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Short communication

## Use of a fluorosurfactant in micellar electrokinetic capillary chromatography

Ronny de Ridder<sup>a,b</sup>, Francesco Damin<sup>a</sup>, Jetse Reijenga<sup>b,\*</sup>, Marcella Chiari<sup>a</sup>

<sup>a</sup>*Institute of Biocatalysis and Molecular Recognition, C.N.R., Milan, Italy*

<sup>b</sup>*Laboratory of Instrumental Analysis, Eindhoven University of Technology, P.O. Box 513, Room STO 3.46, 5600 MB Eindhoven, Netherlands*

### Abstract

A fluorosurfactant, the anionic *N*-ethyl-*N*-[(heptadecafluorooctyl)sulfonyl]glycine potassium salt, trade name FC-129 [CAS 2991-51-7] was investigated for possible application in micellar electrokinetic capillary chromatography (MEKC). The surfactant was characterized with conductometric titration and test sample mixtures were investigated in MEKC systems, and compared with sodium dodecylsulphate. An increased efficiency and interesting selectivity differences were observed. © 2001 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

The use of fluorodetergents in capillary electrophoresis has been reported during the past decade [1–6]. On various occasions, Roeraade and co-workers used mixtures of different ratios of cationic and anionic fluorosurfactants named FC-134 and FC-128 as additives to their capillary zone electrophoresis (CZE) background electrolytes (BGEs) to enhance separation. In doing so, they managed to separate both positively and negatively charged proteins at the same time, without any proteins adsorbing to the capillary wall [1]. Most publications report on the use of fluorosurfactants as such possible low-concentration additives in BGEs [2–6]. No reports on micellar electrokinetic capillary chromatography

(MEKC) applications with the above two fluorodetergents have been encountered in literature.

Yang and Khaledi performed MEKC, using another fluorodetergent, the anionic LiPFOS (lithium perfluorooctanesulfonate) [7]. The retention behavior of 60 different compounds in this system was compared to that in two hydrocarbon detergents, one of them being sodium dodecylsulphate (SDS). This was done using 50 mM ionic strength phosphate buffer at pH 7. Both SDS and LiPFOS were used at a concentration of 40 mM. It was observed that the logarithm of the retention factor for all compounds was systematically lower in the fluorosurfactant system than in SDS.

The fluorosurfactant used in this investigation is the anionic *N*-ethyl-*N*-[(heptadecafluorooctyl)sulfonyl]glycine potassium salt, trade name FC-129. See Fig. 1 for the structural formula of the fluorodetergent compared to that of SDS. There are indications of the possible application in MEKC systems of this component, from the assumption of a

\*Corresponding author. Tel.: +31-40-247-3096; fax: +31-40-245-3762.

E-mail address: j.c.reijenga@tue.nl (J. Reijenga).

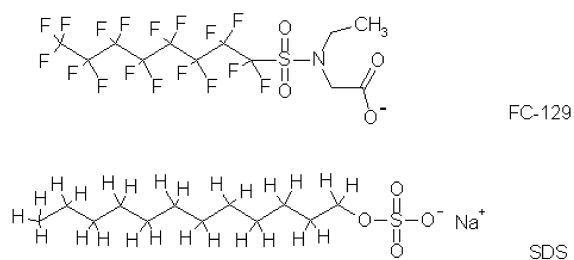


Fig. 1. Structural formulas of FC-129 and SDS for comparison.

relatively low critical micelle concentration (CMC) [8], in comparison to the CMC of, for example, SDS. It is believed that performing MEKC with this fluorosurfactant can provide several new opportunities. The extreme hydrophobicity of the fluorinated carbon chain enables MEKC analysis of compounds that are more non-polar than the limiting compounds of SDS, because a more non-polar environment exists within the micelles formed. The bidentate polar side-chains possibly yield interesting selectivity aspects.

## 2. Experimental

### 2.1. Determination of CMC

The CMC was determined with conductometric titrations in duplicate. A stock solution of 79.45 mM FC-129 in water was prepared. Using an analytical balance type AE166 (Mettler, Switzerland), weighed amounts of 50 or 100 mg were taken from this solution and added to 100 ml of deionized water and the conductivity was measured with a Schott type CG855 conductivity meter (Schott, Hofheim, Germany). The measured specific conductivity was converted into molar conductivity units and subsequently plotted vs. the square root of the analytical detergent concentration, using the purity value given by the manufacturer.

