Application of a New Functionalized MWCNTs for the Construction of Surfactant Potentiometric Sensors

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─────── THIS PAPER IS DEDICATED TO PROF. MIRJANA METIKOŠ-HUKOVIĆ ON THE OCCASION OF HER BIRTHDAY ───────

Abstract: The multi-walled carbon nanotubes (MWCNTs) were noncovalently functionalized with tetraoctadecylammonium tetraphenylborate (TODA-TPB) used as a sensing element and incorporated into a liquid PVC membrane of the new fast, low drift and sensitive potentiometric sensor (FCNSS) for anionic surfactants (ASs). The sensor exhibits a sub-Nernstian response for both dodecyl sulfate (DS) and dodecyl-benzenesulfonate in H_2O and in 10 mM Na_2SO_4.

The lower limits of detection for DS and DBS in H_2O were $1.5 \cdot 10^{-7}$ and $2.0 \cdot 10^{-7}$ M and in 10 mM Na_2SO_4, they were $2.0 \cdot 10^{-7}$ M for both surfactants. The response time of the sensor varied between 8 and 12 s, depending on AS concentration and its signal drift was 2.1 mV/hour. The FCNSS exhibited excellent selectivity for DS against nearly all anions usually found in commercial products. It was successfully employed for end-point detection at potentiometric titrations of ASs in detergent products and effluents.

Keywords: tetraoctadecylammonium tetraphenylborate, MWCNT, anionic surfactant sensor, potentiometric titration, industrial products, effluents.

INTRODUCTION

IN recent years, the global surfactants market experienced steady growth. In 2015 it was valued at approximately USD 30.65 billion.[1] Among all types of surfactants, anionic surfactants (ASs) are the most commonly used ones. Their properties make them essential in a large variety of applications, especially in detergent industry. Analysis of ASs is, therefore, of great importance for industry and environmental protection. The standard methods for their determination are the methylene blue active substances method (MBAS) and the two-phase titration.[2,3] Due to many disadvantages of the standard methods, ASs are usually determined using other analytical approaches (potentiometric titration,[4,5] chromatography,[6,7] flow-injection analysis,[8,9] spectrophotometry,[10,11] biosensors,[12,13] *etc*.). Ion-selective electrodes (ISEs) as sensors in potentiometric titrations represent simple, cheap and rapid alternative to the standard methods. The membrane is the most important part of the electrode, and usually consists of an ionophore as a sensing component, polyvinyl chloride (PVC) and a plasticizer.[14,15] The proportions of these parts can be varied, or some extra additives can be included in the membrane composition with the aim of developing the electrode with better properties (selectivity, limit of detection, response time, accuracy, lifetime, working range, etc.). Lately, the nanomaterials are widely used in various applications, due to their specific properties.[16,17] They are also suitable for modifying the membranes of the ISEs because of their ability to reduce the signal drift, noise and electrical resistance, improve dynamic response and other response characteristics of the electrode and to prevent leaching of the sensing material from the membrane which leads to prolonged lifetime of the electrode.[18,19]

In this paper, multi-walled carbon nanotubes (MWCNTs) were noncovalently functionalized with tetraoctadecylammonium tetraphenylborate (TODA-TPB)

and used as sensing material in the liquid membrane electrode. The new electrode based on MWCNTs was potentiometrically characterized and it's applicability as a sensor for anionic surfactant determination was tested by potentiometric titrations of pure systems, commercial products and effluents.

MATERIALS AND METHODS

Materials

Poly vinyl chloride (PVC), *o*-nitrophenyloctylether (*o*-NPOE), tetrahydrofurane (THF), tetraoctadecylammonium bromide (TODAB), sodium tetraphenylborate (NaTPB), sodium dodecyl sulfate (NaDS) and dodecylbenzenesulfonate (NaDBS), 1,3-didecyl-2-methylimidazolium chloride (DMIC), hexadecyltrimethylammonium bromide (CTAB) and benzethonium chloride (Hyamine 1622) were purchased from Fluka, Switzerland. Cetylpyridinium chloride (CPC) was obtained from Merck, Germany. Hexane and sodium decanesulfonate, dodecanesulfonate and tetradecanesulfonate were products of Sigma-Aldrich, USA. Genapols (T 080, T 110 and T 150) were purchased from Clariant, Switzerland. All the reagents used were of analytical grade except for NaDBS and Genapols which were of technical grade.

Real samples were liquid soap, liquid hand-dishwashing agent, gel detergent and three samples of household effluents.

MWCNTs (OD = 10–20 nm, L = 1–2 μm, 95 + %) were obtained from Io-li-tec, Germany.

Deionized water was used for the preparation of all solutions.

Philips electrode body IS-561 was obtained from Glasblaeserei Moeller, Zurich, Switzerland.

Electrode Preparation

MWCNTs were cleaned with *n*-hexane and dried at 60 °C. In the saturated solution of TODAB, the cleaned MWCNTs were added and stirred on magnetic stirrer until the mixture was homogenous. The mixture was then centrifuged.

The separated MWCNT-TODAB mixture was diluted with distilled water, stirred and NaTPB ($c = 1 \cdot 10^{-3}$ M) was added till mixture MWCNT-TODA-TPB was separated. The separated mixture was dried for 24 hours at 60 °C.

The liquid membrane that consisted of 0.0584 g of PVC, 0.1170 g of *o*-NPOE, 2 mL of THF and 0.0054 g of MWCNT-TODA-TPB mixture was mounted on the electrode body. Sodium chloride ($c = 3$ M) was used as the internal filling solution of the electrode.

