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The Influence of Plasticizers On Determination of Cationic Surfactants In Pharmaceutical Disinfectants By Direct Potentiometric Surfactant Sensor

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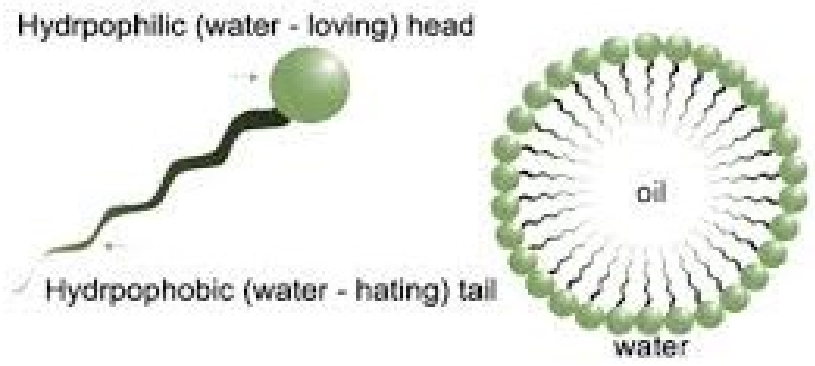
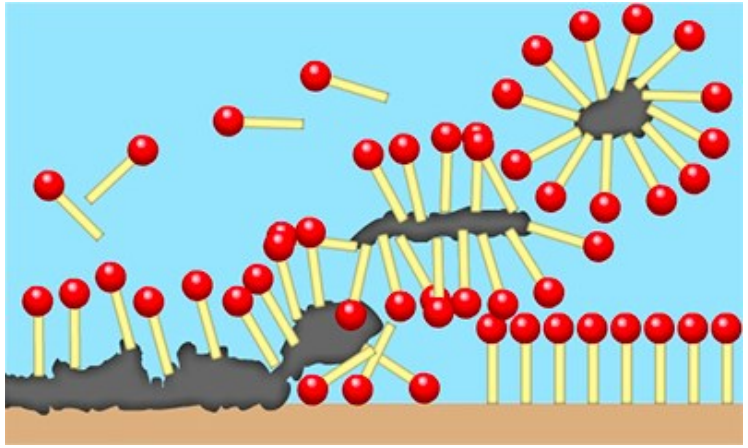
1. Introduction

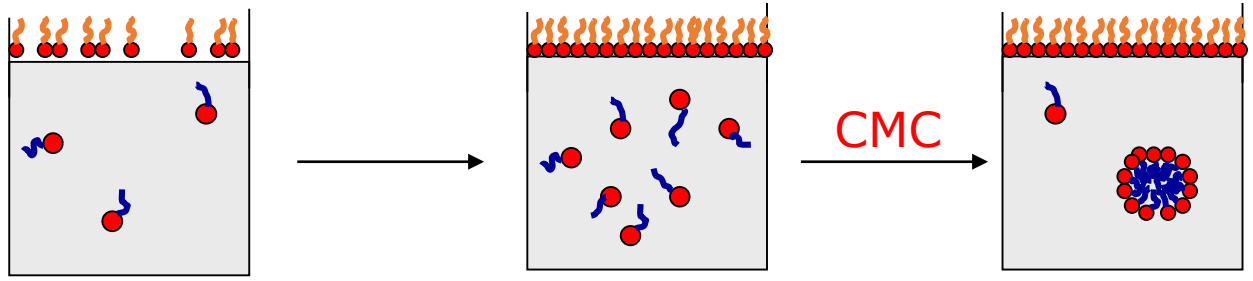
SURFACTANT** = **surf**ace **act**ive **agent





Operating principle

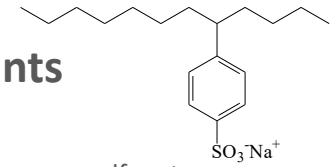
- **Lower the surface tension**
- **Critical micelle concentration**



1. Introduction

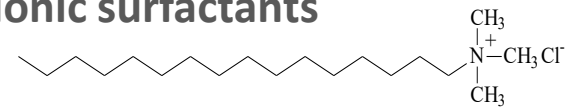
CLASSIFICATION

Anionic surfactants



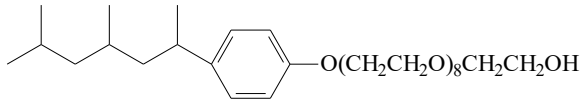
Example: Sodium dodecylbenzenesulfonate

Cationic surfactants



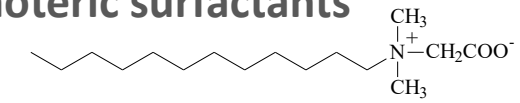
Example: N-Hexadecyltrimethylammonium chloride

