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Potentiometric Titration of Micromolar Levels of Anionic Surfactants in Model Effluents Using a Sensitive Potentiometric Sensor

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Anionic surfactants have been potentiometrically determined at the *ppm* level using a sensitive surfactant sensor based on 1,3-didecyl-2-methylimidazolium-tetraphenylborate as a sensing ion-exchanger. Standard solutions of 3-didecyl-2-methylimidazolium chloride and cetylpyridinium chloride at concentrations of 5 x 10^{-5} M were used as cationic titrants. The sensor exhibited Nernstian slope toward dodecylsulfate and dodecylbenzene sulfonate with slope values of 59.4 ± 0.2 and 58.9 ± 0.4 mV/concentration decade, respectively, and detection limits of 2 x 10^{-7} M. The obtained recoveries of anionic surfactants in model effluents varied between 96.4 and 97.0 % with a detection limit of 0.02 mg/L.

Keywords: surfactant sensor, PVC membrane, anionic surfactant, potentiometric titration, model effluent

1. INTRODUCTION

Anionic surfactants (AS) are the largest group of the surfactants and represent 70% of the annual surfactant production. They are widely used in the industrial and domestic fields; therefore, it is very important to determine the amount of AS in product formulations for quality control, in industrial samples for process control, and in food products and the environment for contamination control.

The standard procedure for the determination of AS is based on a two-phase titration [1] but has many drawbacks, such as the use of carcinogenic organic solvents, the difficulty of AS determination in turbid or colored samples, subjectivity, the lack of automatization, and the existence of many sources of interference. Ion selective electrodes (ISE) sensitive to AS represent a great alternative to the standard procedure. They are used in potentiometric titrations with cationic surfactants as titrants or in direct potentiometry. Many scientists have previously developed different types of ISE that are sensitive to AS: coated wire electrodes [2], liquid membrane electrodes [3], and polyvinyl chloride (PVC) electrodes with different sensor materials [4, 5]. Electrodes with liquid ion exchangers dissolved in organic solvents were the first electrodes used for the determination of AS concentrations [6]. Today, most of the ISE have very similar design: a membrane based on a PVC matrix with plasticizer and an ion pair that represent the sensing component of the membrane. Cutler et al. were the first to make an electrode with sensor material composed of cationic and anionic surfactant [7]. Many articles have reviewed different types of surfactant electrodes in which the sensor materials, including different ion pairs and plasticizers, were varied [8-10].

The biggest challenge in AS analysis is the determination of low levels of AS. The methylene blue active substance method (MBAS) is the standard procedure for the determination of low concentrations of AS in effluents [11]. Due to the disadvantages of the MBAS method, such as long analysis times, interference, and the use of large volumes of chloroform, this method can also be replaced with ISE, which are much more environmental friendly, faster, and less complex [12-19].

Biosensors [20], ISFET sensors [21] and ISE incorporated into a flow injection analysis system (FIA) [22, 23] can also be used for the analysis of low levels of AS.

2. EXPERIMENTAL

2.1. Reagents and Materials

The sensor response characteristics were investigated using sodium dodecylsulfate (NaDDS) and sodium dodecylbenzene sulfonate (NaDBS). Both chemicals were purchased from Fluka (Switzerland). Sodium sulfate solution (Kemika, Croatia) was used as the medium. Solutions of 1,3-didecyl-2-methylimidazolium chloride (DMIC, Fluka, Switzerland) and cetylpyridinium chloride (CPC, Merck, Germany) were used as the titrants. Bioaktiv flower detergent (Saponia, Croatia) was used as a model system.

1,3-didecyl-2-methylimidazolium-tetraphenylborate (DMI-TPB), bis(2-ethylhexyl)phthalate (DOP), *o*-nitrophenyloctylether (*o*-NPOE), and high molecular weight poly (vinyl chloride) (PVC) were purchased from Fluka (Switzerland) and 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) and controlled by the Tiamo software was used as the dosing element to perform the potentiometric titrations. During 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 765 Dosimat (all from Metrohm, Switzerland), in-house software, and the DMI-TPB sensors were all used for the response measurements. A silver/silver (I) chloride electrode (Metrohm, Switzerland) was used as a reference.

