Separation and Quantitative Analysis of Alkyl Sulfate Ethoxymers by HPLC

Julien Morvan[1], Marie Hubert-Roux[2], Valérie Agasse[1], Pascal Cardinael[1,*], Florence Barbot[3], Gautier Decock[3], and **Jean-Philippe Bouillon[1]**

[1]Laboratoire Synthèse et Chromatographie, Sciences et Méthodes Séparatives, UPRES EA 3233, Université de Rouen, rue Tesnières, F-76821 Mont Saint Aignan Cedex, France; [2]CNRS-UMR 6014, Laboratoire de Spectrométrie de Masse Bio-organique, Université de Rouen, rue Tesnières, F-76130 Mont Saint Aignan, France; [3]YSL Beauté Recherche et Industries, route de Noyon, F-60310 Lassigny, France

Abstract

Separation of alkyl sulfate ethoxymers is investigated on various high-performance liquid chromatography (HPLC) stationary phases: Acclaim C_{18} Surfactant, Surfactant C_8, and Hypercarb. For a fixed alkyl chain length, ethoxymers are eluted in the order of increasing number of ethoxylated units on Acclaim C_{18} Surfactant, whereas a reversed elution order is observed on Surfactant C_8 and Hypercarb. Moreover, on an Acclaim C_{18} Surfactant column, non-ethoxylated compounds are eluted in their ethoxymers distribution and the use of sodium acetate additive in mobile phase leads to a co-elution of ethoxymers. HPLC stationary phases dedicated to surfactants analysis are evaluated by means of the Tanaka test. Surfactant C_8 presents a great silanol activity whereas Acclaim C_{18} Surfactant shows a high steric selectivity. For alkyl sulfates, linearity of the calibration curve and limits of detection and quantitation are evaluated. The amount of sodium laureth sulfate raw material found in commercial body product is in agreement with the specification of the manufacturer.

Introduction

Surfactants are amphiphilic molecules possessing hydrophilic and hydrophobic parts. Due to their specific chemical and physical properties, they are widely used in cosmetic products such as shampoos, shower gels, or creams as emulsifier, viscosifier, or texturing agent. These compounds are classified in four groups: anionic, cationic, non-ionic, and amphoteric surfactants, depending on the charge of the hydrophilic part. In personal care products, ethoxylated fatty alcohols (non-ionic) and alkyl sulfates (anionic) are the most widely used (1). Ethoxylated compounds are obtained by condensation of ethylene oxide on fatty alcohols with different alkyl chain lengths (usually ranging from 8 to 18 carbon atoms). Therefore, commercial surfactants are generally complex mixtures. Their composition (distribution of ethoxymers and alkyl chain length) influences their physical and chemical properties (foaming, viscosity, detergency, critical micellar concentration) (2–4). Moreover, quantification of surfactant is important to ensure product quality control and environmental monitoring. Their complete characterization requires the knowledge of: (*i*) hydrophilic moiety; (*ii*) alkyl chain length; (*iii*) ethoxylation degree (if necessary) (3).

Surfactants are described according to usual abbreviations: C_nEO_m, where n is the number of carbon of the alkyl chain and m is the number of condensed ethylene oxide units. The structure of alkyl sulfates is given in Figure 1.

Previously, gas chromatographic methods were used (5,6) for the determination of ethoxylation distribution after derivatization, but were limited by the low volatility of the compounds even at high temperature.

Therefore, HPLC is suitable to analyze complex mixture of surfactants. Several methods have been developed including various HPLC modes and detectors (7–9). Recently, the substitution of refractive index detector by evaporative light scattering detector (ELSD) has enhanced the sensitivity of the method and has allowed the use of solvent gradient (7). Moreover, methods developed with ELSD are more easily transferred to HPLC–MS methods with few or no modifications.

While the selectivity of suppressed conductivity detector is particularly interesting for the quantitation of ionic surfactants in complex mixtures, ion chromatography methods have not offered a good resolution between ethoxymers (10,11). To overcome this drawback, Rocca et al. (12) have collected fractions of surfactant following alkyl chain length by HPLC. The fractions were reinjected on the same column (Kromasil C_{18}) using another elution gradient to separate ethoxymers. Futhermore, two-dimensional HPLC was applied to separate various families of surfactants but the resolution between the anionic ethoxymers remained too low (13). Recently, columns especially dedicated to the analysis of sur-

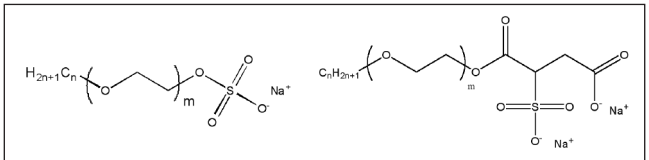

Figure 1. Structures of sodium ethoxylated alkyl sulfates and disodium ethoxylated alkyl sulfosuccinates $8 \leq n \leq 18$, $m \geq 0$.

* Author to whom correspondence should be addressed: email Pascal.Cardinael@univ-rouen.fr.

factants have been developed like Acclaim C_{18} Surfactant (Dionex) and Surfactant C_8 (Alltech) (14,15).

In this study, commercial sodium ethoxylated alkyl sulfates and disodium ethoxylated alkyl sulfosuccinates were analyzed on three columns: Acclaim C_{18} Surfactant, Surfactant C_8, and Hypercarb. In the first part, the chromatographic performances of columns were compared and the influence of the nature of the salt in the mobile phase was investigated. Particular attention was given to the determination of the elution order of oligomers with mass spectrometric detection. To improve the knowledge of these surfactant-specific columns, Tanaka test and comparison with conventional C_8 and C_{18} columns were performed. In a second part, limits of detection (LOD) and quantitation (LOQ) were measured using conductivity detector. The amount of sodium laureth sulfate raw material in a commercial body product was also determined.