The electrode prepared in such a way had a six months lifetime. Between the measurements, the electrode was kept in deionized water.

Apparatus

Centrifuge Centric 200R (Tehtnica, Slovenia) and magnetic stirrer RCT basic (IKA Labortechnik, Germany) were used for sensor material preparation. All potentiometric measurements were performed using the 794 Basic Titrino combined with Metrohm 806 Exchange unit, 801 stirrer with stand and 826 mobile pH meter (all from Metrohm, Switzerland). Tiamo (Metrohm, Switzerland) and in-house software were controlling the 794 Basic Titrino.

Potentiometric Measurements

All measurements were performed at room temperature with the new electrode used as the working electrode and a silver/silver chloride electrode used as the reference. All solutions were magnetically stirred during the measurements. There was no ionic strength or pH adjustments, except in titrations of real samples where pH was adjusted to 3.

The new electrode response characteristics toward NaDS and NaDBS were examined in water and Na$_2$SO$_4$ ($c = 0.01$ M). Measuring of the signal drift was carried out in NaDS ($c = 1$ mM). The total volume of the analyzed solution was always 20 mL during the response measurements.

The potentiometric selectivity coefficients for possible interfering anions ($c = 0.01$ M) were determined using the fixed interference method proposed by the IUPAC.[20]

NaDS, three commercial products and three household effluent samples were used as analytes and four cationic surfactants (CPC, DMIC, CTAB and Hyamine) were used as titrants in the potentiometric titrations. The titrant concentrations used were $4 \cdot 10^{-3}$ M, $4 \cdot 10^{-4}$ M and $1 \cdot 10^{-4}$ M. During all titrations, the total solution volume was 25 mL. Dynamic (DET) and monotonic equivalence point titration mode (MET) were used for potentiometric titration measurements. DET mode was accompanied with a signal drift of 5 mV/min and was used for determination of high concentrations of ASs. The increments of the titrant in MET mode were 0.1 mL. MET mode was used for determination of low concentrations of ASs.

RESULTS AND DISCUSSION

Response characteristics

The analysis of ionic surfactants is most frequently based on the so called antagonist reaction:

$$CAT^+ + AN^- \rightleftarrows CATAN \tag{1}$$

where CAT$^+$ and AN$^-$ are large organic, mostly surfactant cations and anions, respectively.

The formed CATAN product is an ion-pair, slightly dissociated and almost insoluble in water but easily soluble in many organic solvents. In titrimetric methods, ASs are

usually determined using standard solutions of cationic surfactants, as titrants.

The response of the ion-pair based ionic surfactant potentiometric sensors to cationic and anionic surfactants can be defined by the Nernst equation:

$$E = E° + S·\log a\left(CAT^+\right), \quad \text{for cationic surfactants} \quad (2)$$

and

$$E = E° - S·\log a\left(AN^-\right), \quad \text{for anionic surfactants} \quad (3)$$

where $a(CAT^+)$ and $a(AN^-)$ are activities of the cationic and anionic surfactant ions.

The solubility product of a CAT^+AN^- ion pair, used as the sensing element of a sensor membrane is

$$K_{sp} = a\left(CAT^+\right)·a\left(AN^-\right) \quad (4)$$

From Eq. (4), $a(CAT^+) = K_{sp}/a(AN^-)$, and after its insertion into Eq. (2), the following sensor response is obtained:

$E = E° + S · \log K_{sp}/a(AN^-)$, which after rearrangement gives:

$$E = \text{const} - S · \log a\left(AN^-\right) \quad (5)$$

where const $= E°+S · \log K_{sp}$

where $E°$ = constant potential term, S = sensor slope, which for surfactant anion amounts 59.2 mV/decade of activity at 25ºC, and $a(AN^-)$ = activity of the surfactant anion.

It follows from Eq. (5) that the magnitude of the *emf* changes in the course of titration greatly depends on the K_{sp} value of ion-pair formed during titration. Lower K_{sp} values cause a greater *emf* change at the equivalence point, resulting in a more sensitive surfactant determination. If the difference between pK_{sp} values of ion-pairs formed during titration of anionic surfactants mixture is 2–3 units, the effectively separated inflexions are obtained on the titration curve, which enable the determination of individual surfactants in the mixture.

The main application of surfactant potentiometric sensor is for indication of the end-point at ionic surfactant potentiometric titrations (Equation 1).

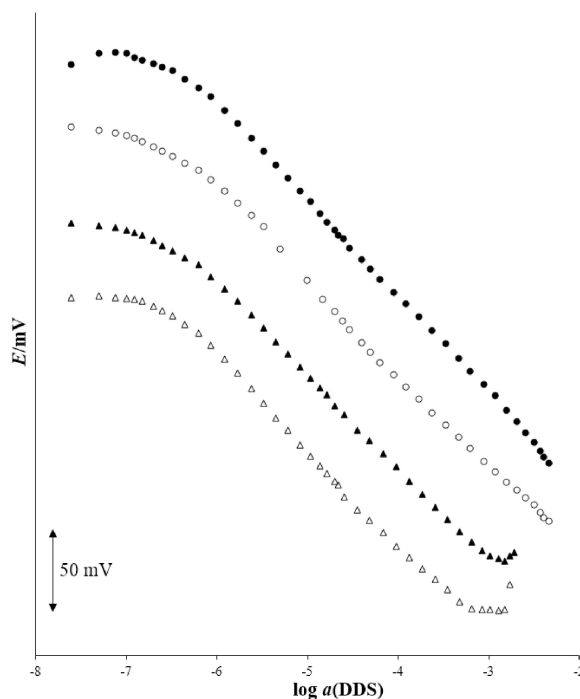The response of the new sensor, based on functiona-

