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A New Microsensor for the Determination of Anionic Surfactants in Commercial Products

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A new potentiometric microsensor for the determination of anionic surfactants (ASs), prepared by the application of a liquid membrane based on the dimethyldioctadecylammonium-tetraphenylborate (DDA-TPB) ion pair as a sensing material on a commercial carbon-based screen-printed electrode (SPE), was developed. The microsensor exhibited sub-Nernstian responses for sodium dodecylbenzene sulfonate (NaDBS, 45.7 mV/decade) and sodium dodecyl sulfate (NaDDS, 50.2 mV/decade) in concentration ranges from $1 \cdot 10^{-7}$ to $2 \cdot 10^{-3}$ M for NaDBS and from $2 \cdot 10^{-7}$ to $7 \cdot 10^{-3}$ M for NaDDS. The detection limit of the new SPE microsensor was $1 \cdot 10^{-7}$ M, which is even lower than the detection limit of a conventional ISE electrode with the same sensor material [1]. The new microsensor is very accurate and selective; thus, different ionic strengths, nonionic surfactants and potentially interfering anions did not have an influence on its performance. Two-component mixtures of ASs and three commercial detergents with different AS contents were successfully titrated using the new microsensor, which resulted in the accurate quantification of ASs in the samples.

Keywords: microsensor, anionic surfactant, potentiometric titration, PVC membrane, screen-printed electrode, commercial products

1. INTRODUCTION

Surfactants or surface active agents are a large group of organic compounds that reduce the surface tension of a liquid or interfacial tension by liquids. They are used in many applications, including in the soap and detergent industry, personal care products, household products, the textile industry, and for crop protection. It is projected that the global surfactant market will reach 22,802 kilotons by volume and $40,286 million by value by 2019, thus growing at a CAGR (compound annual growth rate) of 5.40% by volume and 5.80% by value from 2014 to 2019. In 2013, anionic surfactants (ASs) dominated the global market in terms of volume with 7,080 kilotons [2].

To obtain the best products and thereby prevent contamination of the environment, it is very important to accurately determine AS concentrations. The two-phase titration [3] for higher AS concentrations and the methylene blue active substances (MBAS) method [4] for lower AS concentrations are the standard methods for AS determination. Both methods have many interferences and drawbacks, including the following: they are time consuming, tedious, subjective, use large amounts of carcinogenic organic solvents and cannot be automated.

Great alternatives to standard methods for AS determination are ion selective electrodes (ISEs) [5-8]. ISEs are simple, rapid, accurate, sensitive, inexpensive, environmentally friendly and easily automated potentiometric sensors. There are many types of ISEs, but today most of ISEs have the following design: a membrane based on a polyvinyl chloride (PVC) matrix, including the plasticizers and the sensing material, which is usually an ion pair consisting of two surfactants of opposite charge. By varying the compounds of the ISE, it is possible to construct an electrode with better properties [1, 9-16].

Although ISEs with liquid membranes are good sensors for AS determination and they have a wide range of applications, they have also a few limitations, including the following: it is difficult to produce liquid-membrane ISEs in small sizes, and they have relatively short life-times due to the leaching of the electroactive material. The leaching of the electroactive material into the internal solution can be overcome by using electrodes with a solid inner contact without the inner solution. Such electrodes are less fragile, more robust, more durable and easier to miniaturize than ISEs with liquid membranes [17, 18]. Miniaturization is a current trend in technology as well as in electrode production. Miniaturized electrodes allow measurements with small sample volumes and can be used with portable devices for *in situ* measurements. Considering the above, screen printed electrodes (SPEs) are one of the most promising approaches and are very interesting as electrochemical sensors for the determination of ASs [19, 20].

ASs also can be determined by other methods such as chromatography [21, 22] and biosensors [23].

In this paper, we describe the development of a new miniaturized sensor for AS determination based on a self-made PVC-plasticized liquid-type membrane sensitive to ASs [1] applied on a commercial SPE (SPMS sensor). The new microsensor is compared with a conventional ISE with the same membrane [1] (PMS sensor). We also suggest the application of the new highly sensitive microsensor for the routine analysis of commercial products.

2. EXPERIMENTAL

2.1. Reagents and Materials

The SPMS microsensor response characteristics and the potentiometric titrations were investigated using sodium dodecyl sulfate (NaDDS) and sodium dodecylbenzene sulfonate (NaDBS) from Fluka, Switzerland.

The standard solutions of 1,3-didecyl-2-methylimidazolium chloride (DMIC), hexadecyltrimethylammonium bromide (CTAB) and Hyamine 1622 (benzethonium chloride) purchased from Fluka, Switzerland as well as cetylpyridinium chloride (CPC) purchased from Merck, Germany were used as cationic titrants.

The influence of interfering substances on the response of the SPMS microsensor was investigated using sodium sulfate, sodium carbonate, sodium hydrogen carbonate, sodium nitrite, sodium nitrate, sodium hydrogen sulfate, potassium chloride (Kemika, Croatia), sodium acetate (Gram-mol, Croatia), potassium iodide, sodium hydrogen phosphate, sodium tetraborate (Sigma-Aldrich, USA), sodium phosphate, ammonium sulfamate (ACROS organics, Belgium), sodium benzoate, sodium citrate (Fisher Scientific, UK), ethylenediaminetetraacetic acid disodium salt dihydrate and potassium fluoride (BDH Prolabo, England).

Genapol T 080, Genapol T 110 and Genapol T 150 were used to study the influence of nonionic surfactants on the potentiometric titrations of NaDDS.

Two alkane sulfonates (C_{10} and C_{12}) were used for the differential titration of two-component mixtures.

The applicability of the SPMS sensor to the determination of ASs in real systems was tested using the following three commercial products: compact powdered detergent, gel detergent and liquid hand-dishwashing detergent.

The SPMS microsensor membrane was prepared using dimethyldioctadecylammonium chloride (DDAC), sodium tetraphenylborate (NaTPB), *o*-nitrophenyl octyl ether (*o*-NPOE) and high molecular weight PVC (all Fluka, Switzerland), and then, it was applied on a commercial SPE based on carbon (DropSens, Spain).

2.2. Apparatus and Measurements

Potentiometric titrations were performed using an 808 Titrando all-purpose titrator, a Metrohm 806 exchange unit and Tiamo software (all Metrohm, Switzerland). During the measurements, the solutions were magnetically stirred using an 801 titration stand (Metrohm, Switzerland).

The dynamic response time measurements and measurements of the influences of interferences and ionic strength on the microsensor response were performed using a Metrohm 780 pH meter, a 728 stirrer, a Metrohm 794 Basic Titrino (Metrohm, Switzerland) and in-house software.

2.3. Sensor

Preparation of the SPMS microsensor membrane was the same as the preparation of the membrane based on the DDA-TPB ion pair for a conventional ISE described previously [1], but instead of pouring the membrane into a glass ring, 5 μL of membrane solution was applied on the commercial SPE based on carbon (DRP-C110 electrode, DropSens, Spain). The electrode was dried for 24 hours at room temperature. The microsensor was kept at room temperature between the measurements. The lifetime of the microsensor was relatively long due to the fact that a SPE is a low cost and disposable device (up to 60 measurements were performed with the same microsensor).

2.4. Procedure

A SPE based on a carbon working electrode and silver reference electrode with a PVC-plasticized liquid membrane made by the DDA-TPB ion-pair applied on it was used for all of the potentiometric measurements.