Experimental

Reagents and standards

Acetonitrile (MeCN), methanol (MeOH), and dichloromethane (CH_2Cl_2) were HPLC grade (Acros Organics, Noisy-le-Grand, France). Water was provided by a MilliQ ultrapure system (France). Ammonium acetate, benzylamine, phenol, uracil, phosphoric acid, sodium acetate, and sodium dodecyl sulfate were supplied by Acros Organics (Noisy-le-Grand, France). Butylbenzene, pentylbenzene, triphenylene, and o-terphenyl were purchased from Alfa Aesar (Bischheim, France). Sodium phosphate dibasic, sodium phosphate monobasic, caffeine, and sulphuric acid were obtained from Sigma Aldrich (Saint-Quentin-Fallavier, France). Commercial surfactants, sodium laureth sulfate, and disodium laureth sulfosuccinate were provided by Cognis, Huntsman, and Degussa-Goldschmidt. Body oil was given by YSL Beauté Recherche et Industries (Lassigny, France).

Instrumentation

HPLC analyses were performed on a liquid chromatograph (quaternary pump P2000) equipped with a degasser, an autosampler (AS100) from Thermo Separation Products (Les Ulis, France), and a Polymer Laboratories evaporative light scattering detector PL-ELS2100 (Marseille, France). Data processing was carried out with ChromQuest 2.51 software from ThermoQuest Corporation.

Conductimetric detection was realized using a detector ED50 and a suppressor (AMMS III 4 mm) from Dionex (Voisins-le Bretonneux, France). The solution used to regenerate the suppressor was a 10mM sulfuric acid solution at a flow of 5.0 mL/min. Data were processed with Chromeleon 6.40 SP5 software supplied by Dionex.

HPLC–MS experiments were performed with an Agilent 1200 chromatographic system (Agilent technologies, Waghaeusel-Wiesental, Germany) equipped with a G1379B degasser, a G1312A high-pressure binary pump, a G1329A autosampler and coupled to an Esquire–LC ion-trap mass spectrometer (Bruker Daltonics, Wissembourg, France). The ESI parameters were: capillary voltage, +4 kV; end plate, +3.5 kV; and skimmer 1 voltage, –32.7 V. Nitrogen was used as the drying (9 L/min, 300°C) and nebulizing (30 psi) gas. Helium was the buffer gas and the pressure in the ion trap was 1.2 10^{-5} mbar. Negative ions were detected using the standard scan at normal resolution: the scan speed was 13000 *m/z*/s and the mass resolution was 0.6 U at half peak height (FWHM) over a mass to charge range 50 to 1000 *m/z*.

Columns were purchased from Dionex (Acclaim C18 Surfactant, 250 mm × 4.6 mm, 5 µm), Alltech (Surfactant C8, 250 mm × 4.6 mm, 5 µm), Waters (Xterra MS C18, 250 mm × 2.1 mm, 5 µm), Varian (Polaris Amide C18, 150 mm × 3.0 mm, 3 µm), and Thermo Electron (Hypercarb, 150 × 3.0 mm, 7 µm).

Acclaim C18 Surfactant packing material (pore size: 120Å, carbon percentage: 12%, surface area: 300 m^2/g^{-1}), consisting of hydrophobic chains, tertiary amino groups, and polar amide functional groups, is designed for the separation of various surfactants (14). Surfactant C8 (carbon percentage: 5%) is recommended for analyses of short chain anionic surfactants such as alkyl sulfates and alkyl sulfonates. No further information on packing material characteristics is available.

The Tanaka test was performed using the chromatographic conditions described by Claessens (16). The flow rate was set at

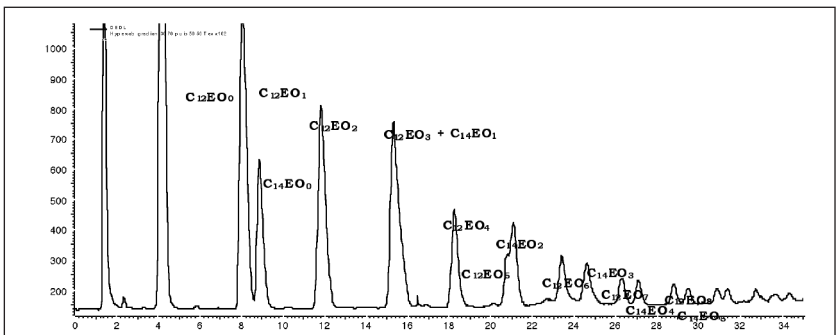

Figure 2. Chromatogram of sodium laureth sulfate (5 g/L) on Hypercarb, 150 mm × 3.0 mm, 0 min: 90% MeOH–10% CH_2Cl_2 with 0.1 mol/L NH_4OAC, 15 min; 70% MeOH–30% CH_2Cl_2 with 0.1 mol/L NH_4OAC, 30 min; 50% MeOH–50% CH_2Cl_2 with 0.1 mol/L NH_4OAC, 0.8 mL/min, evaporative light scattering detector: nebuliser: 40°C, evaporator: 50°C, gas (nitrogen): 1.3 L/min, injection volume: 5 µL.

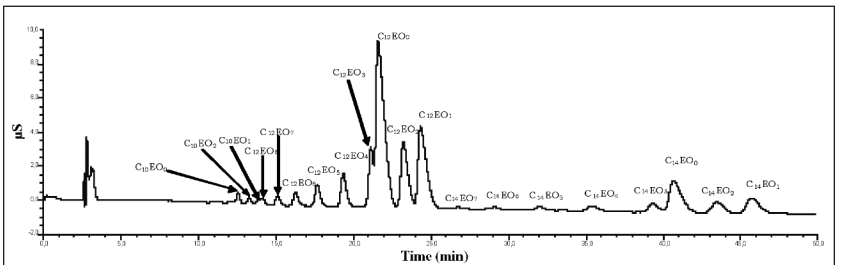

Figure 3. Chromatogram of sodium laureth sulfate (2 g/L) on Acclaim C_{18} surfactant column, 250 mm × 4.6 mm, 5 µm, 50% MeCN, 50% 0.1 mol/L NH_4OAc in water (v/v), 1 mL/min, AMMS III H_2SO_4 5 mmol/L regeneration at 5 mL/min, conductimetric detection, injection volume: 25 µL.