Figure 1. Responses of the FCNSS to DS and DBS in water and in 10 mM Na_2SO_4. Here and in further figures, some curves are displaced laterally and/or vertically for clarity (● DS in water; ○ DS in Na_2SO_4; ▲ DBS in water; △ DBS in Na_2SO_4).

lized nanomaterial (FCNSS) was investigated in solutions of NaDS and NaDBS in a concentration range between $2.5 · 10^{-8}$ and $5 · 10^{-3}$ M in pure aqueous solutions and in 0.01 M Na_2SO_4 (to explore the influence of ionic strength). The measured responses are shown in Figure 1.

At higher concentration region (above $1 · 10^{-3}$ M) the divergences from linearity at some responses are observed, which are caused by the formation of micelles (in the vicinity of critical micellar concentration, CMC). Davies equation was used for calculation of the activity coefficients. The response characteristics of the sensor were estimated by means of linear regression analysis and the results are shown in Table 1.

Table 1. The response characteristics and their statistics of the FCNSS to DS and DBS[a]

Parameters	Slope [mV/decade of activity]	Standard error [mV/decade of activity]	Correl. coeff. [R^2]	Lower limit of detection [M]	Useful conc. range [M]
NaDS in H_2O	$57.1 ± 0.5$	1.5	0.9995	$1.5 · 10^{-7}$	$3.2 · 10^{-7} - 5.0 · 10^{-3}$
NaDS in Na_2SO_4 0.01 M	$54.6 ± 1.0$	3.1	0.9979	$2.0 · 10^{-7}$	$4.5 · 10^{-7} - 5.0 · 10^{-3}$
NaDBS in H_2O	$54.4 ± 0.6$	1.5	0.9993	$2.0 · 10^{-7}$	$4.5 · 10^{-7} - 1.2 · 10^{-3}$
NaDBS in Na_2SO_4 0.01 M	$55.2 ± 1.2$	2.9	0.9972	$2.0 · 10^{-7}$	$3.2 · 10^{-7} - 6.5 · 10^{-4}$

[a] average of 5 determinations ± confidence limits (p = 0.95).

Table 2. The comparison of the new sensor with a few other potentiometric surfactant sensors

Type of the electrode	Ionophore	Analyte	Slope [mV/decade of activity]	Correl. coeff. [R^2]	Lower limit of detection [M]	Useful conc. range [M]	Response time / s	Working pH range	Life time / months
ISE with liquid membrane (FCNSS)	MWCNT-TODA-TPB	NaDDS in H_2O	57.1 ± 0.5	0.9995	$1.5 \cdot 10^{-7}$	$3.2 \cdot 10^{-7} - 5.0 \cdot 10^{-3}$	8	2 - 10	6
		NaDBS in H_2O	54.4 ± 0.6	0.9993	$2.0 \cdot 10^{-7}$	$4.5 \cdot 10^{-7} - 1.2 \cdot 10^{-3}$			
Solid state sensor [21]	MWCNT-OSO$_3$-CP$^{+(a)}$	NaDDS in H_2O	52.9 ± 1.0	0.9993	$1.5 \cdot 10^{-6}$	$3.6 \cdot 10^{-6} - 5.0 \cdot 10^{-3}$	5	3 - 10	6
		NaDBS in H_2O	51.2 ± 1.5	0.9962	$2.5 \cdot 10^{-6}$	$4.2 \cdot 10^{-6} - 9.1 \cdot 10^{-4}$			
ISE with liquid membrane [5]	DDA$^{(b)}$-TPB + 10% C	NaDDS in H_2O	55.3 ± 0.9	0.9987	$2.5 \cdot 10^{-7}$	$3.2 \cdot 10^{-7} - 4.6 \cdot 10^{-3}$	5	3 - 12	5
		NaDBS in H_2O	58.5 ± 1.7	0.9940	$2.0 \cdot 10^{-7}$	$2.5 \cdot 10^{-7} - 1.2 \cdot 10^{-3}$			
All-solid state sensor [19]	DDA-TPB + graphene	NaDDS in H_2O	47.6 ± 0.4	0.9993	$1.5 \cdot 10^{-7}$	$2.5 \cdot 10^{-7} - 4.5 \cdot 10^{-3}$	12	2 - 7	3
		NaDBS in H_2O	59.2 ± 1.5	0.9951	$2.5 \cdot 10^{-7}$	$3.0 \cdot 10^{-7} - 2.5 \cdot 10^{-3}$			
ISE with liquid membrane [22]	L$^{1(c)}$	NaDDS in H_2O	59.5	-	$6.0 \cdot 10^{-7}$	$1.3 \cdot 10^{-6} - 6.8 \cdot 10^{-3}$	3	5 - 8	0.33
ISE with liquid membrane [23]	PPy-DBS$^{(d)}$	NaDBS in H_2O	57.2	-	$2.0 \cdot 10^{-5}$	$3.0 \cdot 10^{-5} - 3.0 \cdot 10^{-3}$	20	3 - 10	6

[a] MWCNT-OSO$_3$-CP$^+$ - MWCNT functionalized with a sulfate group and cetylpyridinium ion.

[b] DDA – dimethyldioctadecylammonium cation.

