Application of surfactants to the supercritical fluid extraction of nitroaromatic compounds from sediments [1]

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Abstract

Supercritical fluid extraction using supercritical carbon dioxide was applied to extract nitroaromatic compounds covering a wide range of polarity from soils having high humic organic matter content. Commercially available non-ionic, anionic and cationic surfactants were utilised as modifiers to enhance analyte solubility in the fluid.

The applied surfactants turned out to have no significant beneficial impact on target analyte recoveries. On the contrary, surfactants exercise a detrimental effect on recovery by the formation of a ''layer'' on the soil or by ''plugging'' micropores, thus hampering analyte desorption. The surfactant deposition onto the soil under supercritical conditions was traced using electrospray ionisation mass spectrometry. The surfactant can be fully solubilised by adding polar methanol modifier to the fluid, but there was no synergetic effect between surfactant and modifier. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Supercritical fluid extraction; Sediments; Nitroaromatic compounds; Surfactants

1. Introduction

Supercritical fluid extraction (SFE) has gained wide acceptance as an alternative to conventional analytical extraction techniques, which are mainly based on the utilisation of organic solvents [1]. The main reasons for this acceptance include the outstanding features of supercritical fluids having diffusivities and viscosities similar to gases and densities similar to liquids, thus enabling rapid mass transfers [2], and the opportunity to vary the solubility of a solute by several orders of magnitude isothermally by adjusting system pressure [3,4]. Carbon dioxide has been preferred for both analytical and technical applications due to its convenient critical point (31.1°C; 7.3 MPa), low cost and low toxicity.

Various modifiers have been used in attempts to compensate for the poor ability of supercritical carbon dioxide ($scCO_2$) to solvate polar organic compounds and to interrupt strong analyte–matrix interactions. The efficiency of modifiers including methanol, organic acids and amines turned out to depend on modifier identity and amount, type of sample matrix and target analyte (see [5] and [6] and references cited therein). Higher-molecular-mass

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modifiers including surfactants have not been a subject of intense research. The amphiphilic oligomers are expected to form microemulsions or self-assemble into reverse micelles or pre-micelle structures (aggregates of 3–10 molecules) [7,8] in the non-polar scCO$_2$ environment, thus tending to stabilise analyte molecules. A precondition for acting as an agent to stabilise analyte molecules is sufficient surfactant solubility in scCO$_2$, which has already been qualitatively investigated for a wide range of surfactants at 50°C and 10–50 MPa [9]. Some surrogates under study, in particular non-ionic ones, were shown to have the capability of forming microemulsions or pre-micelle structures (aggregates of 3–10 molecules). Extremely high solubilities in scCO$_2$ were observed with surfactants that contained highly fluid-philic perfluoropolyether tails [10–12].

In the framework of the present contribution, commercially available and low-cost non-ionic, anionic and cationic surfactants were studied to quantify their solubility in scCO$_2$ and to test their capabilities as SFE modifiers. In addition to the fundamental research focus, it was thought that scCO$_2$ modified with surfactants might be an attractive solvent alternative for many industrial processes, such as the remediation of soils heavily contaminated with priority pollutants [13] including nitroaromatics from ammunition plants [14].

2. Experimental

2.1. Chemicals

Surfactants (all contributed by Henkel, Düsseldorf, Germany or Buna, Schkopau, Germany) under investigation along with their structure are listed in Table 1. Target nitroaromatics (octanol–water coefficient, log K_{ow}, given in brackets to provide an indication of hydrophobicity) include 2-methyl-3-nitroaniline (1.42), 1,2-dinitrobenzene (1.58), 1,3-dinitrobenzene (1.72), 2,4,6-trinitrotoluene (1.86) and 2-nitrotoluene (2.30).

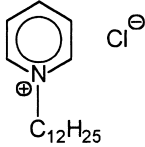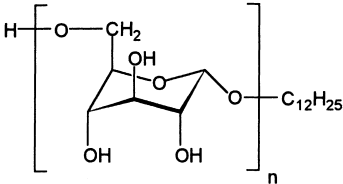### 2.2. Determination of surfactant solubilities in scCO$_2$

Surfactant solubilities were determined by means

of an autoclave (HPM-3; Premex Reactor, Lengnau, Switzerland; see Fig. 1) with a volume of 300 ml. Experiments were conducted statically at 50°C, 75°C and 100°C. The autoclave was filled with 5–30 g of the surfactant to be investigated (depending on solubilities expected on the basis of preliminary experiments), then CO$_2$ was added and both temperature and pressure were set as desired and held at a constant level. After establishing the solubilisation equilibrium (about 4 h), an aliquot of the fluid was taken manually via a three-way valve and flushed into an evacuated vessel (5 ml) made of stainless steel. The volume of the aliquot is regarded as small enough not to disturb the phase equilibrium and large enough to be within the detection limits of the successive analytical determinations. This sampling, which is considered to be adiabatic, was followed by an expansion of the fluid into 20 ml of water at room temperature via a capillary over a couple of hours. The combined aqueous solution, consisting of the above-mentioned 20 ml and the water portion obtained on flushing the sampling apparatus, was analysed according to the procedure detailed below. Despite the high time consumption of this off-line technique, an on-line monitoring was not applied because of a lack of appropriate ''in-situ'' analytical techniques (only UV–Vis appears to be appropriate with reasonable expenditure, and is only applicable to surfactants with chromophores) and serious calibration problems, which become even more pronounced for multicomponent matrices.