The response characteristics of the microsensor to ASs (NaDDS and NaDBS) were investigated by the incremental addition of ASs ($c = 5 \cdot 10^{-4}$ M and $5 \cdot 10^{-5}$ M) into distilled water. Calibration curves were constructed by plotting the potential, *E*, versus the logarithm of the AS activity. Activity coefficients were calculated according to the Davies equation. ASs were added to a sodium sulfate solution (c = 0.001 M, 0.01 M and 0.1 M) to investigate the influence of the ionic strength on the response characteristics of the SPMS microsensor. The influence of different interfering anions (c = 0.01 M) on the response characteristics of the microsensor was investigated by the fixed interference method proposed by the IUPAC [24], and then, the potentiometric selectivity coefficients were calculated.

All titrations were performed in 25 mL of the analyte solution with titrants at concentrations of $4 \cdot 10^{-3}$ M. Although the microsensor can be used with much smaller volumes, all of the measurement conditions were the same as used for a conventional ISE [1] to allow the results to be compared. Three Genapols were added separately in different molar ratios to the titrated NaDDS solutions for investigation of the influence of ethoxylated alcohols on the AS titration curve.

Diluted solutions of the three commercial detergents used were prepared daily, and stock solutions were prepared once per week.

The alkane sulfonates used for the differential titrations of two-component mixtures were added in two molar ratios (C_{10}:C_{12} = 1:1 and 1:2).

The titrator was programmed in the DET (dynamic equivalence point titration) mode, with a signal drift of 5 mV/min and an equilibrium time of 30 s. The wait time before the start of the titration was 120 s. All of the measurements and titrations were performed at room temperature using a magnetic stirrer and without ionic strength adjustment or pH adjustment (except for the commercial system titrations in which the pH was adjusted to 3).

The accuracy and precision of the measurements were tested using the standard addition method, in which NaDDS was added at two concentration levels. As a reference method, a two-phase titration [3] was used.

3. RESULTS AND DISCUSSION

3.1. Response characteristics

The Nernst equation describes the electromotive force of the SPMS microsensor immersed in an AS solution:

$$E = E^0 - S \cdot \log a_{\mathrm{AS}^-} \qquad (1)$$

where E^0 is the constant potential term, S is the sensor slope and a_{AS^-} is the activity of the surfactant anion.

Figure 1 shows the response characteristics of the new AS microsensor in NaDDS and NaDBS solutions. Those two ASs were selected because they are most commonly used in detergent formulations. The activity coefficients were calculated using the Davies equation.

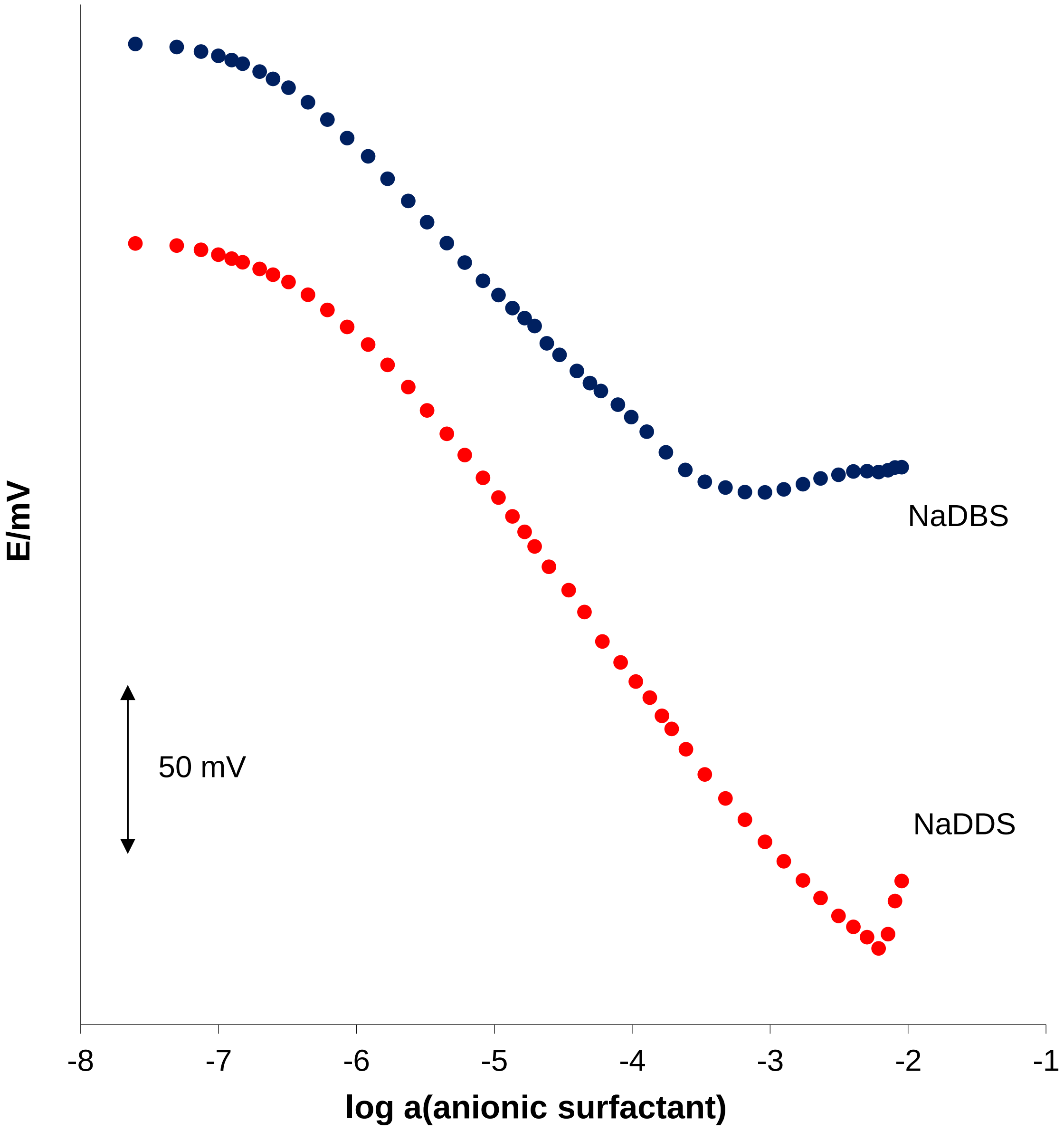

Figure 1. Response characteristics of the new SPMS microsensor in NaDBS and NaDDS solutions. Here and in the following figures, the curves are displaced laterally or vertically for clarity.

The statistical evaluation of the SPMS sensor characteristics compared with those of the PMS sensor [1] are presented in Table 1. The slope values and the correlation coefficients were calculated from the linear range of the calibration graph using linear regression analysis based on a series of five measurements. The detection limits were determined according to the IUPAC recommendations. The SPMS microsensor showed sub-Nernstian responses for NaDBS (45.7 mV/activity decade) in a concentration range from $1\cdot10^{-7}$ to $2\cdot10^{-3}$ M and for NaDDS (50.2 mV/activity decade) in a concentration range from $2\cdot10^{-7}$ to $7\cdot10^{-3}$ M. At higher concentrations of ASs, micellization occurs, resulting in deviations from linearity. The SPMS microsensor has a lower limit of detection and a lower useful concentration range compared to the PMS sensor [1] and other similar sensors presented in recent publications [25-27], which makes it more suitable for the determination of very low concentrations of ASs as well as higher concentrations.

