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The Influence of Plasticisers on Response Characteristics of Anionic Surfactant Potentiometric Sensor

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Six different plasticisers, 2-nitrophenyl octyl ether (P1), bis(2-ethylhexyl) phthalate (P2), bis (2-ethylhexyl) sebacate (P3), 2-nitrophenyl phenyl ether (P4), dibutyl phthalate (P5) and dibutyl sebacate (P6), were incorporated into PVC-based surfactant sensors, and their influence on the determination of anionic surfactants (sodium laurylsulfate (SDS) and sodium dodecylbenzenesulfonate (DBS)) was investigated. Dimethyldioctadecylammonium-tetraphenylborate (DDA-TPB) was used as an ion-pair in the membrane. The sensors containing plasticisers P1– P5 exhibited a sub-Nernstian slope value ranging from −46.4 to −54.8 (mV/decade of activity), while P6 exhibited a super-Nernstian slope value of −66.3 (mV/decade of activity). All the obtained titration curves displayed well defined and sharp inflexion points. Due to the best analytical performance and its low price, the sensor containing dibutyl phthalate (P5) was selected for further investigation. It also provides fast dynamic response and the highest value of potential change at the end-point, allowing reliable end-point location even at low concentration levels of analyte. The linear response renge of the sensor was 6.1×10^{-3} to 7.2×10^{-7} M with the sub-Nernstian slope value of -53.1 ± 0.6 (mV/decade of activity) and the lower detection limit of 3.9×10^{-7} M. The commonly used compounds in product formulations did not interfere with the measurements. Anionic surfactant content was successfully determined in commercial dishwashing detergents.

Keywords: Plasticiser, surfactants, surfactant sensor, direct potentiometry, potentiometric titration

1. INTRODUCTION

Surfactants lower the surface tension. Common methods of determination of the lower surfactant concentrations are: classical methods [1–3] - with many dissadvantages; and ion selective electrodes (ISE) [4–7]. These liquid membrane type surfactant-sensitive electrodes are based on direct potentiomery. The sensing elements – liquid membranes, are typically PVC-based. The basic principle of an ISE is the molecular recognition of charged analyte substances by the lipophilic neutral or charged ligands incorporated into the ISE membranes.

The ISE membrane consists of PVC (as a mechanical support matrix and a ionophore doping agent), the ionophore and lipophilic ionic sites and salts (as electroactive compounds) and a plasticiser (additive with a low molar mass) [8,9]. PVC itself is a large rigid polymer; with addition of a plasticiser, it becomes softer and more flexible. There are also additional benefits of using the plasticiser; it is used as a solvent for the ionophore inside the membrane (the polarity plays important role in retention of the membrane components) [10] enhancing the additive mobility inside the membrane. The typical weight ratio of PVC to plasticiser is 1:2, with up to 1 wt % ionophore used . The plasticiser should possess some important properties: i) it should be insoluble in water, ii) it should prevent ionophore leakage into the analyte (usually the most difficult to prevent [11]), iii) it should be inert to ion exchange [12], iv) it should decrease the PVC glass transition to lower temperatures [13], v) it should ensure simple fabrication with mechanical resistance [14], and vi) it should not oxidise or crystallise in the membrane [15]. A wide variety of organic compounds, most frequently aromatic esters such as phthalates, have been employed as plasticisers [16].

The plasticiser itself is usually not fully inert and enhances the exchange of interferents all the way across the sensing membrane. When comparing the ion exchange rates due to the plasticiser and the ionophore, the plasticiser has a much smaller rate, but the amount of plasticiser present is much greater, which leads to possible interfering action [17]. In ISEs, important properties such as selectivity and lifetime are directly influenced by the plasticiser used. Plasticisers affect the detection limit of different types of electrodes [18] for the Ca^{2+} electrode and a Cd^{2+} electrode [19], or H^+ [15].

The lipophilic properties of the plasticiser should be similar to those of the ionophore used within the sensor membrane matrix. Plasticiser lipophilicity is directly linked to the water penetration coefficient and water flux across the membrane [20].

A plasticiser with high dielectric constant in neutral carrier membranes presents enhanced selectivity to ions with high hydration energy [21].

The PVC liquid membrane electrodes for potentiometric determination of anionic surfactants have been reported by several authors [7,22–24]. Several plasticisers: o-nitrophenyl octyl ether (o-NPOE), o-nitrophenyl decyl ether, o-nitrophenyl dodecyl ether and o-nitrophenyl tetradecyl ether have been incorporated in surfactant ISEs based on a PVC membrane with no added ion exchanger. All plasticisers in PVC-membrane formulations, except o-NPOE, had an improving effect on lowering the limits of detection and on slope sensitivity [25].