2.3. Quantification of surfactants

(a) Surfactant-selective electrodes: The aqueous solution containing the surfactant was diluted with bi-distilled water to give 50 ml volume and titrated with an auto-titrator DL 67 (Mettler–Toledo, Giessen, Germany) using a surfactant-selective electrode 93–42 (Orion, Boston, MA, USA), a reference electrode 90–02 (Orion) and a pH electrode DG 111–SG (Mettler–Toledo). As is already known, the utilisation of surfactant-selective electrodes is based on the measurement of potential changes (in mV) during the process of surfactant-ion pair formation, the marked change at the end point is correlated with the solubility of the precipitated salt. Therefore, according to [15], non-ionic surfactants were ''acti-

Table 1
Surfactants under investigation

Systematic name (Trade name)	Formula
Sodium dodecyl sulphate (Texapon K 1296)	$H_{25}C_{12}-O-SO_3Na$
Sodium dodecyl ethersulphate (Texapon N 28 KC)	$H_{25}C_{12}-(O-CH_2-CH_2)_n-O-SO_3Na$
Sodium diisooctyl sulpho-succinate (Texin DOS 75)	$H_{17}C_8OOC-CH(-SO_3Na)-CH_2-COOC_8H_{17}$
N-Dodecyl pyridiniumchloride (Dehyquart C)	pyridinium ring, $N^{\oplus}-C_{12}H_{25}$, $Cl^{\ominus}$
Nonylphenol ethoxylate (Präwozell N 10)	$H_{19}C_9-C_6H_4-(O-CH_2-CH_2)_n-OH$
Tridecyl ethoxylate (Präwozell F 1315)	$H_{27}C_{13}-(O-CH_2-CH_2)_n-OH$
Dodecyl ethpropoxylate (Präwozell FCE 1214)	$H_{25}C_{12}-(O-CH_2-CH_2)_n-(O-CH(-CH_3)-CH_2)_m-OH$
Dodecyl polyglucose (Plantaren 1200 UPNP)	glucose polymer, $H-[O-CH_2 ... O-C_{12}H_{25}]_n$

vated'' by addition of 1 ml of 0.05 M Ba^{2+} ions to give an ionic crown ether-like complex to be titrated. Advantages of this approach include a distinct jump of the titration curve at the end point and the opportunity to detect non-ionic surfactants in the presence of anionic ones, the latter being commonly
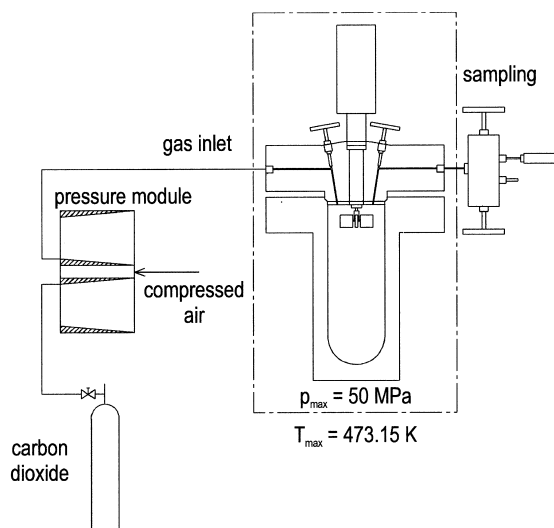
Fig. 1. Schematic presentation of the autoclave used.

precipitated by Ba^{2+} ions. Non-ionic surfactants were titrated with 0.001 M solution of sodium tetraphenylborate, anionic ones with 0.001 M solution of Hyamine (Orion) and the cationic Dehyquart C with 0.001 M solution of sodium dodecylsulphate (Henkel).

