The Analysis of Anionic Surfactants in Effluents Using a DDA-TPB Potentiometric Sensor

Mirela Samardžić[*], Olivera Galović, Sanja Petrušić, Milan Sak-Bosnar

Department of Chemistry, Josip Juraj Strossmayer University of Osijek, Cara Hadrijana 8/A, HR-31000 Osijek, Croatia
[*]E-mail: mirelas@kemija.unios.hr

A new, simple, sensitive, accurate and inexpensive potentiometric sensor for the determination of anionic surfactants (AS) based on the dimethyldioctadecylammonium-tetraphenylborate (DDA-TPB) ion pair as a sensing material was used for end-point detection during the potentiometric titrations of low levels of AS in industrial effluents. Solutions of cetylpyridinium chloride (CPC) at concentrations as low as $5 \cdot 10^{-5}$ M were successfully used as a titrant. The accuracy and precision of the measurements were determined using the standard addition method, and satisfactory results were obtained, with recoveries between 98.3 to 102.0 % in pure AS solutions and 99.0 to 114.5 % in effluents. The AS concentration in effluents ranged between 2.64 and 176.7 mg/L. The results were compared with a standard spectrophotometric Methylene Blue Active Substances (MBAS) method, and they indicated a satisfactory correlation. The influence of the different pH values (2-10) and ionic strengths (0.003-0.301) on the shape of the potentiometric titration curves and the response characteristics of the sensor were examined.

1. INTRODUCTION

Surfactants are chemical compounds with the ability to decrease the surface tension of a solvent. They are widely used in many industries due to their inherent properties. The rate of surfactant production and consumption has been increasing in recent years. In 2012, the surfactant market was estimated to be 27.0 billion US dollars, and it is expected to grow to 36.5 billion by 2017 with a compound annual growth rate of 6.19 % from 2012 to 2017 [1]. The largest consumer of surfactants is Europe. There are four types of surfactants: anionic, cationic, nonionic and amphoteric surfactants. Considering surfactant consumption by product type, anionic surfactants (AS) are the largest group of

surfactants and represent approximately 70 % of the total surfactant market. Considering surfactant consumption by application, soap and detergents represented the largest market for surfactant consumption in 2012 [1].

Due to their widespread use, AS are present in industrial effluents from where they can easily enter the environment, especially rivers and lakes, where they can cause environmental problems. This is one of the main reasons why it is important to accurately determine their concentrations in industrial effluents.

To protect the environment, the European Union makes continuous efforts to control the use and monitoring of surfactants. The allowable AS concentrations in industrial effluents have been significantly reduced [2]. Thus, the methodology that is used to determine AS concentrations must have a very low limit of detection.

The standard method for AS determination in industrial effluents and generally in products with a lower surfactant concentration is the Methylene Blue Active Substances (MBAS) method [3]. The method is tedious, time consuming, subjective and cannot be automated. It has many interferences and it uses large amounts of highly toxic and carcinogenic organic solvents. Considering the efforts that are being made to protect our health and the environment, the use of these types of solvents is unacceptable.

Ion-selective electrodes (ISEs) that are selective for AS and are used as sensors in direct potentiometry and potentiometric titrations represent a promising alternative to the MBAS method [4-7]. Compared to other analytical methods, they are simple, rapid, robust, durable, inexpensive, easily automated, not affected by turbidity or sample color and are environmentally friendly. 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] are some of the types of ISEs that are selective for AS. PVC electrodes are commonly used. Typically, they have a sensing material based on an ion-pair, which is usually composed of a large organic or inorganic cation (most often the cation of a cationic surfactant) and a large organic or inorganic anion (most often the anion of an AS).

Compounds of the electrode can be varied to construct an ISE with better properties, such as better selectivity and reproducibility, a wider linear response range, and a longer lifetime [14-19]. Several highly sensitive ISEs for the determination of AS in industrial effluents and wastewater have been reported [6, 20, 21]

ISEs combined with a flow injection analysis (FIA) system [22, 23], reverse FIA [24], ion-sensitive field-effect transistor (ISFET) sensors [25], chromatography [26, 27] and biosensors [28] are just some of many other methods for AS determination.

In this paper, we describe a new sensor for AS based on dimethyldioctadecylammonium-tetraphenylborate (DDA-TPB) as the sensing element and *o*-nitrophenyl octyl ether (*o*-NPOE) as the plasticizer. The application of this new highly sensitive sensor for the routine analysis of industrial effluents and wastewaters is suggested.

2. EXPERIMENTAL

2.1. Reagents and Materials

NaDDS and NaDBS (both from Fluka, Switzerland) were used for the investigation of the sensor response characteristics and for potentiometric titrations. Cetylpyridinium chloride (CPC), purchased from Merck, Germany, was used as cationic titrant. Hydrochloric acid (Carlo Erba Reagent, Italy) was used to adjust the pH in the industrial effluent samples. Buffers at pH values of 2, 3, 5, 8 and 10 were used to study the influence of different pH values on the shape of the potentiometric titration curves. Sodium sulfate (Kemika, Croatia) was used to study the influence of ionic strength on the response of the sensor and on the titrations of NaDDS and NaDBS.

Five industrial effluent samples with different AS concentrations were used to test the applicability of the sensor for AS determination in real systems with low AS concentrations.

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) combined with a Metrohm 806 Exchange unit controlled by Tiamo software 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.

A Metrohm 780 pH meter, a 728 Stirrer, a Metrohm 794 Basic Titrino and in-house software were used for the response measurements.

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

All parts of the apparatus except the in-house software were purchased from Metrohm, Switzerland.

2.3. Sensor

The sensor contained a DDA-TPB ion-exchange complex used for the preparation of the PVC-based membrane plasticized with *o*-NPOE. A detailed explanation of the preparation of the DDA-TPB complex and the complete sensor has been provided previously [29].

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

The new sensor with DDA-TPB as the sensing material and the external reference electrode were used for all of the potentiometric measurements, and CPC was used as a titrant in all of the potentiometric titrations.

Solutions of CPC at four concentrations: $4\cdot10^{-3}$ M, $1\cdot10^{-3}$ M, $1\cdot10^{-4}$ M and $5\cdot10^{-5}$ M, were used as the titrant, while NaDDS and NaDBS were used as analytes during the potentiometric titrations. The volume of the solution used for all of the titrations was 25 mL.

AS concentrations were determined in five different samples of industrial effluents. If necessary, the samples were diluted before the measurements were conducted. There was no ionic strength adjustment, and the pH was adjusted to 3 in all the measurements.