Table 1. Response characteristics of the new SPMS microsensor for ASs compared to the PMS sensor [1] with ± 95% confidence limits and to other similar sensors presented in recent publications [25-27]

Sensors	Parameters			
	Slope / (mV/conc. decade)	Correl. coeff. (R^2)	Detection limit (M)	Useful conc. range (M)
NaDBS (SPMS microsensor)	45.7 ± 4.8	0.9982	$1\cdot10^{-7}$	$1\cdot10^{-7}$-$2\cdot10^{-3}$
NaDDS (SPMS microsensor)	50.2 ± 0.5	0.9995	$1\cdot10^{-7}$	$2\cdot10^{-7}$-$7\cdot10^{-3}$
NaDBS (PMS sensor)*	59.1 ± 0.3	0.9980	$2\cdot10^{-7}$	$4\cdot10^{-7}$-$2\cdot10^{-3}$
NaDDS (PMS sensor)*	59.0 ± 0.5	0.9999	$2\cdot10^{-7}$	$3\cdot10^{-7}$-$8\cdot10^{-3}$
NaDDS (ISE using a cyclam derivative as ionophore)**	60.0 ± 0.9	-	$4\cdot10^{-6}$	$7.9\cdot10^{-6}$-$2\cdot10^{-3}$
NaDDS (SPE based on [CuSalen]DDS_2)***	56 ± 2	-	$2\cdot10^{-7}$	$4\cdot10^{-7}$-$1\cdot10^{-2}$
NaDDS (SPE based on CP-DDS ion pair)****	53 ± 1	-	$2.5\cdot10^{-6}$	$5\cdot10^{-6}$-$1\cdot10^{-2}$

* Data from [1], ** Data from [25], *** Data from [26], ****Data from [27]

3.2. Interferences

3.2.1. The influence of the ionic strength on the SPMS microsensor response

Real samples of ASs (detergents) usually contain high concentrations of sulfates, carbonates, phosphates, chlorides and other inorganic salts. Because the concentrations of salts are usually much higher than the AS concentration, the influence of the ionic strength on the SPMS microsensor response was investigated (Figures 2 and 3).

Solutions of sodium sulfate at concentrations of 0.001 M, 0.01 M and 0.1 M were used to adjust the ionic strength. The ionic strength in the analyte solution was between 0.003 M and 0.301 M. NaDDS and NaDBS at concentrations of $5\cdot10^{-4}$ M and $5\cdot10^{-5}$ M, respectively, were used as the analytes.

The changes in linearity correspond to the fact that the critical micellar concentration decreases with increasing ionic strength. The reason for this is that the distance between the surfactant ions decreases due to the presence of salt, and consequently, micelles are formed at lower AS concentrations. However, these changes are not significant, and it can be concluded that the new SPMS microsensor can be used for the determination of ASs in samples with different ionic strengths such as commercial products.

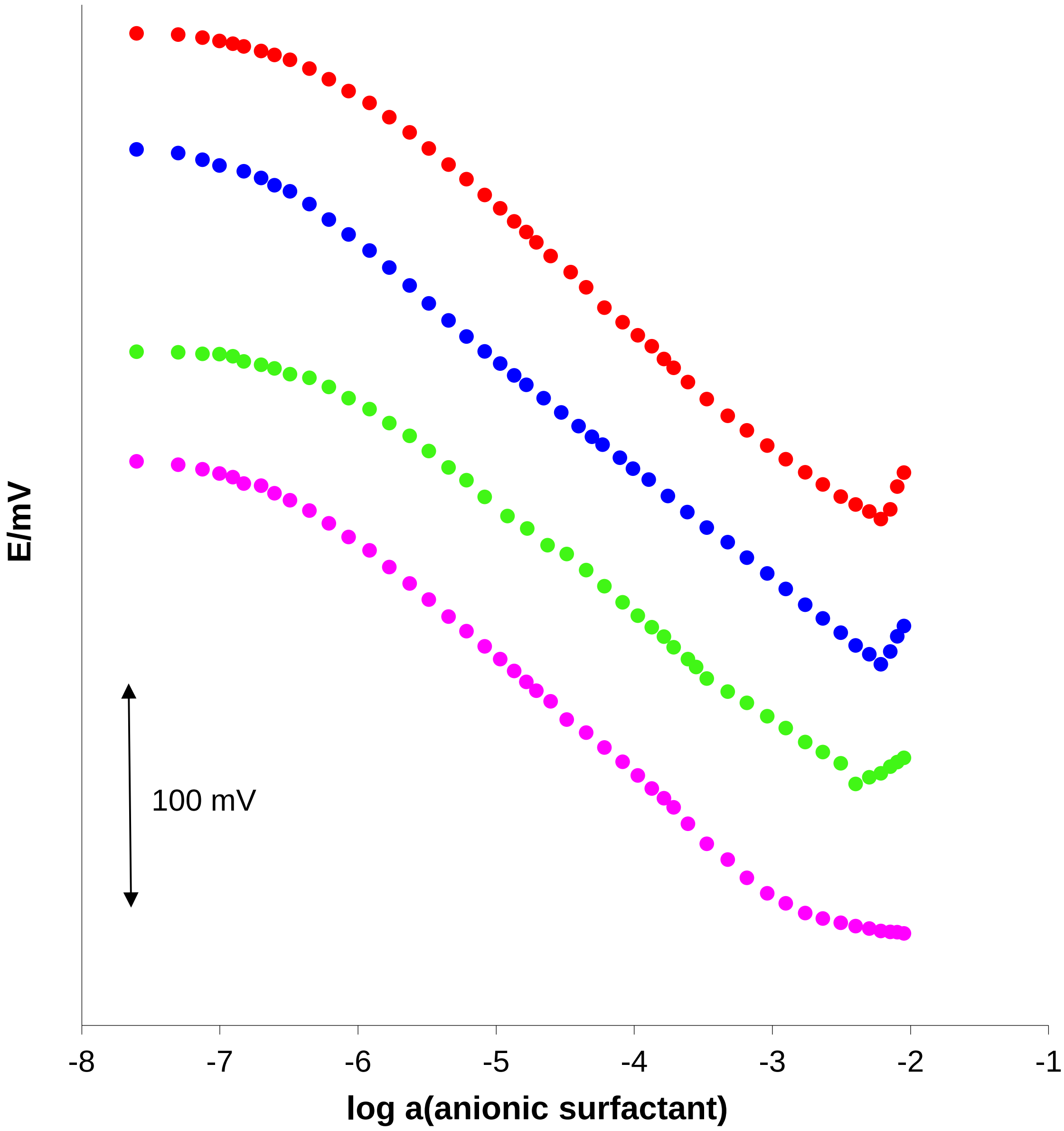

Figure 2. The influence of different ionic strengths on the response characteristics of the SPMS microsensor toward NaDDS (● in H_2O, ● in 0.001 M Na_2SO_4, ● in 0.01 M Na_2SO_4, ● in 0.1 M Na_2SO_4).