Nonionic surfactants



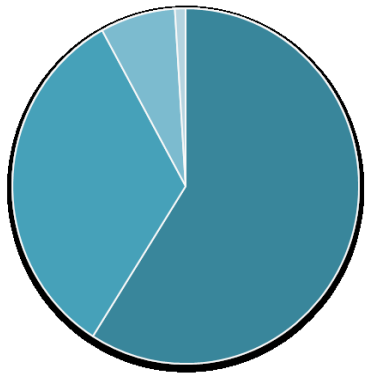
Example: Dodecanol 9-mole ethoxylate

Amphoteric surfactants



Example: Dodecyldimethylammoniomethane carboxylate

COMPLEX MIXTURES



- Anionic surfactant (59)
- Nonionic surfactant (33)
- Cationic surfactant (7)
- Amphoteric surfactant (1)

Global surfactant consumption (%) by surfactant type

- global surfactant market generated revenues of more than US$ 41 billion in 2018

Environmental impact

1. Introduction

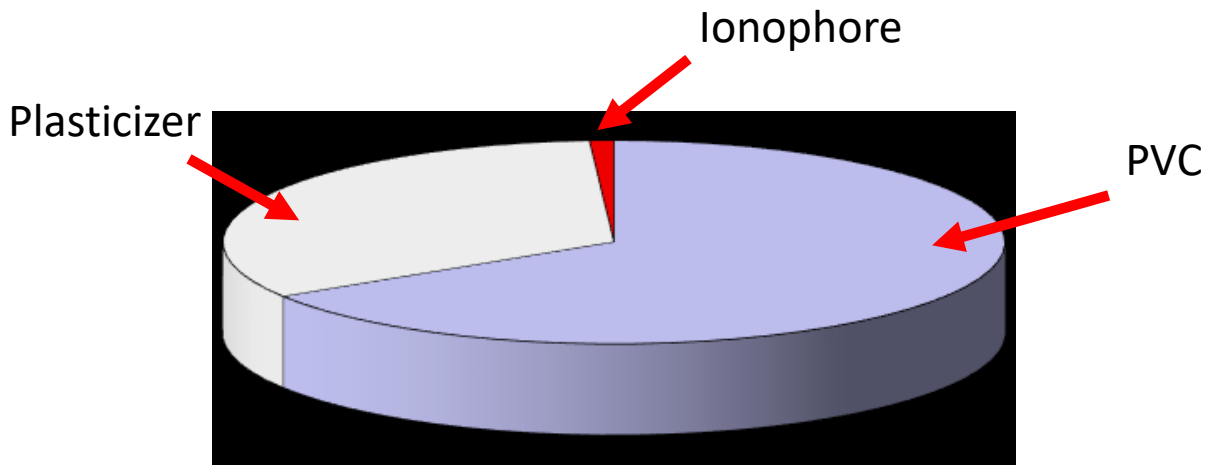
- **Cationic surfactants are used in broad spectra of commercial products as preservatives and disinfectants.**
- **Since classical methods for determination of lower surfactant concentrations [1] have many disadvantages, direct potentiometric sensors for surfactants based on ion selective electrodes with liquid membrane type [2][3] offer an elegant, affordable and reliable substitution.**

1. Introduction

- **Liquid membrane type sensing membranes are typically based on high molecular weight PVC mixed with plasticizer and an ionophore.[4]**
- **Even though the plasticizer has a function to soften the matrix and make it more flexible, it also has an influence on the final direct potentiometric sensor response [5] since in influences the membrane polarity, resistance, ion mobility across the membrane. [6][7]**

1. Introduction

- **The typical weight ratio of PVC to plasticizer is 1:2, with up to 1 wt % ionophore:**



