A New Sensing Material for the Potentiometric Determination of Anionic Surfactants in Commercial Products

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A new potentiometric sensor for the determination of anionic surfactants (ASs) was constructed based on the dimethyldioctadecylammonium-tetraphenylborate (DDA-TPB) ion pair as a sensing material. This sensitive, accurate, selective, rapid, simple and inexpensive sensor exhibited a Nernstian response for sodium dodecyl sulfate (NaDDS, 59.0 mV/decade) and sodium dodecylbenzene sulfonate (NaDBS, 59.1 mV/decade) over the range of $3 \cdot 10^{-7}$ to $8 \cdot 10^{-3}$ M for NaDDS and $4 \cdot 10^{-7}$ to $2 \cdot 10^{-3}$ M for NaDBS. The detection limits for both NaDDS and NaDBS were $2 \cdot 10^{-7}$ M. Different pH values, ionic strengths and commonly used nonionic surfactants, organic anions and inorganic anions did not have a significant influence on the sensor performances or the accuracy of ASs determination. The sensor was successfully applied to ASs determination in three commercial detergents with different percentages of ASs.

1. INTRODUCTION

Surface active agents or surfactants are a large group of chemicals that are widely used in industry, cosmetic products, household products, and so on due to their ability to decrease the surface tension of a solvent. The production and consumption of surfactants have been increasing on a daily basis. By 2018, the surfactant market is estimated to be 41 billion US dollars [1].

Anionic surfactants (ASs) are the largest group of surfactants, with an annual production of approximately 6.5 million tonnes in 2010 [1]. The ASs represent approximately 70% of the total surfactant market.

Due to the large consumption of surfactants, it is important to accurately determinate their concentrations for quality control (commercial products), process control (industrial samples) and contamination control (environmental samples and food products). The standard methods for ASs determination are the two phase titration [2] (for products with a higher surfactant concentration, such as raw materials) and MBAS method [3] (Methylene Blue Active Substances method, which is used for products with a lower surfactant concentration, such as effluents). Both methods are time consuming, subjective and are unable to be automated; these methods also have many interferences and use highly toxic and carcinogenic organic solvents. Because the protection of our environment and health is a current focus, use of these types of solvents is unacceptable. The use of ion-selective electrodes (ISEs) as potentiometric sensors represent an important alternative to standard methods for AS determination [4-7]. ISEs are simple, rapid, inexpensive, easily automated and environmentally friendly. There are many types of ISEs selective to ASs, such as coated wire electrodes [8], liquid membrane electrodes [9], electrochemically modified carbon paste electrodes [10] and polyvinyl chloride (PVC) electrodes, with different sensor materials [11-13]. Currently, ISEs are similarly constructed, having a PVC membrane with a plasticizer and sensing material, which is typically an ion pair composed of two surfactants of opposite charge. All of these compounds can be varied to construct an ISE with better properties, such as better selectivity, accuracy, longer lifetime, and so on [14-19].

In addition, there are many other methods for ASs determination, such as ISEs combined with a flow injection analysis (FIA) system [20, 21], reverse FIA [22], ISFET sensors [23], chromatography [24, 25], biosensors [26], among others.

In this paper, we describe the development of a new ISE based on a self-made PVC-plasticized liquid-type anionic surfactant sensitive membrane prepared from the newly synthesized ion-pair dimethyldioctadecylammonium-tetraphenylborate (DDA-TPB) as the sensing element and *o*-nitrophenyl octyl ether (*o*-NPOE) as the plasticizer. In this report, we also suggest several applications for the new highly responsive sensor, particularly for the routine analysis of industrial raw materials and commercial products.

2. EXPERIMENTAL

2.1. Reagents and Materials

NaDDS and NaDBS (from Fluka, Switzerland) were used for the investigation of the sensor response characteristics and for potentiometric titrations. The standard solutions, purchased from Fluka, Switzerland, of 1,3-didecyl-2-methylimidazolium chloride (DMIC), hexadecyltrimethylammonium bromide (CTAB) and Hyamine 1622 (benzethonium chloride) and cetylpyridinium chloride (CPC), purchased from Merck, Germany, were used as cationic titrants. Sodium hydroxide (T.T.T., Croatia) and hydrochloric acid (Carlo Erba Reagent, Italy) were used to adjust the pH while studying the pH influence on the response of the sensor. 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) were used to study the influence of the interferences on the response of the sensor.

Three commercial products, a compact powdered detergent, gel detergent and liquid hand-dishwashing detergent, were used to test the applicability of the sensor to ASs determination in real systems.

Dimethyldioctadecylammonium chloride (DDAC), sodium tetraphenylborate (NaTPB), *o*-NPOE and high molecular weight PVC (Fluka, Switzerland) were used for the preparation of the sensor membrane.

2.2. Apparatus and Measurements

An all-purpose titrator, 808 Titrando (Metrohm, Switzerland), combined with a Metrohm 806 Exchange unit (Metrohm, Switzerland) controlled by the Tiamo software (Metrohm, Switzerland) was used as the dosing element to perform the potentiometric titrations. During the titrations and measurements, the solutions were magnetically stirred using an 801 Titration stand (Metrohm, Switzerland).

A Metrohm 780 pH meter, a 728 Stirrer, a Metrohm 794 Basic Titrino (Metrohm, Switzerland) and in-house software were used for the response measurements, dynamic response time measurements and measurements of the influence of interferences on the sensor response.

A silver/silver (I) chloride reference electrode (Metrohm, Switzerland) with a 3 M potassium chloride electrolyte solution was used as a reference.

2.3. Sensor

2.3.1. Preparation of the DDA-TPB ion pair and the PVC-plasticized liquid membrane

The DDA-TPB ion pair was prepared by dissolving equimolar amounts of DDAC and NaTPB in 30 mL of dichloromethane, forming a white precipitate. The precipitate was extracted with dichloromethane and dried with anhydrous sodium sulfate. After evaporation at room temperature, the precipitate was dissolved in 10 mL of a 1:1 mixture of diethylether and methanol using an ultrasonic bath. The solvent was evaporated at -18°C. The isolated ion-exchange complex was used as a sensing material for the preparation of the PVC-based membranes plasticized with *o*-NPOE.