2.3. Sensor

Two sensors were used and compared to determine the influence of the plasticizer type. Both sensors contained a DMI-TPB ion-exchange complex, which was used for the preparation of the PVC-based membranes plasticized with DOP or *o*-NPOE. A detailed explanation of the preparation of the DMI-TPB ion-exchange complex has been described previously [16]. Sodium chloride at a concentration of 3 M was employed as the internal filling solution. A silver/silver (I) chloride reference electrode (Metrohm, Switzerland) with a 3 M potassium chloride electrolyte solution was used as a reference. The lifetime of the sensor was more than three months when used daily.

2.4. Procedure

The PVC-plasticized liquid membrane electrodes and the external reference electrode were used for all potentiometric measurements.

Both sensors were used for investigation of the responses to NaDDS and NaDBS. The assays were performed by adding the AS into distilled water and solution of 0.01 M sodium sulfate. The concentrations of AS used were 5 x 10^{-4} M and 5 x 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 volume of solution used for titrations was 25 mL. All titrations were performed with both sensors and titrants at three concentrations: 1 x 10^{-3} M, 1 x 10^{-4} M, and 5 x 10^{-5} M.

A stock solution of the detergent used as the model system was prepared weekly, but the diluted solutions were prepared daily. The model system titrations were performed in 0.1 M sodium sulfate. The standard addition method was performed with two concentrations of AS.

The titrator was programmed to work in DET (Dynamic Equivalence point Titration) Mode with 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 measurements and titrations were performed at room temperature using a magnetic stirrer and without ionic strength adjustment. The pH for the model system titrations was adjusted to 3.

3. RESULTS AND DISCUSSION

The electromotive force of the surfactant sensor dipped into a solution of anionic surfactant (AS) is defined by the Nernst equation:

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

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

It has been shown [17] that the magnitude of the inflection at the equivalence point is strongly dependent upon the solubility product value (K_{sp}) of the ion-exchanger used as sensing material in the sensor membrane:

$$E = E^0 - S \cdot \log K_{sp} / a_{CS^+} \quad (2)$$

Lower K_{sp} values cause a higher potential change at the equivalence point, resulting in a more sensitive surfactant determination. The DMI-TPB ion-exchanger utilized is among the most readily soluble ion-exchangers used in surfactant electrode construction.

3.1. Response characteristics

The response characteristics of two DMI-TPB-based liquid membrane surfactant sensors containing *o*-NPOE and DOP as the plasticizers, respectively, in solutions of two anionic surfactants (NaDBS and NaDDS) are shown in Figure 1.

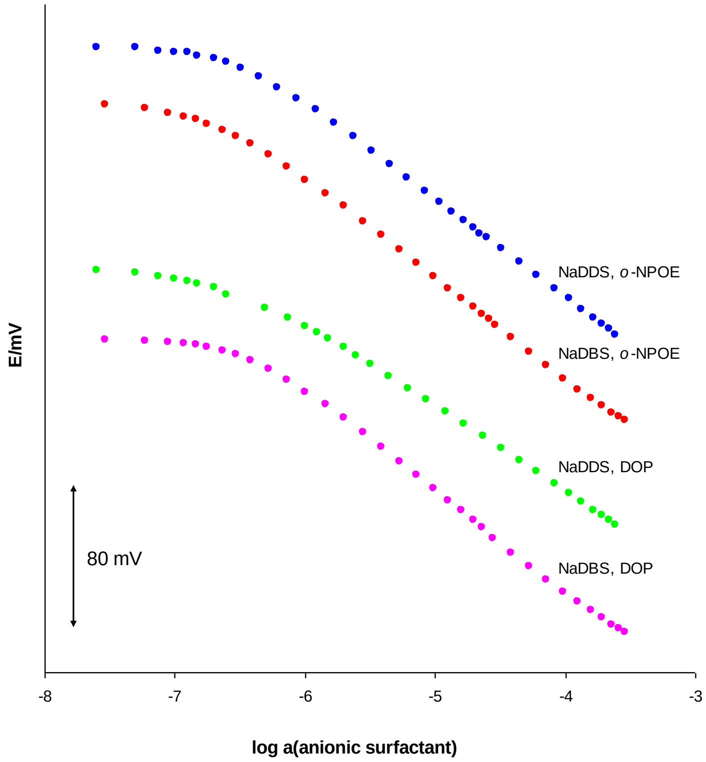

Figure 1. Influence of the plasticizer type on the response characteristics of the DMI-TPB sensor toward NaDBS and NaDDS. Here and in the following figures, some curves are displaced laterally or vertically for clarity.