- **Higher amounts of plasticizer could be interfering to the measurement. [8]**

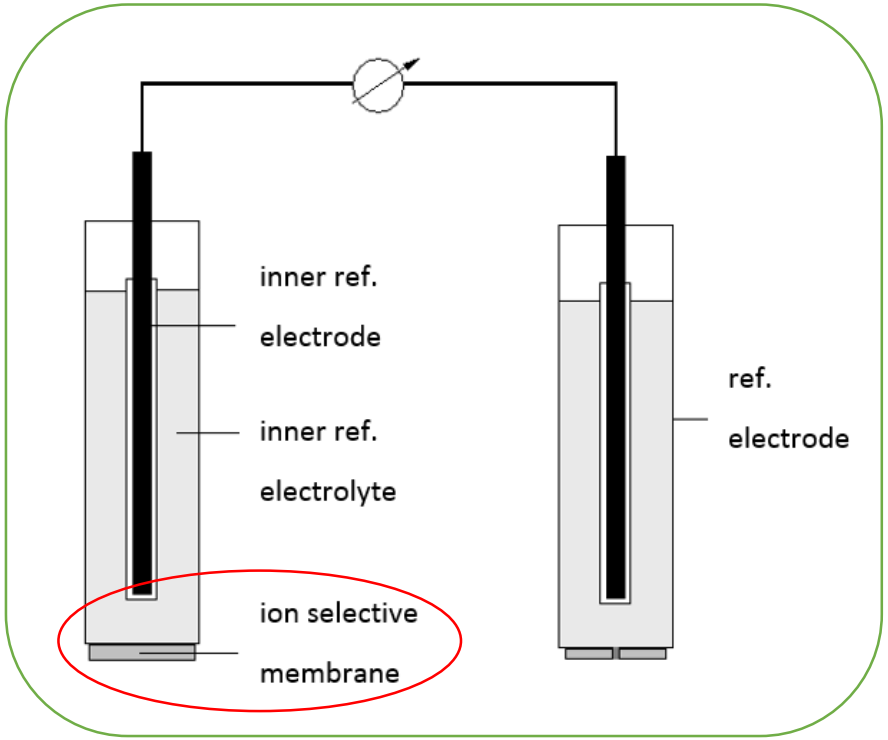
AIM

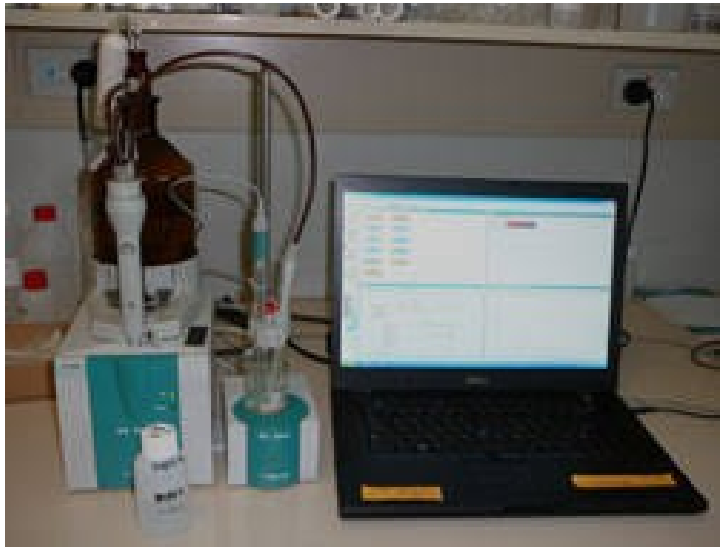
- **Previously we synthesized DMI-TPB ion pair, implement it in the PVC-based liquid membrane surfactant sensor and used it for cationic surfactants quantification in real samples. [9]**

- **In this paper we selected four different plasticizers and implement them in the PVC-based sensing membrane with DMI-TPB as an ionophore to observe the plasticizer influence on the response characteristics of the direct potentiometric surfactant sensor and test the selected membrane formulation on commercial pharmaceutical disinfectants.**

2. Materials and Methods

- **Surfactant ion selective electrodes (surfactant sensors) are electrochemical sensors able to measure surfactant concentration.**
- **Principle: direct potentiometry**
- **There is a logaritmic dependance between surfactant activity and electrode potential.**
- **Instrumentation:**





Working setup

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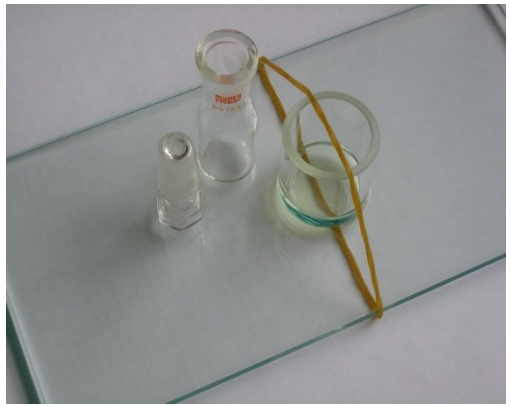
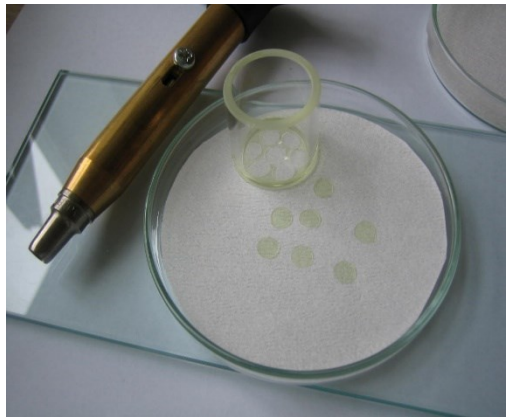
2. Materials and Methods