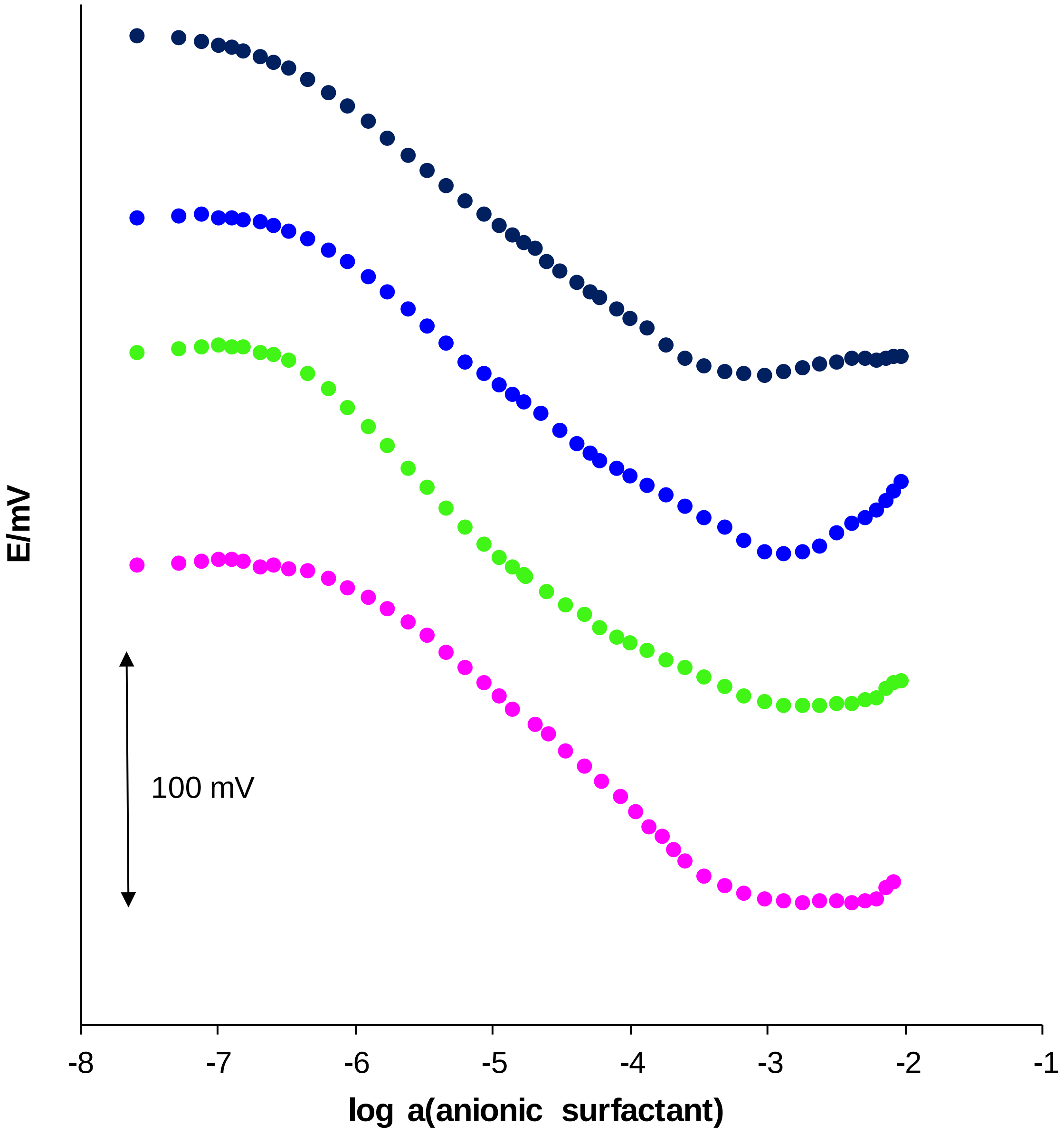

Figure 3. The influence of different ionic strengths on the response characteristics of the SPMS microsensor toward NaDBS (● in H_2O, ● in 0.001 M Na_2SO_4, ● in 0.01 M Na_2SO_4, ● in 0.1 M Na_2SO_4).

3.2.2. The influence of nonionic surfactants on the shapes of the titration curves

Ethoxylated nonionic surfactants (EONS) are a common component in commercial products containing ASs. One of the most commonly used classes of EONS are ethoxylated alcohols, which may exhibit weak anionic character in certain conditions. Considering this, it was necessary to investigate the influence of EONS on the potentiometric titration of ASs.

