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Determination of C_4–C_{14} carboxylic acids by capillary zone electrophoresis
Application to the identification of diamide degradation products and partitioning studies

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Abstract

Capillary zone electrophoresis (CZE) was investigated for the determination of linear saturated carboxylic acid homologues ranging from C_4 to C_{14}. Separation conditions were optimised to overcome the problems of decreasing solubility and decreasing selectivity between successive homologues with increasing chain length. Separations were performed at 20°C, using a 20 kV separation voltage and a pH 8 electrolyte containing 30% methanol. A suitable chromophore (4-aminobenzoate) was added to ensure indirect UV detection of the analytes. Calibration curves and repeatability were established. Minimum detectable concentrations of $3 \cdot 10^{-6}$ mol l^{-1} were achieved. Resolution between successive homologues was better than 2. The electrophoretic mobility of each homologue ($n=7$–14) was assessed and a quasi-linear relationship between the mobility value and $1/n$ was observed. The quantitative analysis of a diamide degradation solution was performed and compared to potentiometric results. The CZE method was also applied to the determination of C_7–C_{14} partitioning between an organic medium containing tributylphosphate in *n*-dodecane and different basic solutions. Their behaviour was established according to the chain length and the pH of the aqueous phase. For C_{10}–C_{14} compounds, results were validated by comparison with gas chromatographic analysis of the organic phases.

Keywords: Partitioning; Carboxylic acids; Dimethyldioctylhexylethoxymalonamide

1. Introduction

Carboxylic acids play an important role in many biological fields. Fatty acids, defined as all saturated and unsaturated aliphatic carboxylic acids containing 6 to 24 carbon atoms, are present in oils and fats coming from plants and animals [1]. Saturated aliphatic carboxylic acids containing 4 to 14 carbon atoms also appear in industrial processes, and specially in the nuclear industry. Nuclear fuel reprocessing plants indeed are presently designed to separate uranium and plutonium from all other elements (actinides and fission products) created during the burning of the nuclear fuel. In order to improve the management of radioactive waste, studies are in progress to seek further separation of the other elements in the flows stemming from the current process. In that framework, a process based on liquid–liquid extraction is tested to isolate simultaneously and selectively minor actinides and lanthanides from the other fission products. This process uses a chelating molecule, namely a diamide, in an

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organic phase [2,3]. As the aqueous solution containing the actinides and fission products is a concentrated nitric acid solution (3 mol l^{-1}), the extracting molecule undergoes degradation through both hydrolysis and radiolysis mechanisms. The formation of degradation products lowers the performances of the extraction solvent. Some of the degradation products, such as secondary amides or monoamides, could be identified directly in the organic phase by gas chromatographic (GC) analysis [4]. However, the GC method was not suited to shorter compounds whose peaks were hindered by the wide solvent peak. Potentiometry enabled the determination of acidic products and showed that carboxylic acids constituted the main degradation products of the diamide. But such a technique only afforded a global result without individual quantification. The restoration of the solvent performances requires the identification of the degradation products, the quantification of the main compounds, and the implementation of appropriate purifying steps. In order to understand the degradation mechanisms of extraction solvents and the behaviour of degradation products during different washing steps, a simple, reliable and robust determination method for carboxylic acids ranging from C_4 to C_{14} is needed.

Carboxylic acid analyses are generally performed by chromatographic methods. However, they often require a derivatisation step prior to the separation, which is time-consuming and may rise problems of incomplete reaction or by-products formation. Most analyses are carried out by GC coupled to flame ionisation detection (FID), after a preliminary esterification of the acids into their methyl or silyl esters so as to enhance their volatility [5–7]. Due to their low UV absorbance, acids separations by high-performance liquid chromatography (HPLC), generally performed as reversed-phase HPLC, also often involve a derivatisation to allow their detection. Many pre- or post-column esterification reagents that confer a high absorbance or fluorescence have been employed [8–10]. Only a few methods have been developed for their direct analysis, including GC analysis on specifically designed stationary phases [11], HPLC analysis with low-wavelength UV detection [12] or supercritical fluid chromatography [13]. For a direct analysis in aqueous media, capillary electrophoresis constitutes an attractive alternative, due to its high resolution power, its rapidity, its easy experimental implementation, its low cost, and the large choice of operating conditions. During the last decade, applications of capillary electrophoresis to the analysis of low-molecular-mass compounds has expanded considerably. Separations of anionic species such as aliphatic carboxylic acids described in the literature are mainly performed by capillary zone electrophoresis (CZE), but a few separations also bring into play micellar electrokinetic chromatography (MEKC) [14–22]. The methods thus differ in the use of micelles or in the speed and the direction of the electroosmotic flow carrying the analytes simultaneously to the migration. Separation of short-chain carboxylic acids containing up to seven carbon atoms have been developed in [14–17]. Difficulties appear in the analysis of medium- and long-chain acids because their solubility in aqueous medium decreases with growing chain length, they tend to form aggregates and the separation selectivity between successive homologues drops rapidly with increasing chain length. Such problems can be solved by optimising the electrolyte composition. The CZE separation of some C_5 to C_{18} carboxylic acids was thus performed in a highly concentrated buffer [18], some C_4 to C_{24} fatty acids were also separated in an electrolyte containing an organic solvent [19], but the methods exhibited a low sensitivity or a poor resolution between successive homologues from C_9. A complexing molecule was also introduced so as to solubilise the acids and enhance the selectivity [20]. In MEKC, the addition of a neutral surfactant or both a neutral and an ionic surfactant together with an organic solvent enabled the separation of C_8 to C_{20} fatty acids [21,22].

The aim of this work was the investigation of CZE for the determination of linear saturated carboxylic acids (LSCAs) ranging from C_4 to C_{14} and differing in only one carbon unit. A simple electrolyte was sought. Separation conditions were optimised to overcome the problems of the lack of a chromophore function on the analytes and of decreasing solubility and decreasing selectivity between successive homologues with increasing chain length. The potential of the method was evaluated for the qualitative and quantitative determination of diamide degradation products in the above-mentioned conditions and

results were compared to those obtained by potentiometry. In order to develop appropriate chemical treatments, the CZE method was also applied to the study of C_7–C_{14} LSCA partitioning between organic and aqueous solutions. The LSCA behaviour was established according to the chain length and the pH of the aqueous phase. For C_{10}–C_{14} compounds, results were validated by comparison with GC of the organic phases.

2. Experimental

2.1. Instrumentation

Capillary electrophoresis experiments were carried out on a ThermoQuest SpectraPhoresis Ultra system (ThermoQuest, San Jose, CA, USA), equipped with a SpectraPhoresis UV3000 absorbance detector. A fused-silica capillary of 40.5 cm (34.5 cm to the detector window)×50 μm I.D.×375 μm O.D. from Thermoquest was employed for the separations.