### 2.2. Electrophoresis

Experiments were carried out on a Spectra-Phoresis 1000 capillary electrophoresis system (Thermo Separation Products, Fremont, CA, USA). Operating conditions were: fused-silica capillary of

400 mm (length to detector 320 mm)  $\times$  50  $\mu$ m I.D.  $\times$  375  $\mu$ m O.D. (Composite Metal Services, Worcester, UK), separation voltage 20 kV with positive inlet polarity, UV detection at 200 nm. Hydrodynamic injection by  $5.17 \cdot 10^3$  N/m<sup>2</sup> pressure.

### 2.3. Chemicals

FC-129 (CAS 2991-51-7) was obtained from Aldrich (Steinheim, Germany) and SDS (CAS 151-21-3) was obtained from Fluka (Buchs, Switzerland). Sodiumtetraborate-10-hydrate (borax; CAS 1303-96-4) and dimethyl sulfoxide (DMSO; CAS 67-68-5) were analytical-grade reagents purchased from Merck (Darmstadt, Germany).

### 2.4. Electrolytes

The buffer solution for CZE measurements was 12.5 mM sodium tetraborate (borax), pH 9.9. Before adding the detergent, the BGE had a ionic strength of 25 mM. The neutral marker in electroosmotic flow (EOF) determination was 1% v/v DMSO in water.

### 2.5. EOF determination

Determination of EOF as a function of detergent concentration was carried out for both FC-129 and SDS. First, the capillary was conditioned with a solution of the detergent in buffer for 1 h. Then, EOF was determined by the injection of a neutral marker (DMSO).

### 2.6. Micelle mobility and migration window determination

BGE containing detergent was saturated with Sudan III by stirring overnight. After adding EOF marker the obtained clear red solution was injected to obtain the micelle migration time.

## 3. Results and discussion

### 3.1. Results of CMC determination

The CMC value of FC-129 was determined by

conductometric titration as described in the Experimental section. The results of one of the duplicate measurements is shown (Fig. 2). The duplicate determinations largely coincided. The CMC thus obtained appears to be 0.5 mM.

Also from the graph, the absolute mobility of the fluorodetergent ion can be calculated, using the potassium value from literature. The mobility at infinite dilution would then be  $-38 \cdot 10^{-9} \text{ m}^2/\text{V s}$ , but considering the impurities present, this can only be considered an approximation.

### 3.2. Results of EOF determination

EOF mobilities were determined in several concentrations of FC-129. SDS was used for comparison.

Only the EOF measured in 10 mM SDS showed a large standard deviation. In both systems the EOF shows little or no dependence on detergent concentration. See Table 1 for EOF mobility vs. detergent concentration used. There were slightly different EOF values at zero detergent concentration in both cases because in each set of experiments, a new capillary was used.

### 3.3. Results of test mixtures

Several test mixtures were used to compare the

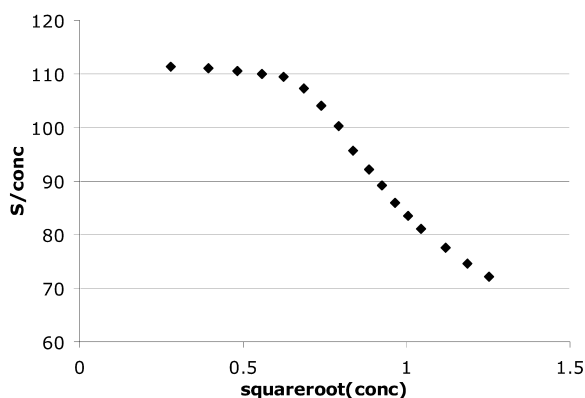


Fig. 2. Conductometric titration of FC-129, specific conductivity [ $\mu\text{S}/\text{cm}$ ] divided by concentration [mM] vs. the square root of the concentration [mM].

