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DETERMINATION OF SURFACTANTS IN ENVIRONMENTAL SAMPLES. PART I. CATIONIC COMPOUNDS

OZNACZANIE SURFAKTANTÓW W PRÓBKACH ŚRODOWISKOWYCH. CZĘŚĆ I. ZWIĄZKI KATIONOWE

Abstract: Compounds from the group of cationic surfactants are widely applied in household, industrial, cleaning, disinfectant, cosmetic and pharmaceutical products as their specific properties (antimicrobial, emulsifying, anticorrosion, softening). After use, cationic surfactants are disposed to wastewater-treatment plants and finally with effluent water to surface waters due to their incomplete degradation. Moreover, they can freely circulate in different environmental compartments including living organisms. It becomes indispensable to recognize in more detail behavior, fate and biological effects of cationic surfactants. This analytical problem can be solved with use sensitive and reliable analytical techniques at sample preparation step and final determination step. In recent years, during isolation analytes from environmental samples mainly were used liquid-liquid extraction (LLE) - liquid matrices or solid-liquid extraction (SLE) - solid matrices. This technique involves application of toxic solvents (chloroform), is time-consuming and interferences are co-extracted. Nowadays, in scientific centers are carried out research to replace this traditional technique. So far, the following techniques were applied: solid-phase extraction (SPE) or its modification (HF-LPME) - liquid samples; accelerated solvent extraction (ASE) and supercritical fluid extraction (SFE) - solid samples. During the determination of total content of cationic surface active agents in environmental samples were used a traditional spectrophotometry technique and potentiometric titration technique. But those techniques are susceptible of interferences on analysis results (anionic and non-ionic compounds). The chromatographic technique (liquid chromatography) applied at the final determination step gives possibility to determine individual cationic surfactants in solvent extracts of environmental samples. The LC systems coupled with mass spectrometers are most powerful tools during such analysis.

Keywords: cationic surfactants, isolation and/or enrichment, final determination, environmental samples

Introduction

Surfactants (usually referred to as surface active substances) are specific organic compounds that contain hydrophilic and hydrophobic group in the molecule. An exhibition of a double affinity (polar - non-polar duality) is typical for amphiphilic substances (Fig. 1).

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The amphiphilicity is a term derives from the Greek word *amphi* and it is meaning *both*. The non-polar hydrophobic part of surfactants molecules usually are a straight or branched hydrocarbon or fluorocarbon chain containing from 8 to 18 carbon atoms [1, 2].

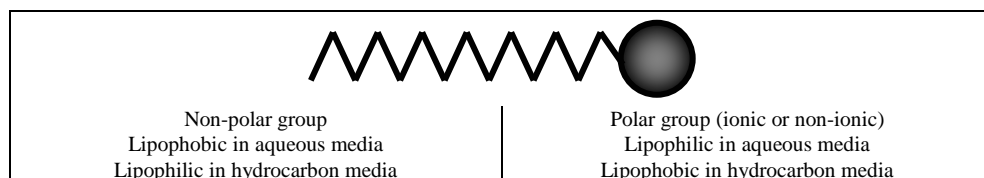


Fig. 1. The schematic structure of compounds from the group of surfactants [1, 2]

The hydrophilic part of surfactants may be [2]:

- negatively charged -> anionic compounds;
- positively charged -> cationic compounds;
- both positively and negatively charged -> amphoteric compounds;
- without formal charge -> non-ionic compounds.

Cationic surface active agents often contain the nitrogen atoms carrying positive charge (mainly in an amine or quaternary ammonium group), which are coupled with one or several long chain of the alkyl type. Quaternary ammonium compounds (QACs) are one of the widest applied group of cationic surfactants. They are organic compounds in which positively charged nitrogen atom is attached covalently to four groups ($R_1R_2R_3R_4N^+$). Different types of functional groups (R_{1-4}) can be attached: one long chain alkyl group and the rest are either methyl or benzyl groups [3]. During the last decade dialkyl dimethyl ammonium salts (eg DTDMAC) used in fabric softeners for household application were replaced by compounds from the group of alkyl ester ammonium salts. They are containing one or more weak ester linkages in the molecular structure [4].

