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Qualitative and quantitative analysis of new alkyl amide arginine surfactants by high-performance liquid chromatography and capillary electrophoresis

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Abstract

A protocol for the qualitative and quantitative analysis of novel arginine-based cationic surfactants using HPLC and CE was studied and compared. The optimization of the analytical conditions was carried out through a systematic variation of the experimental parameters such as mobile phase, eluent conditions, ion pairing and amount of sample for HPLC, and type of buffer, ion strength, type and amount of organic solvent, sample injection time, applied voltage and column washing and conditioning for CE.

Keywords: Surfactants; Arginine alkylamides

1. Introduction

A new family of cationic surfactants [1], the arginine alkyl amide dihydrochloride salts, H–Arg–NH–C_n with $n=10$, 12, 14 and 16, has recently been synthesized and their physico-chemical and antimicrobial properties evaluated [2]. Their molecular structure consists of one hydrophobic chain and one polar head with two cationic groups (Fig. 1). These compounds were designed as new antimicrobial surfactants of low toxicity. It is expected that these new molecules biodegrade more rapidly than the classical alkyltrimethylammonium compounds do, owing to the presence of a labile amide group.

Quantitative determination of H–Arg–NH–C_n homologues by the widely used two-phase titration method [3,4] did not provide satisfactory results. An

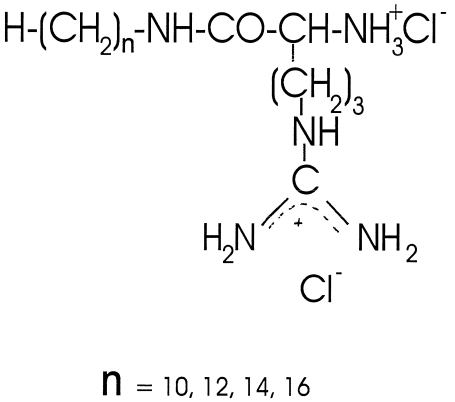

Fig. 1. Structure of H–Arg–NH–C_n surfactant homologues.

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ambiguous titration point was obtained, owing to the presence of two positive charged sites in the molecule (the primary amine hydrochloride salt and the guanidine hydrochloride salt). High-performance liquid chromatography (HPLC) and capillary electrophoresis (CE) methodologies were set up to perform quali- and quantitative analysis of these compounds. Both were compared on the basis of the following analytical parameters: resolution, which indicates the adequate separation (R_s), column efficiency (number of theoretical plates, N), reproducibility expressed as relative standard deviation (RSD) in one day (RSD$<$ 3% indicates the viability of the method) and in day-to-day (RSD$<$5% indicates the viability of the method), linearity interval and detection limit.

The HPLC technique is particularly well suited to separation and quantification of cationic surfactants, such as quaternary ammonium compounds and amines. It provides the most effective means for specifically and sensitively determining them in a range of environmental testing applications [6]. Most of the published methods for HPLC separation of cationic surfactants are based on reversed-phase chromatography with a mobile phase containing a salt. Homologous series of quaternary ammonium salts are separated using ion-pairing reagents [5,7–11]. In this work a propylcyano column and an acetonitrile–water mobile phase containing trifluoroacetic acid (TFA) as ion-pairing reagent were used for the analysis of H–Arg–NH–C_n homologues.

CE is a promising technique for separation and quantification of a wide variety of anionic and cationic surfactants of different alkyl chain lengths [12–19]. Good results for detection and separation of N^{α}-*tert*.-butoxycarbonyl argininyl alkyl amide (C_{10}–C_{16}) monohydrochloride compounds [2,20] as well as for conventional cationic surfactants *N*-alkyl-*N*-benzyl-*N*,*N*-dimethylammonium chloride compounds [21] were obtained in previous studies. Based on these findings, a systematic investigation of buffer systems and instrumental parameters was carried out to optimize both the detection and separation of H–Arg–NH–C_n homologues. Organic solvents such as methanol (MeOH), acetonitrile (ACN) and tetrahydrofuran (THF) were added to buffer solution as cosolvents in order to minimize their molecular aggregation and adsorption on capillary column walls [20,21].

2. Experimental

The following surfactant homologues were analyzed as dihydrochloride salts: arginine decyl amide, arginine dodecyl amide, arginine tetradecyl amide and arginine hexadecyl amide, which will be referred to in the text as C_{10}, C_{12}, C_{14} and C_{16}, respectively. Replicate determinations of different C_n homologues were done in the determination of analytical parameters.