[c] L^1 - 7-methyl-7,13-di-octyl-1,4,10-trioxa-13-aza-7-azonia-cyclopentadecane.

[d] PPy-DBS – dodecylbenzenesulfonate-doped polypyrrole.

The detection limits were estimated according to the IUPAC recommendations.[19]

The investigated sensor revealed a sub-Nernstian response for both DS and DBS in H_2O (57.1 and 54.4 mV/decade of activity, respectively) between $3.2 \cdot 10^{-7}$ and $5.0 \cdot 10^{-3}$ M for dodecyl sulfate (DS) and $4.5 \cdot 10^{-7}$ and $1.2 \cdot 10^{-3}$ M for dodecylbenzenesulfonate (DBS).

It also exhibited a sub-Nernstian response for both DS and DBS in 0.01 M Na_2SO_4 (54.6 and 55.2 mV/decade of activity, respectively) between $4.5 \cdot 10^{-7}$ and $5.0 \cdot 10^{-3}$ M for DS and $3.2 \cdot 10^{-7}$ and $6.5 \cdot 10^{-4}$ M for DBS.

The comparison of the most important analytical and physicochemical characteristics of the new FCNSS with a few other potentiometric surfactant sensors is shown in Table 2. It can be concluded that FCNSS exhibited the longest lifetime combined with the lowest limit of detection and the highest E vs. log$a$(AN⁻) correlation.

Dynamic Response Measurements

The response time of the sensor was estimated by measuring the time needed for the sensor to acquire 90 % of the final value after a sudden change (increase) of surfactant concentration. Figure 2 displays the dynamic responses of the new FCNSS to DS in water.

As shown in Figure 2, the sensor responded within 8 s for changes at a higher concentration level (above $1 \cdot 10^{-4}$ M), and 12 s for changes at lower concentrations (below $1 \cdot 10^{-5}$ M).

Signal Drift

Sensor drift can be defined as a progressive signal variation with time in the electromotive force (emf). It can be caused by various factors, such as temperature changes, stabilizing
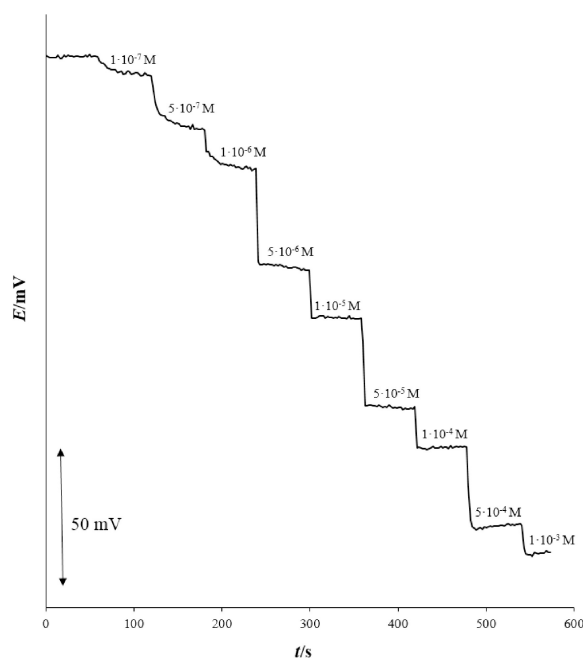

Figure 2. Dynamic responses of the FCNSS to DS in H_2O.

Table 3. The comparison of the potentiometric selectivity coefficients for different anions most frequently used in commercial products for the FCNSS with those obtained using a few other potentiometric surfactant sensors

	Ionophore				
Interference	MWCNT–TODA–TPB (FCNSS)	DDA–TPB + 10 % C[5]	DDA–TPB + graphene[19]	L¹ [22]	PPy–DBS[23]
	pK_{ij}^{pot}				
Chloride	3.91	3.68	4.19	3.82	2.46
Iodide	4.46	4.47	3.47	3.39	2.47
Fluoride	4.45	4.05	3.39	–	2.46
Carbonate	5.32	4.40	4.21	–	–
Hydrogen carbonate	4.17	3.75	2.36	3.45	–
Nitrite	4.52	4.14	3.25	3.71	2.36
Nitrate	4.33	3.85	3.39	3.67	2.20
Sulfate	5.21	5.55	3.75	5.06	–
Phosphate	5.34	4.19	4.43	4.10	–
Dihydrogen phosphate	4.26	4.13	3.26	–	2.39
Borate	5.16	4.12	3.64	–	–
Acetate	4.41	3.78	4.62	3.37	2.15
Benzoate	4.28	3.60	3.14	–	–
Citrate	5.45	4.70	4.26	–	–
Ethylenediamine tetraacetate	5.19	5.48	4.41	–	–
Sulfamate	4.48	4.09	3.77	–	–
Xylene sulfonate	3.59	3.59	2.82	–	–
Toluene sulfonate	4.41	3.89	2.70	–	–

of electronics, aging and contamination of the membrane, memory effects, influence of matrix, sample decomposition, etc. The drift was measured in 1 mM solution of NaDS at 25 ºC and estimated by linear curve fitting on the data set in a designated time interval. It can be defined as the slope of the calculated linear regression line that represented the dependence of *emf* as a function of time.

For the new FCNSS, this dependence is given by the equation

E (mV) = − 0.000581 · t (s) − 157.9, *i.e.* the calculated drift amounted to 2.1 mV/hour.