The electrodes were tested in surfactant solutions at concentrations below 2.5 x 10^{-4} M, although they exhibited a linear response above the concentration of 1 x 10^{-3} M (not shown in the graph).

The sensors were investigated particularly at low concentration ranges (below 1 x 10^{-6} M). Statistical evaluation of the sensor characteristics is given in Table 1.

The sensor containing *o*-NPOE as plasticizer exhibited a Nernstian response for the both surfactant anions investigated, whereas that containing DOP as plasticizer revealed a Nernstian response for NaDBS and a sub-Nernstian response for the NaDDS ion. The detection limits were slightly lower for *o*-NPOE-containing sensor, but the useful concentration range was greater.

Table 1. Response characteristics of the DMI-TPB-based sensor containing different plasticizers (DOP and *o*-NPOE) to the anionic surfactants given together with ± 95 % confidence limits.

PARAMETERS	Plasticizer			
	DOP		*o*-NPOE	
	NaDBS	NaDDS	NaDBS	NaDDS
Slope / (mV/concentration decade)	58.1 ± 0.6	50.0 ± 0.6	58.9 ± 0.4	59.4 ± 0.2
Correl. coeff. (R^2)	0.9995	0.9993	0.9997	0.9999
Detection limit (M)	3 x 10^{-7}	4 x 10^{-7}	2 x 10^{-7}	2 x 10^{-7}
Useful conc. range (M)	5 x 10^{-7} - 5 x 10^{-3}	6 x 10^{-7} - 5 x 10^{-3}	3 x 10^{-7} - 5 x 10^{-3}	3 x 10^{-7} - 5 x 10^{-3}

3.2. Potentiometric titration of low levels of anionic surfactants

The main application of the electrode was the indication of the end-point in ion-pair surfactant potentiometric titrations. Standard solutions of DMIC and CPC were investigated as titrants for the determination of anionic surfactants forming water-insoluble 1 : 1 complexes. Two anionic surfactants (NaDBS and NaDDS) have been titrated potentiometrically using as the end-point detector a DMI-TPB-based sensor containing *o*-NPOE or DOP as the plasticizer. DMIC and CPC, both at concentrations of 1 x 10^{-4} M and 5 x 10^{-5} M, were used as the titrants, and the resulting potentiometric titration curves are shown in Figures 2 and 3, respectively.

The titration curves exhibited well-defined and sharp inflection points with a high potential jump at the equivalence point using 1 x 10^{-4} M titrant.

The titration curves obtained with DMIC as the titrant exhibited a higher potential jump and sharper inflection than those obtained using CPC. The use of *o*-NPOE as a plasticizer in the sensor generated titration curves with a higher potential jump and sharper inflection at the equivalence point than the use of DOP.