For the membrane preparation, the newly synthesized sensor material (0.0018 g) was dissolved in 2 mL of tetrahydrofuran. PVC and 115 μL of *o*-NPOE were mixed and the solution of the sensor material was added. The mixture was dissolved in an ultrasonic bath and poured into a glass ring (i.d. = 24 mm) that was fixed on a glass plate. After 24 hours, small disks (i.d. = 7 mm) were excised from the poured film and used for the sensor preparation.

2.3.2. Sensor preparation

The membrane was mounted on a Philips electrode body IS-561 (Glasblaeserei Moeller, Zurich, Switzerland). Sodium chloride, at a concentration of 3 M, was employed as the internal filling solution. Between measurements, the sensor was placed in deionized water. The lifetime of the sensor was more than four months with daily use.

2.4. Procedure

A Philips electrode with a PVC-plasticized liquid membrane made by the newly synthesized ion-pair and the external reference electrode was used for all of the potentiometric measurements.

An investigation of the responses to NaDDS and NaDBS was performed by incremental addition of ASs into distilled water. The concentrations of ASs used were $5 \cdot 10^{-4}$ M and $5 \cdot 10^{-5}$ M. 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.

The influence of the pH was examined over a pH range of 2 to 12 in solutions of NaDDS and NaDBS at concentrations of $4 \cdot 10^{-3}$ M and $4 \cdot 10^{-4}$ M. The pH values were adjusted with NaOH and HCl, with concentrations of 1 M, 0.1 M and 0.01 M.

The influence of the ionic strength was examined by adding AS in a sodium sulfate solution at the following three concentrations: 0.1 M, 0.01 M and 0.001 M, covering the ionic strengths in the interval 0.003 - 0.301.

The volume of the solution used for all of the titrations was 25 mL. The titrations were performed with titrants at concentrations of $4 \cdot 10^{-3}$ M. Stock solutions of three commercial detergents were prepared weekly and the diluted solutions were prepared daily.

The influence of three ethoxylated alcohols, Genapol T 080, Genapol T 110 and Genapol T 150 was investigated by adding Genapols separately in different molar ratios to the titrated NaDDS solutions. The titrator was programmed to 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 fixed interference method, as proposed by IUPAC [27], was used for the determination of the potentiometric selectivity coefficients. All of the solutions of the interfering anion were at concentrations of 0.01 M.

The standard addition method in which NaDDS was added at two concentration levels was used for the determination of the accuracy and precision of the measurements.

The two-phase titration [2], as an official method, was used as a reference.

3. RESULTS AND DISCUSSION

3.1. Response characteristics

The following Nernst equation describes the electromotive force of the DDA-TPB sensor dipped into a solution of AS:

$$E = E^0 - S \cdot \log a_{AS^-} \tag{1}$$

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

The response characteristics of the DDA-TPB surfactant sensor in solutions of NaDDS and NaDBS are shown in Figure 1. The Davies equation was used to calculate the activity coefficients.
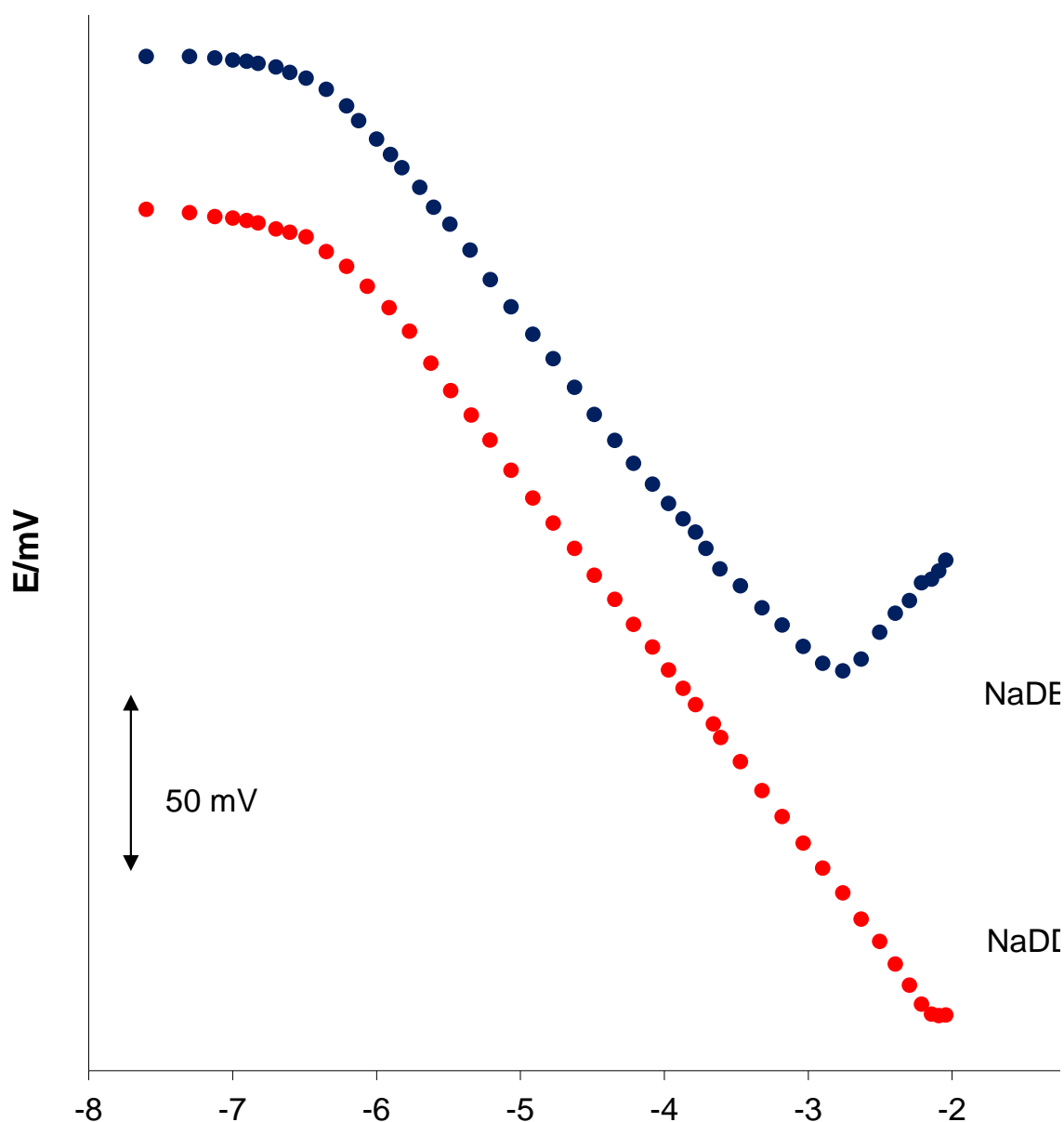
Figure 1. Response characteristics of the DDA-TPB sensor in NaDBS and NaDDS solutions. Here and in the following figures, the curves are displaced laterally or vertically for clarity.
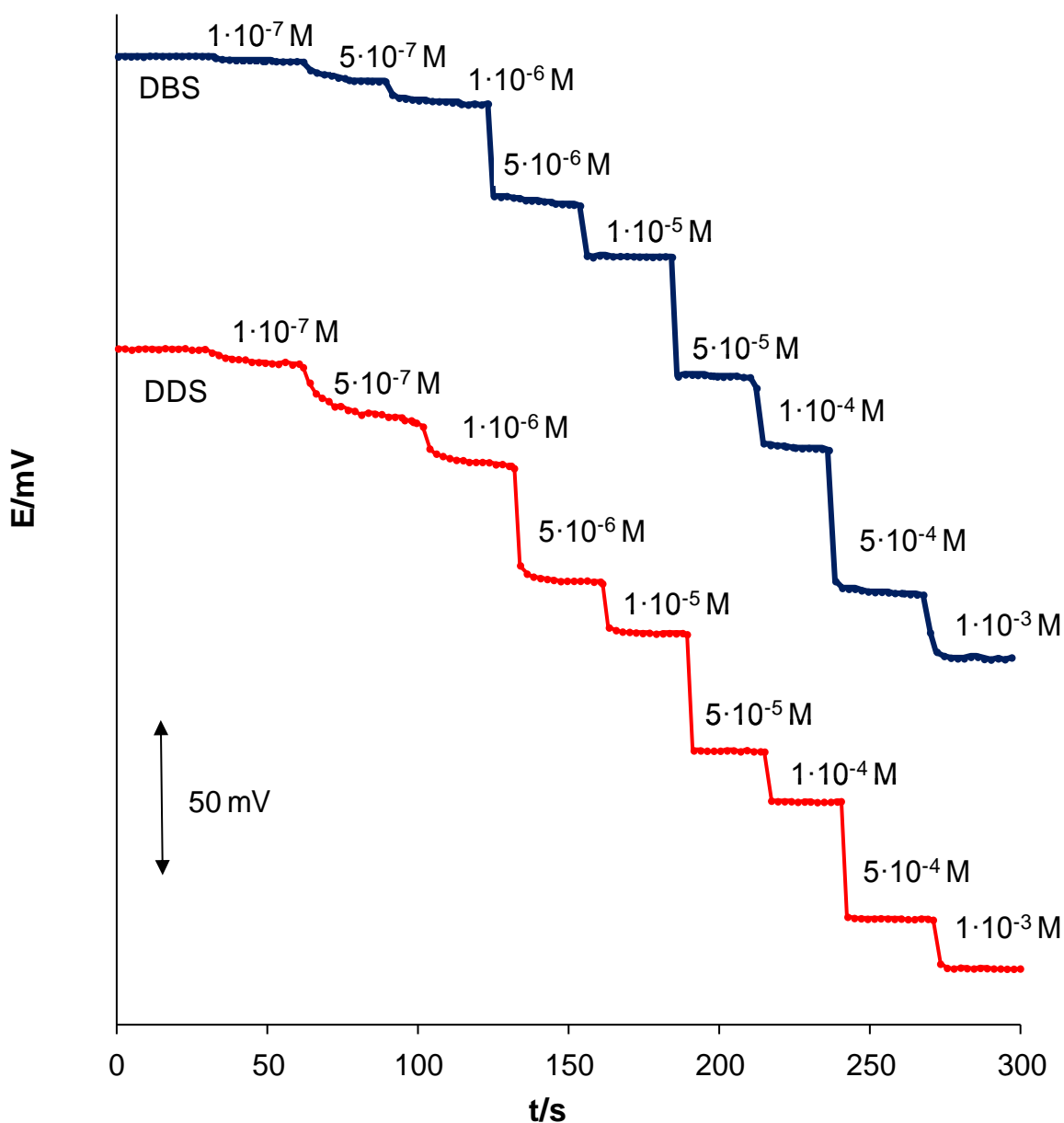
Figure 2. Dynamic response characteristics of the DDA-TPB sensor toward NaDDS and NaDBS.

Table 1 presents the statistical evaluation of the sensor characteristics compared with those of the hexadecyltrioctadecylammonium-tetraphenylborate (HTA-TPB) [28] and 1,3-didecyl-2-methylimidazolium-tetraphenylborate (DMI-TPB) sensors [29].

Linear regression analysis was used to calculate the slope values and the correlation coefficients. All of the calculations were based on a series of five measurements. The sensor investigated showed a Nernstian response for NaDDS (59.0 mV/activity decade) and NaDBS (59.1 mV/activity decade). The sensor exhibited linear responses for both of the ASs anions, even below 10^{-6} M, which can be observed in Figure 1. Micellization occurs at higher surfactant activities, revealing deviations from linearity.

The dynamic response of the DDA-TPB sensor for NaDDS and NaDBS was also evaluated. Figure 2 shows that the sensor responded in a few seconds for each concentration change in the range of $1 \cdot 10^{-7}$ M to $1 \cdot 10^{-3}$ M.

Table 1. Response characteristics of the DDA-TPB sensor for anionic surfactants compared to two other sensors with ± 95% confidence limits

Parameters	NaDBS (DDA-TPB sensor)	NaDDS (DDA-TPB sensor)	NaDDS (HTA-TPB sensor)*	NaDDS (DMI-TPB sensor)**
Slope / (mV/conc. decade)	59.1 ± 0.3	59.0 ± 0.5	58.1 ± 0.3	59.3 ± 0.6
Correl. coeff. (R^2)	0.9980	0.9999	0.9998	0.9993
Detection limit (M)	$2 \cdot 10^{-7}$	$2 \cdot 10^{-7}$	$2 \cdot 10^{-7}$	$3 \cdot 10^{-7}$
Useful conc. range (M)	$4 \cdot 10^{-7}$ - $2 \cdot 10^{-3}$	$3 \cdot 10^{-7}$ - $8 \cdot 10^{-3}$	$3 \cdot 10^{-7}$ - $3 \cdot 10^{-3}$	$4 \cdot 10^{-7}$ - $5 \cdot 10^{-3}$

* Data from [28], ** data from [29].

