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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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Abstract: Ion selective liquid membrane type membranes are usually made of a PVC, ionophore and a plasticizer. Plasticizers soften the PVC but due to their liphopilicity they influence the ionophore, the ion exchange across the membrane, membrane resistance and consequently the analytical signal. The aim of the research was to investigate the influence of 4 different plasticizers, in formulation with the same ionophore, on the analytical properties of the sensor membrane towards two often used cationic surfactants, then select the best membrane formulation and test it on real samples of six pharmaceutical disinfectants containing cationic surfactants.

Keywords: cationic surfactant; surfactant sensor; plasticizer; pharmaceutical disinfectants

1. Introduction

Surface active agents or surfactants are widely used in household and industry for washing, cleaning, disinfection and as emulsifiers. There are four main groups of surfactants: anionic, cationic, amphoteric and nonionic. 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. 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]. The typical weight ratio of PVC to plasticizer is 1:2, with up to 1 wt % ionophore, respectively. Higher amounts of plasticizer could be interfering to the measurement [8]. Previously we synthesized 1,3-didecyl-2-methylimidazolium-tetraphenylborate (DMI-TPB) ion pair (ionophore), 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

2.1. Membrane Preparation and Surfactant Sensor Fabrication

Four different plasticizers were used to manufacture ISE membranes: o-nitrophenyl octyl ether (P1), bis(2-ethylhexyl) phthalate (P2), bis(2-ethylhexyl) sebacate (P3) and dibutyl sebacate (P4); all from Sigma Aldrich, Germany. The membranes were prepared by dissolving 1,3-didecyl-2-methylimidazolium-tetraphenylborate (DMI-TPB) ion pair in small amount of tetrahydrofuran (THF) (Fluka Switzerland). Next the high-molecular-weight PVC (Fluka Switzerland) and corresponding plasticizer were nixed. To this mixture we added previously prepared mixture of ion pair/THF and all was transferred to the ultrasonic bath (Sonoplus Ultrasonic homogenizer with a horn sonicator HD 3100, from Bandelin, Germany) for sonication. The mixture was transferred to 24mm OD mold glass ring. After two days the THF evaporated and the thin plasticized layer was cut in 7mm OD discs (sensor membranes) and stored dry for later use. The same procedure was used for each plasticizer separately. Phillips electrode body (Phillips IS 561, Glasblaeserei Moeller, Switzerland) with 3M sodium chloride (Sigma Aldrich, Germany) inner electrolyte was used to incorporate prepared sensor membranes.

2.2. Surfactant Sensor Response Measurements

Response measurements for cationic surfactants cetylpyridinium chloride (CPC) and cetrimonium bromide (CTAB), both from Sigma Aldrich, Germany, were performed for each membrane with corresponding plasticizer formulation. Instrumentation for direct potentiometric response measurements was a Metrohm 780 pH meter and a Metrohm 794 Basic Titrino with stirrer (Metrohm, Switzerland) and a silver/silver chloride reference electrode (Metrohm, Switzerland) paired with fabricated surfactant sensor. The measurement was performed in deionized water by adding corresponding increments of sodium dodecyl sulfate (DS) (4×10^{-2} M to 4×10^{-4} M) to cover the broad concentration range. The increment interval was from 120 s (for lower concentrations) to 60 s for higher DS concentrations.

2.3. Direct Potentiometric Titrations

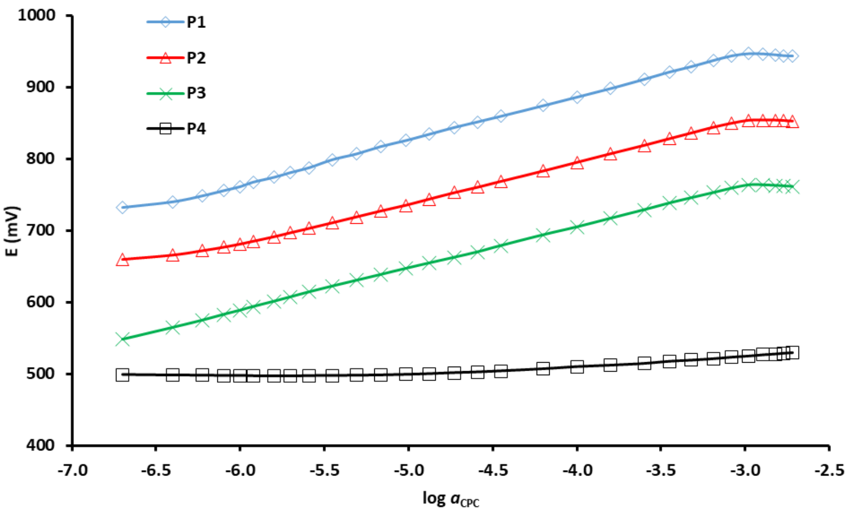
Direct potentiometric titrations of CPC or CTAB were performed with corresponding concentration of DS. A Metrohm 808 Titrando titrator with magnetic stirrer and Tiamo 2.1 software (Metrohm, Switzerland) connected to silver/silver chloride electrode (Metrohm, Switzerland) paired with a corresponding surfactant sensor electrode, were used to perform direct potentiometric titrations. The measuring volume was 25 mL (20 mL deionized water and 5 mL of corresponding surfactant solution). The concentrations of cationic surfactant solutions were 4×10^{-3} M. The titrations of commercial pharmaceutical disinfectants provided in the local drug sore, were performed by the same procedure for selected membrane, with pH adjustment to avoid false result due to the amphoteric surfactants present in formulation.