0.2 mL/min for i.d. 2.1 mm, 0.5 mL/min for i.d. 3.0 mm, and 1 mL/min for i.d. 4.6 mm. The concentrations of the analytes were: pentylbenzene, 5.0 mg/mL; butylbenzene, 5.0 mg/mL; triphenylene, 0.2 mg/mL; o-terphenyl, 0.2 mg/mL; caffeine, 0.5 mg/mL; phenol, 2.0 mg/mL; benzylamine, 1.0 mg/mL; and uracil, 0.2 mg/mL.

Results and Discussion

Analyses of anionic surfactants on various stationary phases

The first part of the study deals with the analyses of ethoxylated alkyl sulfates and alkyl sulfosuccinates (Figure 1) (respectively named sodium laureth sulfates and disodium laureth sulfosuccinates) on columns designed for surfactant analyses (Surfactant C_8 and Acclaim C_{18} Surfactant) and porous graphitic carbon stationary phase (Hypercarb). The selectivity between the ethoxymers (α_{EO}) is calculated in equation 1, where $tr_{CnEOm+1}$ and tr_{CnEOm} are the retention times of sulfate ethoxymers with an alkyl chain length of n carbons and possessing, respectively, m + 1 and m ethylene oxide units. t_0 represents the column dead time which is determined by the injection of uracil.

$$\alpha_{E0} = \frac{tr_{CnEO\ m+1} - t_0}{tr_{CnEOm} - t_0} \qquad \text{Eq. 1}$$

As previously described (17), polyethoxylated alcohols were successfully separated on Hypercarb column using a mixture of CH_2Cl_2–MeCN or ethyl acetate–MeCN. Moreover, the polarizability of the graphitic surface allows the retention of very polar solutes such as inorganic anions (18,19). So, addition of salt(s) in the mobile phase seems necessary to ensure the elution of anionic surfactants. Figure 2 presents the chromatogram of sodium laureth sulfate obtained on Hypercarb in gradient elution (MeOH–CH_2Cl_2) using ammonium acetate (NH_4OAc) as additive. This salt was selected according to its compatibility with ELSD and MS detectors. Moreover, strength elution of an aqueous mobile phase was not sufficient to elute these surfactants in relation to hydrophic interactions between alkyl chain and graphitic surface (17). MeCN is unsuitable to dissolve NH_4OAc. The elution order was determined by HPLC–MS. Alkyl sulfate ethoxymers were eluted in the order of increasing number of ethoxylated units for a fixed alkyl chain length ($\alpha_{EO} > 1$) and following the chain length of fatty alkyl part ($C_{12}E_0$ is eluted before $C_{14}E_0$). This phase presented a very high selectivity α_{EO} in relation to polar interactions between ethylene oxide moieties and porous graphitic carbon surface. However, under these conditions, $C_{14}EO_0$ and $C_{12}EO_1$ as well as $C_{14}EO_2$ and $C_{12}EO_5$ were partially coeluted and $C_{14}EO_1$ and $C_{12}EO_3$ were not separated. So the selectivity between the alkyl chains remained too low to prevent an overlap between C_{12} and C_{14} oligomers. The increase of NH_4OAc content up to 0.2 mol/L had no significant improvement on retention and selectivity.

Recently, Pohl et al. (14) have reported the use of Acclaim C_{18} Surfactant for the separation of various surfactants. Ethoxylated alkyl sulfates were analyzed on this column with 50% MeCN, 50% 0.1 mol/L NH_4OAc in water as mobile phase. The chromatogram obtained, in the same chromatographic conditions, is given in Figure 3. The peak shapes are satisfactory. Elution order was determined by HPLC–MS (Figure 4) using extracted ion currents (EIC) of each ethoxymer. Acclaim C_{18} Surfactant column presents an $\alpha_{EO} < 1$ and non-ethoxylated compounds ($C_{12}EO_0$ and $C_{14}EO_0$) were eluted in the distribution of their ethoxymers (between EO_2 and EO_3). This observation remains difficult to explain. If only pure reversed phase mechanisms were involved in the retention, non-ethoxylated compounds should be the most retained for a given alkyl chain length.

The elution order of alkyl sulfate ethoxymers on Acclaim C_{18} Surfactant (Figure 3) is unusual for a "C_{18} phase". For example, $\alpha_{EO} > 1$ was measured on Xterra MS C_{18} (Figure 5) using the same mobile phase. Moreover, $C_{12}EO_m$ ethoxymers were not well separated for m > 4 on this stationary phase.

On Acclaim C_{18} Surfactant, the separation of ethoxylated alkyl sulfosuccinates was quite similar to those observed for alkyl sulfates but non-ethoxylated compounds were eluted after their ethoxymers (Figure 6).

Stemp et al. (15) have described the separation of ethoxylated alkyl sulfates on Surfactant C_8 using a mixture of 45% MeOH, 55% 0.25 mmol/L NH_4OAc in water (v/v) as mobile phase. The

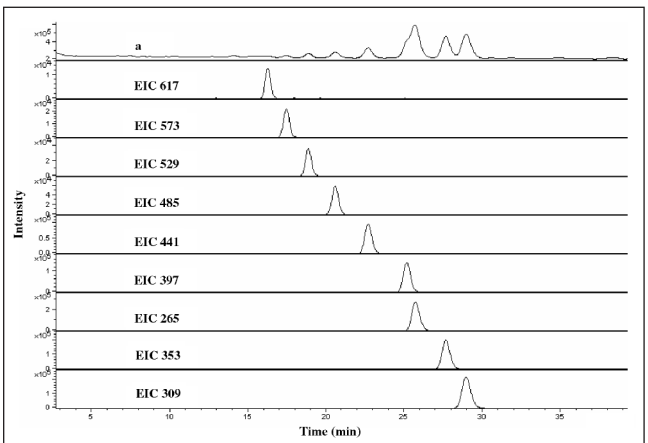

Figure 4. LC–MS chromatogram of sodium laureth sulfate (a) and extracted ion chromatograms of M^- ions of alkyl sulfate ethoxymers.