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 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 the measurements and titrations were performed at room temperature using a magnetic stirrer and without ionic strength adjustment or pH adjustment (except for the industrial effluent titrations, in which the pH was adjusted to 3).

The MBAS method [3], as an official method, was used as a reference.

The influence of pH on the potentiometric titrations was examined over a pH range of 2 to 10 in solutions of NaDDS and NaDBS at a concentration of $4\cdot10^{-3}$ M. The pH values were adjusted with buffers at pH values of 2, 3, 5, 8 and 10.

The influence of the ionic strength on the sensor response characteristics was examined by adding AS in a sodium sulfate solution at the following three concentrations: 0.001 M, 0.01 M and 0.1 M (the ionic strengths were between 0.003 and 0.301). The influence of the ionic strength on potentiometric titration was examined using NaDDS (c = $4\cdot10^{-3}$ M) as the analyte and CPC (c = $4\cdot10^{-3}$ M) as the titrant. Sodium sulfate at concentrations of 0.1 M, 0.01 M and 0.001 M was added to the analyte solution.

3. RESULTS AND DISCUSSION

The electromotive force of the DDA-TPB sensor dipped into a solution of AS is described by the Nernst equation:

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

where E^0 = constant potential term, S = sensor slope and a_{AS^-} = activity of the surfactant anion [30].

The main application of the new sensor described here was the indication of the end-point in AS potentiometric titrations in which a cationic surfactant (CS) was used as a titrant. Before the equivalence point, the sensor responds to the AS concentration, and after the equivalence point, the sensor responds to the CS concentration [21].

The response characteristics of the DDA-TPB surfactant sensor in solutions of NaDDS and NaDBS and the influence of interferences on the response characteristics and potentiometric titration curves have been described previously [29].

3.1. Selection of the titrant concentration

CPC has been shown to be the best titrant for NaDDS and NaDBS titration using the DDA-TPB sensor to indicate the end-point [29].
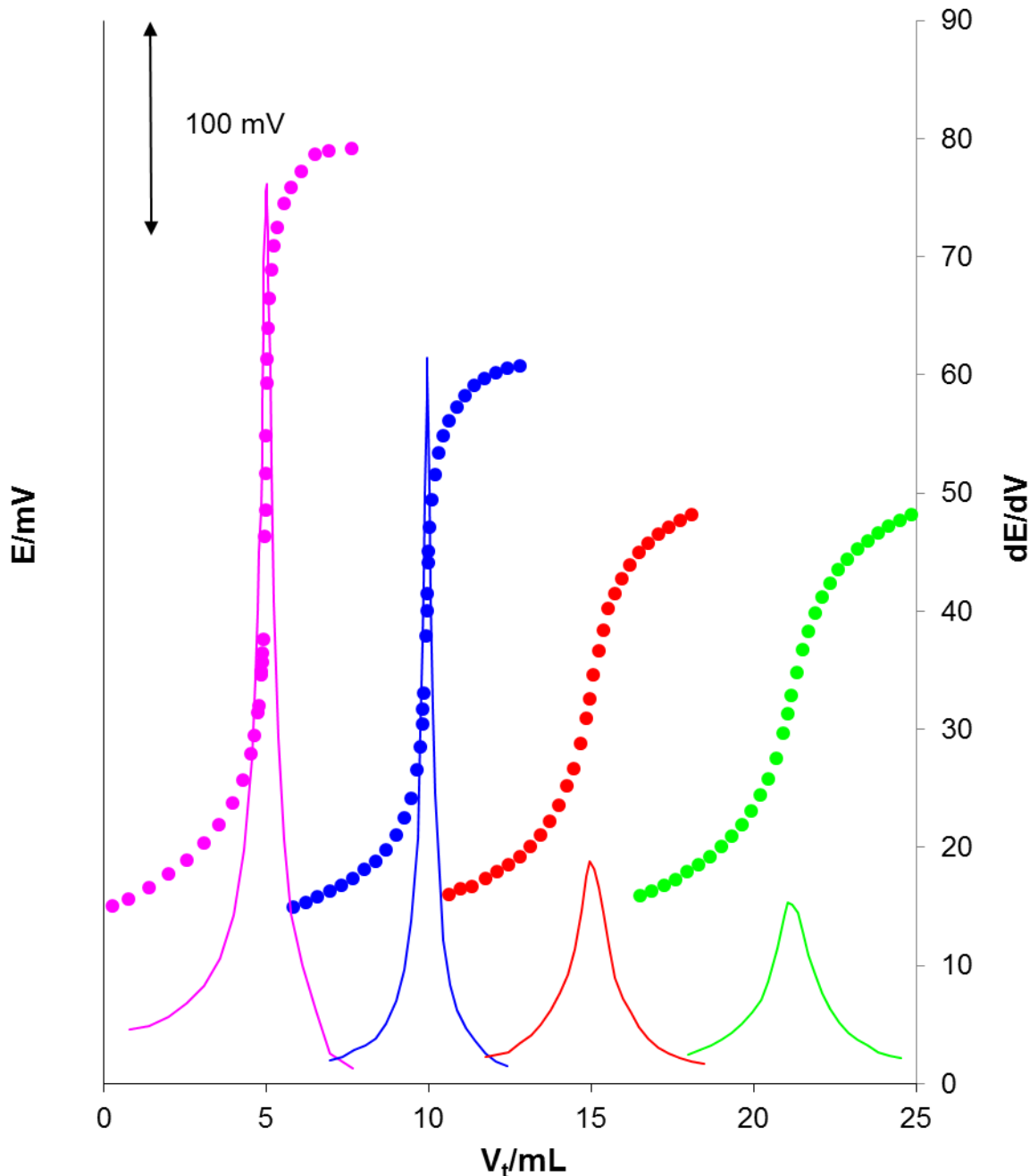