In Table 1 are shown examples of compounds from the group of cationic surfactants.

The examples of compounds from the group of cationic surfactants [5]

Table 1

Quaternary ammonium compounds (QAC)	Esters of quaternary ammonium compounds (EQAC)	Derivatives of pyridine	Derivatives of imidazolines
$R_1R_2R_3R_4N^+X$	$(RCO-O-CH_2CH_2)_2-N^+-R_1R_2$	$[NC_5H_5]^+$	$R_1-C=N-(CH_2)_2-N^+-R_2$
$\begin{array}{c} R1 \\ \\ R2-N^+-R4 \\ \\ R3 \end{array}$			

This class of compounds is dissociated in aqueous solution into amphiphilic cations and mainly the halogen type anions. The amphiphilic structures of surfactants cause their special properties like ability to concentration at surfaces, reduction of the surface tension or formation of micelles. Therefore, they can be applied in various areas of human activity. Cationic surfactants have gained importance because of its bacteriostatic properties. For that reason they are applied as disinfectants and antiseptic agents in different products (cosmetics, medicine, laundry detergents).



Table 2

The effect of several cationic surfactants to different organisms

Class of analytes	Acronym of analytes	Structure of molecule	Test organisms	Toxic parameter		Literature		
				EC ₅₀ * or EC ₅₀ /LD ₅₀ * [mg/dm ³]	LD ₅₀ * [mg/kg]			
Alkyl trimethyl ammonium chloride	C ₁₂ ATMAC	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{R}-\text{N}^+-\text{CH}_3 \\ \\ \text{CH}_3 \end{array} \right] \text{X}^-$	<i>Selenastrum capricornutum</i>	0.19 (96 h)		[8]		
			<i>Microcystis aeruginosa</i>	0.12 (96 h)				
			<i>Navicula pelliculosa</i>	0.20 (96 h)				
	C ₁₆ ATMAC		Rat		250-300	[9]		
			<i>Gammarus</i> sp.	0.1 (48 h)		[10]		
			<i>Drugesia</i> sp.	0.68 (48 h)				
	<i>Dero</i> sp.		0.22 (48 h)					
	C ₁₈ ATMAC		Rat		410	[11]		
			Rat		1000	[9]		
	C ₁₆₋₁₈ ATMAC		Mouse		633	[12]		
			<i>Dunaliella</i> sp.	0.38 (24 h)		[13]		
	C ₁₂₋₂₂ ATMAC		<i>Chlorella pyrenidosa</i>	0.28 (96 h)				
			Rat		>500	[9]		
	Alkyl trimethyl ammonium bromide		C ₁₆ ATMAB	<i>Daphnia magna</i>	1.2-5.8	[14]		
<i>Planorbis corneus</i>		0.73-23						
Dialkyl dimethyl ammonium salts	C ₁₆₋₁₈ 2 DADMAC	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{R}-\text{N}^+-\text{R} \\ \\ \text{CH}_3 \end{array} \right] \text{Cl}^-$ R= two alkyl chains	<i>Selenastrum capricornutum</i>	0.09 (96 h)	[8]			
			<i>Microcystis aeruginosa</i>	0.03 (96 h)				
			Rat		1000	[11]		
			<i>Dunaliella</i> sp.	18 (24 h)		[13]		
			<i>Chlorella pyrenidosa</i>	6 (24 h)				
			<i>Selenastrum capricornutum</i>	0.06 (96 h)		[8]		
			<i>Microcystis aeruginosa</i>	0.05 (96 h)				
			<i>Daphnia magna</i>	0.16-1.06 (48 h)		[15,16]		
			<i>Chironomus riparius</i>	9.02 (96 h)		[17]		
			<i>Lymnaea stagnalis</i>	18 (96 h)				
			<i>Lepomis macrochirus</i>	0.62 (96 h)		[15]		
			<i>Gasterosteus aculeatus</i>	4.5 (96 h)		[17]		
			Alkyl dimethyl benzyl ammonium salts	C ₁₂ ADBMAC	$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_6\text{H}_5-\text{CH}_2-\text{N}^+-\text{R} \\ \\ \text{CH}_3 \end{array} \right] \text{X}^-$	<i>Leuciscus idus melanotus</i>	LC ₀ : 3.5 LC ₁₀₀ : 8.0	[14]
				C ₁₂₋₁₄ ADBMAC		<i>Dunaliella</i> sp.	1.8 (24 h)	[13]
C ₁₂₋₁₈ ADBMAC	<i>Chlorella pyrenidosa</i>	0.67 (96 h)						
C ₁₄₋₁₈ ADBMAC	Rat			525 (Oral)		[12]		
	Mouse			150-340 (Oral)				
Alkyl ester ammonium salts	DEEDMAC	$\left[\begin{array}{c} \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{R} \\ \\ \text{HO}-\text{H}_3\text{C}-\text{H}_3\text{C}-\text{N}^+-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{R} \\ \\ \text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{R} \end{array} \right] \text{X}^-$		<i>Selenastrum capricornutum</i>		2.9 (96)	[19]	
	DEQ		<i>Daphnia magna</i>	14.8 (24 h)				
			<i>Daphnia magna</i>	7.7 (48 h)	[20]			