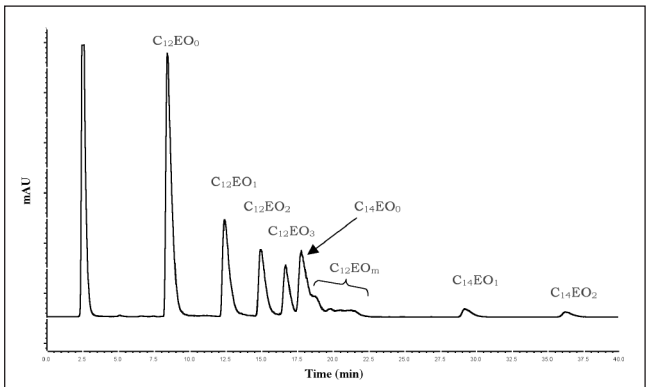

Figure 5. Chromatogram of sodium laureth sulfate (2 g/L) on XTerra MS C_{18}, 250 mm × 2.1 mm, 5 µm, 50% MeCN, 50% 0.1 mol/L NH_4OAc in water (v/v), 0.2 mL/min; evaporative light scattering detector; nebuliser: 40°C; evaporator: 70°C; gas (nitrogen): 1.3 L/min, injection volume: 5 µL.

chromatogram of sodium laureth sulfate on this column achieved with the same operating conditions is presented in Figure 7. The elution order was determined by HPLC–MS. Ethoxylated alkyl sulfates were separated following fatty alkyl chain length and for a fixed alkyl chain length (C_{10}, C_{12}, and C_{14}) were eluted in the order of increasing number of ethoxylated units ($\alpha_{EO} > 1$). Broad and fronting peaks were observed even at low sample concentrations. Despite the overloading, this phase presented good selectivities between the ethoxymers (α_{EO}) and C_{12}/C_{14} alkyl sulfates. Nevertheless, two drawbacks can be mentioned. The first concerns the high retention of C_{16} and C_{18} ethoxymers ($t_r > 90$ min) in the chromatographic conditions used. The second is the elution of C_{12} ethoxymers for EO > 5 in the distribution of C_{14} ethoxymers.

Sulfosuccinate ethoxymers were also separated and eluted with the same elution order in the same operating conditions (data not shown). It can be noted that the analysis of sodium laureth sulfate on Surfactant C_8 using 50% MeCN, 50% 0.1 mol/L NH_4OAc in water (v/v) as the mobile phase did not change the elution order. So, the reversed elution order observed on the Acclaim C_{18} Surfactant cannot be attributed to the nature of the organic solvent and/or the ionic strength.

Therefore, it can be postulated that the Acclaim C_{18} Surfactant and Surfactant C_8 stationary phases present different retention mechanisms for the separation of alkyl sulfate ethoxymers. A study of their chromatographic properties was investigated by means of a chromatographic test. A chromatographic test is needed to investigate the differences in the separation mechanism of Surfactant C_8 and Acclaim C_{18} Surfactant. Various tests dedicated to the classification of stationary phases have been developed by Tanaka (20), Engelhardt (21), Neue (22), Snyder (23), and Lesellier (24) as examples, and their relevance was compared (25). Tanaka (20) test was chosen as it was extensively used [dataset contains more than 200 columns (16,20,26–28)] and its robustness has been fully evaluated (29).

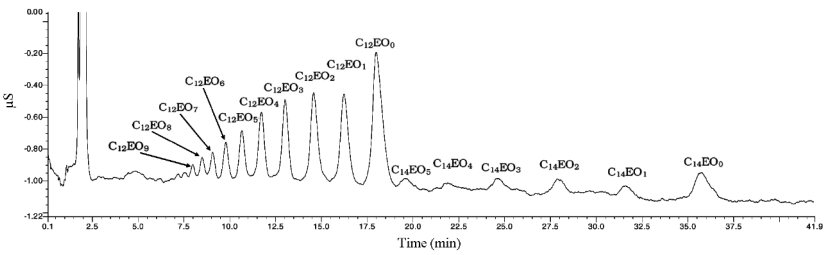

Figure 6. Chromatogram of disodium laureth sulfosuccinate (2 g/L) on Acclaim C_{18} Surfactant, 250 mm × 4.6 mm, 5 µm, 50% MeCN, 50% 0.1 mol/L NH_4OAc in water (v/v), 1 mL/min, AMMS III H_2SO_4 5 mmol/L regeneration, conductimetric detection, injection volume: 25 µL.

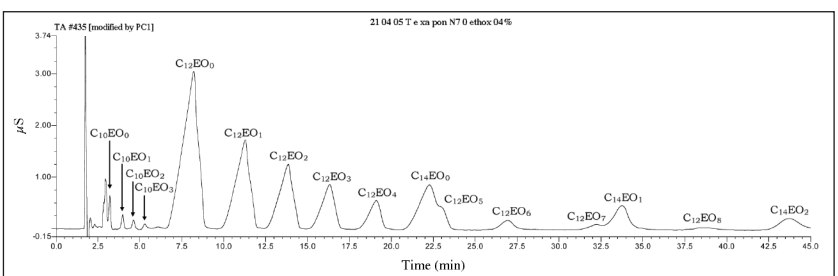

Figure 7. Chromatogram of sodium laureth suflate (3 g/L) on Surfactant C_8 column, 250 mm × 4.6 mm, 5 µm, 45% MeOH, 55% 0.25 mmol/L NH_4OAc in water (v/v), 1 mL/min, AMMS III H_2SO_4 5 mmol/L regeneration at 5 mL/min, conductimetric detection, injection volume: 25 µL.

Tanaka test

The Tanaka protocol comprises six variables for the characterization of selectivity differences between columns (Table I). $k_{pentylbenzene}$ reflects the surface and surface coverage of the phase. α_{CH2} is a measure of the hydrophobic selectivity. $\alpha_{T/O}$ measures the shape selectivity. $\alpha_{C/P}$ gives an evaluation of the number of available silanol groups and the degree of endcapping. $\alpha_{B/P}$ pH 7.6 is an estimation of the total silanol activity. $\alpha_{B/P}$ pH 2.7 is a measure of the acidic activity of the silanol groups (29). The different solutes of Tanaka test were analyzed on Surfactant C_8 and Acclaim C_{18} Surfactant columns.