Figure 1. Potentiometric titration curves of NaDDS and their corresponding first derivatives using the DDA-TPB surfactant sensor as the indicator and CPC as the titrant (at four different concentration levels: ● $4 \cdot 10^{-3}$ M, ● $1 \cdot 10^{-3}$ M, ● $1 \cdot 10^{-4}$ M, ● $5 \cdot 10^{-5}$ M, — $4 \cdot 10^{-3}$ M, — $1 \cdot 10^{-3}$ M, — $1 \cdot 10^{-4}$ M, — $5 \cdot 10^{-5}$ M).
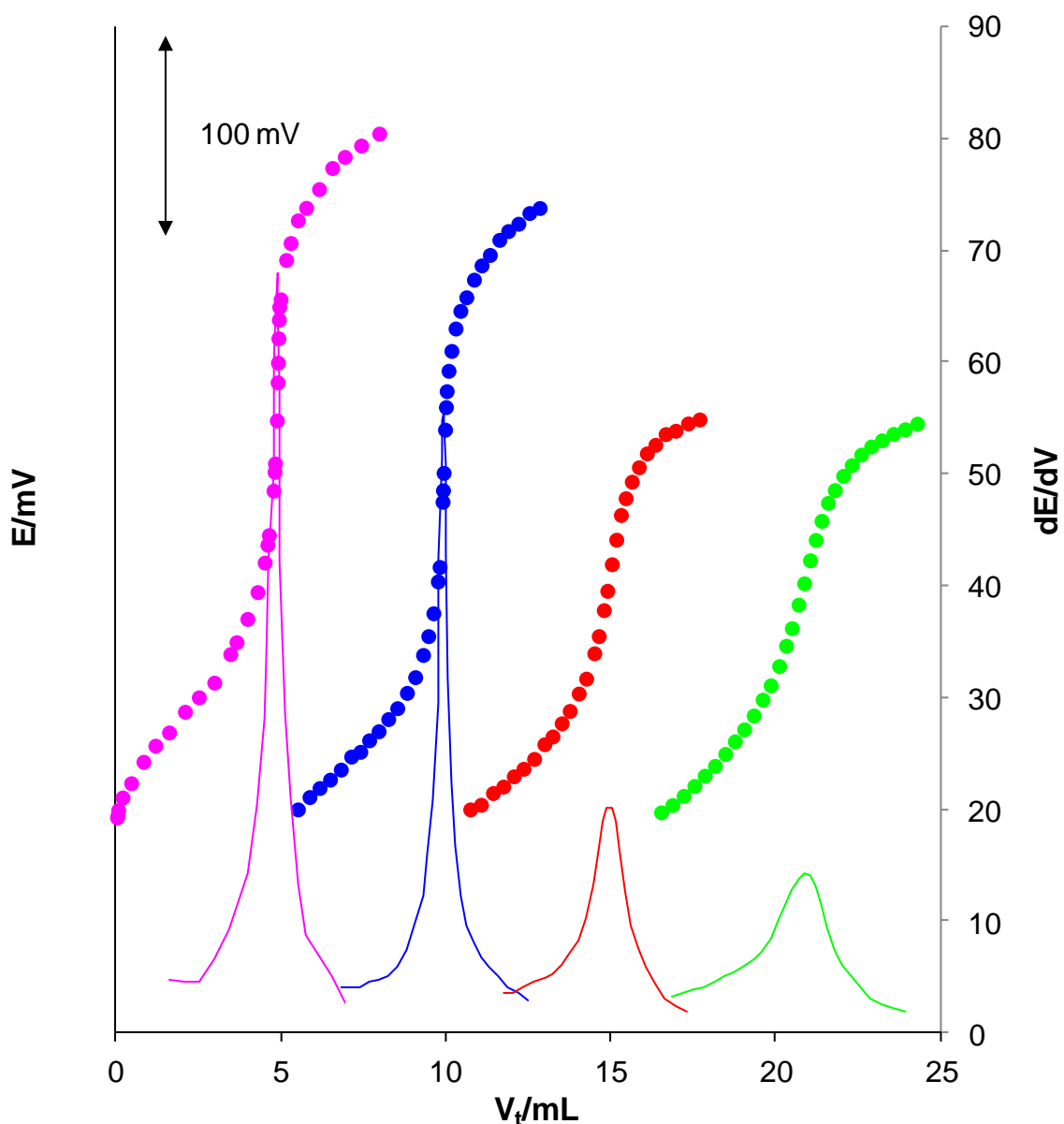
Figure 2. Potentiometric titration curves of NaDBS and their corresponding first derivatives using the DDA-TPB surfactant sensor as the indicator and CPC as the titrant (at four different concentration levels: ● $4 \cdot 10^{-3}$ M, ● $1 \cdot 10^{-3}$ M, ● $1 \cdot 10^{-4}$ M, ● $5 \cdot 10^{-5}$ M, — $4 \cdot 10^{-3}$ M, — $1 \cdot 10^{-3}$ M, — $1 \cdot 10^{-4}$ M, — $5 \cdot 10^{-5}$ M).

Solutions of CPC at four concentration levels: $4 \cdot 10^{-3}$ M, $1 \cdot 10^{-3}$ M, $1 \cdot 10^{-4}$ M and $5 \cdot 10^{-5}$ M were investigated as titrants in potentiometric titrations of NaDDS and NaDBS for the purpose of determining the lowest titrant concentration that can be used to determine the lowest AS concentration. This step was necessary because the AS concentration in effluents and waste waters is usually very low. The results are given in Figures 1 and 2. It should be emphasized that the detection limit for NaDDS and NaDBS was $2 \cdot 10^{-7}$ M (0.06 and 0.07 mg/L, respectively).

All titration curves, even those in which CPC was used at a concentration of $5 \cdot 10^{-5}$ M, exhibited well-defined and sharp inflection points. The potential inflection point jumps for NaDDS

titrations were between 250 mV at $4 \cdot 10^{-3}$ M and 100 mV at $5 \cdot 10^{-5}$ M (Figure 1), whereas those for NaDBS titrations were between 220 mV at $4 \cdot 10^{-3}$ M and 120 mV at $5 \cdot 10^{-5}$ M (Figure 2). The equivalence point volumes were calculated from the derivative curves. The results of these determinations are shown in Table 1. It can be seen that the accuracy of the determinations was satisfactory, even at the lowest titrant concentration.

Table 1. Results of the potentiometric titrations of NaDDS and NaDBS using the DDA-TPB based surfactant sensor as the indicator and CPC as the titrant.

Surfactant investigated	c(CPC)/M	c(taken)/M	c^*(found)/M	Recovery/%
NaDDS	$4 \cdot 10^{-3}$	$8.00 \cdot 10^{-4}$	$7.99 \cdot 10^{-4}$	99.9
	$1 \cdot 10^{-3}$	$2.00 \cdot 10^{-4}$	$1.97 \cdot 10^{-4}$	98.5
	$1 \cdot 10^{-4}$	$2.00 \cdot 10^{-5}$	$1.99 \cdot 10^{-5}$	99.5
	$5 \cdot 10^{-5}$	$1.00 \cdot 10^{-5}$	$1.02 \cdot 10^{-5}$	102.0
NaDBS	$4 \cdot 10^{-3}$	$8.00 \cdot 10^{-4}$	$7.88 \cdot 10^{-4}$	98.5
	$1 \cdot 10^{-3}$	$2.00 \cdot 10^{-4}$	$1.97 \cdot 10^{-4}$	98.5
	$1 \cdot 10^{-4}$	$2.00 \cdot 10^{-5}$	$2.00 \cdot 10^{-5}$	100.0
	$5 \cdot 10^{-5}$	$1.00 \cdot 10^{-5}$	$9.83 \cdot 10^{-6}$	98.3

* Average of 5 determinations.