(b) RP-HPLC: HPLC device (Knauer, Berlin, Germany) consisted of a pump (Maxi–Star K-1000), a degasser, a dynamic mixing chamber, a thermostat (Jetstream 2), a six-port valve (A0634), a UV detector (K-2500) and a light-scattering detector (Sedex 55, detailed in [16]). Analyses were performed using a Kromasil C_4 column (250 mm×4 mm, particle size 5 μm; Knauer) using either isocratic or gradient elution with water–methanol mixtures (see [17]). UV detection of the single surfactant peak, which was indicative of the total surfactant concentration, was used for the surfactants Präwozell N 10 (λ_{max}=226 nm) and Dehyquart C (λ_{max}=258 nm). Light-scattering detection was utilised (double logarithmic calibration, evaporator 40°C, 0.2 MPa nitrogen pressure to ensure the aerosol formation) for the other surfactants which do not contain any significant UV absorbency due to the lack of chromophores. The quantitative calibration of surfactant oligomers by means of light-scattering detection is crucial and will be discussed later.

2.4. Spiking the sediment sample

A municipal river sediment (organic carbon content (OC)=7%) was air-dried and a fraction 63–250 μm was sieved. A total of 600 ml toluene containing 40 mg of each nitroaromatic compound was then added to 400 g sediment to give a spiking concentration of 100 ppm each. After allowing to stand overnight under moderate shaking, the solvent was removed by rotary evaporation.

2.5. SFE

Four hundred milligrams of polluted sediment and the inert Hydromatrix (J.T. Baker, Deventer, The Netherlands), used to retard water physically but not chemically, were filled to capacity into a 2.5 ml cartridge (ISCO, Lincoln, NE, USA). Hydromatrix proved to be free of any extractables and contains no fine particles to clog frits. The extraction was performed using a SFE 260D ISCO device. A second pump was used for continuously adding the methanol modifier. The surfactant (8.5 mg each) was spiked via a diluted 2% (w/w) solution in toluene (which has nearly the same Hildebrand solubility parameter as $scCO_2$) onto the top of the soil which was filled into the cartridge, then the cartridge was sealed and heated. All the soil in the cartridge should be impregnated uniformly with the solution. A capillary restrictor having a fixed flow-rate of 1 ml min^{-1} and held at a constant temperature of 150°C was placed in a vial containing 10 ml methanol trapping solvent. After performing a static approach for 5 min at a specified temperature and pressure (see below), a 30 min dynamic extraction was started. Where necessary, the volume of the trapping solvent was topped up to the initial level during the extraction procedure. The extract was subjected to HPLC to detect target analytes without any purification in order to avoid losses. Aliquots of extracts were also subjected to electrospray mass spectrometry (ESI-MS) to analyse surfactants.

2.6. HPLC of SFE extracts to detect nitroaromatics

Experiments were performed using a DX 500 HPLC device, equipped with a quaternary gradient

system, UV and diode array detector. The 250×4 mm column was filled with 5 μm Zorbax C_{18} RP material. Linear gradient elution was performed with acetonitrile–water mixtures from 20:80 (v/v) to 80:20 for 25 min at a flow-rate of 1 ml min^{-1}. The column was then flushed with methanol–water (90:10, v/v) for approximately 30 min to completely remove surfactant contaminations.

2.7. ESI–MS

Experiments were performed using a MS SSQ 7000 Finnigan device (Bremen, Germany). Standard surfactant samples and methanol extracts obtained by SFE were further diluted with methanol–water–acetic acid and introduced into the ESI interface through a fused-silica capillary column. The MS was operated in a positive-ion mode by applying a spray voltage of 4 kV to the capillary. Full-scan spectra were obtained by scanning the quadrupole from 200–1300 m/z. Calibration of the mass axis was performed using myoglobin. After extraction, the recovered surfactant was quantified by external calibration using various concentrations of the native surfactant under study in methanol.

3. Results and discussion

3.1. Determination of surfactant solubilities in scCO₂

These experiments were aimed at selecting appropriate surfactants with high solubilities for use as modifiers in SFE experiments. Moreover, there is a significant lack of knowledge on solubility data in scCO₂ in the literature.

Solubility experiments were conducted at 50, 75 and 100°C. The low temperatures were chosen in order to achieve low energy consumption for a possible production scale extraction procedure, low thermal stress of the contaminants and high fluid densities. A surfactant decomposition within the applied temperature range could be excluded: gas samples taken from the nitrogen atmosphere of the autoclave filled with surfactants under investigation were analysed on thick-film GLC-capillaries or porous-layer open tubular (PLOT) capillaries (ex-

periments not detailed in this framework). The results gave evidence that all the non-ionic and anionic surfactants are thermostable up to 150°C (applied pressures above 10 MPa) for at least a couple of hours. Dehyquart C decomposes above 150°C dramatically to release pyridine. Texin DOS 75 and Texapon K 1296 produce black-coloured decomposition products that do not display surfactant-like features, that are deposited on the inner autoclave walls.