3. Results and Discussion

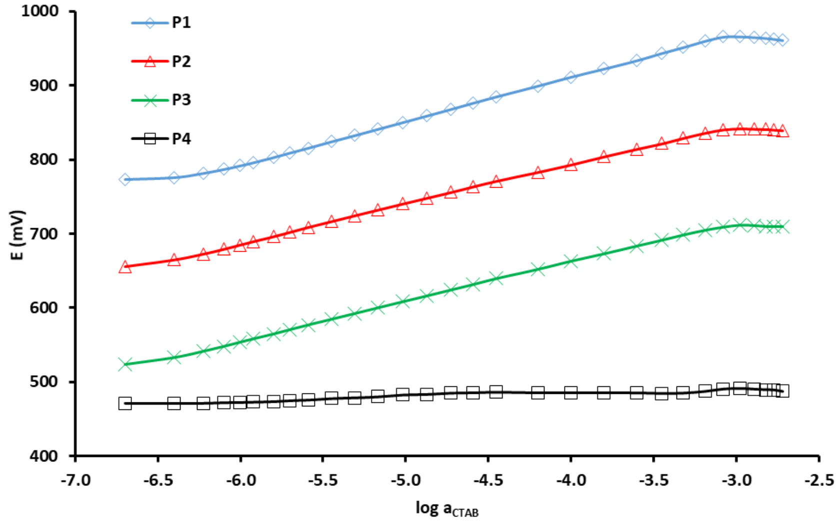
3.1. Response Characterization

The influence of plasticizer type on the response characteristics of the DMI-TPB sensor was tested on two cationic surfactants, CPC and CTAB (Figure 1), in five independent series for each. Four different plasticizers were tested (P1–P4). Cationic surfactants CPC and CTAB were selected since they are often used in commercial product formulations.

The response curves for all plasticizers showed slight distortions when the concentrations of both, CPC and CTAB, were higher, due to the micelle formation.



(**a**)



(**b**)

Figure 1. Influence of the plasticizer type on the DMI-TPB surfactant sensor response characteristics toward cationic surfactants: (**a**) CPC and (**b**) CTAB, 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.

The response curves for CPC in deionized water were shown in Figure 1a. The slope values for plasticizers P1 was the closest to the Nernstian, 57.9 ± 0.4, while the plasticizers P4 obtained the lowest slope value, 12.80 ± 0.2. Correlation coefficients for all four plasticizers were approximately 0.99, within the useful linear concentration range. Plasticizer 3 obtained the highest useful concentration range from 1.3×10^{-3} to 2×10^{-7} M, while plasticizer 4 obtained a very low potential change trough all investigated concentrations. The response curves for CTAB in deionized water are shown in Figure 1b. The slope vales for plasticizers P1 was the closest to the Nernstian, 60.0 ± 0.7, while the plasticizers P4 obtained the lowest slope value. Correlation coefficients for all four plasticizers were approximately 0.99, within the useful linear concentration range. Plasticizers 2 and 3 obtained the highest useful concentration range from 1×10^{-3} to 4×10^{-7} M, while plasticizer 4 obtained a very low potential change trough all investigated concentrations.

3.2. Direct Potentiometric Titrations

The main applications of the surfactant sensors are end-point indications during surfactant direct potentiometric titrations. Two cationic surfactants, CPC and DBS, were determined by direct potentiometric titrations with DMI-TPB surfactant sensor containing formulations of four different plasticizers (P1–P4). The standard DS solution (c = 4×10^{-3} M) was used for direct potentiometric titrations of CPC (c = 4 × 10^{-3} M) and CTAB (c = 4 × 10^{-3} M). The corresponding potentiometric titration curves were presented in Figure 2.