Table 1  
EOF mobilities ( $10^{-9} \text{ m}^2/\text{V s}$ ) and relative standard deviations (RSD) in the anionic MEKC systems

Concentration (mM)	FC-129		SDS	
	$\mu_{\text{EOF}}$	RSD (%)	$\mu_{\text{EOF}}$	RSD (%)
0	61	0.7	42	9.4
2	67	0.5	47	0.4
3	68	0.3	–	–
5	–	–	59	0.3
10	61	1.3	43	10
15	62	1.3	60	1.3
20	–	–	60	0.7
25	–	–	60	0.3

performance of the fluorodetergent with that of SDS. Two detergent concentrations of 15 and 20 mM were used. Samples were analyzed in both systems under the same experimental conditions, and efficiencies (plate numbers) were compared.

A homologue series, ranging from phenol to 2-propylphenol showed better peakshapes in going from 15 mM SDS towards 20 mM FC-129. See Table 2 for the plate numbers of the different compounds in the four systems. All peaks, apart from *o*-cresol (2-methylphenol), show a systematic increase in plate number. The pherograms are shown in Fig. 3. The resolutions are less due to selectivity differences. Take note that the time axes in Fig. 3A and B differ from those in Fig. 3C and D.

In order to determine the migration window and micelle mobility, a number of experiments with Sudan III were performed. The migration windows were calculated as the ratio of micelle and EOF migration times. The migration windows of the two MEKC systems largely coincide. In Table 3 some

Table 2  
Plate numbers for the alkylphenol homologue series in the four MEKC systems

Compound	SDS		FC-129	
	15 mM	20 mM	15 mM	20 mM
Phenol	16 000	23 000	31 000	47 000
<i>o</i> -Cresol	19 000	24 000	43 000	40 000
2-Ethylphenol	22 000	33 000	42 000	55 000
2-Propylphenol	19 000	45 000	58 000	80 000

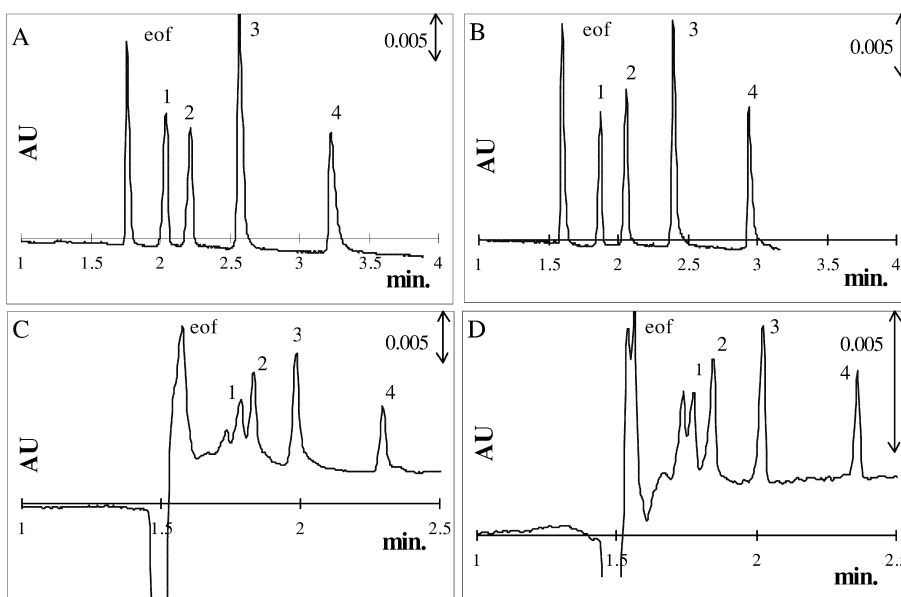


Fig. 3. Separation of the homologue series in 12.5 mM BGE and 15 mM SDS (A), 20 mM SDS (B), 15 mM FC-129 (C) and 20 mM FC-129 (D). Sample concentration: 1 mM each, injection time: 4 s. Peak assignment: 1. phenol, 2. *o*-cresol, 3. 2-ethylphenol, 4. 2-propylphenol.

window sizes and micelle mobilities are listed for the various systems.

A mixture of *ortho*- *meta*- and *para*-cresol was injected in the four systems. In 15 as well as 20 mM SDS the peaks largely coincide, and only *o*-cresol appears as a single peak while the *meta* and *para* form comigrate. In 15 mM FC-129 *o*-cresol appears as an individual peak already and in 20 mM FC-129 moreover, *m*- and *p*-cresol show the first signs of separation as well.