The results obtained on Surfactant C_8 and Acclaim C_{18} Surfactant were compared with those published (26,27) for conventional C_8 and C_{18} phases (respectively, HyPURITY C_8 and Hypersil ODS which are well established and referenced in many HPLC methods) and C_{18} phases possessing embedded polar groups (Polaris Amide C_{18} and Acclaim PA C_{16}).

As expected, α_{CH2} and $k_{pentylbenzene}$ were weaker for the C_8 phases than C_{18} ones apart from Acclaim C_{18} Surfactant, which presented similar value for α_{CH2} (Table II). As Acclaim C_{18} Surfactant and Acclaim PA C_{16} are based on the same silica material, the weak value of $k_{pentylbenzene}$ calculated on Acclaim C_{18} Surfactant seems to be a consequence of the weak carbon percentage of this phase as previously reported for other stationary phases (25).

In addition, $\alpha_{T/O}$ value obtained on Acclaim C_{18} Surfactant phase is very high compared to Hypersil ODS $\alpha_{T/O}$ and close to that measured on Polaris Amide C_{18} and Acclaim PA C_{16}. These results could be explained by the particular nature of Acclaim C_{18} Surfactant phase, which contains tertiary amino groups, and polar amide functional groups (14). The presence of this later group is known to enhance the rigidity of alkyl chains and so improve the shape selectivity (30).

Furthermore, the data obtained on Acclaim C_{18} Surfactant for $\alpha_{C/P}$, $\alpha_{B/P}$ pH 2.7 and $\alpha_{B/P}$ pH 7.6 reveal a poor accessibility to the residual silanol groups or improvement of the endcapping of the silanol groups.

By contrast with Acclaim C_{18} Surfactant, the shape selectivity ($\alpha_{T/O}$) obtained on Surfactant C_8 is equal to 1. In addition, this column presents high values of $\alpha_{C/P}$, $\alpha_{B/P}$ pH 2.7 and $\alpha_{B/P}$ pH 7.6. These results are consistent with a low surface coverage of the phase and a large number of available silanol groups.

To compare more easily the Tanaka test data, radar plots are presented in Figure 8. This representation reveals the opposite character of the phases designed for surfactant analysis. Acclaim C_{18} Surfactant presents a poor silanol activity and high shape selectivity by contrast with Surfactant C_8.

As previously mentioned, alkyl sulfates

ethoxymers were eluted in the order of increasing number of ethoxylated units ($\alpha_{EO} > 1$) on Surfactant C_8 (Figure 7). This elution order can be attributed to the great accessibility of residual silanol groups, which may interact with ethoxylated part of alkyl sulfates. Nevertheless, the same elution order ($\alpha_{EO} > 1$) was observed on XTerra MS C_{18} (Figure 5), which presents a weak silanol activity [weak values of $\alpha_{C/P}$, $\alpha_{B/P}$ pH 2.7 and $\alpha_{B/P}$ pH 7.6 (27)].

To complete this study, the elution order of alkyl sulfates ethoxymers was determined on Polaris amide C_{18} using Acclaim C_{18} Surfactant operating conditions (data not shown). As with Acclaim C_{18} Surfactant, α_{EO} was less than but close to 1 and ethoxymers were less retained. Moreover, non-ethoxylated compounds ($C_{12}EO_0$ and $C_{14}EO_0$) were eluted after their ethoxymers distribution. So, the polar embedded group could be responsible for the ethoxymers elution order ($\alpha_{EO} < 1$) but the elution of non-ethoxylated compounds ($C_{12}EO_0$ and $C_{14}EO_0$) in their ethoxymers distribution remains difficult to explain. The high retention of alkyl sulfate oligomers on Acclaim C_{18} Surfactant was probably due to the presence of tertiary amino groups. So, anionic exchange capacity (18) was measured on Acclaim C_{18} Surfactant and was equal to 9 µeq for the column corresponding to a weak value.

Table I. Mobile Phases Used for Tanaka Test and Corresponding Data

Mobile phase	Data
80% MeOH, 20% water	$\alpha_{CH2} = \alpha_{BB/PB} = k_{butylbenzene}/k_{pentylbenzene}$ $k_{pentylbenzene}$
	$\alpha_{T/O} = k_{triphenylene}/k_{o\text{-}terphenyl}$
30% MeOH, 70% water	$\alpha_{C/P} = k_{caffeine}/k_{phenol}$
30% MeOH, 70% 0.02 mol/L NaH_2PO_4–Na_2HPO_4 pH 7.6	$\alpha_{B/P}$ pH 7.6 = $k_{benzylamine}/k_{phenol}$
30% MeOH, 70% 0.02 mol/L NaH_2PO_4–Na_2HPO_4 pH 2.7	$\alpha_{B/P}$ pH 2.7 = $k_{benzylamine}/k_{phenol}$