The lifetime of the sensor depends on the sample complexity and was approximately five months by using the sensor in aqueous solutions in the absence of strongly interfering matrix components (fats, oils, suspended matter).

Determination of the Potentiometric Selectivity Coefficients

The response of the new surfactant sensor in the presence of interferents can be described by the Nikolskii-Eisenman equation:

$$E = E°\left(A_{det}^- \right) - \frac{RT}{F} \cdot \ln\left[a\left(A_{det}^- \right) + K^{pot}\left(A_{det}^- A_{int}^- \right) a\left(A_{int}^- \right) \right] \text{ (6)}$$

where $K^{pot}(A_{det}^- A_{int}^-)$ is the potentiometric selectivity coefficient and $a(A_{det}^-)$ and $a(A_{int}^-)$ are the activities of the analyte ion (det) and the interfering ion (int), respectively.

For the determination of the potentiometric selectivity coefficients in the investigations described, the fixed interference method (FIM) was applied.[20]

The calculation and optimization of the potentiometric selectivity coefficients was accomplished using *Solver*, a Microsoft Excel analysis tool. The experimental data obtained by the FIM were fitted to the Nikolskii-Eisenman equation.

The list of the potentiometric selectivity coefficients of some inorganic and organic anions usually found in surfactant-based products for the FCNSS compared with those calculated for a few other potentiometric surfactant sensors is shown in Table 3.

At all the selectivity measurements, DS was used as the analyte, in the range from $2 \cdot 10^{-6}$ M to $2 \cdot 10^{-3}$ M, whereas the concentration of the interfering ion was 0.01 M.
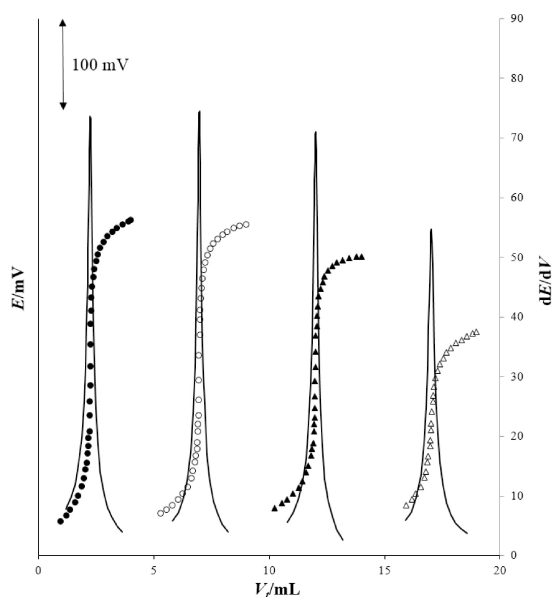
Figure 3. Potentiometric titration curves and their first derivatives for 4 mM DS using different cationic surfactants (c = 4 mM) as the titrants and the new FCNSS as the end-point detector (DMIC (●), CPC (○), CTAB (▲) and Hyamine (Δ)).

The new FCNSS exhibited excellent selectivity for DS over all of the anions investigated. Comparing with other potentiometric surfactant sensors, FCNSS revealed superior selectivity performances.

The Influence of pH

Due to the fact that commercial products based on anionic surfactants may have different pH values, it was necessary to test the applicability of the new electrode over a wide pH range. The new electrode exhibited stable potential without significant deviations in the the pH range between pH 2 and pH 10 (figure not shown).

Selection of the Titrant

Determination of anionic surfactants is usually carried out by titration, thus the selection of an appropriate titrant is of great significance. The most used for this purpose are cationic titrants. The standard solutions (c = 4 · 10^{-3} M) of the following cationic surfactants: Hyamine 1622, CTAB, CPC and DMIC were tested as potential titrants in the investigations presented. A standard solution of NaDS (c = 4 · 10^{-3} M) was applied as the analyte and the new FCNSS served as an end-point indicator (Figure 3).

The results and corresponding statistics are shown in Table 4.

Due to its best analytical performances, CPC was used in further investigations.

The most appropriate titrant concentration for determination of anionic surfactants in different commercial formulations is c = 4 · 10^{-3} M. The new FCNSS exhibited a wide linear working range and low detection limits, which indicates its potential use for determination of low levels of ASs too (in effluents, surface waters etc.). For this purpose, a series of diluted standard CPC solutions of concentrations c = 1 · 10^{-3}, 4 · 10^{-4}, 7 · 10^{-5} and 4 · 10^{-5} M were tested as potential titrants for potentiometric determination of ASs at micromolar level.

Still CPC at a concentration 7 · 10^{-5} M delivered an analytically useful titration curve (figure not shown).

Titration of a Three-component Mixture

Commercial products formulations often contain a combination of two or more anionic surfactants with the aim to improve certain product features. Among the important sensor characteristics belongs its capability to distinguish between individual surfactants in a mixture.

For this purpose a mixture of three alkanesulfonates of different hydrophobic chain length (C$_{10}$, C$_{12}$ and C$_{14}$) was potentiometrically titrated resulting in three well-separated inflexions in the titration curve (Figure 4).