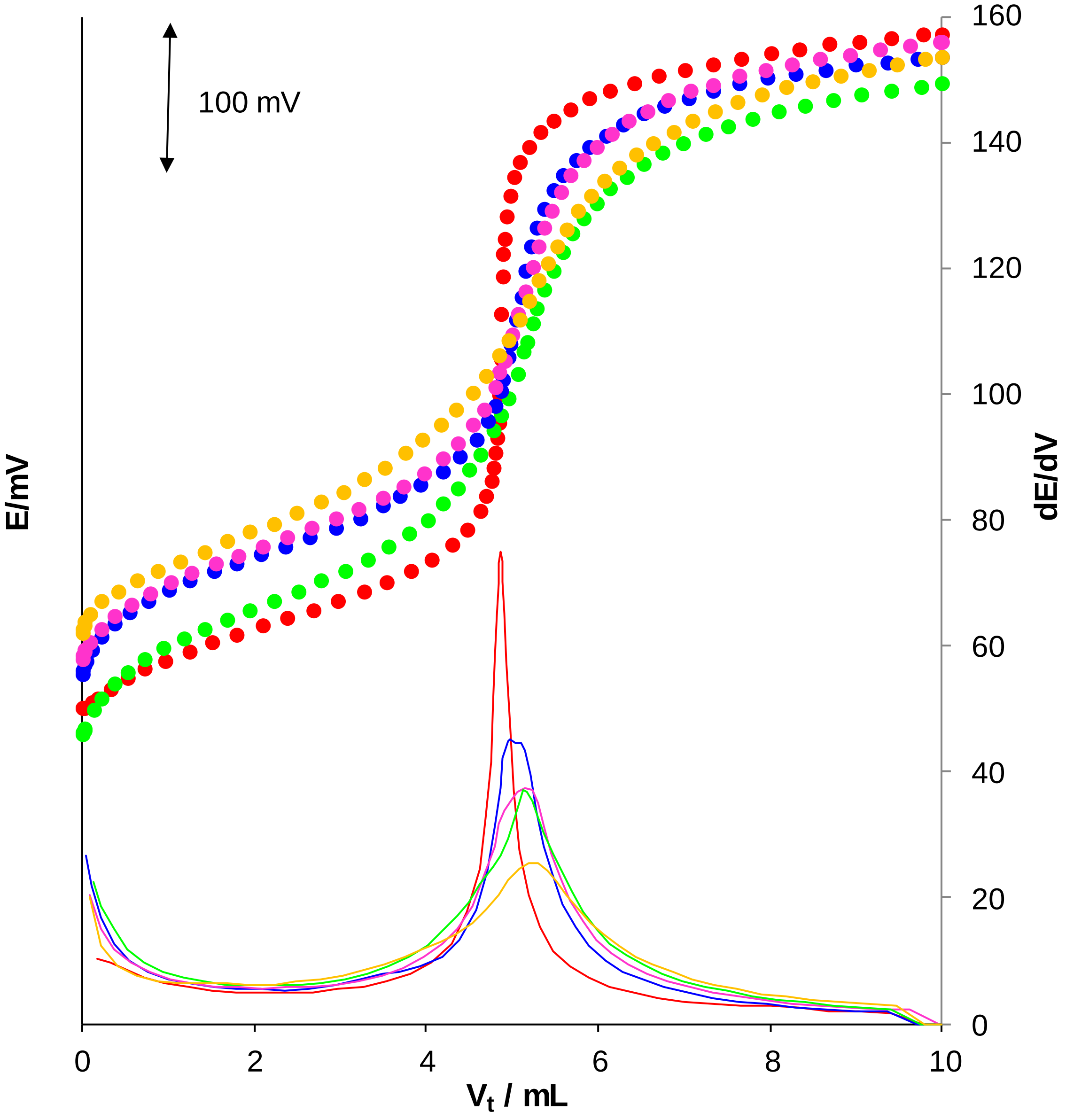

Figure 4. The influence of different amounts of EONS (8 EO groups) on the shapes of the titration curves and their first derivatives for the titration of NaDDS using CPC as the titrant and the SPMS surfactant microsensor as the endpoint indicator (● NaDDS alone, NaDDS:Genapol T 080 molar ratios of ● 1:1, ● 1:2, ● 1:3, ● 1:5, — NaDDS, — 1:1, — 1:2, — 1:3, — 1:5).

Three EONS with different numbers of EO groups (8, 11 and 15) that are commonly used in commercial detergents and cleaning products were selected for this investigation. The EONS were added separately in different molar ratios to the titrated AS solutions.

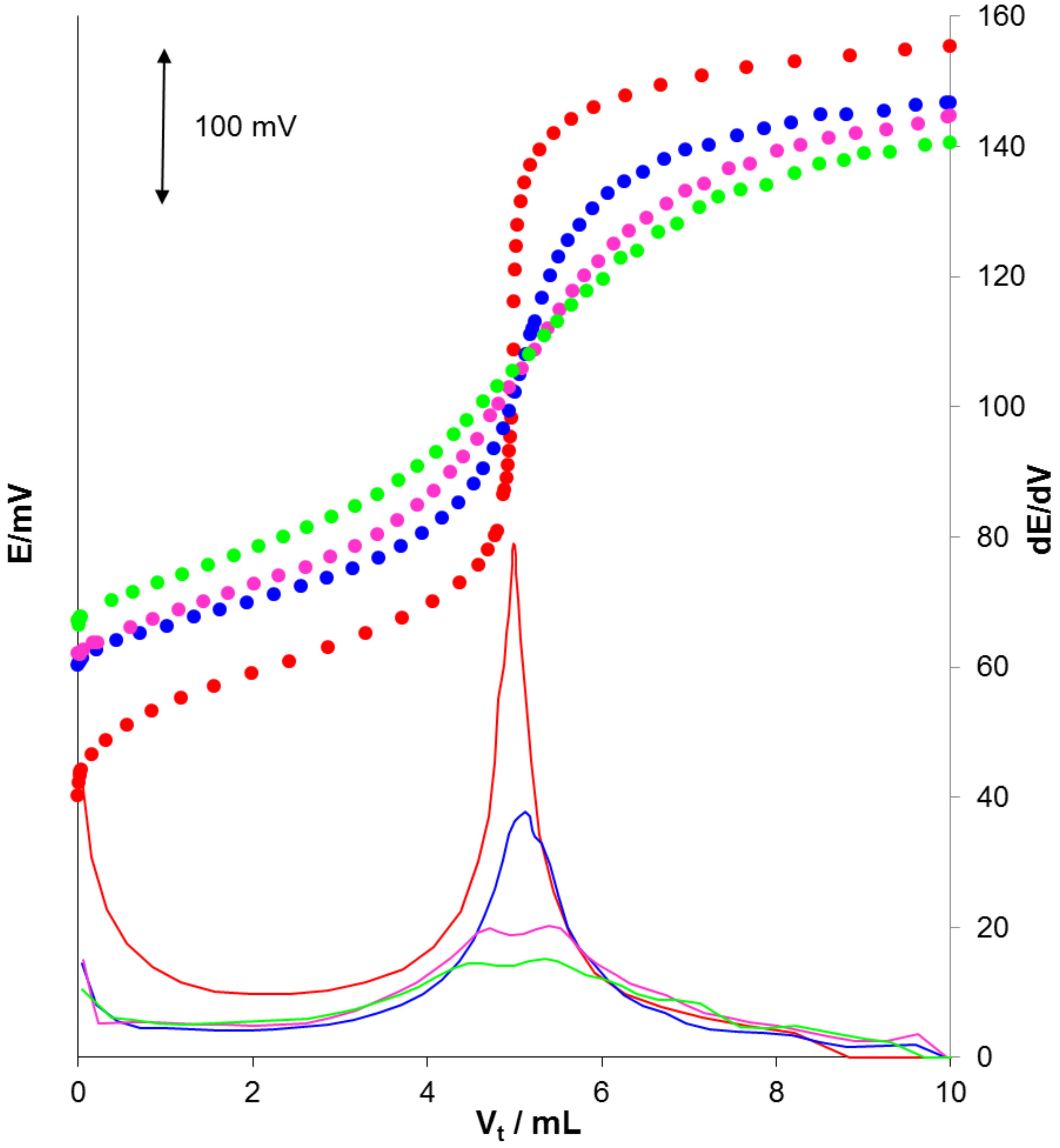

Figure 5. The influence of the nature of the EONS (number of EO groups) at the fixed NaDDS:EONS molar ratio of 1:2 on the shapes of the titration curves and their first derivatives for titrations of NaDDS using CPC as the titrant and the SPMS surfactant microsensor as the endpoint indicator (● NaDDS alone, ● 8 EO groups, ● 11 EO groups, ● 15 EO groups, — NaDDS, — 8 EO groups, — 11 EO groups, — 15 EO groups).

In the first step of this investigation, Genapol T 080 (8 EO groups) was added to the NaDDS solution at different molar ratios (NaDDS:EONS = 1:1, 1:2, 1:3 and 1:5). Figure 4 shows the resulting titration curves and their first derivatives. It can be seen that increasing concentrations of EONS caused decreases in the inflection of the curves. However, the deformation of the titration curve is significant only in molar ratios of EONS:ASs = 5:1 or more (the detected endpoint was 7.4% higher).

In the second step of this investigation, NaDDS solutions were titrated with 3 EONS with different numbers of EO groups (Genapol T 080, Genapol T 110 and Genapol T 150). The molar ratio of EONS:NaDDS was always 2:1. Figure 5 shows the resulting titration curves and their first derivatives. It can be observed that the shape of the titration curve depends on number of EO groups in the molecules of the EONS. Increasing numbers of EO groups caused a decrease in the inflection and more deformed titration curves, which result in less reliable titration endpoints.

Commercial detergents and other cleaning products rarely contain molar ratios of EONS:ASs higher than 5:1; therefore, it can be concluded that EONS are not significant interferences in the potentiometric titrations of ASs in typical detergent formulations.

3.2.3. The influence of different inorganic and organic anions used in commercial products on the SPMS microsensor response and the determination of the selectivity coefficients

The influence of the interfering ions on the response of the surfactant sensor is described by the Nikolskii-Eisenman equation:

$$E = E^{0}_{AS^{-}_{det}} - \frac{RT}{F} \cdot ln\left[a_{AS^{-}_{det}} + K^{pot}_{AS^{-}_{det}AS^{-}_{int}} \cdot a_{AS^{-}_{int}}\right] \qquad (2)$$

where $K^{pot}_{AS^{-}_{det}AS^{-}_{int}}$ is the selectivity coefficient and $a_{AS^{-}_{det}}$ and $a_{AS^{-}_{int}}$ are the activities of the analyte and the interfering ion, respectively.