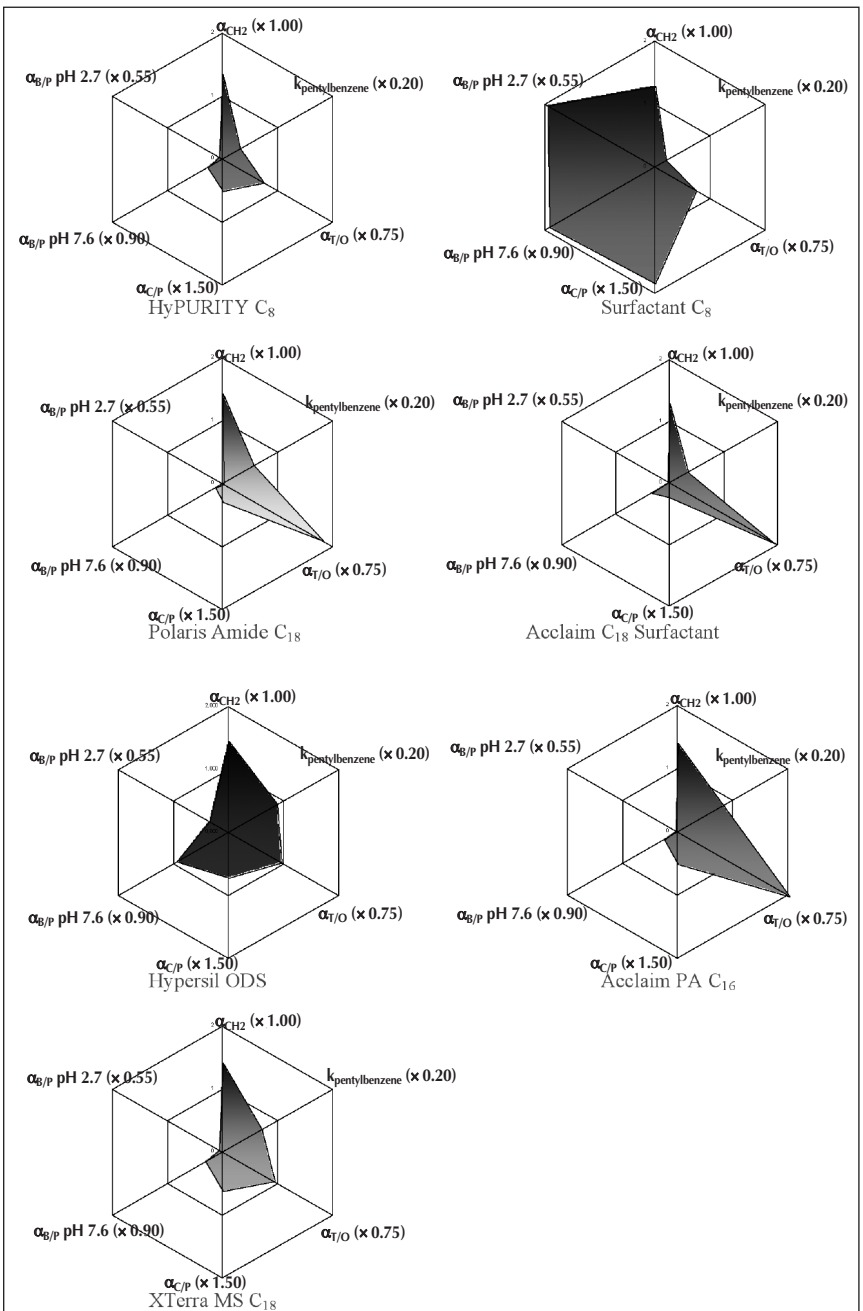

Figure 8. Radar plots of Tanaka test results for HyPURITY C_8, Surfactant C_8, Polaris Amide C_{18}, Acclaim C_{18} Surfactant, Hypersil ODS, Acclaim PA C_{16}, and XTerra MS C_{18}.

Effect of salt in mobile phase

To improve the resolution between oligomers on Acclaim C18 Surfactant column, the influence of the nature of the salt was studied. Lithium acetate (LiOAc), potassium acetate (KOAc), NH_4OAc, and sodium acetate (NaOAc) were selected in order to investigate the role of the cation and pH. For NH_4OAc, evaporative light scattering detection was employed, whereas suppressed conductimetric detection was used for mobile phases containing non-volatile salts (LiOAc, KOAc, and NaOAc). Chromatographic conditions were adapted from those previously used for Acclaim C18 Surfactant [50% MeCN, 50% 0.1 mol/L of salt in water (v/v)]. Chromatograms obtained for laureth sulfate and laureth sulfosuccinate ethoxymers with KOAc and LiOAc were similar to those observed with NH_4OAc (Figures 3 and 5). Nevertheless, with NaOAc (Figure 9), for a given chain length, non-ethoxylated alkyl sulfates were eluted before their respective ethoxymers, and all ethoxymers were coeluted. A similar chromatographic profile was observed with laureth sulfosuccinate (data not shown). This phenomenon could be attributed to the nature of the counter-ion and not to the mobile phase pH, which was similar for NaOAc, KOAc, and LiOAc. As reported by Pohl et al. (14), the pH of the mobile phase does not change the elution order but only influences the retention. As

the same chromatographic conditions, applied on XTerra MS C18 and Surfactant C8, did not allow the co-elution of ethoxymers, a modification of the stationary phase shape selectivity could occur in presence of sodium ion on Acclaim C18 Surfactant. So, $\alpha_{T/O}$ was measured on Acclaim C18 Surfactant with mobile phases containing NaOAc and NH_4OAc. Values were compared to the Tanaka test one (Table III). $\alpha_{T/O}$ values were similar whatever the mobile phases used. So, the nature of the counter ion did not affect the shape selectivity. Thus, the partial co-elution of the ethoxymers could result from a change of the ethoxylated chain conformation due to the presence of sodium in the mobile phase (31). This conformation allowed to a drastic decrease of ethoxymer resolution on Acclaim C18 Surfactant column.

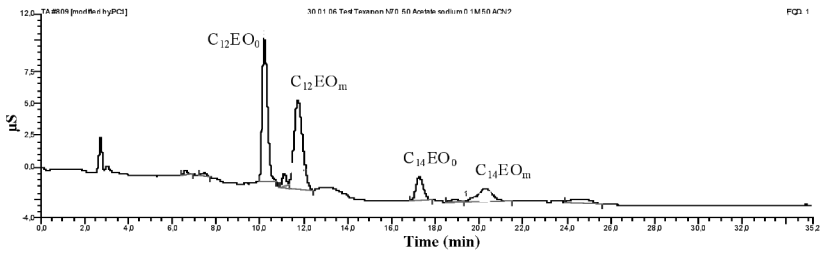

Figure 9. Chromatogram of sodium laureth sulfate (4 g/L) on Acclaim C_{18} surfactant column, 250 mm × 4.6 mm, 5 µm, 50% MeCN, 50% 0.1 mol/L NaOAc in water (v/v), AMMS III H_2SO_4 5 mmol/L regeneration at 5 mL/min, conductimetric detection, injection volume: 25 µL.