An Autosystem gas chromatograph (Perkin-Elmer, Las Vegas, NV, USA) equipped with a split–splitless injector and an FID system was used for GC analyses. Analytical separations were performed on a 15 m×0.53 mm I.D. polar capillary column from Supelco (Bellefonte, PA, USA) coated with a 0.5 μm film of polyethylene glycol modified with nitroterephtalic acid (Nukol).

Separation of aqueous and organic phases in partitioning experiments were carried out by centrifugation with a Jouan C400 Searle apparatus (Jouan, Winchester, VA, USA).

2.2. Chemicals

Standards and chemicals used for the electrolytes were of HPLC grade or analytical-reagent grade. The C_4 to C_{14} linear saturated carboxylic acids standards were supplied by Sigma (St. Louis, MO, USA) or Fluka (Buchs, Switzerland). *p*-Aminobenzoic acid (*p*AB) and triethanolamine were purchased from Fluka, tributylphosphate (TBP) and methanol from Prolabo (Fontenay sous Bois, France), *n*-dodecane from Acros (Acros Organics, NJ, USA). The *N*,*N*′-dimethyl-*N*,*N*′-dioctylhexylethoxymalonamide (DMDOHEMA) and the 2-[methyl(octyl)carbamoyl] hexyloxybutanoic acid (Amide Acid) were synthesised by Panchim (Evry, France). Electrolytes were prepared using LC-quality water obtained by purifying demineralised water in a Milli-Q filtration system (Millipore, Milford, MA, USA).

2.3. Preparation of the diamide degradation samples and the partitioning experiments

The DMDOHEMA diamide, initially at a 0.69 mol l^{-1} concentration in hydrogenated tetrapropylene, was hydrolysed in the presence of 3 mol l^{-1} HNO_3. Vials containing mixtures of diamide and HNO_3 solutions (50:50, v/v) were maintained at 45°C and agitated every day for 1 min, during 1 or 2 months. Acid degradation products were then extracted from the hydrolysed sample using liquid–liquid extractions with 0.3 mol l^{-1} NaOH. Owing to the high concentration of the target compounds, the extraction solution was diluted 500 times before CZE analysis.

Partitioning experiments were performed by stirring 10 ml of organic phase (*n*-dodecane–TBP, 70:30, v/v) containing the target analytes (C_7 to C_{14}) initially at $4{\cdot}10^{-4}$ mol l^{-1} with 10 ml of aqueous NaOH solutions at different pH, until equilibrium was reached. A kinetic study performed at pH 10.9 after contact times of 5 and 30 min showed that equilibrium was reached in 5 min. Both phases were separated by centrifugation at 3000 rpm. The pH of the aqueous phase was measured. The analytes concentration in the aqueous phase was then determined by CZE, the content of the organic phase being assessed by GC.

2.4. Procedures

For CZE analyses, standard solutions containing C_4 to C_{14} carboxylic acids at concentrations ranging from 10^{-2} to 10^{-6} mol l^{-1} were prepared from 0.2 mol l^{-1} stock solutions in methanol. For distribution experiments, stock solutions of the C_4 to C_{14} carboxylic acids were prepared in *n*-dodecane. The 1-ml samples analysed by CZE were prepared as follows: 500 μl of unknown sample (or standard solution)+ 200 μl of 10^{-2} mol l^{-1} *p*-aminobenzoate adjusted to pH 8 with triethanolamine+300 μl of methanol.

In all CZE experiments, samples were injected

using the hydrodynamic mode with a 0.8 p.s.i. pressure applied for 5 s, which corresponds to a 9.6 nl injection volume (1 p.s.i.=6894.76 Pa). Other parameters such as temperature, separation voltage, electrolyte composition were optimised. After optimisation, the following conditions were selected. Analytes were separated in an electrolyte containing 10^{-2} mol l^{-1} *p*-aminobenzoate adjusted to pH 8 with $2.73 \cdot 10^{-2}$ mol l^{-1} triethanolamine (pH and concentrations before the addition of methanol), mixed with methanol (70:30, v/v). A constant voltage of +20 kV was applied. The temperature was set to 20°C. The separation current was 2.6 μA. Analytes were monitored by indirect UV detection at 264 nm. Methanol was used as the electroosmotic flow marker. Between each run, the capillary was rinsed with the electrolyte for 1 min at a 100 p.s.i. pressure, which corresponds to the displacement of 20 capillary volumes. Each analysis was repeated three times. Peak areas corrected by migration times were considered for quantification.

GC analyses of carboxylic acids in organic samples were carried out without any derivatisation of the analytes. A 0.5-μl sample volume was introduced into the column via the split–splitless injector used in the splitless mode, and set at 250°C. The carrier gas was helium, at a 4.4 ml min^{-1} flow-rate. Separations were performed using a temperature gradient raising from 110°C to 160°C at a rate of 8°C min^{-1}, then from 160°C to 165°C at 1°C min^{-1}, then from 165°C to 220°C at 10°C min^{-1} and finally maintained at 220°C for 2 min. The FID temperature was set to 250°C. For quantification, hexadecanoic acid was added to the samples as the internal standard. Each analysis was repeated twice.

2.5. CZE calculations

Electroosmotic mobility m_{eo} was calculated from the electroosmotic time t_{eo} using the relation $m_{eo}=(lL)/(t_{eo}V)$, where L represents the total length of the capillary, l the length to the detector window and V the applied voltage. Electrophoretic mobility m^i_{ep} of the i compound was calculated as the difference between apparent mobility m^i_{app} [obtained from the migration time $t^i_m=(lL)/(m^i_{app}V)$ of the i compound on the electropherogram] and electroosmotic mobility, yielding $m^i_{ep}=lL/V \cdot (1/t^i_m - 1/t_{eo})$.

The mobility at infinite dilution was calculated from the empirical relation valid within the ionic strength range 10^{-3}–10^{-1} mol l^{-1}: $m^i_{ep}=m^{i\infty}_{ep} \exp(-\omega.\sqrt{|z|I})$, where m^i_{ep} is the analyte mobility measured in a I ionic strength electrolyte, z the analyte charge and ω a constant equal to 0.5 for $z=1$ [24].

When repeatability was examined, the relative standard deviation was calculated as 100 times the ratio of the standard deviation to the mean.

Efficiency was measured by the theoretical plate number N defined by $N=(t_m/\sigma)^2$, where σ is the standard deviation of the peak, in minutes. In practice, the peak width at half height ($w_{1/2}$) was measured, and the theoretical plate number was calculated using the relation $N=5.54(t_m/w_{1/2})^2$.

Peak asymmetry was defined at 10% of the peak height.