Table 4. Statistics of NaDS determination obtained using FCNSS as end-point detector and different titrants (c = 4 mM)[a]

	Parameters	Titrants			
		CPC	DMIC	CTAB	Hyamine
Potential jump in EP/mV		323.2	330.0	280.5	191.8
Potential value in EP/mV		−11.3 ± 2.6	−26.2 ± 20.3	−11.7 ± 3.5	−105.7 ± 5.0
First derivative values in EP/ mV/mL		74.6 ± 0.2	73.3 ± 0.4	71.0 ± 0.6	54.4 ± 0.8
Accuracy/%		98.4	112.1	101.0	101.0
Precision	SD	0.550	0.921	0.319	0.782
	RSD	0.0056	0.0082	0.0032	0.0077
	CV	0.559	0.822	0.316	0.774

[a] average of 5 determinations ± confidence limits (p = 0.95).
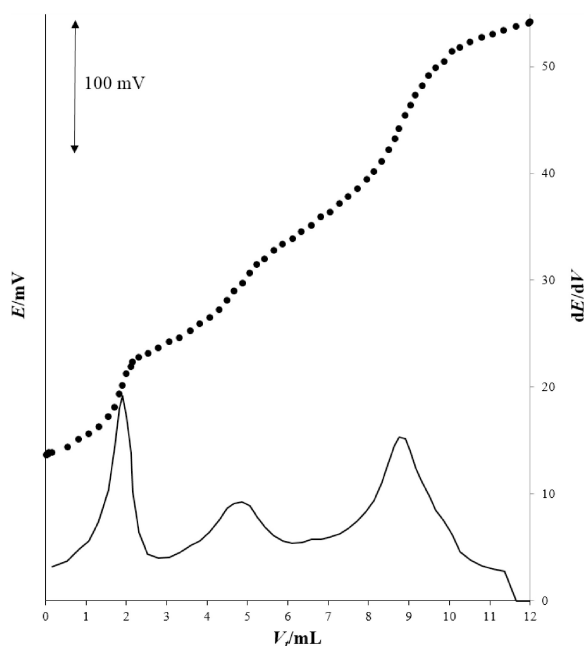
Figure 4. Potentiometric titration curves and their first derivatives for the three-component mixture of alkane sulfonates (C_{10}, C_{12} and C_{14}, c = 1 mM each) using the new FCNSS as the end-point detector and 1 mM CPC as the titrant (C10:C12:C14= 4:3:2).

Although the difference between the surfactants was only two C atoms, the end-points located by means of their first derivative were analytically usable.

The results of the single surfactants content in the mixture are shown in Table 5.

Influence of Nonionic Surfactants

The commercial product formulations are often optimized using a combination of anionic and nonionic surfactants, and from the latter, the ethoxylated nonionic surfactants (EONS) are most commonly used. Their compatibility with other nonionic and anionic surfactants opens up the new possibilities in product development. Among the most frequently used types of EONS are ethoxylated fatty alcohols, which influence the shape of potentiometric titration curves of ASs.

In Figure 5, the influence of the number of EO groups in each particular surfactant on the shape of the titration curves was shown. The molar ratio of NaDS and EONS by all investigations was 1:2, respectively. The explored EONS contained 8, 11 and 15 EO groups. It can be seen that EONS with higher EO content have a stronger influence on the potentiometric titration, but the magnitude of the electrode potential jump at the inflexion was still sufficient for a reliable endpoint location.

Table 5. The results of determination of single alkanesulfonates in a mixture obtained using FCNSS as end-point detector and CPC (c = 1 · 10^{-3} M) as the titrant

Alkan sulfonate	Added [mol]	Found [mol] ± RSD [%][a]	Recovery [%][a]
C10	$4 \cdot 10^{-6}$	$3.98 \cdot 10^{-6} \pm 1.0$	99.5
C12	$3 \cdot 10^{-6}$	$2.88 \cdot 10^{-6} \pm 1.0$	96.0
C14	$2 \cdot 10^{-6}$	$1.95 \cdot 10^{-6} \pm 1.1$	97.5

[a] average of 3 determinations.

The concentration of EONS affected the shape of potentiometric titration curves too, which was demonstrated in the example of Genapol 080 (8 EO groups), as shown in Figure 6.

The extent of the inflexion decreased with increasing concentration of EONS, resulting in slight distortion of the titration curves, but still making location of the end-point reliable.

Titration of Commercial Products and Effluents

The quantification of ASs in various commercial products (household and industrial detergents, cosmetics, pharma-
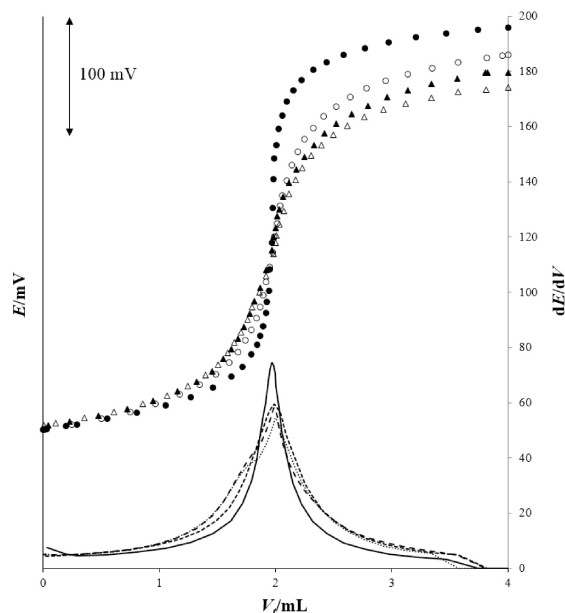