Table 2. Potentiometric selectivity coefficients for different anions used in commercial products obtained by the fixed interference method for the SPMS surfactant microsensor. DDS was used as the primary ion. The concentration of the interfering ion was 0.01 M.

Interference	K^{pot}_{ij}	Interference	K^{pot}_{ij}
Chloride	$2.6 \cdot 10^{-4}$	Dihydrogenphosphate	$4.9 \cdot 10^{-4}$
Iodide	$7.6 \cdot 10^{-4}$	Borate	$3.4 \cdot 10^{-5}$
Fluoride	$1.6 \cdot 10^{-4}$	Acetate	$9.3 \cdot 10^{-5}$
Carbonate	$5.3 \cdot 10^{-5}$	Benzoate	$6.6 \cdot 10^{-4}$
Hydrogencarbonate	$3.7 \cdot 10^{-4}$	Citrate	$1.1 \cdot 10^{-5}$
Nitrite	$2.0 \cdot 10^{-4}$	Ethylenediaminetetraacetate	$1.7 \cdot 10^{-5}$
Nitrate	$3.6 \cdot 10^{-4}$	Sulfamate	$2.2 \cdot 10^{-3}$
Sulfate	$1.9 \cdot 10^{-5}$	Xylensulfonate	$1.2 \cdot 10^{-3}$
Hydrogensulfate	$2.5 \cdot 10^{-4}$	Toluensulfonate	$6.3 \cdot 10^{-4}$
Phosphate	$2.1 \cdot 10^{-5}$		

The determination of the potentiometric selectivity coefficients for the new SPMS surfactant microsensor was performed using the fixed interference method [24]. The response of the electrode was measured in solutions with different analyte activities and a fixed interfering ion activity. NaDDS in a concentration range from 10 μM to 10 mM was used as the analyte in all of the measurements. The concentration of the interfering ion was always 10 mM.

The selectivity coefficients can be determined graphically using experimental data, which is an approximate method. More reliable results can be obtained by the fitting of the Nikolskii-Eisenman equation, which is used as a model, to the experimental data obtained by the fixed interference method using Solver (Microsoft Excel analysis tool). In this investigation, the selectivity coefficients were estimated using Solver.

The selectivity coefficients of certain potentially interfering organic and inorganic anions, which can be expected in commercial products, are presented in Table 2. It can be seen that the new SPMS microsensor showed excellent selectivity for dodecyl sulfate (DDS).

3.3. Potentiometric titration

3.3.1. Titrant selection

The new SPMS microsensor should be used for the determination of ASs in real systems. In this paper, we suggest the application of the new microsensor as an indicator of the endpoint in AS potentiometric titrations. Therefore, it is very important to select the best titrant that will be used for titrations of real samples (detergent solutions).

For the potentiometric titrations of ASs, the titrants usually used are DMIC, CPC, Hyamine and CTAB. In this investigation, to select the best titrant, standard solutions ($c = 4\cdot10^{-3}$ M) of these cationic surfactants (CS) were used for titrations of standard solutions of NaDDS and NaDBS. The resulting titration curves and their first derivatives are presented in Figures 6 and 7 for NaDDS and NaDBS, respectively.

It can be seen that the inflections at the endpoints of the titrations are sharp for all of the titrants. The magnitudes of the potential jumps at the equivalence points are in the range of 170 mV (Hyamine) to 330 mV (DMIC) for NaDDS titrations and in the range of 190 mV (Hyamine) to 240 mV (DMIC) for NaDBS titrations, with the magnitudes of potential jumps for both analytes at the equivalence points ranked according to decreasing values being as follows: DMIC > CPC > CTAB > Hyamine. The CPC titrant exhibited slightly lower potential jumps at the endpoints of the titrations compared to DMIC, but DMIC is significantly more expensive; thus, CPC was selected as the titrant for further investigations.

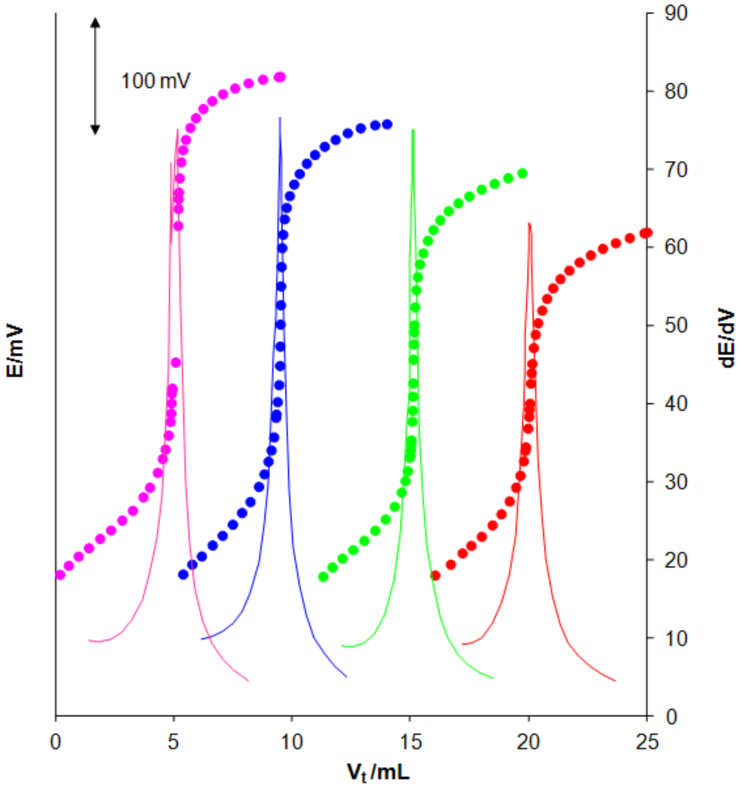

Figure 6. Potentiometric titration curves and the first derivatives of a NaDDS solution (c = $4\cdot10^{-3}$ mol/L) with several cationic surfactants using the new SPMS surfactant microsensor as the endpoint indicator (● DMIC, ● CPC, ● CTAB, ● Hyamine, — DMIC, — CPC, — CTAB, — Hyamine).