PVC liquid membrane preparation: a) setup, b) cutted membrane discs

A)



B)



CATIONIC SURFACTANTS

- cetylpyridinium chloride (CPC)
- cetrimonium bromide (CTAB)

PLASTICIZERS

- o-nitrophenyl octyl ether (P1)
- bis(2-ethylhexyl) phthalate (P2)
- bis(2-ethylhexyl) sebacate (P3)
- dibutyl sebacate (P4)

ION PAIR

1,3-didecyl-2-methylimidazolium-tetraphenylborate (DMI-TPB)

Surfactant sensor with implemented membrane disc on the bottom of the electrode

SIX REAL SAMPLES OF PHARMACEUTICAL DISINFECTANTS PROVIDED BY THE LOCAL STORE

3. Results and Discussion

3.1. Response characterization

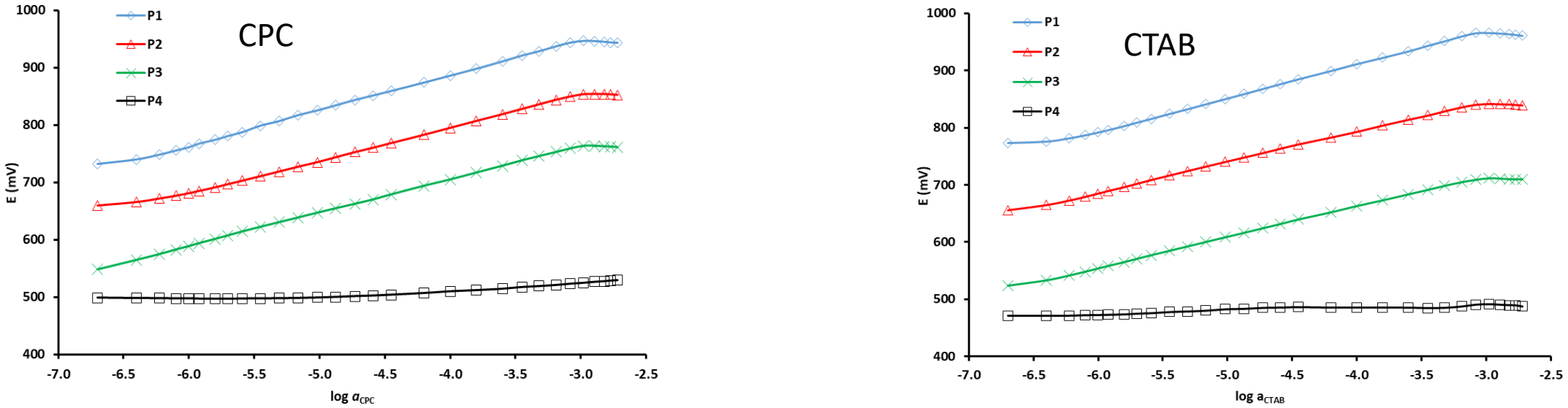


Figure 1. Influence of the plasticizer type on the DMI-TPB surfactant sensor response characteristics toward cationic surfactants: a) CPC (left) and b) CTAB (right), in deionized water. Plasticizers, from top to bottom: 2-nitrophenyl octyl ether (P1), bis(2-ethylhexyl) phthalate (P2), bis (2-ethylhexyl) sebacate (P3), and dibutyl sebacate (P4). The curves have been shifted vertically for clarity.