3.2. The influence of pH on the shape of potentiometric titration curves

The influence of pH on the shape of potentiometric titration curves was examined using NaDDS and NaDBS as analytes and CPC as the titrant. The concentration of all solutions used was $4 \cdot 10^{-3}$ M. The pH values were adjusted using buffers (pH=2, 3, 5, 8 and 10). The different pH values simulated real conditions in different effluent samples. Figures 3 and 4 show the resulting titration curves and their first derivatives for NaDDS and NaDBS. It can be observed that the potentiometric titration curves at all pH values revealed a well-defined inflection point with a significant magnitude of increased potential, which enabled reliable end-point detection at all the investigated pH values. The slightly lower potential jump at the inflexion at pH=5 could be assigned to citrate containing buffer pH=5. It is well known that the magnitude of inflexion at the equivalence point is strongly dependent upon the solubility product value of the ion-pair formed [21]. Citrate probably causes slightly higher solubility of the formed ion-pair and consequently its higher solubility product value, resulting with lower potential jump at the equivalence point, but it doesn't influence the end-point location from the titration curve and its first derivative.
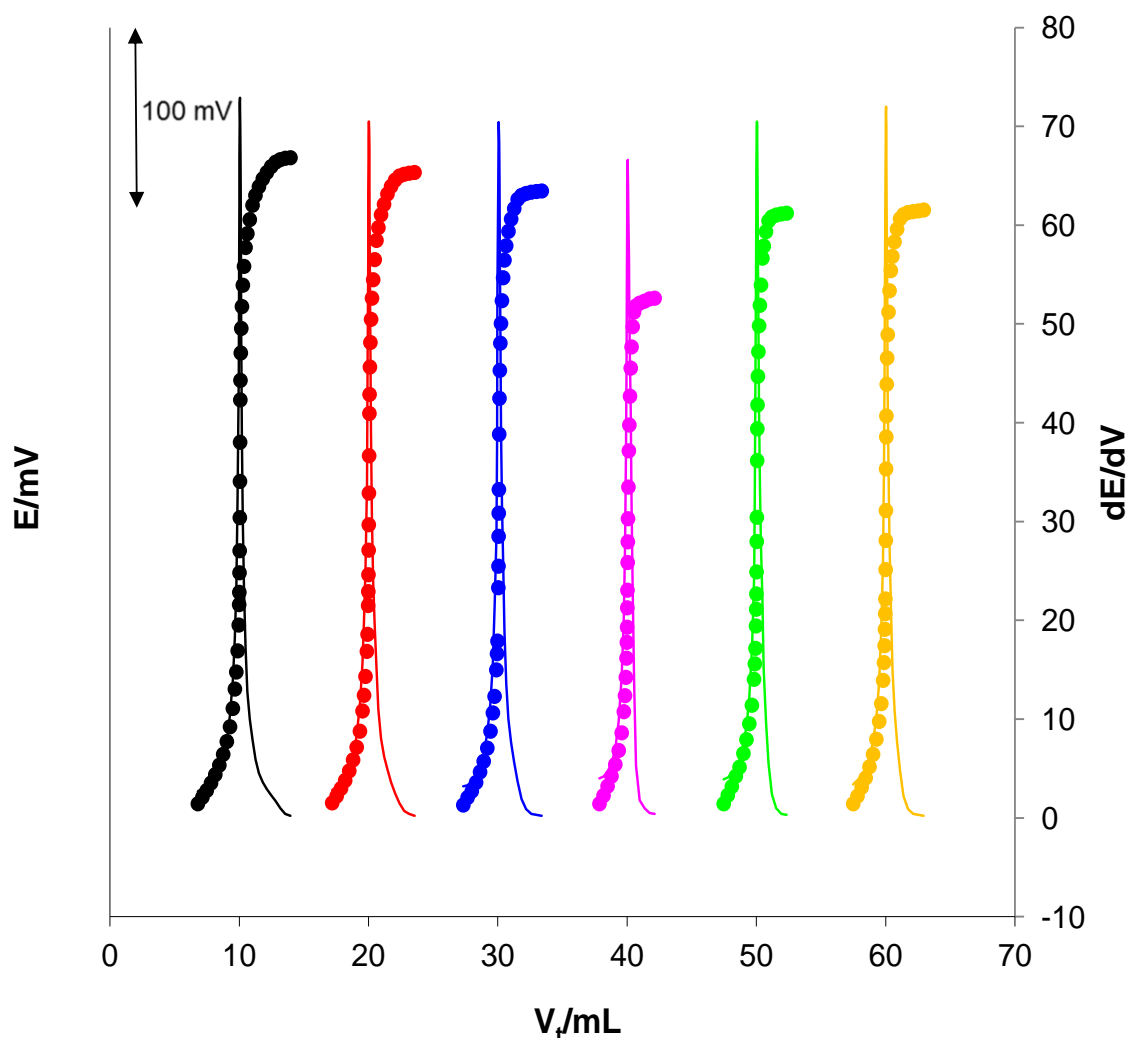
Figure 3. The influence of pH value on the shape of the potentiometric titration curves of NaDDS (c = 4·10^{-3} M) and their corresponding first derivatives using the DDA-TPB surfactant sensor as the indicator and CPC (c = 4·10^{-3} M) as the titrant (● no pH adjustment, ● pH=10, ● pH=8, ● pH=5, ● pH=3, ● pH=2, — no pH adjustment, — pH=10, — pH=8, — pH=5, — pH=3, — pH=2).

3.3. The influence of ionic strength on the response characteristics of the sensor and shape of potentiometric titration curves

High concentrations of inorganic salts (e.g., sulfates, carbonates, phosphates, and chlorides) are commonly found in real effluent samples for the potentiometric determination of AS. Because their concentrations are usually considerably higher than the AS concentration, it was necessary to investigate the influence of ionic strength on the sensor response and the shape of the potentiometric titration curves. For those investigations, solutions of Na_2SO_4 at concentrations of 0.001 M, 0.01 M and 0.1 M were used, which spanned a range of ionic strengths (between 0.003 and 0.301).