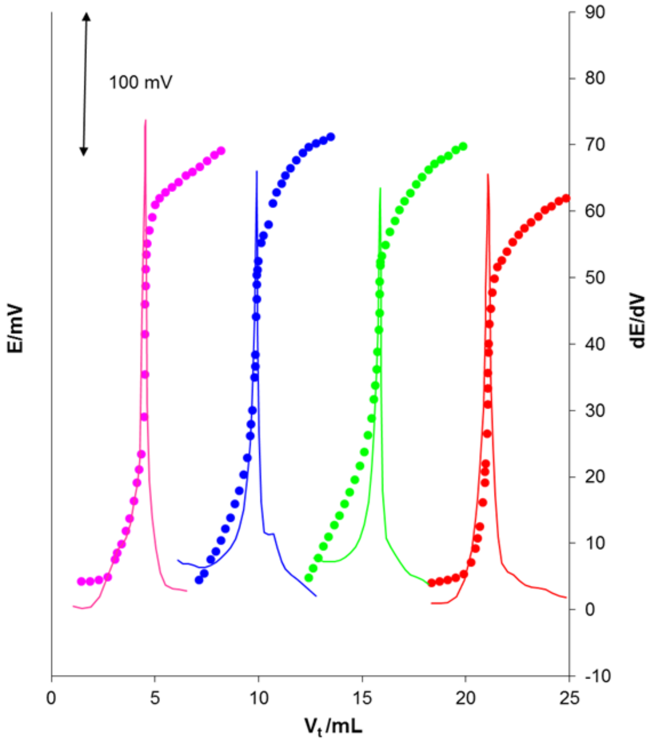

Figure 7. Potentiometric titration curves and the first derivatives of a NaDBS solution (c = $4\cdot10^{-3}$ mol/L) with several cationic surfactants using the new SPMS surfactant microsensor as the endpoint indicator (● DMIC, ● CPC, ● CTAB, ● Hyamine, — DMIC, — CPC, — CTAB, — Hyamine).

3.3.2. Titrations of two-component mixtures

Sodium decanesulfonate (C_{10}) and sodium dodecanesulfonate (C_{12}) were selected for use in differential titrations of two-component mixtures of ASs with the new SPMS microsensor. CPC was used as the titrant. Differential titrations were tested with alkane sulfonates in the following two molar ratios: $C_{10}:C_{12}$ = 1:1 and 1:2. The resulting titration curves and their first derivatives are presented in Figure 8. It can be seen that, although the difference between the sulfonates used was only 2 C-atoms, differential titrations were successfully performed resulting in two well-defined inflection points. The sodium dodecanesulfonate was titrated first because it forms the less soluble ion pair with the CPC.

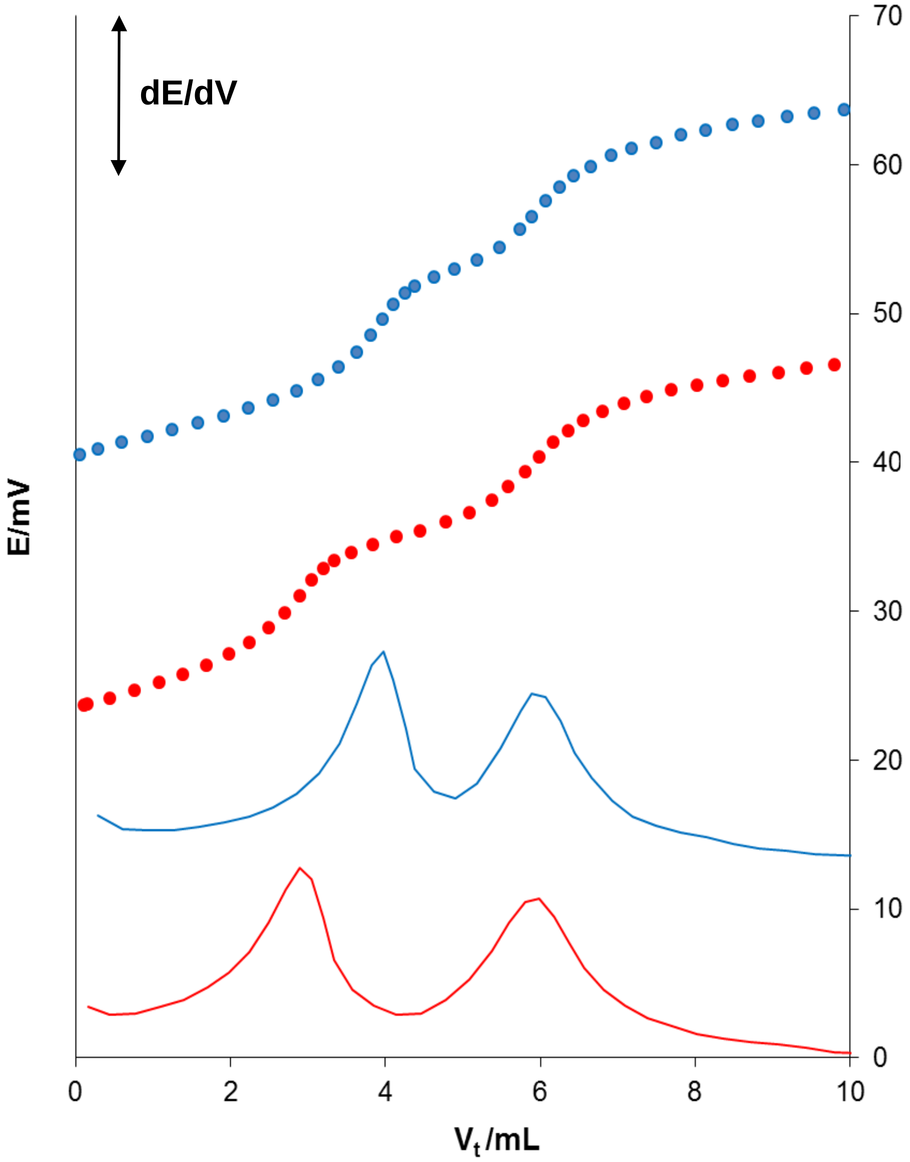

Figure 8. Potentiometric titration curves and the first derivatives of the same two-component mixtures of alkane sulfonates in different molar ratios using the new SPMS microsensor as the endpoint indicator and CPC (c = 1·10^{-3} M) as the titrant (● $C_{10}:C_{12}$ = 1:2, ● $C_{10}:C_{12}$ = 1:1, — $C_{10}:C_{12}$ = 1:2, — $C_{10}:C_{12}$=1:1).

3.3.3. Titrations of commercial products

The main applications of the new SPMS microsensor should be the routine analysis of commercial products based on ASs. For this purpose, three commercial detergents with different AS contents were used. The selected detergents were powdered detergent, gel detergent and liquid hand-dishwashing detergent.