Also a separation of 2-, 3- and 4-ethylphenol was performed. In SDS, the compounds were individually visible, but the peaks still largely coincided. This overlay of the peaks becomes less upon increasing concentration. In FC-129 already at 15 mM three individual, separated peaks are observed. Going to 20 mM gives a further increase in resolution. See Fig. 4 for the chromatograms of this separation.

Table 4 summarizes selectivity and retention factors of the two separations shown above. The

Table 3

EOF mobility and micelle mobility with their standard deviations in  $10^{-9} \text{ m}^2/\text{V s}$  units and the migration window of two anionic MEKC systems in 12.5 mM borax, pH 9.9

	EOF mobility		Micelle mobility		Migration window
	Mean	SD	Mean	SD	
15 mM SDS	63.1	0.6	-39.9	0.8	2.7
20 mM SDS	65.8	-	-40.4	-	2.6
15 mM FC-129	60.3	0.0	-38.6	0.8	2.8
20 mM FC-129	59.1	0.7	-39.4	0.6	3.0

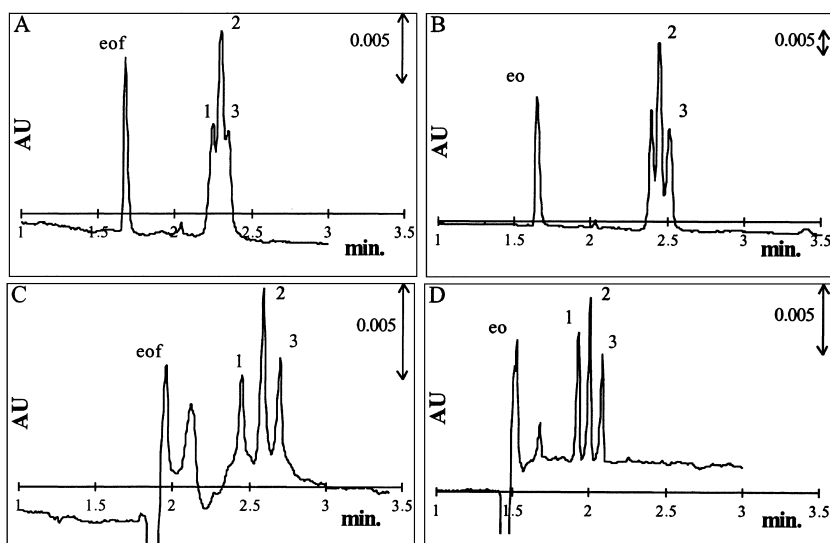


Fig. 4. Separation of an ethylphenol mixture. See legend of Fig. 3. Peak assignment: 1. 2-ethylphenol, 2. 3-ethylphenol and 3. 4-ethylphenol.

Table 4  
Retention factors ( $k$ ) and selectivities ( $s$ ) of test mixture components in the four MEKC systems

	FC-129				SDS			
	15 mM		20 mM		15 mM		20 mM	
	$k$	$s$	$k$	$s$	$k$	$s$	$k$	$s$
<i>o</i> -Cresol	0.32	–	0.26	–	0.42	–	0.56	–
<i>m</i> -Cresol	0.42	1.3	0.31	1.2	0.46	1.1	0.60	1.1
<i>p</i> -Cresol	0.42	1.0	0.33	1.1	0.46	1.0	0.60	1.0
2-Ethylph	0.50	–	0.41	–	0.68	–	1.1	–
3-Ethylph	0.68	1.4	0.50	1.2	0.76	1.1	1.2	1.1
4-Ethylph	0.84	1.2	0.60	1.2	0.84	1.1	1.3	1.1

selectivity seems to be different in the FC-129 and the SDS system, the FC-129 system giving somewhat better results.

#### 4. Conclusions

It was demonstrated that the anionic fluoro-detergent FC-129 has a good MEKC potential. It has been shown that the efficiency of FC-129 exceeds that of SDS at the same and higher detergent concentrations and that interesting selectivity differences for some sample mixtures were observed.

Further experiments will be carried out to characterize the system in terms of selectivity, efficiency and migration window.

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