*EC₅₀ (h) - effective concentration (concentration of the toxic substance that causes specific biological effect of 50% of its maximum value after 24, 48 or 72 hours)

*LD₅₀ (h) - lethal dose (concentration of the toxic substance, which kills 50% of the population after defined hours)



Cationic compounds from the group of surfactants have high adsorptivity to different types of surfaces and they might be applied as: fabric softeners, antistatic agents, corrosion inhibitors or flotation agents [6, 7].

After use, compounds from the group of surfactants and their degradation products are discarded to wastewater-treatment plants (WWTPs). Sometimes surfactants are discarded directly to surface waters and they might be dispersed into different environmental compartments. In wastewater-treatment plants they are completely or partially removed by a combination of different processes (*eg* sorption, biodegradation). But some surfactants have a low biodegradability or their biodegradation products are more toxic than initial compounds. Examples of toxic effect on living organisms are given in Table 2.

After appropriated processes in wastewater-treatment plants the effluents in which can occurred different types of surfactants or their degradation products, are discharged into surface waters [21, 22]. Due to their widespread use and freely migration between phases surfactants (and degradation products) have been detected at various concentrations in different part of environment. The occurrence of surface active agents was confirmed in atmospheric precipitation and deposits, surface waters, sediments, soils, living organisms. Moreover, because of positive charge of the cationic surfactants they are sorbed strongly to the negatively charged solid surfaces of sludge, soil, sediments, metals, plastics and cells membranes [23, 24]. It is become necessary to understand behavior, fate and biological effects of these surfactants in the environment [24-26].

For several reasons, it is complicated to detect, identify and quantify the levels of surfactants once they reach environment. It should pay attention at collection and storage stage of environmental samples. They must be representative of the environmental compartment from which they were taken and the chemical composition of the samples does not change during storage.

The determination of compounds from the group of surfactants in environmental samples causes problems mainly because of:

- the complex matrix composition of sample;
- the low levels of individual surfactants;
- the diverse structures of surfactants molecules;
- the amphiphilic properties of surfactants [5].

The mentioned difficulties might be eliminating by application of suitable isolation and/or enrichment techniques at the sample preparation step. Nowadays, the analytical techniques for the determination of levels of surfactants in environmental samples have been continuously improved with regard to selectivity, sensitivity and reproducibility [6].