The aim of this work is to examine the influence of different plasticisers on the properties of PVC-based surfactant sensors containing a DDA-TPB ion-pair for anionic surfactant determination, and the selection of the most appropriate plasticiser for anionic surfactant determination in commercial products. The sensing membranes were characterised through direct potentiometric response, dynamic response, and the influence of interfering agents and were applied in commercial product titration.

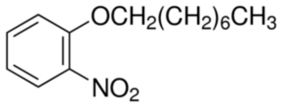
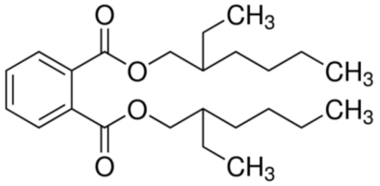
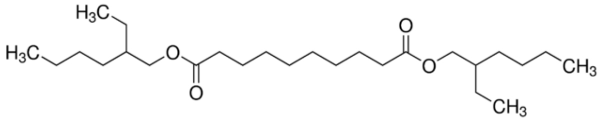
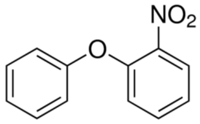
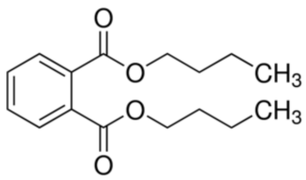
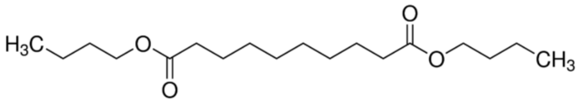
2. MATERIAL AND METHODS

2.1. Reagents

Plasticisers (Table 1) used in this research were *o*-nitrophenyl octyl ether, *o*-nitrophenyl phenyl ether, dibutyl phthalate, dibutyl sebacate, bis(2-ethylhexyl) sebacate and bis(2-ethylhexyl) phthalate, all from Sigma Aldrich, Germany. Other materials for membrane preparation included high-molecular-weight PVC, tetrahydrofuran, both from Fluka Switzerland, and synthesised dimethyldioctadecylammonium-tetraphenylborate (DDA-TPB) ion pair.

For response measurements, two anionic surfactants were used: sodium laurylsulfate (SDS) and sodium dodecylbenzenesulfonate (DBS).

Table 1. Plasticiser name, abbreviation and formula.

PLASTICISER		
NAME	**ABBREVIATION**	**FORMULA**
2-nitrophenyl-octyl-ether	P1	
bis(2-ethylhexyl) phthalate	P2	
bis (2-ethylhexyl) sebacate	P3	
2-nitrophenyl phenyl ether	P4	
dibutyl phthalate	P5	
dibutyl sebacate	P6	

2.2. Membrane preparation

The DDA-TPB ion pair was dissolved in small amount of THF. The exact amounts of PVC and plasticiser were mixed together and the ion-pair solution was added. The obtained mixture was dissolved using an ultrasonic bath (Sonoplus Ultrasonic homogeniser with a horn sonicator HD 3100, from Bandelin, Germany) and poured into a glass ring fixed on a flat glass plate. After THF evaporation (24–48 h), small discs were cut from the mixture and stored dry for later use. The procedure was repeated for all plasticisers.

2.3. Sensor preparation

The membrane was set on the electrode body (Phillips IS 561, Glasblaeserei Moeller, Switzerland). As the inner filling, a solution of 3M sodium chloride was used. The sensors were preconditioned in SDS solution prior to use and kept in deionised water between measurements.

2.4. Lipophilicity calculations

Liphophilicity for all six plasticisers was calculated using the Java based ALOGPS 2.1 online software.

2.5. Response measurements

The response measurements were performed using bespoke software, a Metrohm 780 pH meter and a Metrohm 794 Basic Titrino with stirrer (Metrohm, Switzerland).

For all response measurements, a silver/silver chloride reference electrode was used. The volume of solutions used for measurements was 20 mL. Sensor response characteristics were obtained by incremental addition of the corresponding surfactant (SDS and DBS) solutions to deionised water. The concentrations of surfactant solutions ranged from 4×10^{-2} M to 4×10^{-4} M. The volume of the increments ranged from 0.01 to 4.00 mL, time interval between increments was 120 s for the first 10 increments and 60 s thereafter. Stirring speed was set on 3.