3.2. Interferences

3.2.1. The influence of pH
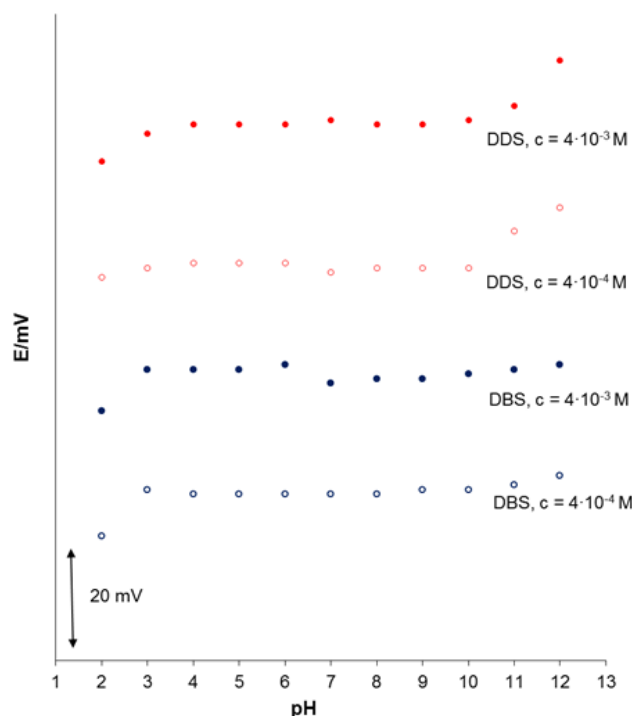
Figure 3. The influence of the pH value on the potentiometric response of the DDA-TPB sensor in NaDDS and NaDBS solutions.

Different commercial products have different pH values. Therefore, the stability of the sensor potential was investigated over a pH range of 2 to 12. The investigations were performed in solutions

of NaDDS and NaDBS at concentrations of $4 \cdot 10^{-3}$ M and $4 \cdot 10^{-4}$ M. The pH values were adjusted with NaOH and HCl, with concentrations of 1 M, 0.1 M and 0.01 M. Figure 3 shows that the sensor potential is very stable and without significant potential deviations over the entire pH range investigated, indicating that the sensor can be used in strongly acidic and alkaline conditions without reducing the measurement accuracy.

3.2.2. *The influence of ionic strength*

The effect of ionic strength on the sensor potential stability was investigated, simulating the practical conditions of different formulated products. The investigations were performed in solutions of NaDDS and NaDBS at concentrations of $5 \cdot 10^{-4}$ M and $5 \cdot 10^{-5}$ M. The ionic strength was adjusted with a solution of Na_2SO_4 and was investigated at three concentration levels of Na_2SO_4 (0.1 M, 0.01 M and 0.001 M). The corresponding ionic strengths for $5 \cdot 10^{-4}$ M NaDDS and NaDBS were 0.301, 0031 and 0.004 for 0.1 M, 0.01 M and 0.001 M Na_2SO_4, respectively.

For $5 \cdot 10^{-5}$ M NaDDS and NaDBS the ionic strengths were 0.300, 0.030 and 0.003 for 0.1 M, 0.01 M and 0.001 M Na_2SO_4, respectively.

There was no difference between the measurements performed in water and those performed in solutions of Na_2SO_4 at different concentrations (data not shown). The results confirmed that the DDA-TPB sensor can be used for measurements in commercial products with different ionic strength.

3.2.3. *The influence of nonionic surfactants*

Common components of liquid and powdered detergents based on anionic surfactants are ethoxylated nonionic surfactants (EONS), especially ethoxylated alcohols. Under certain circumstances, EONS can exhibit a slightly anionic character; therefore, the influence of three ethoxylated alcohols, Genapol T 080 (8 EO groups), Genapol T 110 (11 EO groups) and Genapol T 150 (15 EO groups), on the potentiometric titration of AS was investigated. Genapols were added separately in different molar ratios to the titrated NaDDS solutions.

Figure 4 shows the resulting titration curves and their first derivatives for Genapol T 080. It can be observed that an increase in the EONS concentration decreases the inflection, which slightly disturbs the end-point detection (2.5% higher end-point) for the molar ratios of NaDDS:EONS of 1:5 or more. The data for Genapol T 110 and Genapol T 150 are not shown but also revealed that an increase in the EONS concentration decreases the inflection. A decrease of the inflection also depends on the number of EO groups in the EONS molecule. This trend can be observed in Figure 5 in which the influences of EONS with a different number of EO groups at a fixed NaDDS:EONS molar ratio (1:2) on the potentiometric titration of AS are compared. The EONS with a higher number of EO groups more significantly decrease the inflection of the titration curve.