Sample preparation step

Liquid samples

During determination of cationic surfactants in liquid environmental samples is used the traditional technique liquid-liquid extraction (LLE) at the sample preparation step. This technique requires use of organic solvent - chloroform and reagents to form hydrophobic ion pairs (*eg* disulphine blue dyes (DiSB), patent blue V, bromophenol blue, LAS [5, 27]). Organic solvent allows for transfer ion pair of reagent-cationic surfactants from water to chloroform. It has been considered that this type of extraction technique is the most effective for isolation of cationic compounds from aqueous samples [28].



However, the LLE technique requires time-consuming clean-up step and involves the use of chloroform (toxic agent for living organisms). Because of this, the traditional extraction has to be replaced by other techniques. Only several times the solid-phase extraction (SPE) technique was applied during preparation of extracts from liquid environmental samples during analysis of cationic SAA [29-31]. The cationic analytes are adsorbed on the prepared surface of sorbent:

- octadecyl-bonded silica [28],
- SDS hemimicelles-alumina [30],
- modified polystyrene-divinylbenzene phase [29, 31].

Sometimes during isolation of analytes from very complex matrixes interferences might be removed from sorbent with use of appropriated solvents (mainly acetonitrile, water H₂O). The cationic analytes are eluted from sorbent with use of mixture of non-organic and organic solvents (acetonitrile, methanol, acetic acid, water, ammonium formate buffer) [27].

Researchers in scientific centers are developing new extraction techniques which give possibility to reduce or eliminate use of toxic solvent during preparation of extracts. So far, the hollow-fiber membrane-assisted liquid-phase microextraction [32] or screening colorimetric method (chromo- and fluorogenic processes with use of S2 sorption element and patent blue dye) [33, 34] were investigated at isolation step of cationic analytes from environmental samples.

Solid samples

For several years, concentrations of cationic surfactants in solid samples have been determined using a traditional solid-liquid extraction (SLE) or Soxhlet extraction (isolation takes 5-18 hours). In these techniques was used acidic methanol for isolation of analytes from sewage sludge, soil, and sediment samples. Next extracts after clean-up step were analyzed [27, 35-38].

Alternatively, the ultrasound-assisted extraction (UAE), accelerated solvent extraction (ASE) and supercritical fluid extraction (SFE) were used for isolation of cationic surfactants (benzalkonium chlorides, ditallowdimethylammonium chlorides) from solid environmental samples. Such techniques allow for reduction of the sample preparation time and the quantities of solvents required in the traditional solvent extraction [39, 40].

Final determination step

During the determination of total content of cationic SAA in appropriated extracts was applied a universal spectrophotometry technique. This technique is based on the formation of ion associates (of cationic analytes with anionic ions-pair reagents), isolation of them to organic solvent (LLE with use of chloroform) and measuring of the absorbance of organic phase (after phase separation). The spectrophotometry technique is typically used for routine environmental analysis. But application of mentioned technique is coupled with two main problems: possibility of determination only of total concentration of cationic analytes and the influence of interferences on results (anionic and non-ionic surfactants) [6, 27].

A potentiometric titration technique (PT) with ion-selective detector was applied for determination of cationic surfactants. This technique is based on the changes in electromotive force of solution in measuring cell after the addition of the titrant. During measurement are used ion-selective electrodes for estimation of endpoint of titration, which



are made with different materials (polyvinyl chloride membranes, carbon paste electrodes, coated wire, coated graphite electrodes) [41]. The difficulties with production of electrodes (manual) and their durability, reproducibility and stability of signal, the possibility of determination only total concentration of surfactants, high values of LODs and the influence of interference on results are disadvantage related with PT technique [27].