Resolution between two peaks 1 and 2 was obtained from the electropherogram using the relation $R_s=2(t^2_m-t^1_m)/(w_1+w_2)$, where w refers to the peak width measured at the base, expressed in time units. Using the mobilities, the resolution can be expressed by $R_s=1/4 \cdot |(m_{ep1}-m_{ep2})/(m_{ep}+m_{eo})| \sqrt{N}$, where m_{ep} is the mean value of the effective electrophoretic mobility and N the mean efficiency value [25]. As compounds are completely ionised, effective mobility is equal to the absolute electrophoretic mobility of the carboxylate. Insofar as efficiency is limited by the diffusion, i.e., broadening is controlled by axial diffusion, the resolution can be approximated to $R_s=(Vl)^{1/2}/[4(2LD)^{1/2}] \cdot |m_{ep1}-m_{ep2}|/|m_{ep}+m_{eo}|^{1/2}$, where D is the diffusion coefficient of the analyte [26].

3. Results and discussion

3.1. CZE optimisation

Carboxylic aliphatic acids can be separated either in the co-electroosmotic mode (electroosmotic flow and electrophoretic migration in the same direction) or in the counter-electroosmotic mode (electroosmotic flow and electrophoretic migration in the opposite direction), according to the chain length of the analytes. The co-electroosmotic mode is suitable for short-chain compounds but not for long-chain com-

pounds since all low mobility analytes will migrate with a poor resolution within a small time window limited by the electroosmotic marker. For low mobility species, a better resolution is brought about in the counter-electroosmotic mode, detection occurring either at the anode or at the cathode. A CZE separation in the counter-electroosmotic mode with anodic detection was first tried, using conditions developed for compounds with a slightly higher mobility than our target analytes, namely dicarboxylates containing 2 to 11 carbon atoms [23]. In this configuration, the analytes are carried towards the detector by their own electrophoretic mobility, the electroosmotic flow being in the opposite direction. The separation took place in a pH 9.6 electrolyte containing a cationic surfactant tetradecyltrimethyl ammonium bromide (TTAB) at a $7 \cdot 10^{-5}$ mol l^{-1} concentration, below its critical micellar concentration, so as to slow down the electroosmotic flow. A −30 kV voltage was applied, the temperature was set to 25°C. This method was suited for short and medium-chain-length LSCAs such as C_7, but not for long-chain compounds such as C_{14}, which possessed a too low electrophoretic mobility to make up for the electroosmotic flow, despite the reduction of the latter.

Following this unsuccessful attempt, the LSCA CZE analysis was then developed in the counter-electroosmotic mode with a cathodic detection. The electroosmotic flow carries the analytes towards the detector, whereas their own electrophoretic mobility stands against this migration, which slows them down and allows a better resolution. In this configuration, the applied voltage was positive.

A simple separation system was sought, with an electrolyte containing as few reagents as possible (buffer+chromophore), taking the nature of the analytes into account. The parameters on which the choice was based were the baseline stability, peak symmetry, sensitivity, analysis time and, above all, resolution between successive homologues. As developed in the experimental section, the resolution is proportional to the absolute value of difference in mobility of both analytes $|m_{ep1}-m_{ep2}|$ and inversely proportional to the square root of the absolute value of the sum of the mean electrophoretic mobility and the electroosmotic mobility $|m_{ep}+m_{eo}|$. Several ways of improving the resolution could be to increase the difference between the mobility of successive homologues, or to reduce $|m_{ep}+m_{eo}|$, that is to say to reduce the electroosmotic flow by adding an electroosmotic flow modifier (solvent, surfactant), using a high concentration buffer, or decreasing the temperature. The effect of these factors was examined below.

First of all, the electrolyte composition was optimised. This included particularly its pH, the nature of the chromophore enabling analytes indirect detection and the proportion of organic solvent necessary to make the long-chain acids soluble and well separated.

As the LSCAs have very close pK_a values between 4.8 and 5 at 25°C [27], their separation could not be based on differences in their effective charges. Their analysis should rather be carried out with the anionic form, so as to maximise their mobility. A basic electrolyte at pH 8.0 was then implemented. In order not to introduce in the electrolyte other anions than the chromophore, a cationic buffer was selected. Triethanolamine, with a pK_a value of 7.8 at 25°C, was thus employed to fix the pH.

Due to the lack of chromogenic centre in the analytes, a chromophore had to be introduced in the electrolyte to ensure their indirect UV detection. To optimise the sensitivity, the chromophore should carry a charge of the same sign as the analytes, possess a mobility close to the one of the analytes and a high molar absorptivity. Three chromophores, whose characteristics are listed in Table 1, were investigated at a 10^{-2} mol l^{-1} concentration. Using chromate, the C_7 carboxylate was scarcely detected

Table 1
Some data of the chromophores investigated for the indirect absorbance detection of LSCAs

Chromophore	Chromate	Benzoate	4-Aminobenzoate (*p*AB)
Absolute mobility at 25°C ($\cdot 10^5$ cm^2 s^{-1} V^{-1}) [20,23]	81.1/88	33.6	31
Detection wavelength (nm)	264	254	264
Molar absorptivity (l mol^{-1} cm^{-1})	3900	800	8900

and C_{14} could not be observed, despite a high concentration (10^{-2} mol l^{-1}). Chromate was not suited to the analysis of the C_7–C_{14} LSCAs because of a too large gap between chromophore and analytes mobilities. In the presence of benzoate, used for the separation of low mobility acids in [18], the C_7–C_{14} LSCAs exhibited sharp and symmetric peaks, thanks to an appropriate mobility. However, the low molar absorptivity of benzoate resulted in a poor sensitivity. Finally, *p*AB, which had been used for the separation of some long-chain dicarboxylic acids [23], proved to be the best suited to the separation. Sharp and symmetric peaks were obtained, with a tenfold increase in sensitivity, compared to benzoate. *p*-AB was therefore selected.

The main problem with long-chain carboxylic acids is their low solubility in aqueous medium as soon as the chain length exceeds seven carbon atoms. In a merely aqueous electrolyte, the peak height of C_{13} and C_{14} was reduced, indicating an incomplete solubilisation or aggregate formation. Moreover, resolution between successive homologues was far inadequate (lower than 1) and decreased with the chain length, the C_{10}–C_{14} LSCAs being hardly separated. To overcome both insolubility and resolution problems, a given proportion of organic solvent or/and specific reagents can be introduced in the electrolyte [20,22]. Methanol, which solubilises the analytes and is miscible with water, was added to the electrolyte. Different concentrations were tested, namely 10, 30 and 50% (v/v). Methanol percentage should not be too high because its addition to the electrolyte reduces the electroosmotic flow and thus lengthens migration times. The presence of methanol modifies both the electrolyte viscosity and the zeta potential. As shown in Fig. 1, the electroosmotic flow decreased from 72 $cm^2\ s^{-1}\ V^{-1}$ in the absence of methanol to 53, 40 and 29 $cm^2\ s^{-1}\ V^{-1}$ in the presence of 10, 30 and 50% methanol, respectively, at 30°C. However, even with the low values obtained with 50% of methanol in the electrolyte, the electroosmotic flow remained sufficient to carry the analytes towards the detector. As a consequence, analysis time increased with the methanol percentage. Migration time of one of the slowest compound (C_7) raised from 1.83 min in the absence of methanol to 2.79, 4.69 and 7.46 min in the presence of 10, 30 and 50% methanol, respectively, at 30°C, with an applied voltage of 28 kV. When 30% of methanol was introduced in the electrolyte, C_4 to C_{12} LSCAs were completely solubilised whatever their concentration (highest concentration studied of $4{\cdot}10^{-4}$ mol l^{-1}), C_{13} and C_{14} exceeding their solubility limit at $1–2{\cdot}10^{-4}$ mol l^{-1}. The addition of organic solvent also improves significantly the resolution between successive homologues, up to a 30% proportion. As an example, the resolution between C_7 and C_8 increased from 1.0 to 1.90 and 2.80 in an electrolyte containing, respectively, 0, 10 and 30% of methanol, at 30°C, with a 28 kV separation voltage. A 50% proportion of methanol was not recommended since it increased the background noise and the resolution was not better (2.82). The increase in the methanol percentage in the electrolyte actually induced a strong reduction of the electroosmotic flow, as is shown in Fig. 1A, due to a decrease of the medium relative permittivity as well as an increase of its viscosity (the viscosity of