Table II. Comparison of the Results of the Tanaka Test (26,27)

	Acclaim C_{18} Surfactant	C_8 Surfactant	Hypersil ODS	HyPURITY C_8	Polaris Amide C_{18}	Acclaim PA C_{16}
$k_{pentylbenzene}$	1.68	1.04	4.44	1.59	2.87	4.16
α_{CH2}	1.30	1.29	1.45	1.35	1.43	1.40
$\alpha_{T/O}$	2.60	1.00	1.28	1.00	2.43	2.71
$\alpha_{C/P}$	0.16	1.24	0.48	0.34	0.20	0.34
$\alpha_{B/P}$ (pH 7.6)	0.37	2.12	1.04	0.30	0.15	0.27
$\alpha_{B/P}$ (pH 2.7)	< 0.05	3.55	0.64	0.11	–0.02	0.04

Table III. Shape Selectivity ($\alpha_{T/O}$) Measured on Acclaim C18 Surfactant with Various Mobile Phases

Acclaim C_{18} Surfactant	$\alpha_{T/O}$
80% MeOH, 20% water	2.60
80% MeOH, 20% 0.1 mol/L NH_4OAc in water	2.53
80% MeOH, 20% 0.1 mol/L NaOAc in water	2.47

Table IV. Slopes of Calibration Curves, Regression Coefficients (r^2), LOD, and LOQ Values for C_8EO_0, $C_{10}EO_0$, $C_{12}EO_0$, $C_{14}EO_0$, and $C_{16}EO_0$

Alkyl sulfate	r^2	Slope (µS/mg/L)	LOD (mg/L)	LOQ (mg/L)
C_8EO_0	0.9992	15000	0.06	0.19
$C_{10}EO_0$	0.9996	14500	0.07	0.24
$C_{12}EO_0$	0.9994	13630	0.11	0.35
$C_{14}EO_0$	0.9994	10780	0.25	0.84
$C_{16}EO_0$	0.9991	9330	0.97	3.24

Quantification of laureth sulfates in a shower gel

Most of alkyl sulfate ethoxymers standards are not commercially available. Therefore, factor response for each ethoxymer and consequently their relative mass percentages cannot be determined. Nevertheless, the HPLC method described in this paper was used to quantify laureth sulfate raw material amounts in commercial body product, which does not contain any other anionic alkyl surfactant. Analyses were performed on Acclaim C18 Surfactant using 50% MeCN, 50% 0.1 mol/L of NH4OAc (v/v). Suppressed conductivity detection was chosen because of its usefulness and selectivity. For this application, the high sensitivity of mass spectrometry detection was not required. In a first part, the linearity, the limits of detection (LOD) and quantitation (LOQ) were estimated for non-ethoxylated alkyl sulfates, which were commercially available (Table IV). The linearity of the relationship between concentration and area was studied on 6 levels with a series of standard solutions prepared from non-ethoxylated alkyl sulfates (C_8EO_0, $C_{10}EO_0$, $C_{12}EO_0$, $C_{14}EO_0$, and $C_{16}EO_0$). The concentration range was from 0.01 to 0.40 g/L. LOD and LOQ were calculated from calibration equations using a signal-to-noise ratio (respectively S/N ≥ 3 and S/N ≥ 10) and they are expressed as a concentration (mg/L). Calibration slopes, regression coefficients (r^2), LOD and LOQ values are listed in Table IV. Slope values decrease with an increase of the alkyl chain length. These results confirm that alkyl sulfates present different response factors with conductimetric detection. LOD and LOQ were, respectively, below 0.97 and 3.24 mg/L. The worst values were obtained for $C_{16}EO_0$, which was the most retained and presented the broader peak. However, these values were suitable for the quantitation of alkyl sulfates raw material as lauryl sulfates in cosmetic products.

The chromatographic method (Figure 3) was applied to quantify the amount of sodium laureth sulfates. According to the concentration and the distribution of alkyl sulfate ethoxymers in the sodium laureth sulfate raw material are unspecified, the calibration required the preparation of standards with the laureth sulfate raw material used for the formulation. The linearity of the relationship between concentration and the areas sum (y) of eight $C_{12}EO_m$ ethoxymers ($0 \le m \le 7$) and four $C_{14}EOm$ ethoxymers ($0 \le m \le 3$) was estimated on 5 levels of concentration (x) by injection of solutions prepared from sodium laureth sulfate raw material. The calibration curve ($y = 11.5x$) shows good linearity ($r^2 = 0.9996$) in the concentration range from 1 to 8 g/L. The mass percentage of laureth sulfate raw material in the body oil is equal to 10.0 ± 0.4%. This result is in good agreement with the specification of the product given by the manufacturer.

Conclusion

This study has shown that columns (Acclaim C18 Surfactant and Surfactant C8) dedicated to surfactant analysis have opposite characteristics which were evaluated using Tanaka test. Acclaim C18 Surfactant has a high shape selectivity and develops anion exchange interactions. Surfactant C8 presents a great accessibility to the residual silanol groups which favors interactions with ethoxylated part of surfactants. Nevertheless, the peak shape remains unsatisfactory. Despite several coelutions, Hypercarb highlights a great selectivity between the ethoxymers possessing the same alkyl chain length. Finally, a convenient HPLC method using suppressed conductimetric detection was developed allowing the quantification of sodium laureth sulfate raw material in body oil.

Acknowledgements

This work was supported by a grant from the Conseil Régional de Haute Normandie (France) and YSL Beauté Recherche et Industries company (Lassigny, France).