The flow injection analysis (FIA) was applied for the determination of cationic compounds from the group of surfactants (dodecyltrimethylammonium bromide - DTAB, tetradecyltrimethylammonium bromide - TTAB, cetyltrimethylammonium bromide - CTAB) in the environmental samples. This technique is based on the enhancement of color intensity of the complex formed between analytes and Fe(III)-SCN^- [42].

Mentioned analytical difficulties might be solved at the final determination stage with the chromatographic techniques. Nowadays, the most commonly use technique during analysis of individual cationic surfactants in solvent extracts of environmental samples is liquid chromatography (LC). Typically, this technique is coupled with four types of detectors: ultra-violet (UV) [43], conductometric (CD) [44, 45], fluorescence (FL) [28], mass spectrometry (MS) [30, 31] or tandem mass spectrometry (MS-MS) [28, 29].

The concentration of cationic surfactants in environmental samples

So far, in various research centers are conducted studies consist mainly on analysis of anionic and nonionic surface-active agents. However, there is limited information on the levels of cationic analytes, which are widely used in many areas of human life (such as antistatic agents, preservatives, disinfectants), and thus they are emitted into different ecosystems.

Table 3

The analytical procedures used for determination of cationic surfactants and their levels in environmental samples

Analytes	Type of sample	Isolation technique	Final determination technique	Concentration of analytes	Literature
Solid samples					
QAC	River sediment	Sohxlet extraction	HPLC-MS-MS	n.d. - 3.6 mg/kg	[40]
	Sewage sludge			22-103 mg/kg	
DTDAC	Marine sediment	SLE or ASE	HPLC-UV or HPLC-FL	880-1140 mg/kg or 30.3-42.3 mg/kg	[28]
	Sewage sludge			3300 mg/kg or 3290 mg/kg	
Liquid samples					
Sum of cationic analytes	Sea water	LLE	Spectrophotometry	> 31 $\mu\text{g}/\text{dm}^3$	[46]
BAC DDAC* ATAC*	Wastewater	LLE	HPLC-MS-MS	0.014-0.63 $\mu\text{g}/\text{dm}^3$ n.d. - 0.83 $\mu\text{g}/\text{dm}^3$ n.d. - 1.1 $\mu\text{g}/\text{dm}^3$	[47]
BAC	River water	SPE	HPLC-MS-MS	1.2-36.6 $\mu\text{g}/\text{dm}^3$	[29]
DTAB CTAB CPC	Wastewater	-	FIA	3-5 mg/dm^3	[42]
	Pond water	-		1.6-3.5 mg/dm^3	
	Ground water	-		0.5-1.3 mg/dm^3	

*DDAC - Dialkyl Dimethyl Ammonium Chloride

*ATAC - Alkyl Trimethyl Ammonium Chloride



The analytical techniques used for determination of cationic surfactants and their concentrations in solid and liquid environmental samples are presented in Table 3. In the sediment samples (from river and sea) and sewage sludge content of cationic surfactants were determined from the values below the detection limit up to 42.3 mg/kg, 22 to 3300 mg/kg, respectively. In wastewater samples, the total concentration of cationic surface active agents was determined from 3 to 5 mg/dm³ and for individual analytes from 0.12 to 3.5 µg/dm³. In groundwater samples and surface water samples (pond water) the total concentration of compounds from the group of cationic surfactants has been determined from 0.5 to 1.3 mg/dm³ and 1.6-3.5 mg/dm³, respectively.

Summary

Cationic surface active agents play an important role in many areas of human activity as ingredients of detergents, personal care products, fabric softeners, emulsifiers or biocides. Due to their commonly application, specific and toxic properties, it is a crucial analytical problem to monitor their presence, behavior and fate in various parts of environment.