Präwozell FCE 1214 and Texin DOS possess the highest solubilities of the investigated non-ionic and anionic surfactants, respectively, and were therefore investigated further along with the cationic Dehyquart C. Our work has also been focused on fitting these solubility data into a model, on the basis of which surfactant solubilities may be predicted. A widely accepted empirical approach to predict solubilities in supercritical fluids in correlation with fluid density and temperature has been proposed by Mitra and Wilson [18] (see Eq. (1)).

$$\ln c = A\rho + BT + C \tag{1}$$

where c is the concentration of the surfactant in scCO₂, ρ is the fluid density, T is the temperature (K) and A, B, C are constants (obtained by multivariable linear regression)

The constant A is a measure for the influence of fluid density (which is also associated with temperature and pressure, in turn) on solubility; B expresses the direct influence of temperature via the surfactant vapour pressure and Brownian molecular movement on solubility. (Surprisingly, the vapour pressures of non-ionic surfactants under study were very high: for example, the vapour pressure of FCE 1214 was 169 mbar at 60°C). The constant C is arbitrary. On the basis of measured data and utilisation of this approach, unknown non-ionic surfactants may be classified according to their hydrophilie/lipophilie (HLB concept, detailed in [19]). Roughly speaking, the HLB value expresses the ratio of hydrophilic and lipophilic domains in the surfactant molecule.

Fig. 2a depicts the solubility behaviour of the non-ionic FCE 1214 within the temperature range given above. The solubility data cover a range of two orders of magnitude (0.001 up to 0.2 M) which equals 0.1 up to 10% (w/w) and are all below the
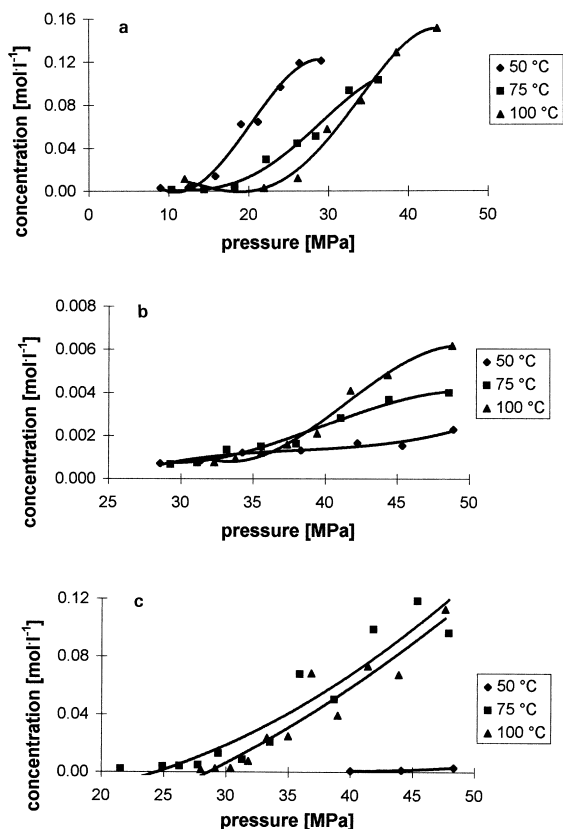
Fig. 2. Solubility of surfactants in scCO$_2$ at various temperatures: (a) non-ionic surfactant FCE 1214; (b) anionic surfactant Texin DOS 75; (c) cationic surfactant Dehyquart C.

inversion point.[2] This gives strong evidence that fluid density plays the key role in controlling solubility. According to Eq. (1), a correlation between solubility on the one hand and density and temperature on the other hand was established for non-ionic FCE 1214. Table 2 (upper part) indicates the usefulness of this approach to describe solubility behaviour of this surfactant in scCO$_2$. The experimental data given in Fig. 2a for the non-ionic surrogate fit well into the Mitra–Wilson concept (see Eq. (1)). The small B coefficient for the non-ionic surfactant gives strong evidence that there is little direct influence of temperature via vapour pressure and Brownian movement on the solubility (as already stated above),

thus the fluid density is regarded as being the decisive parameter to predict the solubility within the investigated temperature and pressure range. The good applicability of the Mitra–Wilson model allows the prediction of solubilities, which was performed exemplarily for FCE 1214 in the temperature range 50–100°C and pressure range 15 to 50 MPa based on results given in Table 2 (Fig. 3)