2.6. Potentiometric titration measurements

For potentiometric titrations, a titrator with 20 mL exchange unit was used, along with a titration stand magnetic stirrer, all from Metrohm, Switzerland. Tiamo software (Metrohm, Switzerland) was used for the control of the titrator.

A silver/silver chloride electrode (Metrohm, Switzerland) was used as reference electrode in all titrations. The volume of solutions used for measurements was 25 mL (20 mL deionised water and 5 mL corresponding surfactant solution). The concentration of surfactant solutions was 4×10^{-3} M.

The titrations of commercial samples were performed by the same procedure, with pH adjustment to pH 3.

2.7. Interferences

The potentiometric selectivity coefficients for the interfering anion ($c = 1 \times 10^{-2}$ M) were determined by the fixed interference method, as proposed by IUPAC [26].

3. RESULTS AND DISCUSSION

3.1. Membrane lipophilicity

Lipophilicity was calculated using the Java based ALOGPS 2.1 online software with interactive on-line prediction of logP [27], and compared with literature data. The highest lipophilicity value of 10.08 was obtained by the P3, and the lowest, 3.39, by the P4. Other plasticiser lipophilicity values were: P1, 5.80; P2, 7.60; P5, 4.79; and P6, 6.30. Plasticiser lipophilicity is directly linked to the water penetration coefficient and water flux across the membrane [20].

3.2. Response characterisation

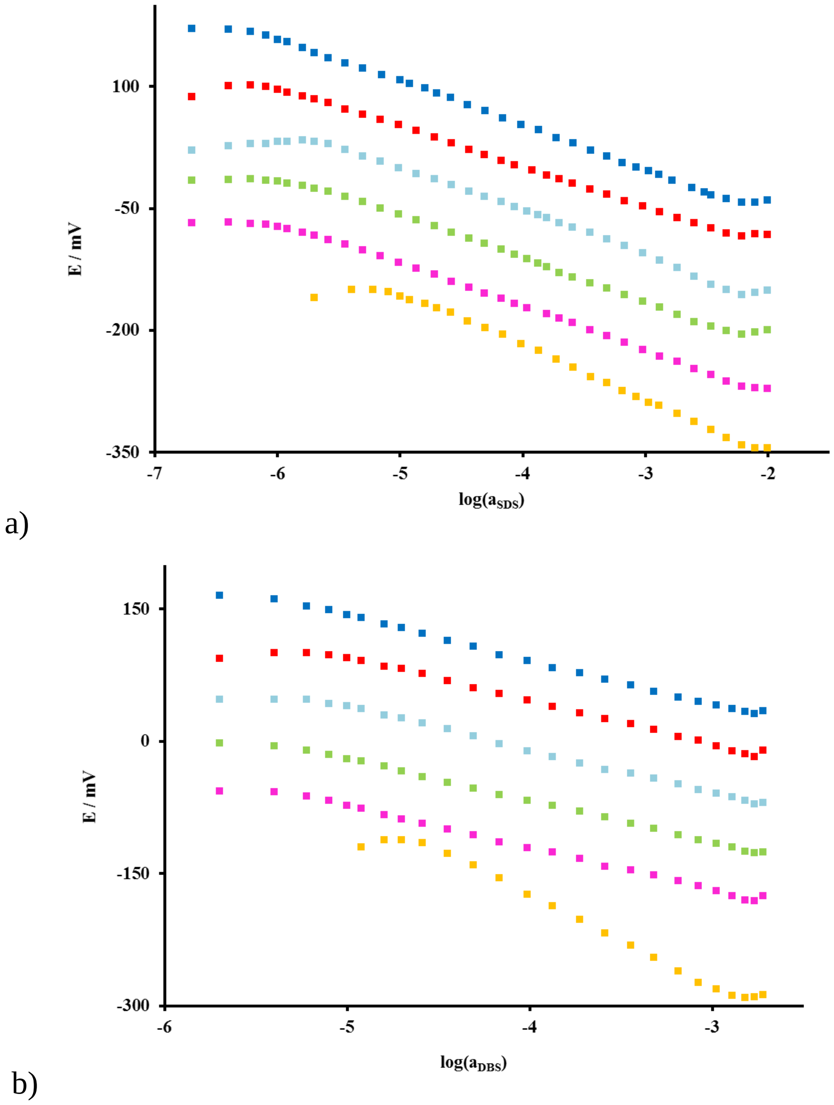


Figure 1. Influence of the six different plasticiser types on the response characteristics of the surfactant DDA-TPB sensor toward anionic surfactants in deionised water: a) SDS and b) DBS. Plasticisers, from top to bottom: 2-nitrophenyl octyl ether (P1), bis(2-ethylhexyl) phthalate (P2), bis (2-ethylhexyl) sebacate (P3), 2-nitrophenyl phenyl ether (P4), dibutyl phthalate (P5) and dibutyl sebacate (P6). The curves have been shifted vertically for clarity.