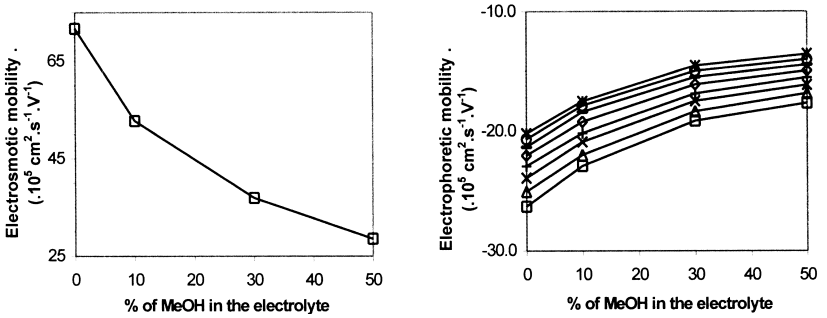

Fig. 1. Dependence of the electroosmotic and electrophoretic mobilities on the methanol percentage in the electrolyte, at 30°C. – □ – C_7, – △ – C_8, – × – C_9, – + – C_{10}, – ◇ – C_{11}, — – — C_{12}, – ○ – C_{13}, ✱ C_{14}.

the methanol–water mixture increases from 0 to 40% and then diminishes). The absolute value of the electrophoretic mobilities is also reduced, but far less strongly, as this can be noticed in Fig. 1B, so that the main term affected by methanol increase in the expression of the resolution is $|m_{ep}+m_{eo}|$, the variation in the term $|m_{ep1}-m_{ep2}|$ being negligible. As the former term is strongly reduced, resolution increases. A 30% methanol proportion was the added to the electrolyte, resulting in a good analyte solubilisation and an improved resolution.

Other parameters such as the applied voltage and the temperature also influence the analysis time, efficiency and resolution. A strong dependence on the temperature was observed. When the temperature was reduced from 30 to 20°C, a 30% increase in efficiency was noticed and resolution between C_7 and C_8 raised by about 25%, due to the increase in viscosity with temperature. However, analysis time also lengthened by about 30% because of a reduction of the mobilities. In order to improve the resolution, temperature was set to 20°C. The voltage value, investigated at 20, 28 and 30 kV, had little effect on the efficiency and on the resolution. A +20 kV voltage was then applied for the analyses.

Fig. 2 illustrates the CZE separation of a standard solution of C_4 to C_{14} LSCAs performed in the above optimised experimental conditions. Due to the CZE configuration selected, the LSCAs were detected in the order of decreasing chain length.

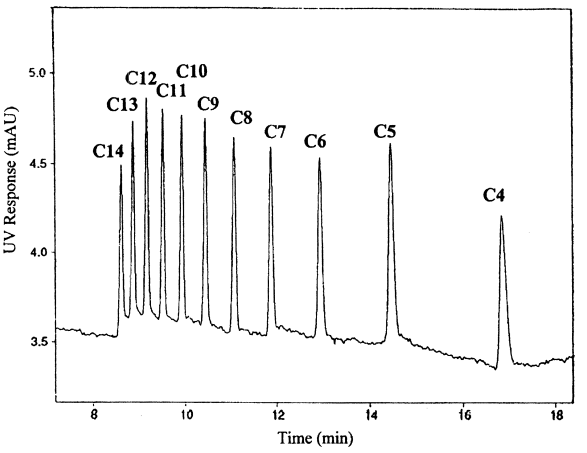

Fig. 2. CZE separation of a standard solution containing (C_4) butanoate, (C_5) pentanoate, (C_6) hexanoate, (C_7) heptanoate, (C_8) octanoate, (C_9) nonanoate, (C_{10}) decanoate, (C_{11}) undecanoate, (C_{12}) dodecanoate, (C_{13}) tridecanoate and (C_{14}) tetradecanoate, at $5\cdot10^{-5}$ mol l^{-1} each. Experimental conditions: hydrodynamic injection with 0.8 p.s.i. pressure for 5 s, fused-silica capillary, 40.5 cm (34.5 cm to the detector window)×50 μm I.D., electrolyte, 10^{-2} mol l^{-1} *p*-aminobenzoate+$2.7\cdot10^{-2}$ mol l^{-1} triethanolamine (pH 8.0)–methanol (70:30, v/v), separation voltage, +20 kV, temperature, 20°C, indirect UV detection at 264 nm.

3.2. Quantitative aspects

The performances of the CZE analytical method were evaluated with respect to repeatability, linearity and detection limits. Some parameters characterising the quality of the separation were also assessed, including the efficiency, the peak asymmetry factor and the resolution between successive peaks.

The repeatability of migration time, enabling the identification of the analyte, and the repeatability of peak areas corrected by migration time, enabling its quantification, were determined using results obtained for three CZE analyses of samples containing each LSCA standard (C_4 to C_{14}). Results obtained at eight different concentration levels ranging from $2\cdot10^{-4}$ to $5\cdot10^{-6}$ mol l^{-1} are reported in Table 2. Within one set of experiments, migration times were very reproducible. The relative standard deviation on migration time is in the order of 0.5–1%, whatever the analytes concentration in the range investigated. Consequently, only the results obtained at 10^{-4} mol l^{-1} are indicated in Table 2. The relative standard deviation of areas corrected by migration time ranges from 1 to 10% over the concentration range $2\cdot10^{-4}$–10^{-5} mol l^{-1}, which is satisfactory considering the repeatability usually mentioned in the literature [25], and enables an accurate quantification. The precision drops when the concentration comes closer to the detection limit.