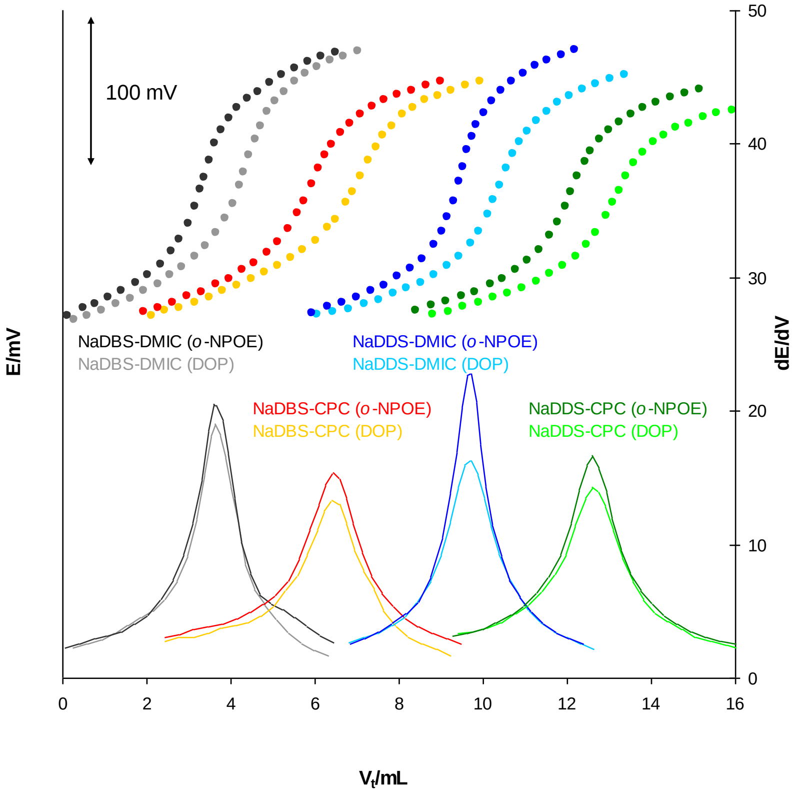

Figure 2. Potentiometric titration curves and their derivatives of NaDBS and NaDDS obtained with DMI-TPB sensors containing different plasticizers (DOP and *o*-NPOE) and DMIC and CPC as the titrants at concentrations of 1 x 10^{-4} M.

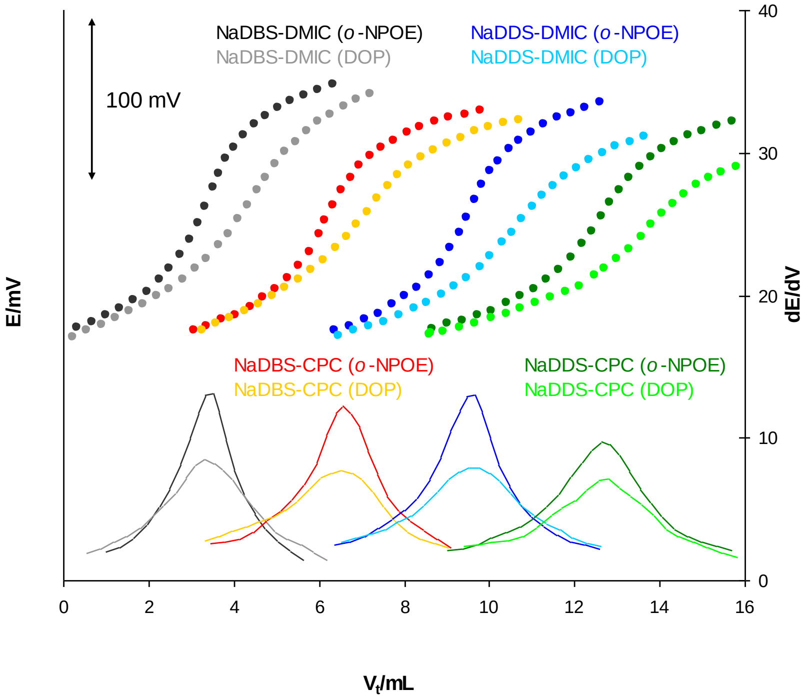

Figure 3. Potentiometric titration curves and their derivatives of NaDBS and NaDDS obtained with DMI-TPB sensors containing different plasticizers (DOP and *o*-NPOE) and DMIC and CPC as the titrants at concentrations of 5 x 10^{-5} M.

The use of 5 x 10^{-5} M titrant gave a less pronounced but usable potential break at the equivalence point and still facilitated reliable end-point detection. The results of these determinations are given in Table 2. Satisfactory accuracy and precision values were obtained even at the lowest titrant concentration (5 x 10^{-5} M). There were no significant differences between the accuracy of the results obtained with of any of the titrants and any of the plasticizers used in the sensors investigated with a titrant concentration of 1 x 10^{-4} M. With a titrant concentration of 5 x 10^{-5} M, the accuracy of the results was greater with the sensor containing *o*-NPOE as the plasticizer.

Table 2. Results of the potentiometric titrations of NaDBS and NaDDS using DMI-TPB-based sensors containing different plasticizers (DOP and *o*-NPOE) and DMIC and CPC as the titrants (both at concentrations of c = 1 x 10^{-4} M and c = 5 x 10^{-5} M).