The influence of ionic strength on response characteristics was investigated for NaDDS and NaDBS and is displayed in Figures 5 and 6. The point of the change in the linear portion of the calibration graphs at the higher concentration region corresponds to the critical micellar concentration (CMC). In both figures, it can be seen that CMC decreases with increasing salt concentrations and ionic strength, which is caused by increased micellar size.
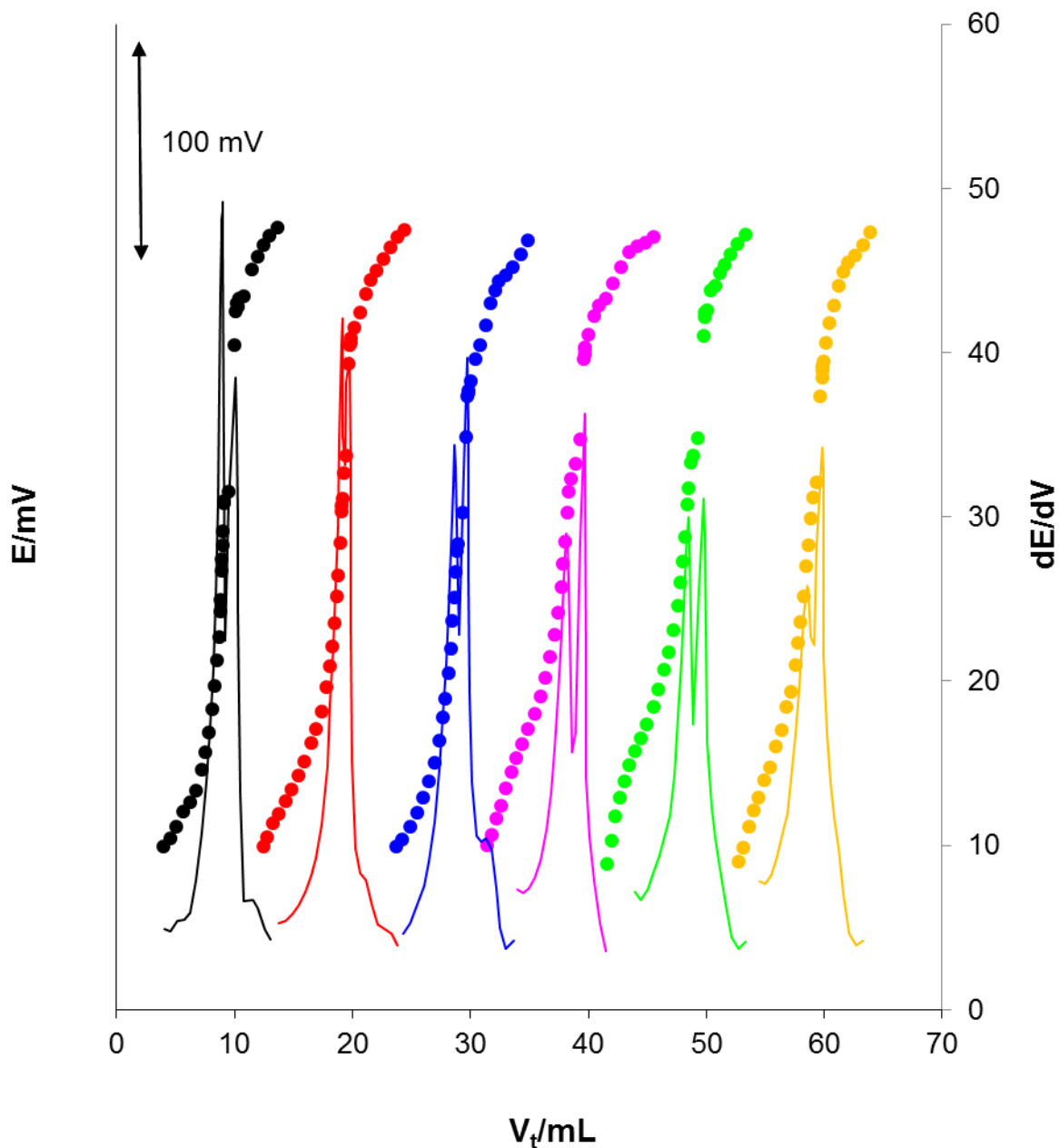

Figure 4. The influence of pH value on the shape of the potentiometric titration curves of NaDBS (c = $4 \cdot 10^{-3}$ M) and their corresponding first derivatives using the DDA-TPB surfactant sensor as the indicator and CPC (c = $4 \cdot 10^{-3}$ M) as the titrant (● no pH adjustment, ● pH=10, ● pH=8, ● pH=5, ● pH=3, ● pH=2, — no pH adjustment, — pH=10, — pH=8, — pH=5, — pH=3, — pH=2).
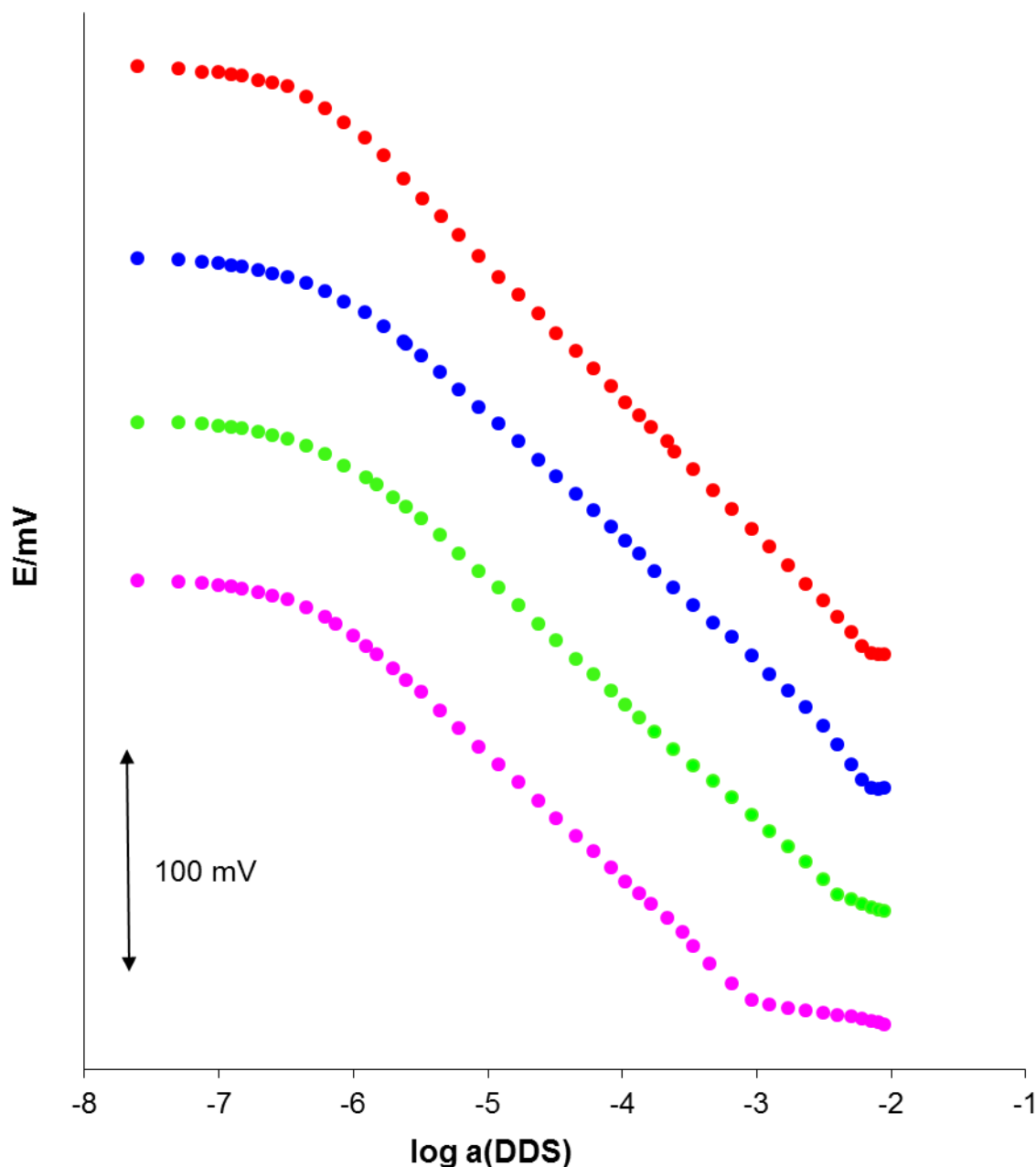
Figure 5. The influence of different ionic strength on the response characteristics of the DDA-TPB sensor toward NaDDS (● in H_2O, ● in Na_2SO_4 0.001 M, ● in Na_2SO_4 0.01 M, ● in Na_2SO_4 0.1 M).