Similar experiments were conducted with the ionic surrogates. According to data given in the literature [9], a lower solubility in comparison with non-ionic surfactants was expected beforehand. This assumption was confirmed by our experiments: solubility isotherms of the anionic Texin DOS 75 indicate that solubility is between 1 and 6 mM (Fig. 2b). It is striking that the data points start near the inversion point (in the range of 30 MPa to a little above 35 MPa, where the solubility isotherms cross each other) and therefore a pronounced solubility–temperature correlation is obtained. Attention should be paid to the relatively large B coefficient (Table 2) which indicates that, in contrast to the non-ionic member, the temperature is the dominant influence on solubility rather than the density. As for the non-ionic surfactant, a good correlation coefficient is evident (see Table 2), emphasising again the usefulness of the empirical concept. In contrast to the Texin DOS 75 surfactant, the Texapon K 1296 (sodium dodecyl sulphate) anionic surrogate shows solubilities in the applied temperature and pressure range below 0.2 mM, which is close to the detection limit of titration. The solubility of the surfactant Texapon N 28 (see Table 1) lies between them. This finding does not fit into the HLB concept. Under the valid assumption that this approach may also be applied to ionic surfactants, the HLB values were calculated based on increments given in [21]: Texin DOS: 40.65, Texapon N 28: 40.66, Texapon K 1296: 40.0. According to this ranking, the latter would be expected to have the best solubility in scCO$_2$, which is not the case.

A very peculiar case is the cationic surfactant, the solubility of which is strongly dependent on temperature (Fig. 2). Whereas at 50°C and pressures between 40 and 50 MPa a negligible solubility results (about 3 mM), the solubility at 75°C is greater by almost two orders of magnitude (about 110 mM at 50 MPa), which is close to the solubilities of non-ionic surfac-

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[2]This point is based on the adverse impacts of fluid density and surfactant vapour pressure on solubility [20].

Table 2
Application of Mitra–Wilson approach to describe surfactant solubilities for the non-ionic surfactant FCE 1214, the anionic surfactant Texin DOS 75 and the cationic surfactant Dehyquart C

T (K)	A	B	C	r
Präwozell FCE 1214				
323.15	14.171 ± 1.326		-14.230 ± 1.054	0.975
348.15	9.427 ± 0.950		-10.139 ± 0.644	0.966
373.15	13.344 ± 1.530		-12.256 ± 1.026	0.963
323.15–373.15	12.912 ± 0.710	0.025 ± 0.004	-21.427 ± 1.792	0.970
Texin DOS 75				
323.15	10.994 ± 1.289		-16.708 ± 1.178	0.967
348.15	15.523 ± 1.233		-19.127 ± 1.013	0.982
373.15	18.679 ± 1.274		-20.118 ± 0.952	0.986
323.15–373.15	15.395 ± 1.057	0.061 ± 0.004	-40.378 ± 2.214	0.960
Dehyquart C				
323.15	45.365 ± 6.620		-49.316 ± 6.229	0.990
348.15	21.123 ± 1.819		-20.612 ± 1.433	0.965
373.15	26.742 ± 3.112		-23.207 ± 2.238	0.944
323.15–373.15	17.587 ± 3.806	0.104 ± 0.020	-55.020 ± 9.576	0.741

tants (Fig. 2a). This unusual behaviour might be attributed to the surfactant melting process which is assumed to be between 50°C and 75°C as supported by the literature (melting point at 50–51°C according to [22] or 86.0°C according to [23,24]; no remarks on surfactant purity and oligomer distribution are given) and the fact that we are faced with a technical product which probably has some impurities which decrease the melting point. Obviously, this change in aggregation state stimulates the solubility process. A further temperature increase turned out to be of minor importance for solubility enhancement. Therefore, these findings do not fit into the empirical

Mitra–Wilson concept. As usual with empirical models and equations, the theoretical background of the constants (in this case A, B and C) is not fully defined. The utilisation of another empirical correlation method [25] proved not to provide benefits for description of the solubility isotherms. However, the process of solubilisation can be described in more detail because an additional parameter was inserted to take into account the temperature dependence of the reaction enthalpy (consisting of evaporation and solvation energy of the solute). This topic is outside the scope of this contribution and will be outlined later.

3.2. Surfactants as modifiers

Based on the results obtained above, the three surfactants from the autoclave studies were used as modifiers to test their benefits for enhancing the analyte solubility and stimulating desorption kinetics. As is already known [2], analyte solubility in the fluid is commonly the limiting factor in extracting highly contaminated soils and sediments whereas desorption kinetics is important in aged environmental samples with low contamination. The amount of surfactant (8.5 mg) added onto the SFE cartridge, which was flushed with 30 ml fluid, is far below the surfactant solubility measured in autoclave experi-
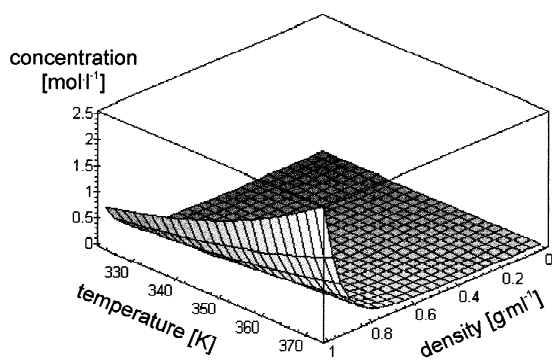

Fig. 3. Interpolation of non-ionic surfactant FCE 1214 solubility in scCO$_2$.