Titrant	Plasticizer											
	DOP						*o*-NPOE					
	Surfactant investigated						Surfactant investigated					
	NaDBS			NaDDS			NaDBS			NaDDS		
	Taken (µg)	Found* (µg)	Recov.* (%)	Taken (µg)	Found* (µg)	Recov.* (%)	Taken (µg)	Found* (µg)	Recov.* (%)	Taken (µg)	Found* (µg)	Recov.* (%)
DMIC												
c = 1 x 10^{-4} M	172.0	169.8±0.9	98.7	144.0	142.0±1.1	98.6	172.0	170.4±0.8	99.1	144.0	142.4±0.8	98.9
c = 5 x 10^{-5} M	86.0	82.2±0.8	95.6	72.0	69.3±1.2	96.3	86.0	83.7±0.8	97.3	72.0	70.3±0.4	97.6
CPC												
c = 1 x 10^{-4} M	172.0	170.5±1.7	99.1	144.0	141.8±1.6	98.5	172.0	170.2±0.8	99.0	144.0	142.2±1.4	98.8
c = 5 x 10^{-5} M	86.0	82.4±0.8	95.8	72.0	69.0±1.0	95.8	86.0	84.2±0.7	97.9	72.0	70.7±0.8	98.2

* average of 5 determinations ± C.I. (Confidence Interval)

3.3. Titration of model effluent formulations

A diluted solution of a NaDBS-based detergent product was used as a model effluent for further investigation. The influence of the ingredients this product on the determination of anionic surfactant was investigated by the addition of known amounts of NaDBS and NaDDS to the product solution. Standard solutions of DMIC and CPC, both at a concentration of 5 x 10^{-5} M, were used as the titrants for the titration of anionic surfactants using the DMI-TPB-based sensor containing *o*-NPOE as a plasticizer.

Known amounts of the NaDBS and NaDDS solutions were added in the model effluent (ME) solution and titrated potentiometrically using the sensor as described for end-point indication. The ME solution contained 0.1 M Na_2SO_4 as the ionic strength regulator, and its pH was adjusted to 3 using 0.1 M HCl. The resulting potentiometric titration curves using DMIC and CPC as the titrants are shown in Figures 4 and 5, respectively.

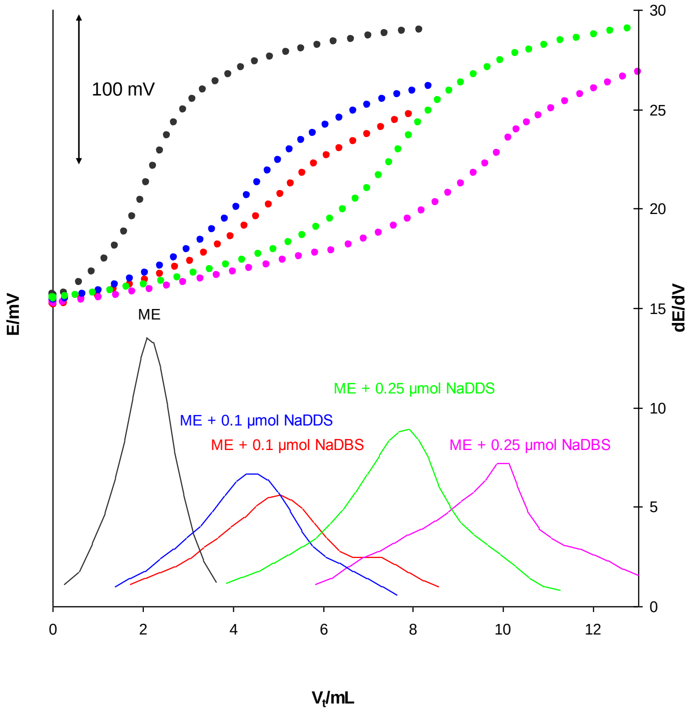

Figure 4. Titration curves of model effluent (ME, diluted solution of NaDBS-based powder detergent) and the corresponding first derivatives with the addition of known concentrations of NaDBS and NaDDS, using the DMI-TPB surfactant sensor as the indicator and DMIC ($c = 5 \times 10^{-5}$ M) as the titrant.