The influence of ionic strength on the shape of the potentiometric titration curves was investigated using NaDDS (c = $4 \cdot 10^{-3}$ M) as the analyte and CPC (c = $4 \cdot 10^{-3}$ M) as the titrant. The resulting curves are shown in Figure 7. It can be observed that Na_2SO_4 did not influence the shape of the potentiometric titration curves and titrant volumes, even in solutions of 0.1 M Na_2SO_4 where the salt concentration was approximately 100-fold higher than the NaDDS concentration.
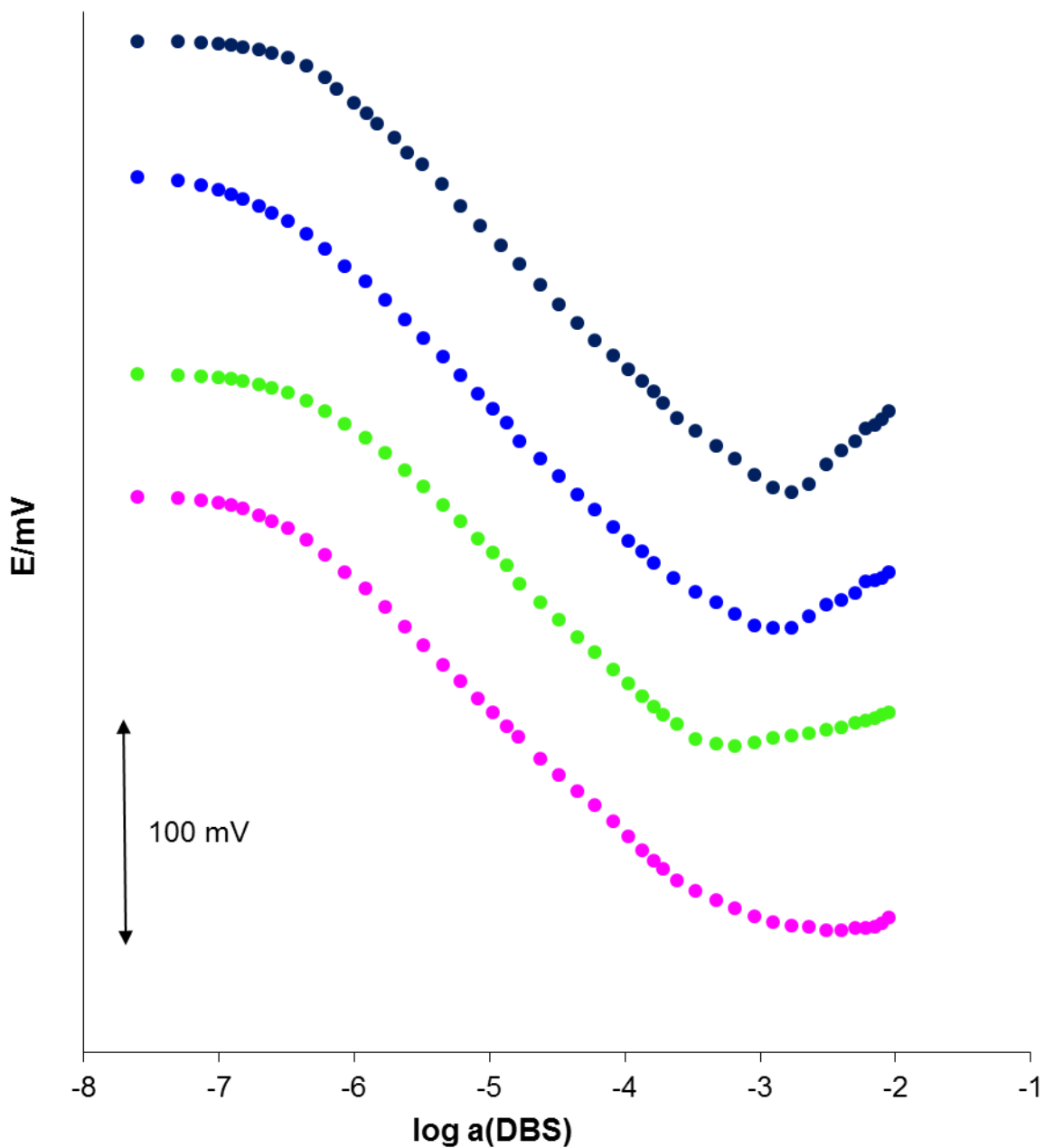
Figure 6. The influence of different ionic strength on the response characteristics of the DDA-TPB sensor toward NaDBS (● in H_2O, ● in Na_2SO_4 0.001 M, ● in Na_2SO_4 0.01 M, ● in Na_2SO_4 0.1 M).