Table 3
Recoveries of nitroaromatics without utilisation of surfactants as modifiers

Extraction parameter $T/p/\rho$ ($^{\circ}$C/MPa/g ml^{-1})	Methanol modifier (%, v/v)	Recovery of target analytes (%) [a]				
		2-NT	1,2-DNB	1,3-DNB	TNT	2-M-3-NA
100/34.5/0.71	0	92	76	71	54	44
100/34.5/0.71	1	96	74	72	50	47
100/30.5/0.71	10	106	89	88	78	69

[a] Data replicate of two: R.S.D. between 4 and 11%; target analytes in shorthand designation; spike concentration of nitroaromatics: 100 ppm each (see text).

ments. (We proceed from the valid assumption that the solubilised surfactant in the autoclave represents the oligomer distribution of the original surfactant as evidenced by ESI-MS, see below.) Nitroaromatics with different numbers of nitro groups in the molecule were chosen as target spike analytes because (i) they are capable of entering into a wide range of polar interactions with soils and sediments including charge transfer interactions and hydrogen bonding, which are unlikely to be broken by non-polar scCO$_2$ and (ii) their relevance as hazardous pollutants (see [26] and references cited therein).

Table 3 gives the recoveries of the spiked nitroaromatics dependent on the methanol modifier at 100°C. Extractions were conducted without surfactant addition. Improvements of recoveries of nitroaromatic were marginal when extending the extraction time to 60 min. The addition of the methanol modifier turned out to be much more important than raising the temperature or the density, therefore the latter two parameters are not detailed further. The similarity between data obtained without methanol

and 1% methanol (extraction time 30 min) indicate that desorption phenomena do not play the key role, because the addition of 1% modifier (no significant increase in solubility for nitroaromatics) would be capable of efficiently interrupting analyte–matrix interactions. (However, humic matrix swelling via methanol modifier addition also plays a role; this will be outlined later.) The recovery of picric acid was negligible in all cases (also for surfactant as modifier; see Table 4), possibly due to the formation of bound residues [27] on the soil matrix. Obviously, there was no complete extraction of the spiked target analytes with the exception of nitrotoluene, but the recoveries measured by us are higher than those given in [28] for loamy soils, which were also spiked with nitroaromatics. When turning to samples subjected to weathering and ageing processes, the recoveries will become even worse [29,30], but this is outside the scope of this paper.

Table 4 lists extraction results obtained by addition of the non-ionic surfactant FCE 1214. There is strong evidence that the surfactant has an adverse

Table 4
Recovery of nitroaromatics with non-ionic surfactant FCE 1214 as modifier

Extraction parameter $T/p/\rho$ ($^{\circ}$C/MPa/g ml^{-1})	Methanol modifier (%, v/v)	Recovery of target analytes [a]				
		2-NT	1,2-DNB	1,3-DNB	TNT	2-M-3-NA
100/34.5/0.71	0	0.68	0.70	0.75	0.72	0.69
100/34.5/0.71 [b]	0	0.74	0.80	0.75	0.79	0.82
100/30.5/0.71	10	0.93	0.88	0.95	0.98	0.89
140/50.0/0.71	0	0.89	0.80	0.85	0.83	0.74
140/47.8/0.71	10	1.05	0.99	1.06	0.97	0.97
100/51.5/0.85	0	0.76	0.75	0.77	0.82	0.74
100/50.0/0.85	10	0.97	0.94	1.01	0.98	0.97

[a] Referred to data obtained without surfactant; data replicate of two.
[b] Dynamic extraction time = 90 min.

effect on recoveries when using the fluid without methanol modifier. On increasing the fluid density, no significant improvement will result. However, on adding modifier to 10%, the recoveries for nitro-aromatics using either $scCO_2$ and surfactant-modified fluid approach each other. In all cases, the recovery was not significantly improved by adding surfactant to the methanol-modified fluid, i.e. no synergetic effect occurs. Therefore, addition of methanol modifier turned out to be more beneficial than adding the surfactant. Similar findings were also obtained when utilising the anionic surfactant Texin DOS 75 and the cationic surfactant Dehyquart C; therefore these results are not discussed further.

Three possible reasons for the poorer recovery of surfactant-modified $scCO_2$ in comparison with the non-modified fluid are:

1. The analyte solubility in the surfactant-modified fluid becomes poorer which is quite unlikely.
2. The increase of organic carbon contributed by the surfactant, which cannot be solubilised and that is therefore deposited on the soil, leads to stronger sorption of nitroaromatics. However, according to our experience the OC content does not play the key role in organic analyte recovery, and furthermore the surfactant contribution to OC is at most 20% (8.5 mg surfactant having about 70% OC deposited on 400 mg soil having 7% OC).
3. The surfactant acts as a limiting factor for analyte desorption from the matrix rather than as a ''normal'' sorbent.