Figure 5. The titration curves and their first derivatives for DS using 4 mM CPC as the titrant and the new FCNSS as the end-point detector in the presence of EONS of different EO group contents at a fixed DS:EONS molar ratio of 1:2 (●, — DS alone; ○, --- 8 EO groups; ▲, — — 11 EO groups; Δ, ···· 15 EO groups).
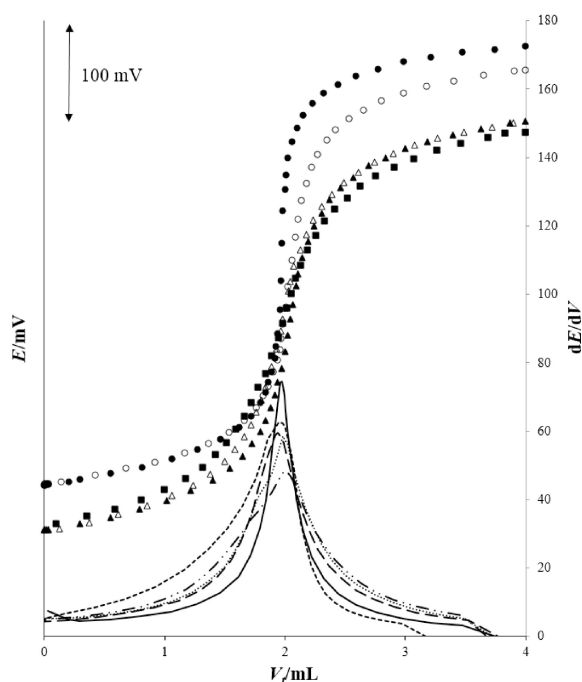
Figure 6. The influence of concentration of EONS (8 EO groups) on the titration curves and their first derivatives for the DS titration using 4 mM CPC as the titrant and the new FCNSS as the end-point detector (●, — DS alone; DS:Genapol T 080 at molar ratios of ○, --- 1:1; ▲, — — 1:2; Δ, •••• 1:3, and ■, —•·— 1:5).

Figure 7. Titration curves for three commercial detergents with the addition of known amounts of 4 mM DS obtained using 4 mM CPC as the titrant and the new FCNSS as an end-point detector (● liquid soap, ○ liquid soap + 2 mL DS, ■ liquid hand-dishwashing detergent, □ liquid hand-dishwashing detergent + 2 mL DS, ▲ gel detergent, Δ gel detergent + 2 mL DS).

ceuticals, etc.) is one of the principal uses of surfactant potentiometric sensors.

For this purpose, three commercial products (liquid soap, liquid hand-dishwashing detergent, gel detergent) were titrated with a 4 mM CPC solution as the titrant. The new FCNSS was used as an end-point detector.

The influence of the matrix, accuracy and precision of the determination were tested using the standard addition method by adding one or more increments of the standard NaDS solution to sample aliquots. The obtained potentiometric titration curves exhibited well-defined inflections resulting in reliable end-point detection (Figure 7).
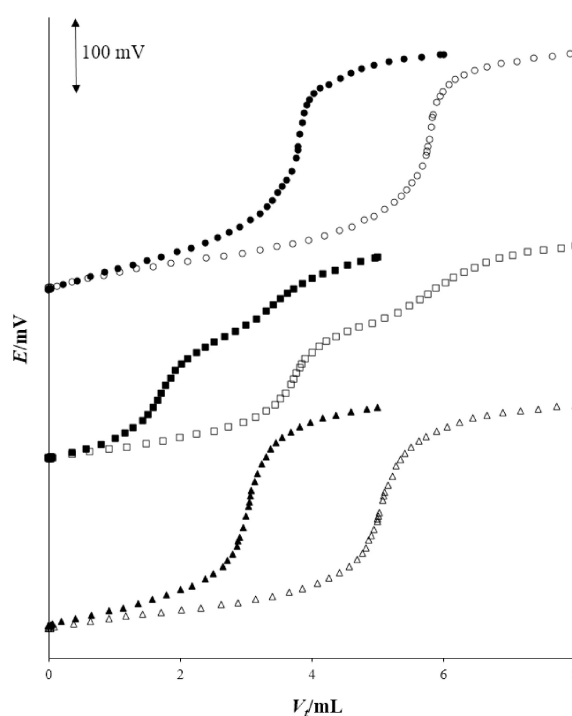
The pH value of the sample solutions was adjusted to 3 before titration. No ionic strength adjustment was necessary. The results and corresponding statistics of the determination of ASs in the products investigated are shown in Table 6. The obtained recoveries ranged from 98.2 to 100.4%, indicating a satisfactory accuracy of the determination of ASs.

The ASs content was also determined using the standard two-phase titration method and the results obtained were compared with those acquired using the new FCNSS (Table 7).

Table 6. Results of the potentiometric determinations of ASs in the commercial detergents and with the addition of known amounts of NaDS solution, using 4 mM CPC as the titrant and the new FCNSS as the end-point detector

Detergent type	AS found [mol L−1] ± RSD [%][a]	NaDS added [mol]	NaDS found [mol] ± RSD [%][a]	Recovery [%][a]
1	$1.01 \cdot 10^{-3} \pm 0.5$	$8.00 \cdot 10^{-6}$	$7.86 \cdot 10^{-6} \pm 0.3$	98.2
2	$1.39 \cdot 10^{-3} \pm 1.1$	$8.00 \cdot 10^{-6}$	$8.03 \cdot 10^{-6} \pm 0.3$	100.4
3	$1.22 \cdot 10^{-3} \pm 0.3$	$8.00 \cdot 10^{-6}$	$8.01 \cdot 10^{-6} \pm 0.3$	100.1

[a] average of 5 determinations ± confidence limits (p = 0.95).