References

1. A.M. Raymond. The global outlook for surfactants from a U.S. perspective. World Surfactants Congress, 4th, Barcelona, June 3–7, **1:** 21–32 (1996).
2. M.F. Cox. Effect of alkyl carbon chain length and ethylene oxide content on the performance of linear alcohol ethoxylates. *J. Am. Oil Chem. Soc.* **66:** 367–74 (1989).
3. M.F. Cox. Effect of alkyl carbon chain length and ethylene oxide content on the performance of linear alcohol ether sulfates. *J. Am. Oil Chem. Soc.* **66:** 1637–46 (1989).
4. K.L. Matheson, T.P. Matson, and K. Yang. Peaked distribution ethoxylates—their preparation, characterization and performance evaluation. *J. Am. Oil Chem. Soc.* **63:** 365–70 (1986).
5. F. Ventura and P. de Voogt. Separation and detection. GC and GC-MS determination of surfactants. *Compr. Anal. Chem.* **40:** 51–76 (2003).
6. A.H. Silver and H.T. Kalinoski. Comparison of high-temperature gas chromatography and carbon dioxide supercritical fluid chromatography for the analysis of alcohol ethoxylates. *J. Am. Oil Chem. Soc* **69:** 599–608 (1992).
7. K. Rissler. High-performance liquid chromatography and detection of polyethers and their mono(carboxy)alkyl and -arylalkyl substituted derivatives. *J. Chromatogr. A* **742:** 1–54 (1996).
8. J.J. Morelli and G. Szajer. Analysis of surfactants: part I. *J. Surfactants Deterg.* **3:** 539–52 (2000).
9. T.M. Schmitt. HPLC analysis of surfactants. *Chromatogr. Sci. Ser.* **78:** 789–804 (1998).
10. L.M. Nair and R. Saari-Nordhaus. Recent developments in surfactant analysis by ion chromatography. *J. Chromatogr. A* **804:** 233–39 (1998).
11. M.G. Kunitani and L.M. Kresin. Analysis of alkyl sulfates in protein solutions by isocratic and gradient ion chromatography. *Anal. Biochem.* **182:** 103–108 (1989).
12. G. Cretier, C. Podevin, and J.L. Rocca. Analysis of aliphatic alcohol ethoxylates in terms of alkyl and ethylene oxide chain lengths by reversed-phase liquid chromatography with evaporative light scattering detection. *J. Chromatogr. A* **874:** 305–10 (2000).
13. O.P. Haefliger. Universal two-dimensional HPLC technique for the chemical analysis of complex surfactant mixtures. *Anal. Chem.* **75:** 371–78 (2003).
14. X. Liu, C.A. Pohl, and J. Weiss. New polar-embedded stationary phase for surfactant analysis. *J. Chromatogr. A* **1118:** 29–34 (2006).
15. A. Stemp, V.A. Boriraj, P. Walling, and P. Neill. Ion-chromatographic characterization of ethoxylated anionic surfactants. *J. Am. Oil Chem. Soc.* **72:** 17–22 (1995).
16. H.A. Claessens, M.A. van Straten, C.A. Cramers, M. Jezierska, and B. Buszewski. Comparative study of test methods for reversed-phase columns for high-performance liquid chromatography. *J. Chromatogr. A* **826:** 135–56 (1998).
17. P. Chaimbault, C. Elfakir, and M. Lafosse. Comparison of the retention behavior of polyethoxylated alcohols on porous graphitic carbon and polar as well as apolar bonded-silica phases. *J. Chromatogr. A* **797:** 83–91 (1998).
18. T. Takeuchi, T. Kojima, and T. Miwa. Ion chromatography of inorganic anions on graphitic carbon as the stationary phase. *J. High Resol. Chromatogr.* **23:** 590–94 (2000).
19. C. Elfakir, P. Chaimbault, and M. Dreux. Determination of inorganic anions on porous graphitic carbon using evaporative light scattering detection. Use of carboxylic acids as electronic competitors. *J. Chromatogr. A* **829:** 193–99 (1998).
20. K. Kimata, K. Iwaguchi, S. Onishi, K. Jinno, R. Eksteen, K. Hosoya, M. Araki, and N. Tanaka. Chromatographic characterization of silica C18 packing materials. Correlation between a preparation method and retention behavior of stationary phase. *J. Chromatogr. Sci.* **27:** 721–28 (1989).
21. H. Engelhardt and M. Jungheim. Comparison and characterization of reversed phases. *Chromatographia* **29:** 59–68 (1990).
22. U.D. Neue. Stationary phase characterization and method development. *J. Sep. Sci.* **30:** 1611–27 (2007).
23. J.J. Gilroy, J.W. Dolan, and L.R. Snyder. Column selectivity in reversed-phase liquid chromatography IV. Type-B alkyl-silica columns. *J. Chromatogr. A* **1000:** 757–78 (2003).
24. E. Lesellier, C. West, and A. Tchapla. Classification of special octadecyl-bonded phases by the carotenoid test. *J. Chromatogr. A* **1111:** 62–70 (2006).
25. E. Lesellier and C. West. Description and comparison of chromatographic tests and chemometric methods for packed column classification. *J. Chromatogr. A* **1158:** 329–60 (2007).
26. E. Cruz, M.R. Euerby, C.M. Johnson, and C.A. Hackett. Chromatographic classification of commercially available reverse-phase HPLC columns. *Chromatographia* **44:** 151–61 (1997).
27. M.R. Euerby and P. Petersson. Chromatographic classification and comparison of commercially available reversed-phase liquid chromatographic columns containing polar embedded groups/amino endcappings using principal component analysis. *J. Chromatogr. A* **1088:** 1–15 (2005).
28. M.R. Euerby and P. Petersson. Chromatographic classification and comparison of commercially available reversed-phase liquid chromatographic columns using principal component analysis. *J. Chromatogr. A* **994:** 13–36 (2003).
29. P. Petersson and M.R. Euerby. An evaluation of the robustness of the Tanaka characterization protocol for reversed-phase liquid chromatography columns. *J. Sep. Sci.* **28:** 2120–29 (2005).
30. X. Liu, A. Bordunov, M. Tracy, R. Slingsby, N. Avdalovic, and C. Pohl. Development of a polar-embedded stationary phase with unique properties. *J. Chromatogr. A* **1119:** 120–37 (2006).
31. W.R. Melander, A. Nahum, and C. Horvath. Mobile phase effects in reversed-phase chromatography. III. Changes in conformation and retention of oligo(ethylene glycol) derivatives with temperature and eluent composition. *J. Chromatogr. A* **185:** 129–52 (2006).

Manuscript received February 28, 2008;
Revision received June 30, 2008.