2.1. HPLC

A Merck–Hitachi HPLC instrument was used, which consisted of an injection valve fitted with a 20-μl loop, an intelligent pump L-6200, a UV–Vis detector L-4250 at 210 nm wavelength and a Chromato-Integrator D-2500. The separations were carried out on a LiChrocart 250×4 mm, LiChrospher 100 CN (particle size 5 μm) column at room temperature. The flow-rate through the HPLC column was set to 1.0 ml/min.

Ultrapure deionized water was obtained from a Millipore Milli-Q system. Acetonitrile (ACN) (for chromatography), TFA (for spectroscopy) and HFBA (heptafluorobutyric acid) were supplied by Merck.

The calibration set consisted of seven concentrations ranging from 6.000 to 0.144 m*M*, each in duplicate. The dilution solvent for each C_n homologue was 0.075% (v/v) TFA in water (eluent A), except for C_{16} which was diluted in 0.1% (v/v) TFA in ACN–water (4:1) (eluent B) because of its poor solubility in water. Qualitative analysis was performed with a solution of the four homologues in eluent B, using the following concentrations: C_{10}: 0.152 m*M*, C_{12}: 0.152 m*M*, C_{14}: 0.155 m*M* and C_{16}: 0.156 m*M*.

2.2. CE

An Applied Biosystems Model 270A (Foster City, CA, USA) apparatus consisting of the following functional assemblies was employed: a UV–Vis detector, an uncoated fused-silica capillary column of 72 cm×50 μm I.D., which was obtained from Composite Metal Services, an automatic injection system which injects in an hydrodynamic mode by

vacuum, and a buffer reservoir at the capillary end compartment. Peaks were UV detected at 210nm and recorded on a Shimadzu C-R6A Chromatopac Chart Recorder. The column was thermostated between 25–31°C.

Buffers were prepared from ultrapure deionized water produced by a Millipore Milli-Q system and from the following chemicals of analytical grade: THF, ACN, MeOH and citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$) from Merck, and sodium dihydrogenophosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$) from Fluka. Electrolyte salts were dissolved in the appropriate volume of water and adjusted to the desired pH, and then the specific volume of organic cosolvent was added. Finally and prior to utilization, they were filtered through a 0.22-μm membrane filter from Millipore.

Prior to use, new capillary columns were subjected to a standard wash cycle using 1 *M* NaOH for 30 min and water for 10–15 min. Between injections, the following cleaning methods were tried: (i) water for 10–15 min, (ii) analysis buffer for 10 min and (iii) water for 5 min, methanol for 30 min, water for 5 min and analysis buffer for 10 min. The last cleaning method was the best and is discussed below. Finally, the capillary was equilibrated with the operating buffer for 15 min before sample injection. The separation was initiated by applying a voltage between the two capillary ends, which were immersed in reservoirs containing the operating buffer.

Qualitative analysis was performed with a solution of the four homologues dissolved in water–methanol (7:1) using the following concentrations: C_{10}: 2.51 m*M*; C_{12}: 2.49 m*M*; C_{14}: 2.59 m*M*; C_{16}: 2.60 m*M*.

3. Results and discussion

3.1. Qualitative aspects

3.1.1. HPLC

A gradient elution from 50% to 100% B in 25 min gave satisfactory results for qualitative and quantitative HPLC analysis of these compounds. The retention factors k' obtained for the C_{10}, C_{12}, C_{14} and C_{16} homologues were 1.25, 1.93, 2.64 and 3.35, respectively, using the following solvent system: A: 0.1% (v/v) TFA in water, B: 0.11% (v/v) TFA in ACN–water (4:1). The hydrophobicity of these surfactants is directly related with the alkyl chain length. Hence, the retention factor increases with the number of methylene groups in the hydrophobic tail. The use of TFA in mobile phases was necessary: no retention of C_{12} and C_{14} was observed using mobile phases without this ion pairing reagent. When a much more hydrophobic counterion was used, i.e., HFBA, the retention time increased considerably (i.e., t_R=from 7.96 min to 21.14 min for C_{12}) and broad peaks were obtained.

Two different isocratic eluents were tested to decrease the analysis time: (a) A–B (44:56) and (b) A–B (42:58). Both a and b elution conditions gave satisfactory separation and quantification analysis of the compounds in 25 min. Shorter retention times were obtained with the isocratic elution system b (C_{10}: 5.56 min, C_{12}: 6.84 min, C_{14}: 8.48 min and C_{16}: 10.72 min) than the isocratic elution system a (C_{10}: 6.22 min, C_{12}: 7.98 min, C_{14}: 10.27 min and C_{16}: 13.47 min).