Calibration curves were drawn using standard solutions at the same concentration ($2\cdot10^{-4}$ to $5\cdot10^{-6}$ mol l^{-1}). Linear regression data were obtained on the whole range for C_4 to C_{12}, the upper limit of the working range being 10^{-4} mol l^{-1} for C_{13} and C_{14}. These data are reported in Table 3. At a given concentration, the response of all the LSCAs (time corrected peak area and peak height) are nearly identical. Such a result could be expected as these compounds are homologues carrying the same charge, hence yielding the same response when

Table 2
Precision for migration times (t_m) and for peak areas corrected by migration times (A/t_m) of LSCAs, expressed as relative standard deviation (RSD) (%), according to the concentration (three repetitions at each concentration level)

Concentration (mol l^{-1})	RSD t_m,	RSD A/t_m							
	$1\cdot10^{-4}$	$2\cdot10^{-4}$	$1\cdot10^{-4}$	$7.5\cdot10^{-5}$	$5\cdot10^{-5}$	$2.5\cdot10^{-5}$	$1\cdot10^{-5}$	$7.5\cdot10^{-6}$	$5\cdot10^{-6}$
C_4	1.0		2.5	1.1	2.6				
C_5	0.9		4.0	2.2	5.3				
C_6	0.8		3.8	4.4	3.2				
C_7	1.1	5.5	3.4	4.3	6.1	2.1	8.4	23.9	27.1
C_8	1.0	1.6	2.6	4.1	2.8	4.1	10.2	15.3	31.7
C_9	0.9	3.0	1.5	6.2	0.4	2.2	9.1	19.5	13.8
C_{10}	0.9	3.3	3.3	2.8	7.0	5.3	0.5	24.0	11.2
C_{11}	0.8	2.4	1.7	3.1	0.5	10.0	7.3	9.0	16.8
C_{12}	0.8	2.6	8.6	1.3	0.8	8.0	13.2	19.8	36.8
C_{13}	0.7		7.2	5.1	6.2	16.0	8.1	36.3	29.3
C_{14}	0.7		7.5	2.6	5.8	1.4	14.1	17.9	10.9

Operating conditions as in Fig. 2.

monitored by UV indirect detection. The correlation coefficients are satisfactory. The detection limits, defined for a signal-to-noise ratio equal to three, were measured on the peak heights. Using this method, it proved possible to detect $3\cdot10^{-6}$ mol l^{-1} of each acid.

Efficiency was measured at low concentration, in the order of $5\cdot10^{-5}$ mol l^{-1}, because the plate number decreased with increasing injected amount, beyond a threshold concentration value. Peak dissymmetry also increased with increasing concentration, beyond this threshold value. Actually, as the analyte mobility is not strictly identical to the chromophore mobility, the analyte peak is not symmetric because of local heterogeneity of electric field near the analyte zone. When the analyte amount is higher than the separation capacity, peak dissymmetry increases, the contribution of migration to the analyte zone broadening rising more and more towards the contribution of diffusion. Consequently, beyond a threshold concentration, peak dissymetry is more and more pronounced, leading to a reduction of efficiency and resolution. Efficiency, peak asymmetry and resolution were measured at $7.5\cdot10^{-5}$, $5\cdot10^{-5}$, and $2.5\cdot10^{-5}$ mol l^{-1}, respectively. Peak symmetry improved slightly at the lowest concentration, but resolution and efficiency did not show any significant difference. Results obtained at

Table 3
CZE linear regression data of peak areas corrected by migration time versus injection concentration of LSCAs

Compound	Slope (10^6 mAU l mol^{-1})	Intercept (mAU)	Correlation coefficient (R^2)
C_4	7.52	−13	0.999
C_5	8.98	−2	0.998
C_6	7.92	−8	0.999
C_7	7.55	−18	0.998
C_8	8.27	−25	0.997
C_9	8.21	−13	0.998
C_{10}	8.36	−24	0.997
C_{11}	8.54	−31	0.996
C_{12}	7.97	−8	0.996
C_{13}	7.69	2	0.999
C_{14}	7.77	−16	0.991

C_7 to C_{14} acids were studied in the concentration range $5\cdot10^{-6}$ to $2\cdot10^{-4}$ mol l^{-1}, C_4 to C_6 acids in the concentration range $5\cdot10^{-5}$ to $1\cdot10^{-4}$ mol l^{-1}.

Table 4
Efficiency (theoretical plate number) with a 34.5 cm capillary (length to the detector window), peak asymmetry and resolution, at the $5 \cdot 10^{-5}$ mol l^{-1} concentration level

Compound	Plate number	Asymmetry	Resolution
C_4	99 000 (±6000)	1.39 (±0.031)	9.61 (±0.12)
C_5	116 000 (±4000)	1.18 (±0.040)	7.48 (±0.08)
C_6	128 000 (±7000)	1.05 (±0.012)	6.16 (±0.09)
C_7	140 000 (±8000)	0.99 (±0.006)	4.91 (±0.21)
C_8	143 000 (±7000)	0.91 (±0.005)	4.16 (±0.23)
C_9	132 000 (±15 000)	0.88 (±0.009)	3.71 (±0.18)
C_{10}	138 000 (±12 000)	0.84 (±0.017)	3.20 (±0.13)
C_{11}	147 000 (±16 000)	0.83 (±0.032)	2.82 (±0.14)
C_{12}	132 000 (±8000)	0.80 (±0.003)	2.42 (±0.08)
C_{13}	130 000 (±7000)	0.82 (±0.041)	2·10 (±0.12)
C_{14}	114 000 (±21 000)	0.80 (±0.018)	

The figures in the table are mean values obtained for three repetitions, the standard deviations are indicated in parentheses. Operating conditions as in Fig. 2.

the $5 \cdot 10^{-5}$ mol l^{-1} level are reported in Table 4. A high efficiency of about 400 000 plates per meter is achieved with all LSCAs. Peak asymmetry is not pronounced. It is more important for longer-chain compounds (asymmetry factor of 0.80 for C_{14}, whose mobility is lower than the chromophore's), then asymmetry decreases with decreasing chain length, until C_7. The C_7 peak is symmetric, indicating a mobility identical to the one of the chromophore. When reducing chain length from C_7, the opposite variation is observed. Asymmetry grows when the carbon chain shortens, with asymmetry factors higher than 1, as the analytes mobility becomes greater than the chromophore's (asymmetry factor of 1.39 for C_4). Resolution between successive homologues is satisfactory and all the better as the LSCAs are shorter. Even for the longest compounds, resolution is higher than 2 at $5 \cdot 10^{-5}$ mol l^{-1}, indicating the return to the baseline between successive peaks.