In commercial product ratios, ASs:EONS ratios are typically lower; thus, it can be concluded that EONS do not significantly interfere with the potentiometric titration of ASs.
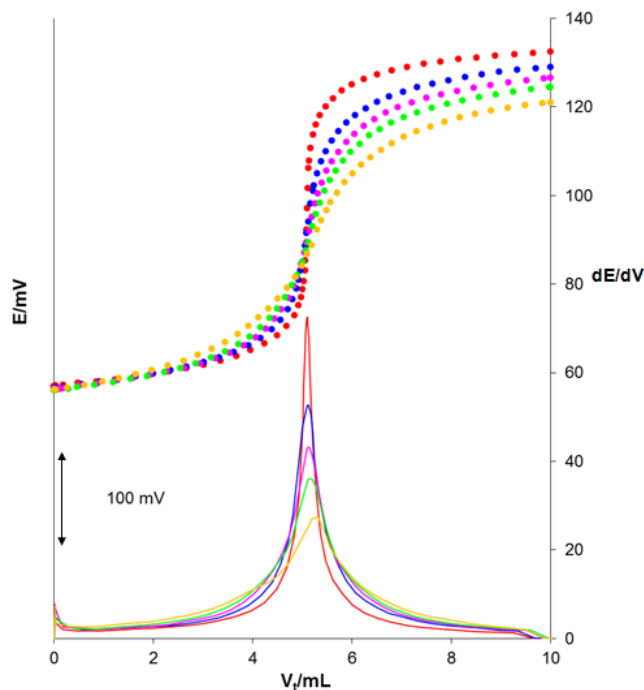
Figure 4. The influence of different amounts of EONS on the shape of the titration curves and their first derivatives of NaDDS using CPC as the titrant and the DDA-TPB surfactant sensor as the end-point indicator (● NaDDS alone, NaDDS:Genapol T 080 molar ratios of: ● 1:1, ● 1:2, ● 1:3, ● 1:5, — NaDDS, — 1:1, — 1:2, — 1:3, — 1:5).
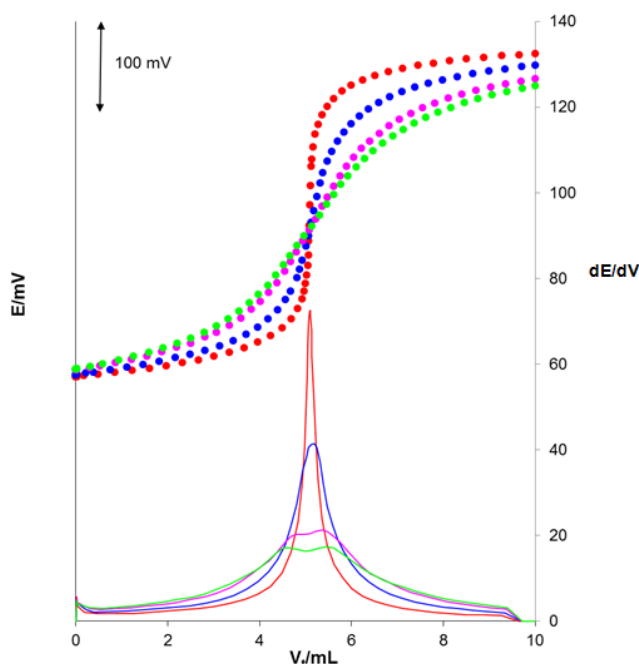
Figure 5. The influence of the EONS nature (the number of EO groups) at a fixed NaDDS:EONS molar ratio of 1:2 on the shape of the titration curves and their first derivatives of NaDDS using CPC as the titrant and the DDA-TPB surfactant sensor as the end-point indicator (● NaDDS alone, ● 8 EO groups, ● 11 EO groups, ● 15 EO groups, — NaDDS, — 8 EO groups, — 11 EO groups, — 15 EO groups).

3.2.4. The influence of different inorganic and organic anions used in commercial products and the determination of the selectivity coefficients

The following Nikolskii-Eisenman equation describes the influence of the interfering ions on the response of the surfactant sensor:

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

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.

The fixed interference method proposed by IUPAC [27] was used for the determination of the potentiometric selectivity coefficients. In all of the measurements, dodecyl sulfate (DDS) was used as a primary ion in the concentration range of 10 μM and 10 mM. All of the solutions of the interfering anion were at concentrations of 10 mM.

Table 2. Potentiometric selectivity coefficients for different anions used in commercial products obtained by the fixed interference method for the DDA-TPB liquid membrane surfactant electrode. DDS was used as the primary ion. The interference concentration was 0.01 M.

Interference	K^{pot}_{ij}	Interference	K^{pot}_{ij}
Chloride	$3.5 \cdot 10^{-5}$	Dihydrogenphosphate	$3.8 \cdot 10^{-5}$
Iodide	$1.1 \cdot 10^{-4}$	Borate	$1.5 \cdot 10^{-5}$
Fluoride	$5.6 \cdot 10^{-5}$	Acetate	$5.8 \cdot 10^{-5}$
Carbonate	$2.1 \cdot 10^{-5}$	Benzoate	$4.8 \cdot 10^{-5}$
Hydrogencarbonate	$4.6 \cdot 10^{-5}$	Citrate	$5.3 \cdot 10^{-6}$
Nitrite	$7.5 \cdot 10^{-5}$	Ethylenediaminetetraacetate	$9.8 \cdot 10^{-6}$
Nitrate	$5.5 \cdot 10^{-5}$	Sulfamate	$9.3 \cdot 10^{-5}$
Sulfate	$9.6 \cdot 10^{-6}$	Xylensulfonate	$1.3 \cdot 10^{-4}$
Hydrogensulfate	$4.1 \cdot 10^{-5}$	Toluensulfonate	$1.2 \cdot 10^{-4}$
Phosphate	$6.7 \cdot 10^{-6}$		

The selectivity coefficients were estimated by fitting of the Nikolskii-Eisenman equation, which was used as a model, to the experimental data obtained by the fixed interference method.

Solver, a Microsoft Excel analysis tool, was used to calculate the minimum sum of the squared residuals by varying the values of E^0, S and $K^{pot}_{AS^-_{det}AS^-_{int}}$.

Table 2 presents the selectivity coefficients of certain potentially interfering organic and inorganic anions typically present in commercial products, which were determined for the DDA-TPB

surfactant selective sensor. It can be concluded that the new DDA-TPB ion-pair based sensor exhibits excellent selectivity performances for DDS.