Because of the finding that recoveries were significantly improved when extending dynamic extraction time up to 90 min (Table 4), we concluded that the surfactant impact is towards desorption kinetics. Therefore, it is assumed that the surfactant remains on the soil thus forming a quasi layer/film on it (which must be penetrated by the analyte molecules) and/or clogging the micropores. (The clogging of pores will become even more pronounced if micelles have formed.) Obviously, the interactions between the soil matrix and the surfactant are strong enough in the non-polar fluid environment at high temperatures to retard the surfactant from becoming soluble in the fluid. Unfortunately, sorption data of surfactants on soils and sediments in non-polar supercritical media could not be found in the literature. (Partition coefficients of surfactants in

water–oil systems were recently measured [31], but the results of this paper cannot be transferred to our topic.)

In contrast, sorption from aqueous solutions has been the subject of intense research [32–35]. Based on the fact that there is an incremental contribution of each methylene group in the n-alkane series towards partition coefficient referred to OC (K_{OC}) on soils [36], we assume the same holds also true for surfactant oligomers: The higher the surfactant oligomer molecular weight, the higher the partition coefficient. Recently, surfactants have been treated as ''quasi soils'' in the framework of exciting methodological studies, which will probably foster studies concerned with the fate of environmental chemicals [37].

To investigate further the surfactant influence on limiting analyte desorption from the soil, after the extraction process the methanol trapping solvent samples were subjected to ESI-MS to quantify surfactant recovery and to study the oligomer profile. ESI-MS (see [38]) was the method of choice because even non-ionic surfactants can be electrically charged in the gaseous phase. (A comparison of RP-HPLC and ESI-MS to study oligomer profile of surfactants and to quantify surfactants is outside the aim of this paper and will be outlined later [39].) Table 5 gives the results obtained with the non-ionic FCE 1214; those for the other non-ionic surfactants investigated are similar. Interpretation of ESI spectra revealed that there is no significant fragmentation, preferred peaks include $(M+H)^+$. The interpretation was complicated by the series of sodium adducts of the surfactant beside the native alcohols. Fig. 4 depicts the discrimination when using $scCO_2$ without any methanol modifier. As expected (see above), the competing sorbing effect of the soil overcomes surfactant solubility in the non-polar fluid, the effect being more pronounced with oligomers having higher molecular weight. The oligomer profile in the trapping solvent after extraction with 10% methanol addition is almost identical to that of the native surfactant (Fig. 4b). In general, the discrimination of oligomers with high molecular mass (Fig. 4) coincides well with poorer recovery of nitroaromatics when using surfactants in the non-polar $scCO_2$. The finding that high methanol modifier ratios are necessary to extract the non-ionic surfactant FCE 1214

Table 5
Recovery of surfactant FCE 1214 in the trapping solvent measured by ESI-MS [a]

Extraction parameter $T/p/\rho$ (°C/MPa/g ml^{-1})	Methanol Modifier (%, v/v)	Recovery [b] (%)	Oligomer profile
100/34.5/0.71	0	24	Strong discrimination above M_r 400
100/345/0.71 [c]	0	28	See above
100/34.5/0.71	1	38	Discrimination above M_r 400
100/30.5/0.71	10	95	No discrimination
140/50.0/0.71	0	54	Strong discrimination above M_r 550
140/50.0/0.71	1	78	See above
140/47.8/0.71	10	104	No discrimination
100/51.5/0.85	0	28	Equivalent to 100/34.5/0.71
100/50.0/0.85	10	106	No discrimination

[a] Each 8.5 mg surfactant FCE 1214 was spiked into the top level of 400 mg solid matrix as described in the text; data average of two replicates.
[b] The intensities above all signals from $m/z = 220$–1050 were summed up and normalised to a standard surfactant solution.
[c] Dynamic extraction time = 90 min.

coincides well with data given in [40], according to which scCO$_2$ modified with 30% methanol is appropriate to extract a cationic surfactant from sludges.