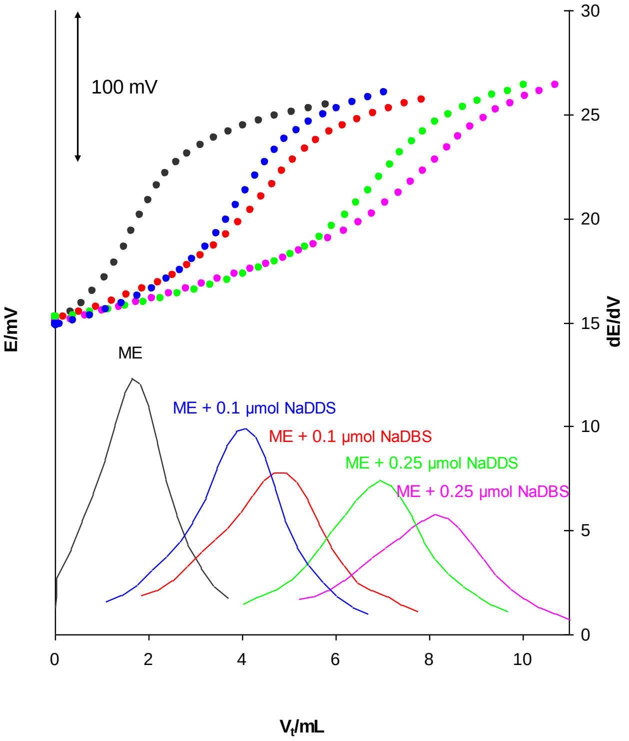

Figure 5. Titration curves of model effluent (ME, diluted solution of NaDBS-based powder detergent) and the corresponding first derivatives with the addition of known concentrations of NaDBS and NaDDS, using the DMI-TPB surfactant sensor as the indicator and CPC ($c = 5 \times 10^{-5}$ M) as the titrant.

All of the titration curves are analytically usable, although the titration curves obtained using DMIC as the titrant exhibited a slightly higher potential break at the equivalence point compared to those obtained using CPC. The results of the determinations for both titrants, DMIC and CPC, are given in mass units (μg) and as the concentration in the titrated solutions (μM and mg/L), together with the corresponding accuracy and precision statistics (Table 3).

Table 3. Results of the potentiometric titrations of model effluents (diluted solution of a commercial detergent) with the addition of known concentrations of NaDBS and NaDDS, using the DMI-TPB based surfactant sensor as the indicator and DMIC and CPC as the titrants (both at a concentration of $c = 5 \times 10^{-5}$ M).

Titrant	Analyte										
	Model effl.	NaDBS					NaDDS				
	Found* (μg)	Added (μg)	Found* (μg)	c* (μM)	c* (mg/L)	Recov. (%)	Added (μg)	Found* (μg)	c* (μM)	c* (mg/L)	Recov. (%)
DMIC	34.7±0.9	50.7	48.9±1.3	5.69±0.15	1.96±0.05	96.4	34.4	33.2±0.7	4.60±0.10	1.33±0.03	96.5
		123.5	119.7±2.0	9.56±0.23	4.78±0.08	96.9	89.9	87.2±1.3	12.09±0.18	3.49±0.05	97.0
CPC	33.9±0.9	41.8	40.5±0.9	4.71±0.10	1.62±0.04	96.9	30.8	29.8±0.7	4.13±0.10	1.19±0.03	96.8
		108.7	105.2±1.5	12.23±0.17	4.21±0.06	96.8	72.9	70.7±1.2	9.81±0.17	2.83±0.05	97.0

* average of 5 determinations ± C.I.

The estimated limit of detection for both surfactants investigated was 0.02 mg/L. The anionic surfactant concentrations in the solutions investigated were between 10^{-5} and 10^{-6} M.

4. CONCLUSIONS

A sensitive surfactant sensor based on 1,3-didecyl-2-methyl-imidazolium-tetraphenylborate (DMI-TPB) as a sensing ion-exchange complex was used for end-point detection during the potentiometric titration of anionic surfactants in model effluents. Two plasticizers, *o*-nitrophenyloctylether (*o*-NPOE) and bis(2-ethylhexyl)phthalate (DOP), and two titrants, 3-didecyl-2-methylimidazolium chloride (DMIC) and cetylpyridinium chloride (CPC), were tested. Sodium dodecylsulfate (NaDDS) and sodium dodecylbenzene sulfonate (NaDBS) were titrated. The best performances were exhibited by a sensor containing *o*-NPOE as a plasticizer. Both titrants, DMIC and CPC, gave analytically usable titration curves even at a concentration of 5×10^{-5} M, although DMIC exhibited slightly a higher potential jump at the equivalence point, enabling the reliable determination of anionic surfactants at the *ppm* level.

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