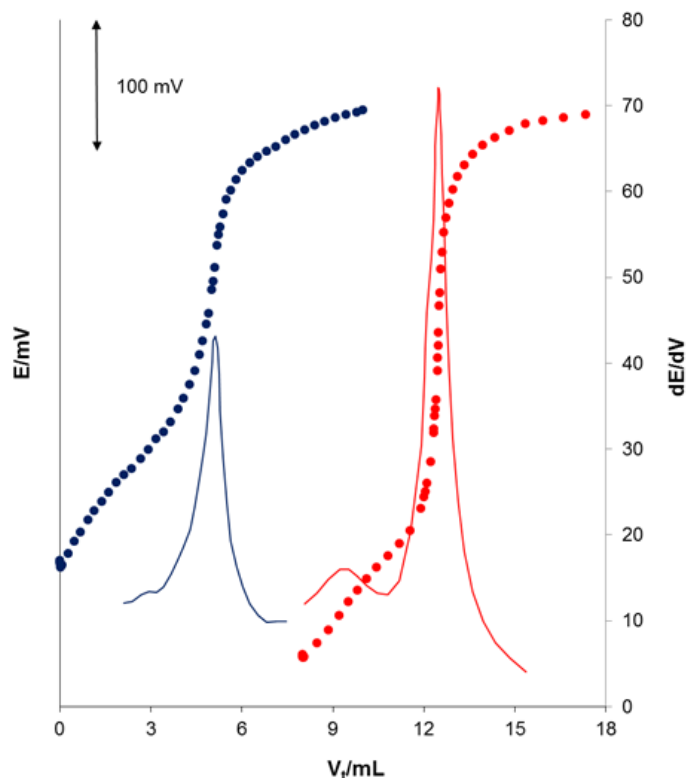### 3.3. Potentiometric titration

3.3.1. Titrant selection
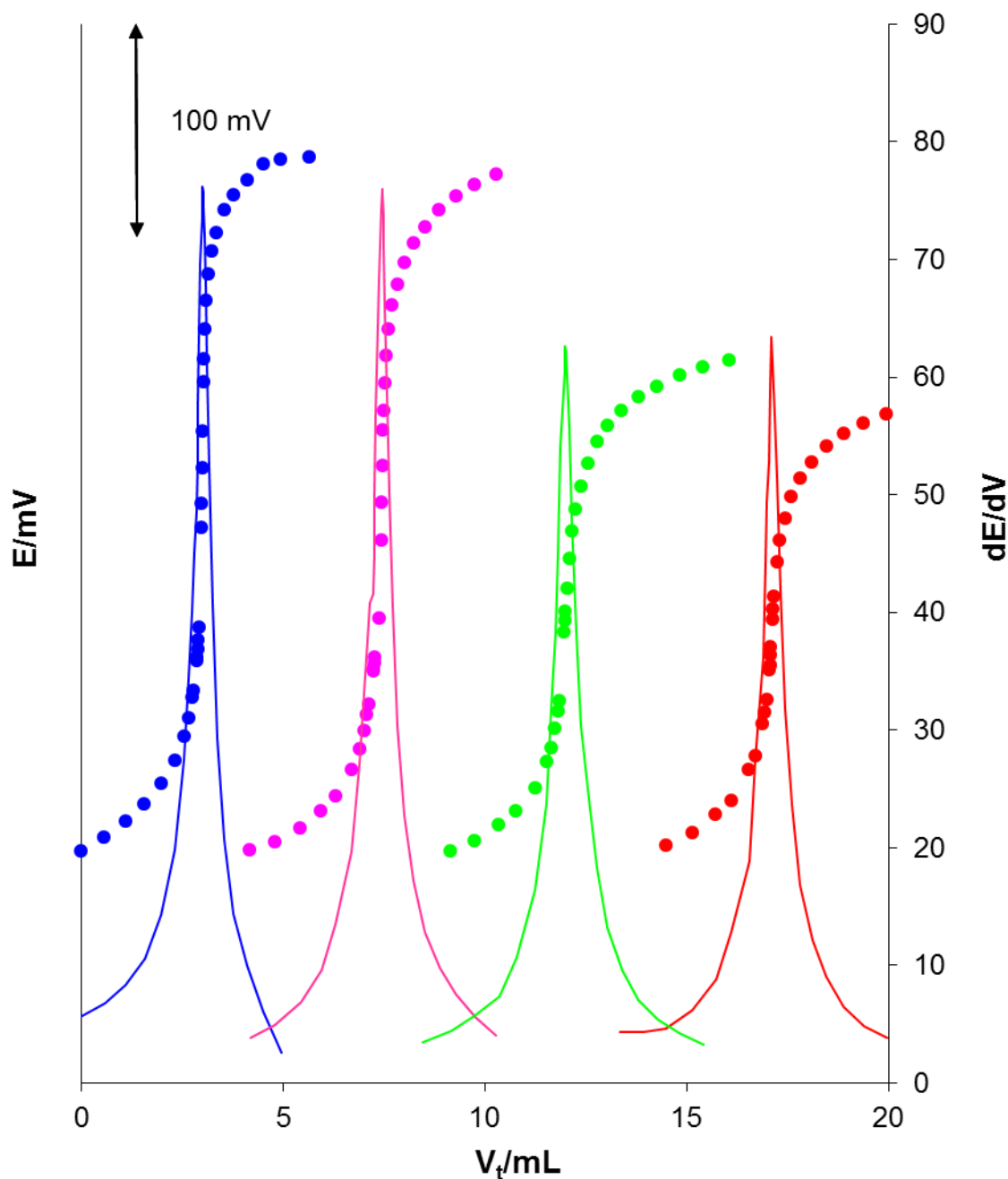
Figure 6. Potentiometric titration curves of the NaDDS solution (c = 4·10^{-3} M) with several cationic surfactants using the DDA-TPB surfactant sensor as the end-point indicator and their first derivatives (● CPC, ● DMIC, ● CTAB, ● Hyamine, — CPC, — DMIC, — CTAB, — Hyamine).

The primary application of the new DDA-TPB sensor was as an indicator of the end-point in ASs potentiometric titrations. During the titration, AS react with the cationic surfactant (CS), used as a titrant, resulting in the formation of a water insoluble ion-pair complex. Before the equivalence point, the change in the sensor potential is in response to the decrease in the AS concentration, according to equation (1). After the equivalence point, all of the ASs are precipitated and the change in the sensor potential is in response to the increase in the CS concentration.

DMIC, Hyamine, CPC and CTAB are cationic surfactants that are commonly used as titrants for the potentiometric titration of anionic surfactants. The selection of the best titrant was investigated using the standard solutions (c = $4 \cdot 10^{-3}$ M) of these cationic surfactants as the titrant and NaDDS and NaDBS solutions as the analytes (c = $4 \cdot 10^{-3}$ M for both of the ASs). Figure 6 presents the resulting titration curves for NaDDS as the analyte (the results for NaDBS are not shown). It can be observed that the inflections are sharp and the magnitudes of the potential jumps at the equivalence points are in the range of 240 mV for Hyamine to 350 mV for CPC and DMIC. CPC and DMIC have very similar potential jumps at the equivalence point. Both CPC and DMIC show excellent titration properties, but DMIC is significantly more expensive; thus, CPC was selected as the titrant for further investigations.