Table 7. Results of the potentiometric determinations of ASs content in the commercial detergents using 4 mM CPC as the titrant and the FCNSS as an end-point detector compared to the results obtained using the two-phase titration method

Detergent type	AS content using FCNSS [%][a]	AS content using two-phase titration [%][b]
1	3.53	3.23
2	9.67	9.63
3	8.47	8.41

[a] average of 5 determinations.

[b] average of 3 determinations.

A satisfactory agreement was found between the results obtained using the potentiometric method and those obtained by the standard two-phase titration.

The new FCNSS was tested on three different samples of industrial effluents. All of the samples were filtered and the pH was adjusted to 3 before titration. The ionic strength was not adjusted.

The standard addition method was used to determine the accuracy, precision and influence of the matrix on the ASs determination.

The corresponding titration curves are displayed in Figure 8 and they revealed a satisfactory inflexion at the end-point using 0.1 mM CPC as the titrant. The volume of titrant at the end-point was calculated from the derivative curves or by Savitzky-Golay-Barak method. The results of the determinations are shown in Table 8.

The obtained recoveries were in the range between 87.3 and 103.8 %, which is acceptable for the determination of ASs in effluents. The differences in recoveries for some effluents are caused by dissimilarities in their complexity.

The results obtained with the new FCNSS compared with those obtained by the standard MBAS procedure are shown in Table 9.

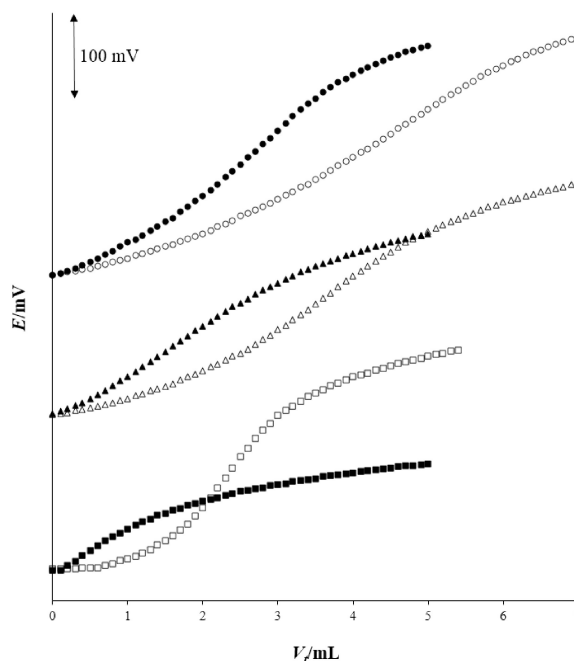It can be concluded that a satisfactory correlation existed between the both methods.

Figure 8. Titration curves for industrial wastewaters with the addition of known amounts of 0.1 mM DS obtained using 0.1 mM CPC as the titrant and the new FCNSS as an end-point detector (● sample 1, ○ sample 1 + 2 mL DS, ▲ sample 2, △ sample 2 + 2 mL DS, ■ sample 3, □ sample 3 + 2 mL DS).

CONCLUSION

A new anionic surfactant sensitive sensor was prepared, containing multi-walled carbon nanotubes noncovalently functionalized with tetraoctadecylammonium tetraphenyl-borate, that was used as sensing material and embedded in a PVC liquid membrane. The sensor responded fast and revealed a considerably reduced signal drift compared to conventional ion-pair based sensors. Its main use is for end-point detection at the potentiometric titration of anionic surfactants. The resulting titration curves exhibited a clear inflexion providing a reliable end-point evaluation. The new sensor revealed outstanding selectivity for DS against almost all particular anions usually present in commercial

Table 8. Results of the potentiometric determination of ASs in industrial wastewater and with the addition of known volumes of standard NaDS solution using the FCNSS as an end-point detector and 0.1 mM CPC as the titrant

Wastewater sample	AS found [mol L^{-1}] ± RSD [%][a]	NaDS added [mol]	NaDS found [mol] ± RSD [%][a]	Recovery [%][a]
1	$2.76 \cdot 10^{-5} \pm 3.1$	$2.00 \cdot 10^{-7}$	$2.08 \cdot 10^{-7} \pm 5.0$	103.8
2	$1.65 \cdot 10^{-5} \pm 4.5$	$2.00 \cdot 10^{-7}$	$1.81 \cdot 10^{-7} \pm 3.5$	90.4
3	$3.55 \cdot 10^{-6} \pm 11.9$	$2.00 \cdot 10^{-7}$	$1.75 \cdot 10^{-7} \pm 3.6$	87.3

[a] average of 5 determinations ± confidence limits (p = 0.95).

Table 9. Comparison of results of ASs content obtained with the new FCNSS and those obtained using the MBAS method

Wastewater sample	AS content using FCNSS [mg L⁻¹][a)	AS content using MBAS method [mg L⁻¹][b)
1	9.64	9.82
2	5.75	5.63
3	1.24	1.40

[a] average of 5 determinations.

[b] average of 3 determinations.

formulations based on anionic surfactants. The nonionic surfactants, commonly found in the commercial formulations, can affect the titration of anionic surfactants, resulting in a decrease of inflexion at titration curves, but still providing reliable end-point de-tection. The new sensor succeeded in single potentiometric determination of alkanesulfonates in their three-compo-nent mixture. It was successfully tested for the potentio-metric titration of ASs in the detergent products and industrial effluents, and the results obtained were in good accordance with those obtained using standard methods.

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