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High temperature liquid chromatography and liquid chromatography–mass spectroscopy analysis of octylphenol ethoxylates on different stationary phases

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Abstract

Temperature was investigated as active parameter in the liquid chromatography (LC) analysis of octylphenol ethoxylates. Significant differences in selectivity were observed when the oligomers were analyzed by reversed phase LC (RPLC) on silica-, zirconia- and polystyrene/divinylbenzene based stationary phases at low (ambient), medium and elevated temperature with acetonitrile/water as mobile phase. As ascertained by LC–mass spectroscopy (MS), in most cases the elution order of the oligomers was completely reversed comparing ambient and high temperature separations. On a graphitized carbon type column, the selectivity remained unchanged, regardless the analysis temperature. Also in normal phase LC, the elution order remained unaffected by temperature variations both for acetonitrile/water and methanol/water mixtures as mobile phase. Surprisingly, when reversed phase LC on a octadecylsilicagel column at different temperatures was repeated with methanol instead of acetonitrile as mobile phase ingredient, the reversal of elution order did not take place. Results are evaluated in terms of thermodynamic parameters.

Keywords: LC; LC–MS; Temperature; Octylphenol ethoxylates; Selectivity

1. Introduction

The use of elevated temperatures and temperature programming in liquid chromatography (LC) is gaining momentum in recent years [1–9]. At the present time, the number of applications of high (or elevated) temperature LC is still limited mainly because of lack of suitable stationary phases and equipment. Of utmost importance is adequate control of mobile phase and column temperature. In this respect, problems could be circumvented by using packed capillary columns exhibiting low heat capacity and negligible radial temperature gradients. Instrumentation for elevated temperature conventional LC became recently available to efficiently heat the entering mobile phase to the same temperature as the column (oven) temperature. In this way, loss of separation and efficiency due to thermal mismatch between mobile and stationary phase is eliminated. The effluent temperature is actively controlled by a Peltier element to stabilize and protect the detector.

Presently, the limiting factor in using high temperature in conventional LC is the stability of bonded silica-based stationary phases. Silica-based stationary phases usually are stable at temperatures up to 90 °C; although some novel reversed phase material can be used up to 120 °C [8,9]. When using water in the mobile phase as in reversed phase type separations, loss of bonded phase from the silica support due to hydrolysis is more pronounced at high temperatures [10]. Stationary phases with higher temperature stability are based on materials other than silica e.g. graphitized carbon types, zirconium oxide based phases and polystyrene/divinylbenzene phases.

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Alkylphenol ethoxylates are important technical nonionic surfactants widely used in industrial and household applications. The production process generally does not generate one discrete molecule, but a disperse distribution of compounds. Quality and application area of the product is greatly determined by the chain length distribution and the purity of the synthesized product. To determine these characteristics, several separation techniques can be applied. Reversed phase LC (RPLC) and normal phase LC (NPLC) with UV detection are by far the most popular techniques for these analyses.

Analyses are normally carried out at ambient temperatures or temperatures slightly higher than ambient. Using acetonitrile–water as mobile phase in RPLC, a chain length distribution separation is obtained which is controlled by hydrophobic interaction [11]. The large, less hydrophobic oligomers elute before oligomers with a smaller degree of polymerization. For normal phase separations, this elution order is opposite and the larger oligomers are more retained on the column. When the reversed phase analysis is carried out at moderately elevated temperatures (e.g. 50 °C) with the same mobile phase composition, the selectivity between oligomers with different chain lengths is significantly reduced and consequently, little or no oligomeric separation takes place. At higher temperatures than this 'critical' temperature a chain length distribution separation reappears, however, with inversed elution order compared to analyses at ambient temperature.

At present, the reason for this phenomenon is not completely obvious, but size-exclusion effects seem not to cause this reversal. The effect is most interesting since reversed selectivity by temperature can be achieved on the same instrument, with the same column, and with the same mobile phase composition. Several publications describe this selectivity change for polymers with ethylene oxide (EO) units. Melander et al. [12] observed more than 20 years ago increased retention of PEG 400 at elevated temperature in RPLC. Escott and Mortimer operated an ODS column at 80 °C for a separation of a blend of PEGs and they reported an improved resolution compared to ambient temperature [13]. Lochmüller et al. [14] also observed an increased retention of PEO samples with increased temperature in RPLC on a silica-based C18 stationary phase with a mobile phase composed of water and acetonitrile. The group of Greibrokk applied inverse temperature programming in RP-packed capillary LC for improved separation of PEG oligomers [15]. Cho et al. [16] recently reported on the temperature dependence of retention of poly(ethylene oxide) (PEO) and fatty alcohol ethoxylates (FAE) [17] in RPLC. Significant selectivity changes caused by changes in analysis temperature were observed. Kamiusuki et al. [18] have reported on the separation of octylphenol ethoxylates on branched fluorinated silica gel columns. The oligomers were separated according to increasing number of ethylene oxide units. The mobile phase was a mixture of water and methanol. Increasing the temperature from 40 to 70 °C resulted in a shorter retention time, however, without affecting selectivity.

The aim of this study was to investigate the potential of using temperature as active variable in the LC analysis of octylphenol ethoxylates using the present state-of-the-art in column technology and instrumentation.

2. Experimental

2.1. Chemicals and samples

All solvents used were HPLC grade from Biosolve Ltd. (Valkenswaard, The Netherlands). Triton X-100 from Sigma-Aldrich (Bornem, Belgium) was dissolved in water/acetonitrile, 1/1 (v/v) for RPLC analyses and in water/acetonitrile, 1/9 (v/v) for NPLC analyses.

2.2. Instrumental

Analyses were performed using an Agilent 1100 Series LC equipped with a diode array detector (Agilent Technologies, Waldbronn, Germany) set at 225 nm. All analyses were carried out in the isocratic mode. The column temperature was controlled with a Polaratherm Series 9000 oven equipped with a mobile phase preheater and cryo-option (Selerity Technologies, Salt Lake City, UT, USA). The preheater temperature was set equal to the oven temperature and the effluent temperature at 40 °C.

The mass spectrometer was an Agilent 1100 Series Quadrupole MSD version SL equipped with an atmospheric pressure chemical ionization (APCI) source (Agilent Technologies, Waldbronn, Germany). Positive ionization was

Table 1
LC columns with details on column dimensions and packing material

Column (stationary phase)	Dimensions $L \times$ I.D. (particle size)	Base material	Pore size (Å)
Agilent Zorbax StableBond (C18)	150 mm × 3.0 mm (3.5 μm)	Silica, sterically protected	80
Agilent Zorbax StableBond (C18)	150 mm × 4.6 mm (3.5 μm)	Silica, sterically protected	300
Agilent Zorbax StableBond (phenyl)	150 mm × 3.0 mm (3.5 μm)	Silica, sterically protected	80
Selerity Blaze (C8)	150 mm × 4.6 mm (3 μm)	Silica, poly dentate	100
Zirchrom PBD (polybutadiene)	150 mm × 2.1 mm (3 μm)	Zirconium oxide	300
Polymer Laboratories PLRP-S (polystyrene/divinylbenzene)	150 mm × 2.1 mm (3 μm)	Polystyrene/divinylbenzene	100
Thermo Electron Hypercarb (graphitized carbon)	100 mm × 3.0 mm (5 μm)	Graphitized carbon	250
Phenomenex Ultremex 3 Silica (silica)	75 mm × 4.6 mm (3 μm)	Silica	80