation

Before injection the shampoos were diluted approximately 1:10 to 1:20 with water and suspended matter was removed by filtration with a membrane syringe filter (0.45 μm , Hewlett-Packard). The calibration solutions were prepared in the same way. The dilution depends on the expected concentration in the formulations.

3. Results and discussion

Fig. 3 shows a typical chromatogram of commercially available shampoos containing alkylbetaine (left) or cocamidopropylbetaine (right). The distribution of the fatty acid homologues corresponds to the surfactant raw materials used. It is evident that the selectivity of the column achieves excellent separation of the shampoo matrix. Thus all the non-ionic or anionic components are eluted long before the betaines.

Although the cocamidopropylbetaines are separated better than the alkylbetaines under the conditions described, the separation efficiency was satisfactory in both cases.

For the quantitative determination the cali-

bration curves were plotted according to the external standard method based on the areas of the C₁₂ homologues in each case. In the concentration range for shampoos (0.1-2% by weight), when dilution is taken into account, the linearity according to the equation $y = mx + b$ is very good. The regression data for alkylbetaine ($m = 7.21$, $b = -0.608$, correlation coefficient = 0.99991) and cocamidopropylbetaine ($m = 78.92$, $b = 8.84$, correlation coefficient = 0.99984) were obtained with 5 data points each.

The results of the quantitation of the betaines in two commercially available shampoos are summarized in Table 1. Both alkylbetaine in shampoo 1 and cocamidopropylbetaine in shampoo 2 can be determined with a high degree of precision and accuracy.

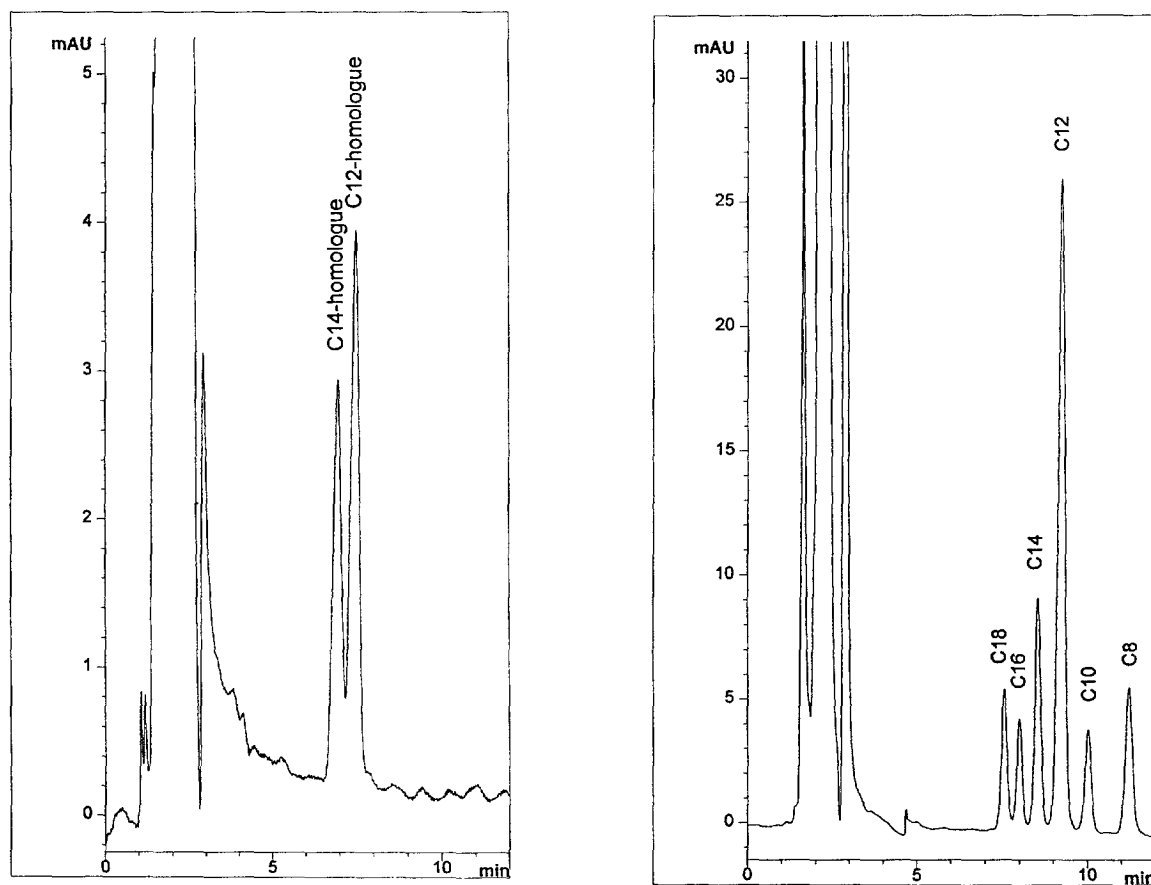


Fig. 3. Chromatograms of shampoos with alkylbetaine (left) and cocamidopropylbetaine (right) under the analytical conditions described above.

Table 1

Values obtained in the determination of alkylbetaine and cocamidopropylbetaine in commercially available shampoos with mean, standard deviation and expected value

Measurement No.	Percentage (w/w) of alkylbetaine in shampoo 1	Percentage (w/w) of cocamidopropylbetaine in shampoo 2
1	5.01	5.04
2	4.88	5.06
3	4.94	5.04
4	4.89	5.03
5	4.96	4.97
6	5.09	5.05
7	4.76	4.99
8	5.08	5.06
Mean	4.95	5.03
S.D.	0.11	0.033
Expected	5.0	5.0

4. Conclusions

The method described here for the determination of the amphoteric surfactants with betaine structure is rapid and uncomplicated on the one hand, and also precise and robust on the other, as we ascertained in the analysis of numerous shampoos and shower foams. For us, this method represented a considerable improvement over the methods previously presented in papers on this subject. It is also eminently suitable for use as a routine method in production quality control.

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