During last years, several techniques have been applied for the trace analysis of cationic surface active agents in environmental samples. At sample preparation step analytes were isolated mainly with use of liquid-liquid extraction (liquid samples) or solid-liquid extraction (solid samples). To reduce disadvantages of those techniques (use of toxic solvents, time-consuming, necessity of high volume samples) during preparation of extracts are studied such solution techniques like solid phase extraction and membrane-assisted liquid-phase microextraction or accelerated solvent extraction, respectively. At final determination step for estimate total concentration of cationic surfactants in appropriated extracts was applied a universal spectrophotometry technique. Individual analytes were determined with use of liquid chromatography coupled with different detection systems (MS, MS-MS, FL, UV).

The cationic surfactants or their degradation products can be emitted into different ecosystems. The presence of these substances was confirmed in solid (bottom sediment, sewage sludge) and liquid (wastewater, sea water, river water, ground water) environmental samples. But in literature were presented only some information about occurrence of this class of compounds. The research in this field give possibility to better understand the human health risks associated with the group of cationic surfactants.

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OZNACZANIE SURFAKTANTÓW W PRÓBKACH ŚRODOWISKOWYCH CZEŚĆ I. ZWIĄZKI KATIONOWE

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Abstrakt: Związki z grupy kationowych surfaktantów ze względu na swoje właściwości (bakteriobójcze, grzybobójcze, emulgujące, antykorozyjne, zmiękczejące) są szeroko wykorzystywane w gospodarstwach domowych oraz przemyśle jako środki myjące, dezynfekujące i produkty farmaceutyczne. Po zastosowaniu w różnych dziedzinach działalności człowieka kationowe surfaktanty są kierowane do oczyszczalni ścieków, a następnie do wód powierzchniowych wraz z oczyszczoną wodą (ze względu na ich niecałkowitą degradacją). Ponadto, mogą one swobodnie migrować pomiędzy różnymi elementami środowiska, w tym w żywych organizmach. Zatem istotne staje się poznanie w sposób bardziej szczegółowy zachowania, losu oraz efektów względem organizmów żywych związków z grupy kationowych surfaktantów. To zagadnienie analityczne może być rozwiązane z użycie czułych i selektywnych technik analitycznych na etapie przygotowania próbek do analizy oraz na etapie oznaczania końcowego. W ciągu ostatnich lat na etapie izolacji analitów z próbek środowiskowych wykorzystywane były głównie techniki ekstrakcji w układzie ciecz-ciecz (LLE) - ciekłe próbki lub ciało stałe-ciecz (SLE) - stałe próbki. Ta technika obejmuje zastosowanie toksycznych rozpuszczalników (chloroformu), jest czasochłonna oraz substancje przeszkadzające są współekstrahowane. Obecnie w wielu ośrodkach naukowych są prowadzone badania mające na celu zastąpienie tych tradycyjnych technik. Jak dotąd wykorzystywano następujące techniki analityczne: ekstrakcja do fazy stałej (SPE) bądź jej modyfikacja (HF-LPME) - ciekłe próbki; przyspieszona ekstrakcja za pomocą rozpuszczalnika (ASE) lub ekstrakcja za pomocą rozpuszczalnika w stanie nadkrytycznym (SFE) - stałe próbki. W celu oznaczenia sumarycznej zawartości surfaktantów w próbkach środowiskowych były najczęściej wykorzystywane tradycyjne techniki: spektrofotometrii oraz miareczkowania potencjometrycznego. Jednak stosowanie tych technik wiąże się z ich podatnością na obecność substancji przeszkadzających (anionowych i niejonowych związków). Zastosowanie na etapie oznaczania końcowego techniki chromatograficznej (chromatografii cieczowej) umożliwia oznaczenie pojedynczych kationowych środków powierzchniowo czynnych w ekstraktach rozpuszczalnikowych przygotowanych z próbek środowiskowych. Chromatografia cieczowa w połączeniu ze spektrometrią mas jest obecnie jednym z najbardziej uniwersalnych narzędzi analitycznych wykorzystywanych podczas tego typu analiz.

Słowa kluczowe: kationowe surfaktanty, izolacja i/lub wzbogacanie, etap oznaczania końcowego, próbki środowiskowe