3.5. Titration of industrial effluents

Five samples of industrial effluents with different AS concentrations were used for these investigations. The samples were collected in different places and at different times. If necessary, the samples were diluted before the measurements were conducted. There was no ionic strength adjustment, and the pH value was adjusted to 3 in all the measurements. To determine the influence of

the sample components on the determination of AS, known amounts of NaDDS were added to the investigated solutions.
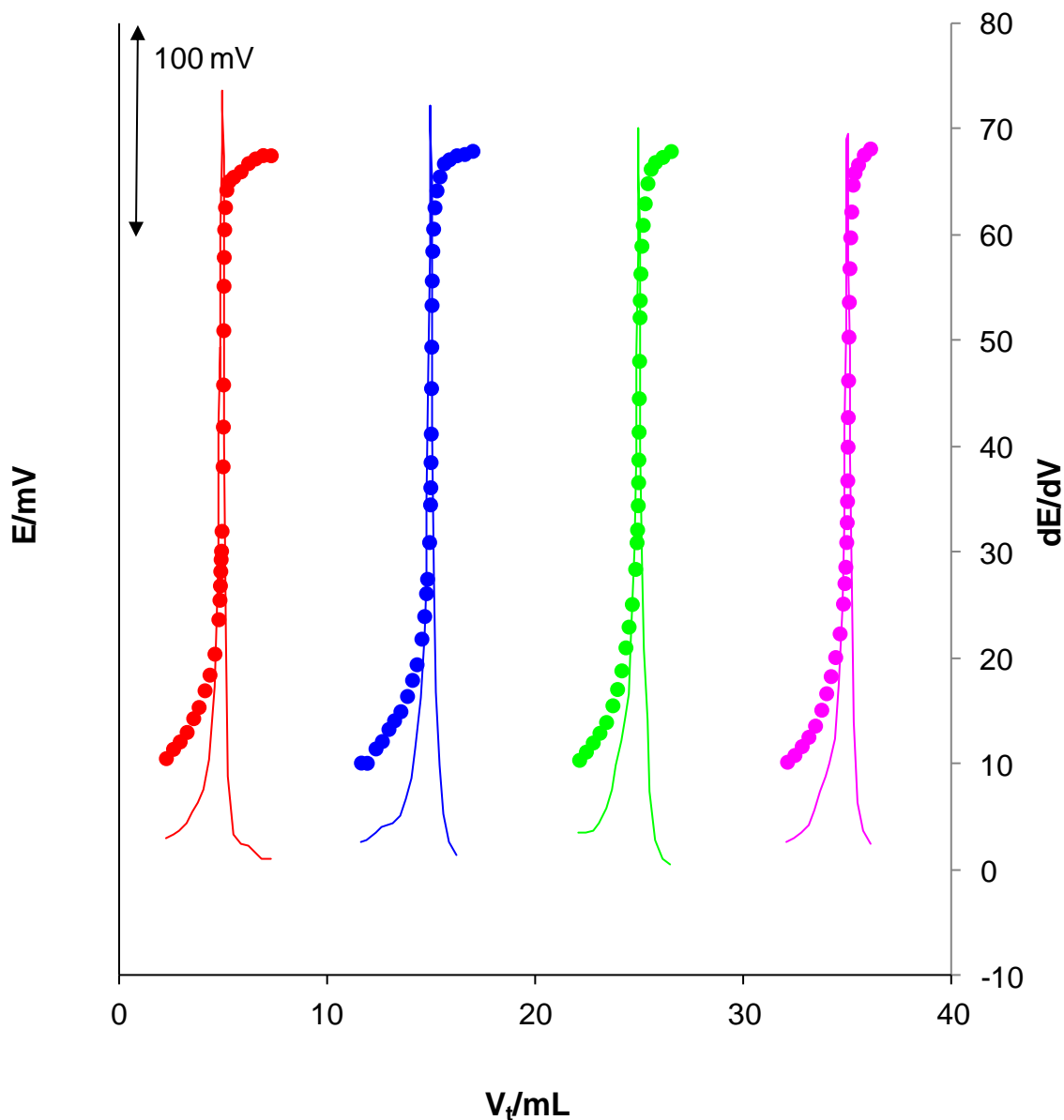

Figure 7. The influence of different ionic strengths on the shape of the potentiometric titration curves of NaDDS ($c = 4 \cdot 10^{-3}$ M) and their corresponding first derivatives using the DDA-TPB surfactant sensor as the indicator and CPC ($c = 4 \cdot 10^{-3}$ M) as the titrant (● no ionic strength adjustment, ● in Na_2SO_4 0.001 M, ● in Na_2SO_4 0.01 M, ● in Na_2SO_4 0.1 M).