Electrophoretic mobility of each compound was determined, and the variation according to the chain length was studied. Absolute electrophoretic mobilities of LSCAs were obtained in a 10^{-2} mol l^{-1} *p*AB+$2.7 \cdot 10^{-2}$ mol l^{-1} triethanolamine (pH 8) electrolyte, without any methanol, at 30°C. Absolute mobilities at infinite dilution were then deduced from the previous values using an empirical relation detailed in the Experimental section [24]. These values, reported in Table 5, match the C_{10} mobility of $-22.1 \cdot 10^{-5}$ cm^2 V^{-1} s^{-1} mentioned in Ref. [22]. Mobility decreases with increasing chain length. The variation in mobility at infinite dilution versus the carbon number inverse is quasi-linear, as shown in Fig. 3. This indicates that the friction coefficient of these homologues is actually proportional to the

Table 5
Absolute electrophoretic mobility m^i_{ep} of carboxylates in a 10^{-2} mol l^{-1} *p*AB+$2.7 \cdot 10^{-2}$ mol l^{-1} triethanolamine, pH 8 electrolyte, and absolute mobilities at infinite dilution $m^{i\infty}_{ep}$, at 30°C

Compound	m^i_{ep} ($\cdot 10^{-5}$ cm^2 V^{-1} s^{-1})	$m^{i\infty}_{ep}$ ($\cdot 10^{-5}$ cm^2 V^{-1} s^{-1})
C_7	−26.3	−27.7
C_8	−25.1	−26.4
C_9	−23.9	−25.2
C_{10}	−22.9	−24.1
C_{11}	−22.0	−23.2
C_{12}	−21.3	−22.4
C_{13}	−20.7	−21.7
C_{14}	−20.1	−21.1

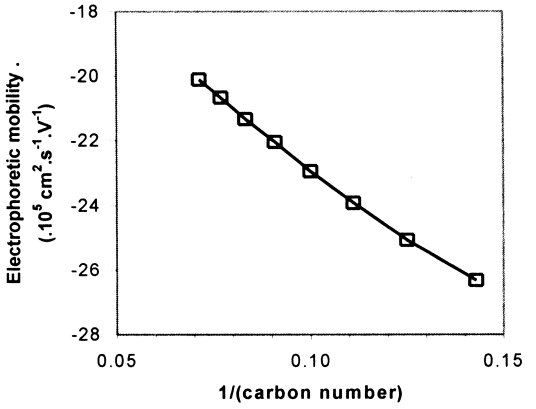

Fig. 3. Dependence of the eletrophoretic mobility of the carboxylate homologues $C_{n-1}H_{2n-1}COO^-$ on their chain length.

segment number of the chain, hence a mobility inversely proportional to the segment number.

3.3. Qualitative and quantitative analysis of LSCAs in diamide degradation solutions; comparison with potentiometric results

The method developed above was applied to the determination of LSCAs contained in diamide solutions degraded through their contact with a nitric acid solution. The structure of the DMDOHEMA diamide is presented in Fig. 4. This diamide, initially at 0.69 mol l^{-1} in hydrogenated tetrapropylene, was hydrolysed in the presence of 3 mol l^{-1} HNO_3 for a 1 or 2 month period. Acid degradation products were then extracted from the hydrolysed sample using a 0.3 mol l^{-1} NaOH solution, which was analysed by CZE after a proper dilution to match the optimal quantification range of the method. The NaOH content in the injected sample did not exceed $3\cdot10^{-3}$ mol l^{-1} and did not disturb the determination. LSCAs coming from the diamide degradation were identified by both migration times and spiking the sample with standards. The compound already identified by GC, namely the amide acid, was added to the standard solution of C_4–C_{14} carboxylic acids. The CZE analysis of the diamide sample hydrolysed during 1 month is illustrated in Fig. 5. Quantification was performed using the calibration curves. Similar results were obtained using spiked concentrations. The results of the identification and the quantification are gathered in Table 6. Standards such as C_4, C_5, C_6, C_7 and amide acid could be determined. Three unknown compounds, probably long-chain compounds if one considers their mobility, were detected. Compound 4 possesses the same migration time as the C_{11} standard. With regard to the diamide structure, it may correspond to a carboxylic acid containing 10 carbon atoms and one oxygen or nitrogen atom in its chain. The mobility of such a species must be very close to that of the C_{11} LSCA. A more powerful detection method than indirect UV detection, such as mass spectrometry, is required to conclude as to the identity. Unknown compounds were quantified assuming that they yielded the same response by indirect UV detection as the standards. This hypothesis was justified by a similar response for all LSCAs and the amide acid.

The comparison of the determination after a 1 month hydrolysis period and after a 2 month period

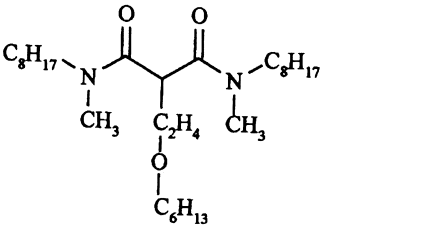

Fig. 4. Structure of the DMDOHEMA diamide.

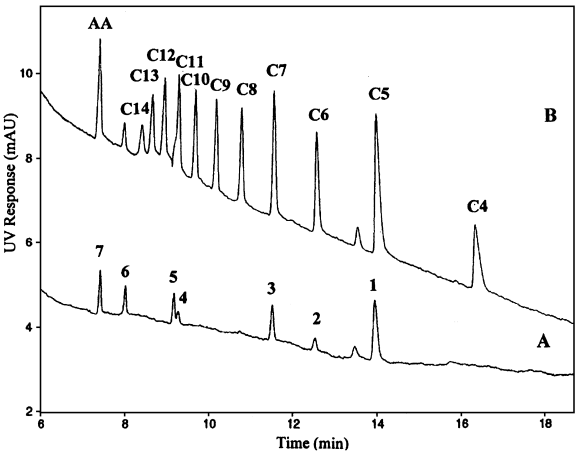

Fig. 5. CZE analysis of the degradation products of the DMDOHEMA diamide. Sample hydrolysed for a 1 month period, diluted 500 times (A) non-spiked, (B) spiked with 10^{-4} mol l^{-1} of each standard. Experimental conditions as in Fig. 2.