Therefore, the quantitative analysis optimization of the C_n mixture was carried out, using the following analysis conditions: solvent system: A: 0.075% (v/v) TFA in water, B: 0.1% (v/v) TFA in ACN–water (4:1); isocratic eluent: A–B (42:58).

3.1.2. CE

The development of the separation and detection method was carried out through a systematic variation of the following experimental and instrumental parameters: the buffer and the organic cosolvent, the temperature and the capillary cleaning method.

3.1.3. Influence of buffer solution

Initial attempts to separate the C_n homologues were performed using a sodium citrate buffer solution 50 m*M*, pH 2.5. Nevertheless, the separation of the peaks was not achieved with any of the organic modifiers (MeOH, ACN and THF) and the applied voltages assayed. Sodium dihydrogenphosphate buffer solution 50 m*M*, containing ACN or THF with a pH range 4.5–6.5 was probed.

An increase in pH decreases the migration time [because of the increase in electroosmotic flow (EOF)], leading to sharp peaks but insufficient peak resolution. Three possible explanations of the differ-

ent CE selectivity obtained with sodium citrate buffer and sodium dihydrogenphosphate buffer could be offered. First, the different ampers produced: at 25 kV applied voltage, a 50 m*M* aqueous sodium citrate solution produced 31 μA, while 50 m*M* sodium dihydrogenphosphate produced 21 μA. Second, the effect of buffer on the EOF. Third, the effect of buffer on the pH value generated [22]. Thus, qualitative and quantitative analysis was accomplished using 50 m*M* sodium dihydrogenphosphate buffer, pH 4.5, which gave the best results.

As expected, the four cationic surfactant compounds were eluted from the capillary column in order of decreasing charge-to-mass ratio, i.e., in order of increasing alkyl chain length due to their different electrophoretic mobilities in the voltage gradient inside the buffer filled capillary.

3.1.4. Influence of the organic cosolvent and electrolyte concentration

Samples of each C_n homologue were analyzed using NaH_2PO_4 50 m*M* buffer solutions (pH 4.5) containing MeOH, ACN and THF in the proportions of 10%, 25%, 50% and 75%. The experimental parameters were: applied voltage 5 or 15 kV and an injection time 0.5 s.

MeOH was not able to avoid the adsorption and aggregation effects of C_n surfactant homologues giving peak broadening for both C_{10} and C_{12} and absence of detection for C_{14} and C_{16}, even at high MeOH concentrations. However, ACN and THF promoted the migration and separation of all compounds. The best results were obtained with 50% ACN or THF, which was the minimum amount of cosolvent required to avoid peak broadening. The optimum applied voltage was 5 kV for ACN and 15 kV for THF. Finally, ACN was chosen as the best cosolvent because the peak broadening and the RSD values for migration time were lower than in THF: one day reproducibility RSD was 0.01% for ACN and 3% for the THF; day-to-day reproducibility RSD was 1.4% for ACN and 5% for THF.

Resolution, efficiency, peak area and method reproducibility were studied as a function of the electrolyte concentration of the buffer NaH_2PO_4 (50, 75 and 100 m*M*). The electrolyte concentration was irrelevant to the resolution and to the symmetry of the peaks. Nevertheless, on increasing the concentration of the electrolyte, peak area increases (i.e., from 76 mV at NaH_2PO_4 50 m*M* to 198 mV at NaH_2PO_4 100 m*M* for C_{14}). The values of *N* calculated from the electropherograms were quite close for the three electrolyte concentrations. Hence, a minimum band broadening was obtained when a concentration of 50 m*M* NaH_2PO_4 was used.

Migration time reproducibility as a function of electrolyte concentration was also studied. The 50 m*M* NaH_2PO_4 electrolyte concentration provided the lowest RSD values: one day reproducibility RSDs were 0.01, 0.85 and 0.3% for 50, 75 and 100 m*M*, respectively; day-to-day reproducibility RSDs were 1.4, 2.2 and 2.1% for 50, 75 and 100 m*M*, respectively. But, since the 100 m*M* NaH_2PO_4 electrolyte concentration provided the highest sensitivity without a critical loss of method efficiency and reproducibility, this was later used for the development of the quantitative analysis.