Although the phenomena we are faced with in this context (surfactant in the non-polar supercritical fluid/soil system) are quite different to environmental studies (sorption of surfactants on soils/sediments from aqueous solutions), some similarities are quite
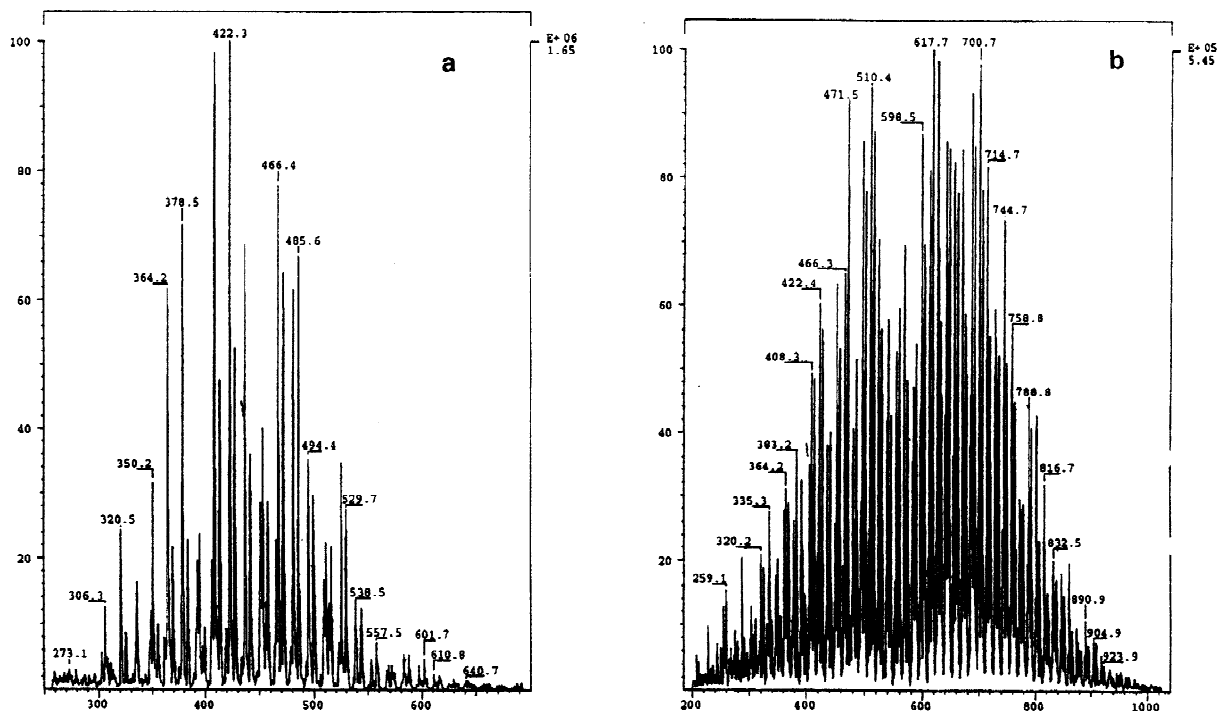

Fig. 4. Oligomer profile of surfactant FCE 1214 in the methanol trapping solvent as measured by ESI-MS (normalised intensity vs. m/z). Extraction at 140°C/$\rho = 0.71$ g ml^{-1} without methanol modifier (a) and with addition of 10% modifier (b).

striking [41–47]. As an example, results in [47] also indicate a cosorbent-behaviour (or more precisely: desorption barrier behaviour) of the non-ionic Triton-X on aquifer materials. However, a great deal of work (including the investigation of micelle formation for surfactants in $scCO_2$) still has to be done in order to clarify this behaviour.

3.3. An alternative concept for detecting nitroaromatics in solutions containing surfactants

GC and HPLC are the most widely applied methods for the detection of nitroaromatics (see [48,49]). Enrichment of target analytes has been predominantly performed by solid-phase extraction or liquid–liquid extraction, both of which sometimes give rise to low recoveries (in particular for polar metabolites such as nitrophenols or nitroanilines) and anomalous results if surfactants are present [50]. For our specific interests of detecting nitroaromatics in organic trapping solvents, GC analysis of these extracts is inappropriate due to the presence of surfactants. HPLC analysis requires a cumbersome flushing step after each run to remove the surfactant and may be prone to peak overlapping of target analytes and surfactant oligomers.

Therefore, we applied the solvent-free solid-phase microextraction (SPME), which is comprehensively detailed in [51], in the headspace mode to exclude the surfactant. However, this approach is restricted to aqueous solutions and to volatile nitroaromatics. Approaches to extend the accessibility towards non-volatile, polar surrogates by in-situ derivatization in water (or methanol–water up to a 1:1, v/v ratio) are now in progress and will be published later, e.g. [52]. Preliminary results using fibres coated with polyacrylate indicate that the target analytes listed in Table 3 can be analysed by this approach in the low ppb level. Fibre desorption was done both in the hot GC injector and by methanol–water (80:20, v/v) in the SPME–HPLC interface (the interface is outlined in [53]). SPME sampling was performed above the headspace of methanol–water (1:1, v/v) trapping solvent at 40°C. The sensitivity can be enhanced by salt addition. Attention should be paid to establishing the fibre–headspace–solution three-phase equilibrium: the distribution of target analytes between headspace and methanol–water is kinetically hin-dered by the surfactant. (The latter topic is detailed in [54].)

Acknowledgements

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