Table 6
Qualitative and quantitative CZE determination (±standard deviation, $n=3$) of the acid degradation products of the DMDOHEMA diamide hydrolysed for a 1 or 2 month period

Compound	Identification	Concentration (mol l^{-1})			
		CZE analysis[a]		Initial sample[b]	
		1 month hydrolysis	2 month hydrolysis	1 month hydrolysis	2 month hydrolysis
0	Butanoic acid (C_4)	n.d.	$1.3\ (\pm0.3)\cdot10^{-5}$	–	$1.3\cdot10^{-3}$
1	Pentanoic acid (C_5)	$6.2\ (\pm0.15)\cdot10^{-5}$	$51\ (\pm3)\cdot10^{-5}$	$31\cdot10^{-3}$	$51\cdot10^{-3}$
2	Hexanoic acid (C_6)	$1.3\ (\pm0.1)\cdot10^{-5}$	$6.7\ (\pm0.3)\cdot10^{-5}$	$6.5\cdot10^{-3}$	$6.7\cdot10^{-3}$
3	Heptanoic acid (C_7)	$3.3\ (\pm0.15)\cdot10^{-5}$	$14\ (\pm1)\cdot10^{-5}$	$16.5\cdot10^{-3}$	$14\cdot10^{-3}$
4	Unknown (same mobility as C_{11})	$1.2\ (\pm0.1)\cdot10^{-5}$	$6\ (\pm0.7)\cdot10^{-5}$	$6\cdot10^{-3}$	$6\cdot10^{-3}$
5	Unknown (mobility between the ones of C_{11} and C_{12})	$3.0\ (\pm0.15)\cdot10^{-5}$	$10.5\ (\pm0.5)\cdot10^{-5}$	$15\cdot10^{-3}$	$10.5\cdot10^{-3}$
6	Unknown (higher mobility than C_{14})	$2.9\ (\pm0.15)\cdot10^{-5}$	n.d.	$14.5\cdot10^{-3}$	–
7	Amide acid	$4.6\ (\pm0.2)\cdot10^{-5}$	n.d.	$23\cdot10^{-3}$	–
Total CZE×dilution factor[b]				$112\cdot10^{-3}$	$88\cdot10^{-3}$
Total potentiometry				$119\cdot10^{-3}$	$97\cdot10^{-3}$

n.d., Not detected, i.e., the concentration is below $3\cdot10^{-6}$ mol l^{-1}.
[a] Concentration in the sample analysed by CZE.
[b] Concentration in the initial sample, corresponding to the product of the concentration determined by CZE and the dilution factor. Dilution factor = 500 for the sample hydrolysed during 1 month, 100 for the sample hydrolysed during 2 months.

underlines that the longer degradation products, such as amide acid or compound 6, still undergo hydrolysis and disappear to form shorter products. As hydrolysis continues, the amount of shorter compounds such as C_4 and C_5 increases.

The whole acid content in each sample was calculated taking into account the dilution factor for CZE analysis. These values are in good agreement with the total content assessed by another technique, potentiometry, which, however, could not offer individual quantification because of too close pK_a values. Such an agreement also validates the way unknown compounds were quantified.

3.4. Partitioning of LSCAs between an aqueous solution and dodecane–TBP; comparison with GC analysis

To restore the extraction properties of diamide containing solvents or of other solvents where carboxylic acids appeared owing to hydrolysis or radiolysis, elimination of acids through basic liquid–liquid extractions can be implemented. Washing solutions containing sodium hydroxide at three different concentrations (pH 8.4, 10.8 and 11.9) were tested and their efficiency towards the elimination of the carboxylic acids was compared. The partitioning of C_7–C_{14} LSCAs was studied by stirring an organic phase of *n*-dodecane–TBP (70:30, v/v) (TBP is the extracting molecule used in the present process), initially containing the eight target analytes at $4\cdot10^{-4}$ mol l^{-1} with NaOH solutions until equilibrium was reached. The LSCAs being initially under their molecular form in the organic phase, the extraction pH is the pH of the aqueous solution measured at equilibrium. After phase separation, the analyte concentrations in the aqueous phase were determined by CZE, the content of the organic phase being assessed by GC. The C_4–C_6 LSCAs were completely extracted in the aqueous phase under these conditions.

In order to validate the CZE results, a GC method was actually developed for the analysis of LSCAs in organic solutions. The direct analysis of the free acids, without any derivatisation step, could be performed using a polar Nukol column. The GC method enabled the detection of C_{10} to C_{14} up to $5\cdot10^{-6}$ mol l^{-1}, that is to say 1% of the analyte

remaining in the organic phase, and C_7 up to $5 \cdot 10^{-5}$ mol l^{-1}, which is far too high for the traces remaining in the organic phase, according to the CZE results. The C_8 and C_9 compounds, eluted at the same time as the humps of the TBP solvent, could not be determined. The GC separation of a C_7–C_{14} LSCAs standard solution in *n*-dodecane–TBP (70:30, v/v) is presented in Fig. 6. The chromatogram highlights that LSCAs separation by CZE occurs in the reverse order to that obtained by the chromatographic method.

Concerning the CZE analysis of aqueous solutions, these samples may contain TBP, which is soluble up to 10^{-3} mol l^{-1} in aqueous solution [28], and sodium hydroxide at various concentrations between 10^{-6} and 10^{-2} mol l^{-1}. The effect of both components on the LSCAs determination was examined. Analysis of a pH 10.8 aqueous solution in equilibrium with *n*-dodecane–TBP (70:30) initially containing the LSCAs was compared to the analysis

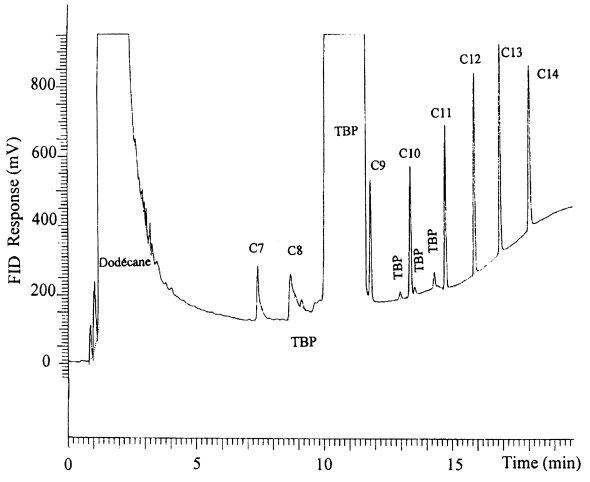

Fig. 6. GC separation of a standard solution containing (C_7) heptanoic acid, (C_8) octanoic acid, (C_9) nonanoic acid, (C_{10}) decanoic acid, (C_{11}) undecanoic acid, (C_{12}) dodecanoic acid, (C_{13}) tridecanoic acid, (C_{14}) tetradecanoic acid and (C_{16}) hexadecanoic acid, at 10^{-3} mol l^{-1} each, in *n*-dodecane–TBP (70:30, v/v). Experimental conditions: 15 m×0.53 mm I.D. Nukol column, split–splitless injector, 250°C, injection volume, 0.5 μl, FID, 250°C, carrier gas, helium 4.4 ml min^{-1}, temperature gradient, 110°C to 160°C at 8°C min^{-1}, 160°C to 165°C at 1°C min^{-1}, 165°C to 220°C at 10°C min^{-1}, maintained at 220°C for 2 min.

of a standard solution. TBP, as a neutral species, migrated at the same time as the electroosmotic flow and did not induce any change in migration time nor in C_7 or C_8 peak area, whose extraction from the organic phase is quantitative at this pH value. Sodium hydroxide in the sample however may disturb the determination both because of the difference between sample and electrolyte basicity, which locally modifies the capillary surface charge density, and because of a high ionic concentration in the sample. The comparison of LSCA analyses in matrices containing 0, 10^{-2}, $5 \cdot 10^{-2}$ and 10^{-1} mol l^{-1} NaOH showed a baseline greatly affected by NaOH at concentrations higher than $5 \cdot 10^{-2}$ mol l^{-1}, as well as a degradation of peak shapes and alteration of migration times. For such studies, the NaOH concentration should not exceed $5 \cdot 10^{-2}$ mol l^{-1}. At the pH values examined in this work, perturbations caused by the difference between sample and electrolyte pH were negligible.