3.1.5. Effect of temperature and capillary cleaning method on resolution and reproducibility

The temperature has a very important influence on CE reproducibility. By using 50 m*M* NaH_2PO_4, pH 4.5 and 50% ACN buffer, the migration time decreased about 1 min/°C and the resolution and peak broadening worsened when the temperature was increased. The most appropriate temperature for an adequate separation was 25°C.

Owing to the high adsorption capacity of cationic surfactants, it was crucial to use a highly effective cleaning method. When the surfactant adsorption takes place on the column wall, an important loss in resolution occurs after a few number of analyses. A variety of cleaning methods using 0.1 *M* NaOH buffer, 0.1 *M* H_3PO_4 and methanol were tried but all were unsuccessful. Finally, a sequence of cleaning steps was chosen, avoiding both the resolution loss and the abnormal decrease in capillary life: a flush with deionized water for 5 min, methanol for 30 min and deionized water for 5 min. Water before and after rinses with methanol was necessary to avoid a precipitation of the electrolyte salts inside the capillary column. Rinses with methanol eliminate any surfactant that could remain adsorbed on the capillary walls.

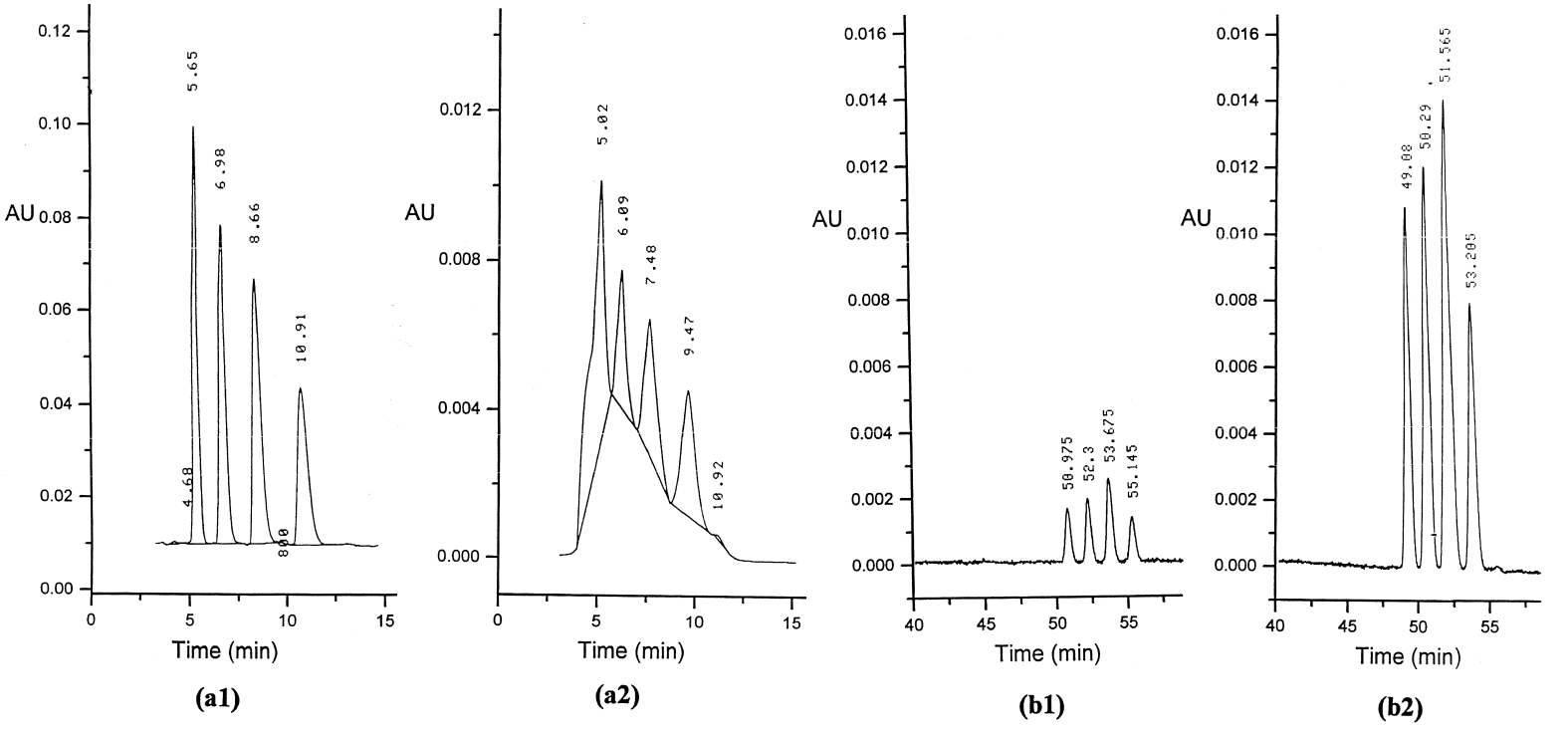

Fig. 2. HPLC chromatograms at concentration levels of 0.15 m*M* (a1) and 3 m*M* (a2), and CE electropherograms at concentration levels of 0.3 m*M* (b1) and 2.5 m*M* (b2), of a mixture of C_{10}, C_{12}, C_{14} and C_{16}, respectively. The analysis conditions are: for HPLC, solvent system: A: 0.075% (v/v) TFA in water, B: 0.1% (v/v) TFA in ACN–water (4:1); isocratic elution: 58% B; sample solvent: B eluent; injected volume: 20 μl; sample μg: 1.1–1.4 and 23.2–28.2 for a1 and a2, respectively; for CE, NaH_2PO_4 100 m*M*, pH 4.50, 50% ACN, applied voltage of 5 kV, a sample injection time of 0.6 s (injected volume in the order of nl) and temperature of 25°C.

3.1.6. Comparative study of R_s, N and reproducibility obtained by HPLC and CE

Fig. 2 shows the HPLC chromatograms and the CE electropherograms of a mixture of C_{10}, C_{12}, C_{14} and C_{16} at two concentration levels using the best analysis conditions for each technique.