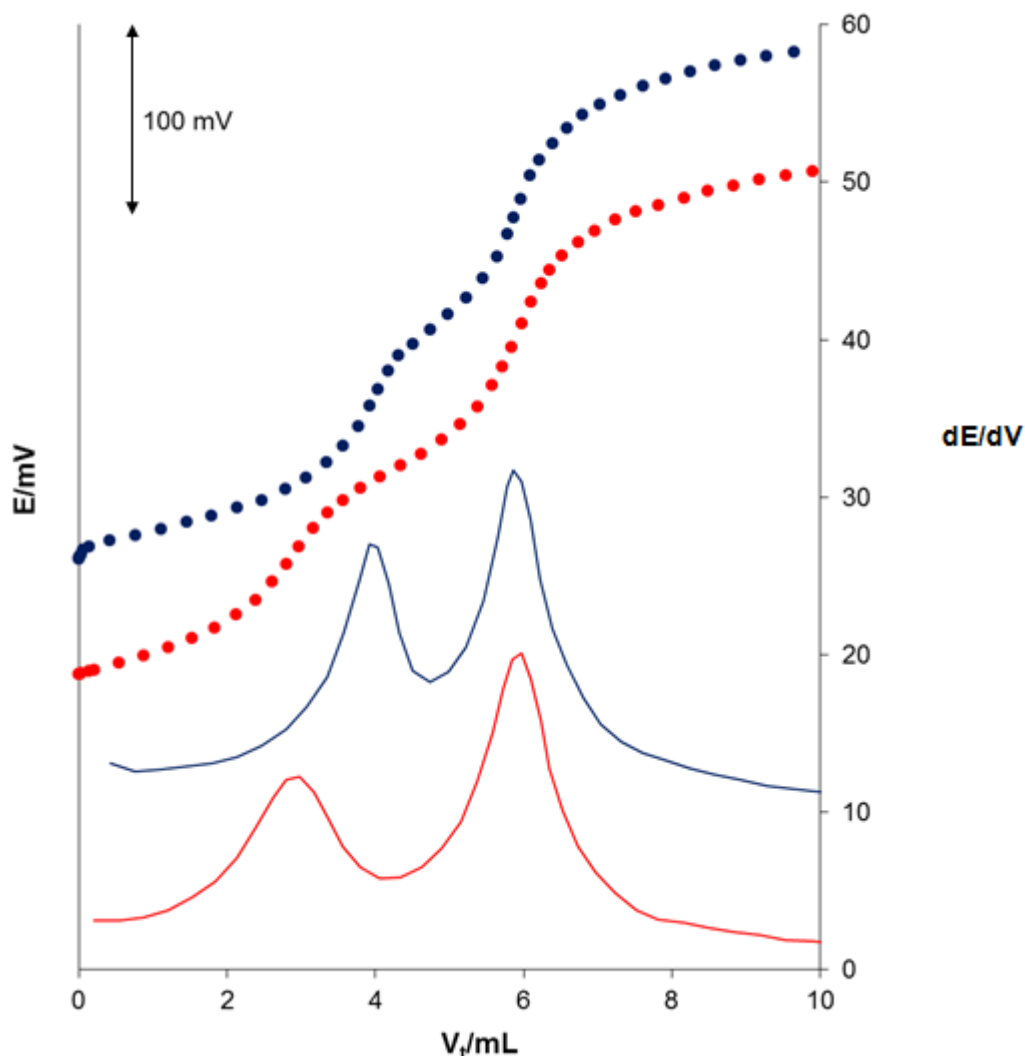*3.3.2. Titration of technical grade anionic surfactants*

Figure 7. Potentiometric titration curves and their first derivatives of technical grade ASs using the DDA-TPB sensor as the end-point indicator and CPC (c = $4 \cdot 10^{-3}$ M) as the titrant (● NaDBS, ● NaDDS, — NaDBS, — NaDDS).

The two most frequently used technical grade ASs (NaDDS and NaDBS) were potentiometrically titrated with the new DDA-TPB sensor as the end-point indicator. A standard solution of CPC was used as the titrant. Figure 7 shows the resulting titration curves and their first derivatives. It can be observed that the inflection points in the titration curves for both of the ASs investigated were well defined and sharp, with excellent potential jumps at the equivalence point.

The results of the determinations were compared with those obtained using the standard two-phase titration method and are shown in Table 4.

### 3.3.3. Titration of two-component mixtures

Figure 8. Potentiometric titration curves and their first derivatives of the same two-component mixtures of alkan sulfonates in different molar ratios using the DDA-TPB sensor as the end-point indicator and CPC ($c = 1 \cdot 10^{-3}$ M) as the titrant (● $C_{10}:C_{12}=1:2$, ● $C_{10}:C_{12}=1:1$, — $C_{10}:C_{12}=1:2$, — $C_{10}:C_{12}=1:1$).

The DDA-TPB sensor was tested for the differential titration of two-component mixtures of alkan sulfonates. Two mixtures of the same sulfonates ($C_{10} + C_{12}$) in different molar ratios ($C_{10}:C_{12} =$

1:1 and 1:2) were used. Figure 8 presents the corresponding titration curves and their first derivatives. It can be observed that the difference in the two C-atoms between the sulfonates is sufficient to exhibit two well-defined inflection points. The first inflection is related to the sulfonate that forms a slightly soluble ion pair with the cationic titrant. Generally, this sulfonate is the one with a greater number of C-atoms (longer hydrocarbon chain).