Results of LSCAs determination in aqueous and organic solutions, expressed as the percentage of the initial concentration, are reported in Table 7. The total percentage of C_{10}–C_{14} compounds determined in both aqueous and organic solutions is about 100 for each LSCA, at each pH. The comparison with GC analysis of the organic phases thus confirms and validates the reliability of the CZE analysis of aqueous solutions.

The studied compounds are surfactants consisting of a long hydrophobic carbon chain ended with a polar, ionic, group. They thus present an affinity for the hydrophobic organic medium and the hydrophilic aqueous medium, and partition between both media. Huge variations could be observed in the LSCAs distribution between both solutions according to the chain length and according to the pH of the aqueous extracting solution. On the one hand, at a given pH value, shorter compounds are more easily extracted in the aqueous solution because of their lower hydrophobicity. At pH 10.8 for example, the whole amount of C_7–C_9 LSCAs is extracted in the aqueous solution, but extraction of longer compounds is not quantitative and the proportion decreases with the chain length, with, respectively 96, 80 and 51% of C_{10}, C_{11} and C_{12} in the aqueous solution, C_{13} and C_{14} remaining mainly in the organic phase (78 and 92%, respectively). Consequently, a pH 10.8 wash-

Table 7
Effect of pH and chain length on the partition of the LSCAs between the organic phase composed of *n*-dodecane–TBP (70:30, v/v) and the aqueous basic phase

	pH		
	8.35	10.75	11.85
Aqueous phase (%)			
C_7	99 (±8)	97 (±2)	95 (±3)
C_8	80 (±5)	97 (±1)	95 (±2)
C_9	41 (±7)	99 (±2)	95 (±2)
C_{10}	15 (±3)	96 (±1)	98 (±3)
C_{11}	7.5 (±2)	80 (±4)	97 (±4)
C_{12}	1.6 (±0.3)	51 (±0.5)	93 (±1)
C_{13}	1.3 (±0.2)	21 (±0.5)	78 (±3)
C_{14}	0.7 (±0.3)	6 (±0.5)	41 (±1)
Organic phase (%)			
C_{10}	87 (±3)	5 (±1)	0 (±0.2)
C_{11}	96 (±1)	18 (±1)	2 (±0.2)
C_{12}	100 (±0.5)	48 (±0.5)	10 (±0.2)
C_{13}	99 (±1)	78 (±1)	29 (±0.5)
C_{14}	100 (±0.5)	92 (±1)	60 (±0.5)
Total (%)			
C_{10}	102	102	98
C_{11}	104	98	99
C_{12}	101	100	103
C_{13}	100	99	107
C_{14}	101	98	101

Proportion extracted in the aqueous phase (±standard deviation, $n=3$), determined by CZE, proportion remaining in the organic phase (±standard deviation, $n=2$), determined by GC, and total percentage in both phases. Proportions are expressed as the percentage of the initial concentration ($4\cdot10^{-4}$ mol l^{-1}).

ing is efficient when short- and medium-chain acids are present. On the other hand, the amount of longer-chain compounds extracted grows with the basicity of the medium. The whole amount of C_{11} is present in the organic phase at pH 8.4, whereas only 2% remains in this phase at pH 11.9. The pH of the aqueous washing solution can then be chosen according to the nature of the acids: if C_{11} or C_{12} are present, a pH 11.9 washing solution is necessary for their total elimination. It should be noticed that C_{13} and C_{14} extraction was not limited by their solubility at these pH values since a pH 11.9 experiment conducted with a $2\cdot10^{-4}$ mol l^{-1} initial concentration displayed identical LSCA proportions in the aqueous phase.

4. Conclusions

This work proposes a simple and reliable CZE approach to the determination of carboxylic acid homologues containing 4 to 14 carbon atoms in aqueous media. Unlike most chromatographic methods, no sample pretreatment, such as derivatisation or liquid–liquid extraction, is required, and a single electrolyte is employed instead of gradient conditions. Besides, this technique presents economic advantages such as the rapidity of the separations, the low cost of consumable equipment, the negligible organic solvents or electrolyte consumption, and the minute analysed sample volume, which prove to be very attractive in the nuclear field. The optimisation of the separation parameters has led to operate at 20°C, using a 20 kV separation voltage, in a pH 8.0 electrolyte containing *p*-aminobenzoate as a chromophore to ensure indirect UV detection and 30% methanol to overcome the problems of solubility and mediocre selectivity between successive homologues for long-chain compounds. Such choices yield a good quality separation, displaying symmetric peaks with a high efficiency, in the order of 400 000 plates/m, and a fine resolution between successive homologues, beyond 2 whatever the analytes. The repeatability of migration time, in the order of 0.5 to 1%, and of surface areas corrected by migration times, in the order of 1 to 10%, are satisfactory to ensure a reliable identification and quantification. CZE furnishes detection limits of the same order of magnitude as chromatographic methods (GC–FID), and minimal detectable concentrations of $3\cdot10^{-6}$ mol l^{-1} are achieved. It has been checked that the sample matrix components, such as TBP or sodium hydroxide up to $5\cdot10^{-2}$ mol l^{-1}, do not interfere with LSCA determination. The electrophoretic mobility of each homologue ($n=7$–14) has been evaluated and a quasi-linear relationship between the mobility value and $1/n$ has been observed. This correlation enables the prediction of the mobility, and hence migration time, of LSCA homologues which were not examined in this work. Applications to the identification and the quantification of LSCAs in diamide degradation solutions have brought to the fore the formation of acid standards during diamide hydrolysis, but also of unknown products. In that case, the non-specificity of the indirect UV detection proves

useful to quantify unknown compounds. A good agreement with the potentiometric evaluation of the whole acid content validates the CZE procedure. A second validation has been obtained with the application of the CZE method to the partitioning of C_7–C_{14} LSCAs between an organic solution of *n*-dodecane–tributylphosphate (70:30, v/v) and different basic aqueous solutions. For C_{10}–C_{14} compounds, CZE results are confirmed by an excellent agreement with gas chromatography analysis of the organic phases. The establishing of C_7–C_{14} LSCAs behaviour according to the chain length and the pH indicates that efficient basic washings can be implemented to eliminated these compounds (up to C_{12}) from the organic phase, the pH needed for a total elimination depending on the length of the acids. Work is under way to determine the elimination conditions for longer-chain LSCAs.

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