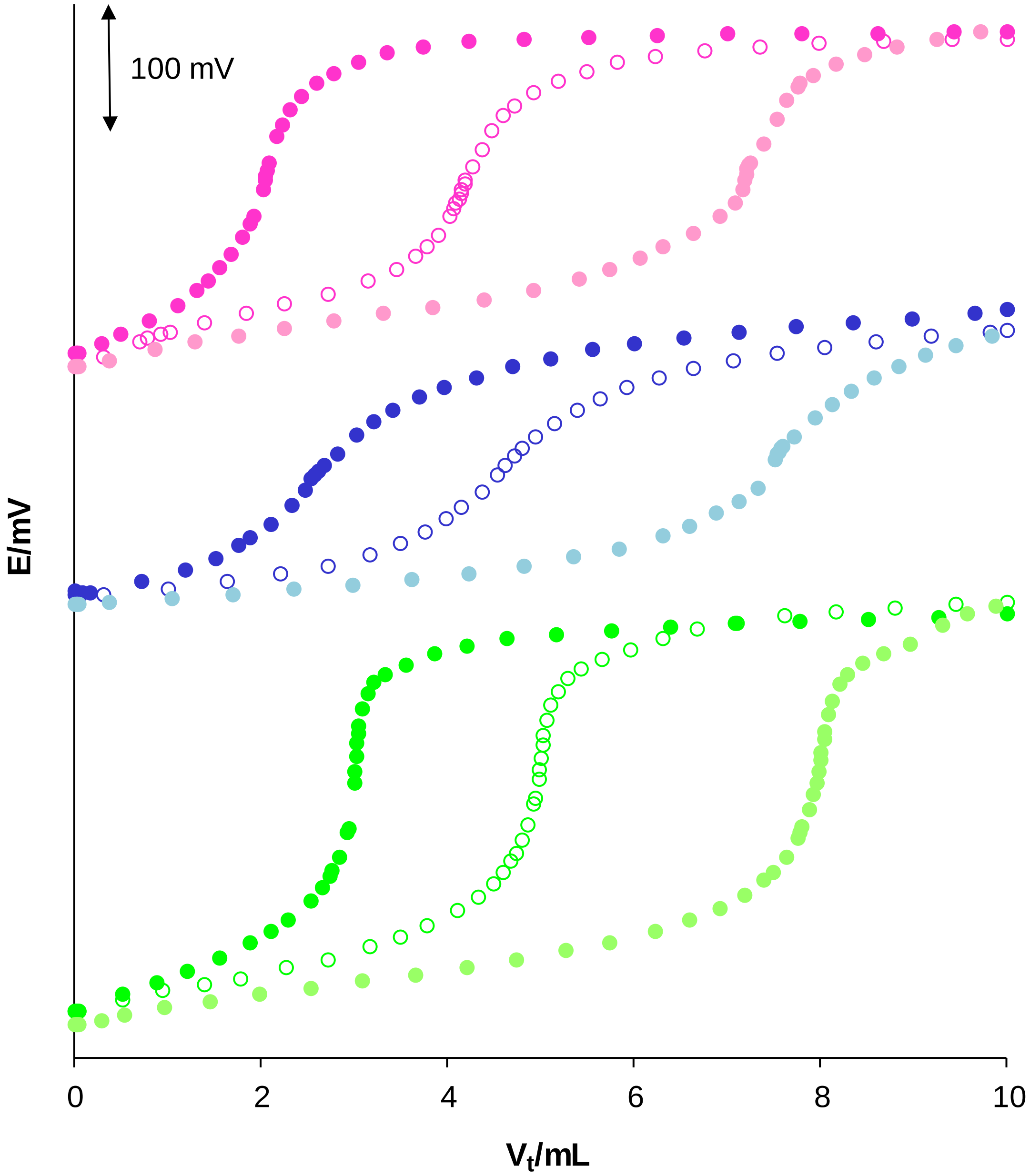

Figure 9. Titration curves of three commercial detergents with the addition of known concentrations of NaDDS (● powdered detergent, ○ powdered detergent + 2 mL NaDDS, ● powdered detergent + 5 mL NaDDS, ● gel detergent, ○ gel detergent + 2 mL NaDDS, ● gel detergent + 5 mL NaDDS, ● liquid hand-dishwashing detergent, ○ liquid hand-dishwashing detergent + 2 mL NaDDS, ● liquid hand-dishwashing detergent + 5 mL NaDDS).

A standard solution of CPC was used as the titrant. The pH values of the commercial detergents varied between 8 and 11. Therefore, to make sure that the titrated analytes were only ASs (not ASs and soaps), the pH values were adjusted to 3 in all of the measurements. The accuracy of the measurements and the influence of the ingredients from the commercial detergents on the determination of the ASs were tested by the known addition method. NaDDS, at a concentration of $4\cdot10^{-3}$ M, was added to the solutions of all three detergents in known amounts. Figure 9 presents the corresponding titration curves.

Table 3. The results of the potentiometric titrations of the commercial detergents with the addition of known concentrations of NaDDS using the SPMS surfactant microsensor as the indicator and CPC (c = $4\cdot10^{-3}$ M) as the titrant compared to the results obtained for the same measurements with the PMS sensor [1].

		SPMS microsensor				**PMS sensor***			
		ASs found (mol/L)	NaDDS			ASs found (mol/L)	NaDDS		
			Added (mol)	Found (mol)	Recovery (%)		Added (mol)	Found (mol)	Recovery (%)
Detergent type	Gel detergent	$6.71\cdot10^{-4}$	$8\cdot10^{-6}$	$8.31\cdot10^{-6}$	103.9	$6.71\cdot10^{-4}$	$8\cdot10^{-6}$	$8.34\cdot10^{-6}$	104.3
			$2\cdot10^{-5}$	$2.00\cdot10^{-5}$	100.0		$2\cdot10^{-5}$	$2.00\cdot10^{-5}$	100.0
	Powdered detergent	$8.15\cdot10^{-4}$	$8\cdot10^{-6}$	$8.23\cdot10^{-6}$	102.9	$9.20\cdot10^{-4}$	$8\cdot10^{-6}$	$8.34\cdot10^{-6}$	104.3
			$2\cdot10^{-5}$	$2.09\cdot10^{-5}$	104.5		$2\cdot10^{-5}$	$2.04\cdot10^{-5}$	102.0
	Liquid hand-dishwashing detergent	$2.39\cdot10^{-3}$	$8\cdot10^{-6}$	$8.00\cdot10^{-6}$	100.0	$2.32\cdot10^{-3}$	$8\cdot10^{-6}$	$8.08\cdot10^{-6}$	101.0
			$2\cdot10^{-5}$	$2.01\cdot10^{-5}$	100.5		$2\cdot10^{-5}$	$2.01\cdot10^{-5}$	100.5

* Data from [1]

Table 4. The results of the potentiometric titrations of commercial products using the SPMS surfactant microsensor and the PMS sensor [1] as indicators compared with the results obtained using the two-phase titration method.

	% AS (found)		
Sample	**SPMS microsensor**	**PMS sensor***	**Two-phase titration**
gel detergent	2.31	2.31	2.41
powdered detergent	5.95	6.25	5.27
liquid hand-dishwashing detergent	16.47	15.92	15.83

* Data from [1]

It can be seen that all of the titration curves revealed good inflection points with potential jumps of good magnitudes, which enable the quantification of the AS contents in the tested commercial products. Table 3 presents the corresponding results compared with results obtained by a

PMS sensor [1]. It can be concluded that the new SPMS microsensor can be successfully applied for the determination of ASs in real systems. The new microsensor is accurate, and ingredients from the commercial detergents do not affect the determination of the ASs. The results obtained by the new microsensor are very similar to the results obtained by the conventional sensor, but are even better. The results were also compared with the reference method proposed by IUPAC (two-phase titration), which can be seen in Table 4. These results also confirm that the new SPMS microsensor works equally as well as the conventional PMS sensor [1]. Comparing the results with the reference method, no significant differences were found.

4. CONCLUSIONS

A new microsensor for the determination of ASs based on the DDA-TPB ion pair as the sensing element, PVC as the polymer matrix and o-NPOE as the plasticizer implemented into a carbon-based SPE was developed. Its primary application is endpoint detection by the potentiometric titration of ionic surfactants. The results were compared with those obtained by the two-phase titration method and with the conventional surfactant ISE [1], and they showed satisfactory mutual agreement.

This microsensor is a simple, sensitive and accurate device that can be successfully applied for the determination of ASs in real systems (commercial detergents). It has many advantages compared to the conventional ISE, such as its low-cost, which allows for its mass production, and its ability to make measurements using small sample volumes, which leads to a reduced cost of chemicals and a smaller amount of waste chemicals. Due to its miniaturized dimensions, the new SPE microsensor could also be used as a specific detector in microfluidic techniques, such as FIA and SIA.

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