3.3.4. Titration of commercial products

Three commercial detergents, powdered detergent, gel detergent and liquid hand-dishwashing detergent, with different ASs contents were used to test the sensor applicability for ASs determination in real systems. CPC ($c = 4 \cdot 10^{-3}$ M) was used as the titrant and the DDA-TPB sensor was used as the end-point indicator. The pH value was adjusted to 3 in all of the measurements. Known amounts of NaDDS ($c = 4 \cdot 10^{-3}$ M) were added to the detergent solutions to investigate the influence of the ingredients from the formulated products on the determination of ASs. The corresponding titration curves and the results are shown in Figure 9 and Table 3, respectively. It can be observed that the potentiometric titration curves for the three detergents revealed a good inflection point with good magnitudes of potential jumps.
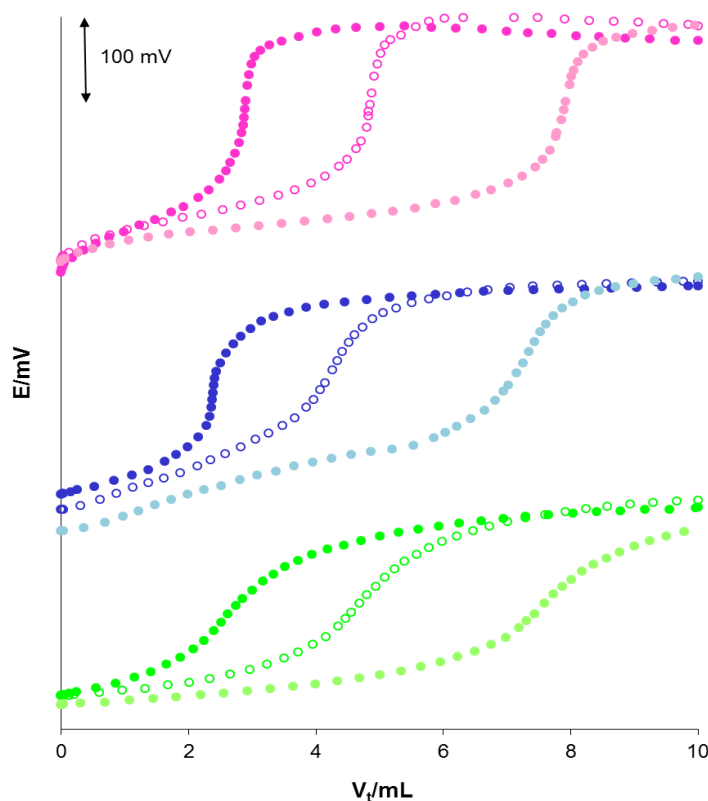
Figure 9. Titration curves of three commercial detergents with the addition of known concentrations of NaDDS (● powdered detergent, ○ powdered detergent + 2 mL NaDDS, ● powdered detergent + 5 mL NaDDS, ● gel detergent, ○ gel detergent + 2 mL NaDDS, ● gel detergent + 5 mL NaDDS, ● liquid hand-dishwashing detergent, ○ liquid hand-dishwashing detergent + 2 mL NaDDS, ● liquid hand-dishwashing detergent + 5 mL NaDDS).

Table 3. The results of the potentiometric titrations of the commercial detergents with the addition of known concentrations of NaDDS using the DDA-TPB based surfactant sensor as the indicator and CPC (c = $4 \cdot 10^{-3}$ M) as the titrant.

		Detergent type					
		Gel detergent		Powdered detergent		Liquid hand-dishwashing detergent	
	AS found (M)	$6.72 \cdot 10^{-4}$		$9.08 \cdot 10^{-4}$		$2.31 \cdot 10^{-3}$	
NaDDS	Added (mol)	$8 \cdot 10^{-6}$	$2 \cdot 10^{-5}$	$8 \cdot 10^{-6}$	$2 \cdot 10^{-5}$	$8 \cdot 10^{-6}$	$2 \cdot 10^{-5}$
	Found (mol)	$8.34 \cdot 10^{-6}$	$2.00 \cdot 10^{-5}$	$8.34 \cdot 10^{-6}$	$2.04 \cdot 10^{-5}$	$8.08 \cdot 10^{-6}$	$2.01 \cdot 10^{-5}$
	Recovery (%)	104.3	100.0	104.3	102.0	101.0	100.5

The results were compared with those obtained using the standard two-phase titration method, and no significant differences were found, as shown in Table 4.

Table 4. The results of the potentiometric titration of technical grade ASs and commercial products compared with those obtained using the two-phase titration method.

	% AS (found)	
Sample	DDA-TPB sensor	Two-phase titration
NaDDS, technical grade	87.27	87.82
NaDBS, technical grade	42.11	41.89
gel detergent	2.31	2.41
powdered detergent	6.25	6.27
liquid hand-dishwashing detergent	15.92	15.82

4. CONCLUSIONS

A new, simple, sensitive, accurate and inexpensive ASs sensitive sensor was prepared by incorporating DDA-TPB as the sensing ion-exchange complex in a PVC-membrane. The useful concentration range of the sensor was between $3 \cdot 10^{-7}$ and $8 \cdot 10^{-3}$ M for NaDDS and between $4 \cdot 10^{-7}$ and $2 \cdot 10^{-3}$ M for NaDBS. In these concentration ranges, the sensor exhibited a Nernstian response for both ASs (59.0 mV/decade for NaDDS and 59.1 mV/decade for NaDBS). The detection limit of the new sensor was $2 \cdot 10^{-7}$ M. The sensor responded within a few seconds for each NaDDS and NaDBS concentration change over a range of $1 \cdot 10^{-7}$ M to $1 \cdot 10^{-3}$ M.

The influence of the ionic strength and pH values over the range of 2 to 12 on the sensor response was negligible. Commonly used concentrations of nonionic surfactants in commercial products did not affect the shape of the titration curves or the accuracy of the ASs determination. The selectivity coefficients for the new surfactant sensor were determined by fitting the Nikolskii-Eisenman equation to the experimental data obtained by the fixed interference method. None of the anions investigated that are commonly used in commercial products based on ASs interfered with the DDA-TPB electrode response for NaDDS.

The primary application of the new sensor was as an indicator of the end-point in the potentiometric titration of commercial products based on ASs. The performance of the sensor was shown through the potentiometric titration of NaDDS and NaDBS of analytical and technical grades, which were successfully titrated. In addition, the sensor was successfully used for the differential titration of a two-component mixture of ASs that differed in only two C-atoms. As the primary goal of this study, three commercial detergents with different ASs contents were successfully titrated. The results were evaluated using the known addition method and compared with those obtained by the two-phase titration method, which showed a satisfactory agreement. All of the investigations resulted in potentiometric titrations curves with good inflections and good magnitudes of potential jumps, enabling reliable equivalence point detection using the first derivative method.

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