The corresponding titration curves are shown in Figure 8, and the results are presented in Table 2. It can be seen that the potentiometric titration curves for all of the effluent samples revealed a robust inflection point with satisfactory magnitudes of increases in potential.
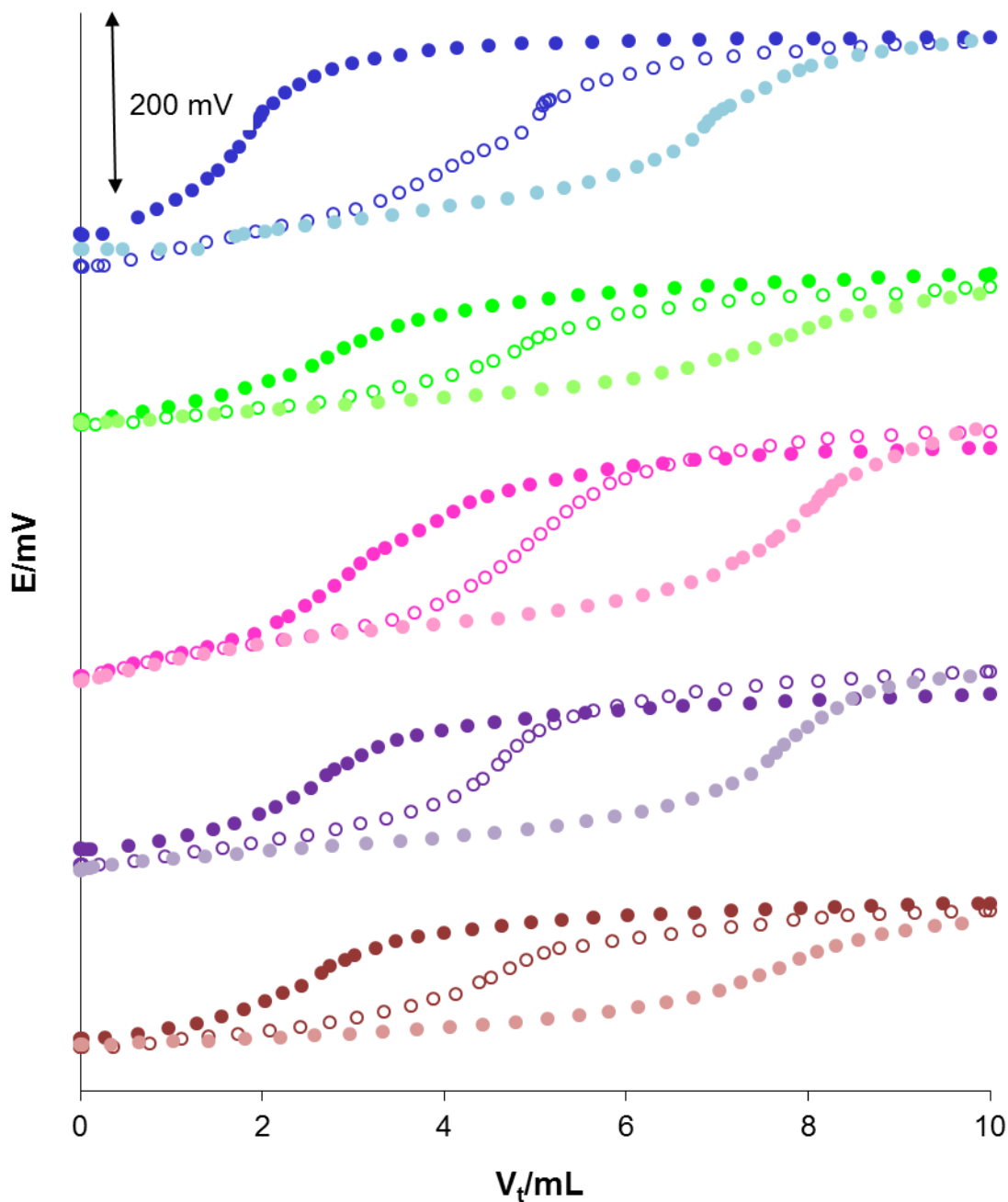
Figure 8. Titration curves of five industrial effluents samples with known addition of NaDDS (c = $1 \cdot 10^{-3}$ M) (● sample 1, ○ sample 1 + 2 mL NaDDS, ● sample 1 + 5 mL NaDDS, ● sample 2, ○ sample 2 + 2 mL NaDDS, ● sample 2 + 5 mL NaDDS, ● sample 3, ○ sample 3 + 2 mL NaDDS, ● sample 3 + 5 mL NaDDS, ● sample 4, ○ sample 4 + 2 mL NaDDS, ● sample 4 + 5 mL NaDDS, ● sample 5, ○ sample 5 + 2 mL NaDDS, ● sample 5 + 5 mL NaDDS).

The discrepancy of the results for the effluents with lower levels of AS concentration is expectedly higher, but still analytically valid.

The obtained results were compared with those obtained by an official spectrophotometric MBAS method [3] (Table 3), and they exhibited a satisfactory positive correlation. The results are expressed as NaDBS concentration, which is conventionally used as a standard AS for the MBAS method [20].

Table 2. Results of the potentiometric titrations of the industrial effluents with the addition of known concentrations of NaDDS using the DDA-TPB based surfactant sensor as the indicator and CPC as the titrant.

Effluent sample	Calculated AS (M)[*]	NaDDS		
		Added (mol)	Found[*] (mol)	Recovery (%)
	$5.30 \cdot 10^{-4}$	$8 \cdot 10^{-6}$	$8.16 \cdot 10^{-6}$	102.0
		$2 \cdot 10^{-5}$	$1.98 \cdot 10^{-5}$	99.0
	$9.49 \cdot 10^{-6}$	$2 \cdot 10^{-7}$	$2.26 \cdot 10^{-7}$	113.0
		$5 \cdot 10^{-7}$	$5.27 \cdot 10^{-7}$	105.4
	$5.70 \cdot 10^{-4}$	$8 \cdot 10^{-6}$	$7.94 \cdot 10^{-6}$	99.3
		$2 \cdot 10^{-5}$	$2.00 \cdot 10^{-5}$	100.0
	$9.67 \cdot 10^{-5}$	$2 \cdot 10^{-7}$	$2.29 \cdot 10^{-7}$	114.5
		$5 \cdot 10^{-7}$	$5.11 \cdot 10^{-7}$	102.2
	$5.52 \cdot 10^{-5}$	$2 \cdot 10^{-7}$	$2.08 \cdot 10^{-7}$	104.0
		$5 \cdot 10^{-7}$	$5.14 \cdot 10^{-7}$	102.8

[*]Average of 5 determinations

Table 3. The results of the potentiometric titration of industrial effluents compared with those obtained using the MBAS method.

Effluent sample	AS content (mg/L)	
	DDA-TPB sensor[*]	MBAS method
1	147.4 ± 2.7	139.2
2	2.64 ± 0.02	2.42
3	176.7 ± 3.3	168.2
4	24.4 ± 0.8	23.7
5	15.2 ± 0.3	14.2

[*]Average of 5 determinations

4. CONCLUSIONS

A new, simple, fast, sensitive, accurate and inexpensive AS responsive potentiometric sensor based on an DDA-TPB ion-exchange complex as the sensing element in a PVC-membrane was used as the end-point detector during the potentiometric titrations of low levels of AS. The solutions containing low levels of AS were successfully titrated with CPC as a titrant. The titrations were performed in pure solutions of NaDDS and NaDBS and in five samples of industrial effluents.

Titration curves for NaDDS and NaDBS were usable and showed pronounced inflections and increases in potential, even for a titrant concentration of $5 \cdot 10^{-5}$ M.

Industrial effluents were titrated without pretreatment except for adjusting the pH to 3. All of the measurements resulted in potentiometric titration curves with clearly defined inflections and satisfactory magnitudes of increases in potential, enabling reliable equivalence point detection using

the first derivative method. Accuracy and precision of the measurements were verified by the standard addition method, and satisfactory results were obtained.

The AS content in industrial effluents was also determined by the standard extraction-spectrophotometric MBAS method. The results were compared with those obtained by the DDA-TPB sensor, and they indicated a satisfactory correlation.

The influence of pH values on the shape of the potentiometric titration curves was examined across a pH range from 2 to 10. The analytically valid potentiometric titration curves were obtained at all pH values enabling reliable end-point detection. There was no influence of ionic strength on the response characteristics of the sensor and the shape of the potentiometric titration curves, even in solutions where the salt concentration was approximately 100-fold higher than the AS concentration.

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