3. Results and Discussion

3.2. Direct potentiometric titrations

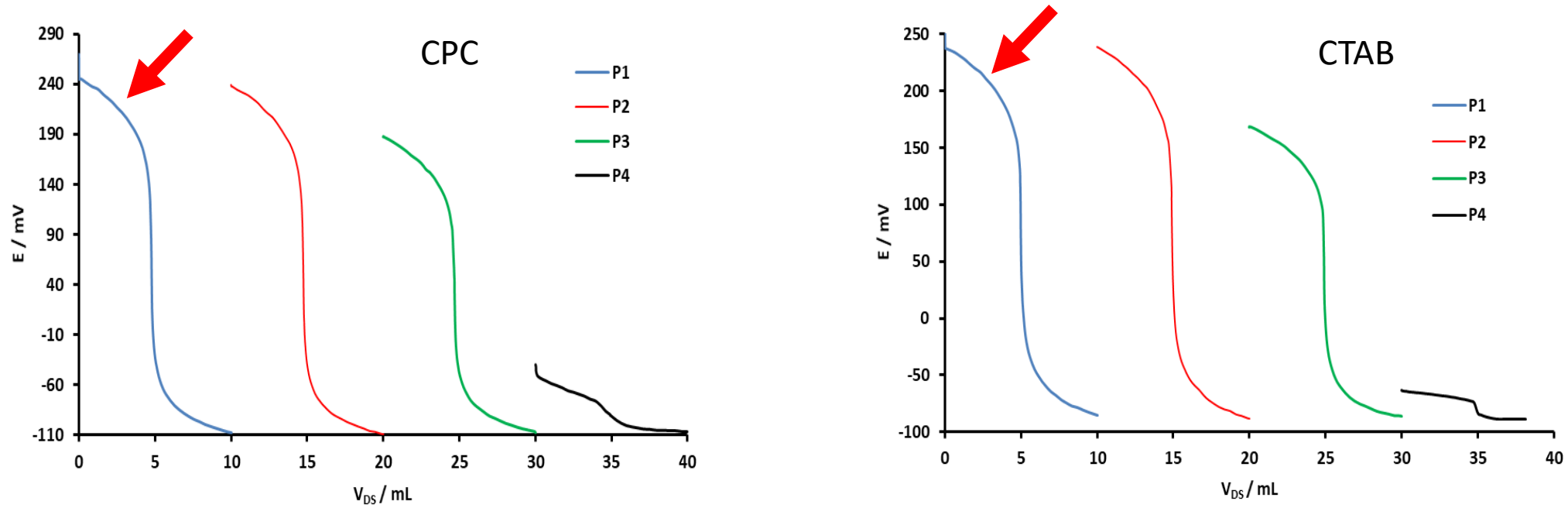


Figure 2. Direct potentiometric titration curves for a) CPC (c=4 × 10^{-3} M) and b) CTAB; with DS (c=4 × 10^{-3} M) obtained by the use of DMI-TPB sensor and for different plasticizers, from left to right: 2-nitrophenyl octyl ether (P1), bis(2-ethylhexyl) phthalate (P2), bis (2-ethylhexyl) sebacate (P3) and dibutyl sebacate (P4). The curves have been shifted vertically for clarity.

3. Results and Discussion

3.3. Titration of pharmaceutical disinfectants

- The DMI-TPB sensor containing plasticizer P1 was selected as an end-point indicator in potentiometric titration of cationic surfactants in six commercial pharmaceutical disinfectants since it presented the best characteristic.
- The standard solution of anionic surfactant DS ($c=4 \times 10^{-3}$ M) was used as a titrant. PVC liquid membrane Direct Potentiometric Surfactant Sensor (DPSS) was used as a reference [10].
- For determinations in six disinfectant samples, no significant differences were observed between the means of both the DMI-TPB sensor containing plasticizer P1 and the DPSS at the 95% confidence level.
- A sufficient well agreement was observed for all results (Table 1).

3. Results and Discussion

3.3. Titration of pharmaceutical disinfectants

Table 1. The results of potentiometric titrations of cationic surfactants in pharmaceutical disinfectants by DS (c = 4 mM) as titrant and a DMI-TPB sensor containing plasticizer P1 as an indicator, in comparison with the results obtained with referent Direct Potentiometric Surfactant Sensor (DPSS).

Product	ANIONIC SURFACTANT CONTENT[1]			
	DMI-TPB sensor with P1		DPSS[2]	
	%	RSD (%)	%	RSD (%)
A	4.3223	0.91	4.2483	0.93
B	5.1313	0.62	5.3013	0.64
C	4.7646	0.72	4.7021	0.67
D	4.7222	0.88	4.5819	0.93
E	0.0684	0.35	0.0672	0.36
F	0.1494	0.25	0.1502	0.27

[1] Average of 5 determinations

[2] DPSS described in ref. [10]

4. Conclusion

- Four different plasticizers were incorporated into the PVC-based liquid membrane surfactant sensors with DMI-TPB as an ionophore.
- Membranes were characterized by their response on cationic surfactant CPC and CTAB, and direct potentiometric titrations of CPC and CTAB with anionic surfactant DS as a titrant.
- Sensor membrane containing plasticizer 2-nitrophenyl octyl ether (P1) showed the best properties and was used for titration of six pharmaceutical disinfectants obtained from the local store.
- The results of showed good agreement with conventional reference direct potentiometric sensor developed previously by the same group.

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Thank you for your attention!