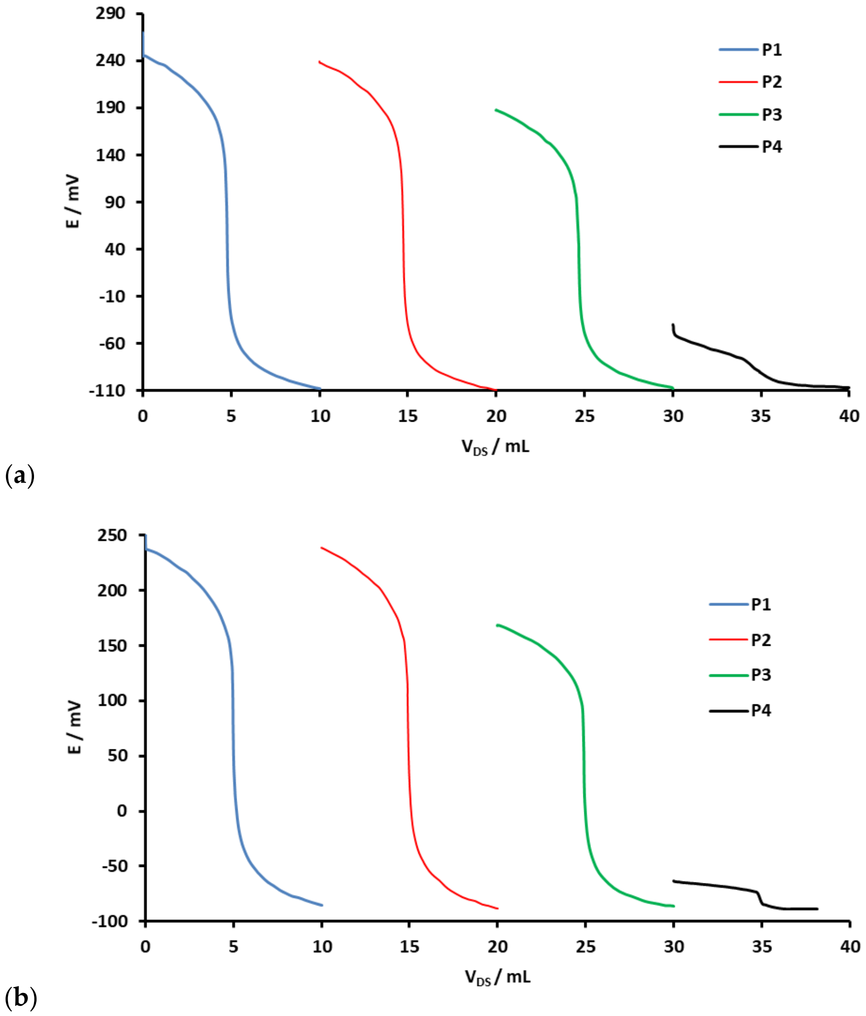


Figure 2. Direct potentiometric titration curves for (**a**) CPC (c = 4 × 10^{-3} M) and (**b**) CTAB; with DS (c = 4 × 10^{-3} M) obtained by the use of DMI-TPB sensor and for different plasticizers, from left to right: 2-nitrophenyl octyl ether (P1), bis(2-ethylhexyl) phthalate (P2), bis (2-ethylhexyl)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

The titration curves of CPC (c = 4 × 10^{-3} M) with DS (c = 4 × 10^{-3} M), using DMI-TPB sensors containing four different plasticizers, exhibited well-defined and sharp inflexion points (Figure 2a). Only the sensor membrane containing the P4 plasticizer obtained small signal change, but still with potential jump at expected equivalence point volume values. This was expected due to low slope exhibited for P4 formulation shown in Figure 1a. The highest value of potential change at the end-point was demonstrated by the sensor containing P1 plasticizer.

The titration curves of CTAB (c = 4 × 10^{-3} M) with DS (c = 4 × 10^{-3} M), using DMI-TPB sensors containing four different plasticizers, exhibited well-defined and sharp inflexion points (Figure 2b). Only the sensor membrane containing the P4 plasticizer obtained small signal change, but still with better than obtained for CPC in Figure 2a. The highest value of potential change at the end-point were demonstrated by the sensors containing P1 and P2 plasticizer.

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 × 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).

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. Conclusions

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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Conflicts of Interest: The authors declare no conflict of interest.

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