Table 1 shows that both HPLC and CE techniques gave satisfactory and similar R_s values. At a high concentration level (2.5 m*M*) only CE provided good separation of the four C_n compounds. At a low concentration level (0.15 m*M*) both techniques gave good separation. Qualitative reproducibility in one day as measured from six replicate determinations resulted in an RSD of less than 3% for all compounds and for both techniques. Qualitative reproducibility in day to day as measured from five replicate determinations resulted in an RSD less than 5% for all compounds and for both techniques. Thus, elution time reproducibility was similar and satisfactory, indicating that the separation of the four analytes was reproducible by both techniques. Elution time values obtained by HPLC (a mean value of 6 min) were 10-times shorter than those of CE (a mean value of 51 min), thus providing faster analyses than CE.

N values obtained by both techniques were not comparable because of the large differences between the elution times. However, the high value of *N* obtained by CE indicates a minimum band broadening despite the fact that the analytes were moving through the capillary column for a long time.

Table 1
R_s values, *N* values, elution time reproducibility in one day and in day-to-day[a]

	HPLC[b]	CE[c]
$R_{sC_{10}-C_{12}}$	1.2	1.2
$R_{sC_{12}-C_{14}}$	1.3	1.3
$R_{sC_{14}-C_{16}}$	1.5	1.6
Elution time reproducibility in one day: t_M(min)±RSD (%)		
	HPLC[d]	CE[e]
C_{10}	5.21±0.17	49.25±0.18
C_{12}	6.32±0.36	50.30±0.28
C_{14}	7.89±0.12	51.60±0.14
C_{16}	–	53.17±0.20
Elution time reproducibility in day-to-day: t_M(min)±RSD (%)		
	HPLC[d]	CE[e]
C_{10}	5.24±0.55	48.64±1.21
C_{12}	6.47±1.90	49.59±1.93
C_{14}	7.98±1.50	50.79±1.88
C_{16}	–	52.13±2.11
	HPLC	CE
N[f]	4681	59 000

[a] The analysis conditions are: for HPLC, solvent system: A: 0.075% (v/v) TFA in water, B: 0.1% (v/v) TFA in ACN–water (4:1); isocratic elution: 58% B; for CE, NaH_2PO_4 100 m*M*, pH 4.50, 50% ACN, applied voltage of 5 kV, a sample injection time of 0.6 s and temperature of 25°C. The above results were obtained by analyzing a mixture of the four C_n compounds at the following concentrations: [b]0.15 m*M*; [c]2.5 m*M*; [d]1.2 m*M*; [e]1 m*M*.

[f] *N* value was calculated from the C_{14} peak at the concentration 0.144 m*M* for HPLC and 2.5 m*M* for CE.

