Quantification of Stepantex of ^{1}H NMR spectroscopy

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Introduction

Stepantex is a component of the washing powder Minidou and has a softener capacity. It is a mixture, which contains esteramines, quaternary esters, triethanolamine and quaternary triethanolamine. Stepantex is synthesized by a quaternization reaction of esters with a quaternization agent: dimethylsulfate (DMS). The objective is to determinate the mass percentage of these quaternary esters in the Stepantex mixture which contains three sorts of quaternary esters: mono, di and tri- quaternary esters.
Several analysis techniques can be used. However ^{1}H NMR spectroscopy is the most appropriate for this mixture because there is no ionization competition like in MS spectroscopy. Moreover it is more repeatable compared to the Liquid Chromatography.

Experimental conditions

The first goal was to collect pure quaternary esters by the Liquid Chromatography with a NH2 preparation column (250 mm x 10 mm, particle diameter: 5 µm) and a fraction collector coupled to the UV detector. The mobile phase used is consisted of 85 per cent of hexane, 10 per cent of methanol, 5 per cent of tetrahydrofuran (THF) and 0.05 per cent of trifluoroacetic acid (TFA). This mobile phase is not polar because through contact of water, Stepantex causes an emulsion.

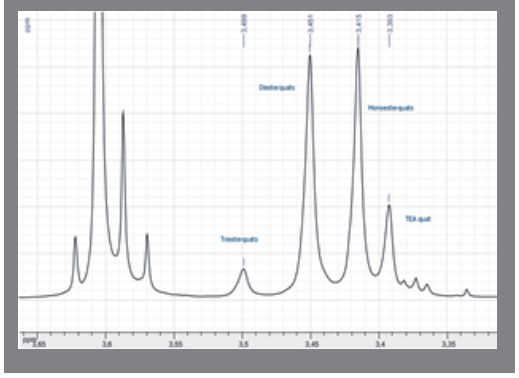
The experimental conditions used were:
Flow rate: 5 mL/min
Injection volume: 500 µL
Detection wavelength: 220 nm

Results and discussion

Quaternary esters fractions NMR spectra were individually recorded on a 400 MHz spectrometer. Each sample purity was then checked. Those spectra were compared to the NMR spectrum of Stepantex mixture.
The three quaternary esters were collected (5 to 10 mg) and analyzed in a mixture of solvents acetone – chloroform (70-30) in a volume of 600 µL. This mixture guarantees a good splitting of resonances in proton and carbon spectra. The ^{1}H spectra obtained serve as outer reference for the ERETIC quantification method. To ensure the quantification is reliable, all the spectra were recorded with the same parameters: scans number (64), gain (101.6) and relaxation period (5s).
Finally, nine samples of Stepantex mixture were prepared. We measured the mono, di and tri- quaternary esters' mass percentages contained in the mixture in order to assess the reproducibility and repeatability of the experiment. Also, we have taken into account the content in counter-ion (methosulfate) has to be taken into account to measure the quantity of active matter present in the Stepantex mixture.

Three types of quaternary esters were distinctly separated (see figure). The integration of each characteristic peak and the use of the ERETIC method allow quantifying the proportions of each quaternary ester in the Stepantex mixture, without using a separative chromatography step.

Figure — Stepantex ^{1}H NMR spectrum, zoom on the characteristic chemicals shifts of mono, di and tri- quaternary esters (3.40 to 3.50 ppm, 400 MHz)



Conclusion

To conclude, the Stepantex mixture contains:
- (36.1± 2.6)% of mono quaternary esters
- (54.4% ± 2.4)% of di quaternary esters
- (9.5% ±1.0)% of tri quaternary esters.

Those mass percentages, determined on nine samples, considering counter-ion and represent active matter 70 per cent in the Stepantex mixture.

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