3.2. Quantitative aspects

Prior to the study of the method linearity, the peak area reproducibility was confirmed by using the optimum analysis conditions obtained by both techniques. For CE, it was observed that values of sample injection time <1 s provided inadequate reproducibility values. Therefore, the following experiments by CE were done with a sample injection time of 1 s. Results obtained are shown in Table 2. Peak area reproducibility was similar and satisfac-

Table 2
Peak area reproducibility in one day and in day-to-day[a]

	HPLC[b]	CE[c]
Peak area reproducibility in one day: area (mV)±RSD (%)		
C_{10}	1285±0.20	75.73±0.92
C_{12}	1257±0.37	91.63±0.44
C_{14}	1363±0.21	125.85±0.75
C_{16}	–	67.45±0.56
Peak area reproducibility in day-to-day: area (mV)±RSD (%)		
C_{10}	1292±0.34	74.44±2.24
C_{12}	1267 ±1.0	89.70±2.67
C_{14}	1380±1.3	122.56±3.36
C_{16}	–	64.48±5.69

[a] The analysis conditions are: for HPLC, solvent system: A: 0.075% (v/v) TFA in water, B: 0.1% (v/v) TFA in ACN–water (4:1); isocratic elution: 58% B; for CE, NaH_2PO_4 100 m*M*, pH 4.50, 50% ACN, applied voltage of 5 kV, a sample injection time of 0.6 s and temperature of 25°C.

[b] 1.2 m*M*.

[c] 1 m*M*.

Table 3
Linearity of response for the cationic surfactants analyzed by HPLC (separately analyzed) and CE (a mixture of the four compounds)[a]

	Linear range (m*M*)		Least-squares equation, $y=mx+b$; m (mV/m*M*), b (mV)		Correlation coefficient	
	HPLC	CE	HPLC	CE	HPLC	CE
C_{10}	0.148–6.11	0.10–2.0	$m=1001.20$ $b=37.28$	$m=82.04$ $b=-3.52$	0.99991	0.9992
C_{12}	0.144–5.99	0.12–2.45	$m=995.61$ $b=39.56$	$m=80.59$ $b=-1.95$	0.99984	0.9995
C_{14}	0.048–6.06	0.15–2.97	$m=1073.93$ $b=27.92$	$m=90.39$ $b=-1.45$	0.99996	0.9996
C_{16}	0.144–5.95	0.10–2.07	$m=661.32$ $b=94.27$	$m=66.83$ $b=-0.23$	0.99439	0.9982

[a] The analysis conditions are: for HPLC, solvent system: A: 0.075% (v/v) TFA in water, B: 0.1% (v/v) TFA in ACN–water (4:1); isocratic elution: 58% B; for CE, NaH_2PO_4 100 m*M*, pH 4.50, 50% ACN, applied voltage of 5 kV, a sample injection time of 0.6 s and temperature of 25°C.

tory, except for C_{16} whose RSD value with CE was slightly higher than the accepted value of 5%. This could be due to the high capacity of this compound for adsorption to the capillary walls.

The linearity interval, regression equation and the correlation coefficient for each C_n homologue using HPLC and CE are shown in Table 3. The linear relationship between peak area versus sample concentration was confirmed for the four compounds using both techniques. The linear relationship was rather good and more sensitive for HPLC than for CE.

While the values of the slope for C_{10}, C_{12} and C_{14} homologues were very similar, the slope for the C_{16} homologue was considerably inferior using both HPLC and CE techniques. Given that the molar extinction coefficient for the H–Arg–NH–C_n compounds measured by UV (210 nm) in methanol was the same for all homologues, this effect could be attributed to the high adsorption capacity of the C_{16} surfactant on the stationary phase of HPLC or on the wall of the capillary column in CE.

The lowest value for the correlation coefficient for both techniques corresponded to the longest homologue C_{16}, probably owing to its highest peak broadening and asymmetry given the high adsorption capacity of this compound.

The detection limit of the method for these cationic surfactants, defined at signal-to-noise ratio (S/N)≥3, was 0.007 m*M* by HPLC and 0.05 m*M* by CE.

4. Conclusions

The qualitative and quantitative analysis of the series of arginine alkyl amide dihydrochloride surfactant homologues (C_{10}–C_{16}) was successfully achieved by HPLC and CE.

With CE it should be emphasized that the use of organic modifiers is essential for obtaining resolution between the homologues of long-chain cationic surfactants.

HPLC is, in general, more suitable for the quantitative analysis of these compounds because it provides shorter analysis times, better linear relationships and higher sensitivity.

Acknowledgements

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