The influence of plasticiser type on the response characteristics of the DDA-TPB sensor was tested on two anionic surfactants, SDS and DBS (Figure 1), in five independent series for each. Six different plasticisers were tested (P1– P6). SDS and DBS were selected since they are the most frequently and widely used anionic surfactants in commercial product formulations.

3.2.1. Surfactant sensor response to SDS

Table 2 presents a statistical evaluation of the potentiometric responses of the surfactant sensors to SDS in deionised water for the PVC membranes formulation containing six different plasticisers (P1 to P6), given with ± 95% confidence limits. The response curves for all six plasticisers revealed slight distortions at higher SDS concentrations influenced by formation of micelles. The slope and the correlation coefficients values for SDS and DBS were calculated using linear regression analysis. Potentiometric response curves for P1– P5 exhibited a sub-Nernstian slope value ranged from −46.4 to −54.8 (mV/decade of activity), while P6 exhibited a super-Nernstian slope value −66.3 (mV/decade of activity). Correlation coefficients for all six plasticisers were within 0.99, in the useful linear concentration range. Potentiometric response curves for P1 and P2 exhibited the broadest useful concentration range of 6.1×10^{-3} to 5.9×10^{-7} M, while P6 evidenced the narrowest useful linear concentration range, from 6.1×10^{-3} to 9.8×10^{-6} M.

Table 2. Statistics of the response characteristics of surfactant sensor to SDS in deionised water for six different plasticisers: 2-nitrophenyl octylether (P1), bis(2-ethylhexyl) phthalate (P2), bis (2-ethylhexyl) sebacate (P3), 2-nitrophenyl phenyl ether (P4), dibutyl phthalate (P5) and dibutyl sebacate (P6), given together with ± 95 % confidence limits.

Parameters	**PLASTICISER TYPE**					
	P1	**P2**	**P3**	**P4**	**P5**	**P6**
Slope / (mV/decade of activity)	-53.5 ± 0.4	-46.4 ± 0.6	-54.8 ± 1.1	-53.5 ± 0.6	-53.1 ± 0.6	-66.3 ± 1.2
Intercept (mV)	-161.5 ± 2.5	-350.4 ± 5.4	-272.2 ± 5.1	-325.4 ± 3.3	-383.2 ± 1.8	-485.7 ± 5.7
Standard error	1.6	1.8	2.3	1.5	1.9	2.5
Correlation coefficient (R^2)	0.9994	0.9932	0.9969	0.9992	0.9989	0.9983
Detection limit (M)	3.2×10^{-7}	3.2×10^{-7}	1.5×10^{-6}	1.0×10^{-6}	3.9×10^{-7}	5.7×10^{-6}
Useful conc. range (M)	6.1×10^{-3} – 5.9×10^{-7}	6.1×10^{-3} – 5.9×10^{-7}	6.1×10^{-3} – 2.6×10^{-6}	6.1×10^{-3} – 1.9×10^{-6}	6.1×10^{-3} – 7.2×10^{-7}	6.1×10^{-3} – 9.8×10^{-6}

Despite the apparently greater slope value, the sensor containing P6 was eliminated due to its significantly narrower useful linear concentration range. The lowest detection limits were shown by the sensors containing P1 and P2, and amounted to 3.2×10^{-7} M.

3.2.2. Surfactant sensor response to DBS

Table 3 presents a statistical evaluation of the direct potentiometric responses of the surfactant sensors to DBS in deionised water for the PVC membranes formulation containing six different plasticisers (P1 to P6), given together with ± 95 % confidence limits. The response curves for all six plasticisers revealed slight distortions at higher DBS concentrations due to formation of micelles. Potentiometric response curves for P1 – P5 exhibited a sub-Nernstian slope value ranged from −47.3 to −50.6 (mV/decade of activity), while P6 exhibited the highest slope value of −103.3 (mV/decade of activity).

Sensors containing P1 and P4 exibited the broadest useful concentration range of 1.8×10^{-3} to 4.9×10^{-6} M, while P6 showed the narrowest useful linear concentration range, from 1.2×10^{-3} to 3.6×10^{-5} M.

The sensor containing P6, having greatest super-Nernstian slope value, was eliminated due to its considerably narrower useful linear concentration range.

The lowest detection limit was shown by the sensor containing P4, and amounted 3.0×10^{-6} M.

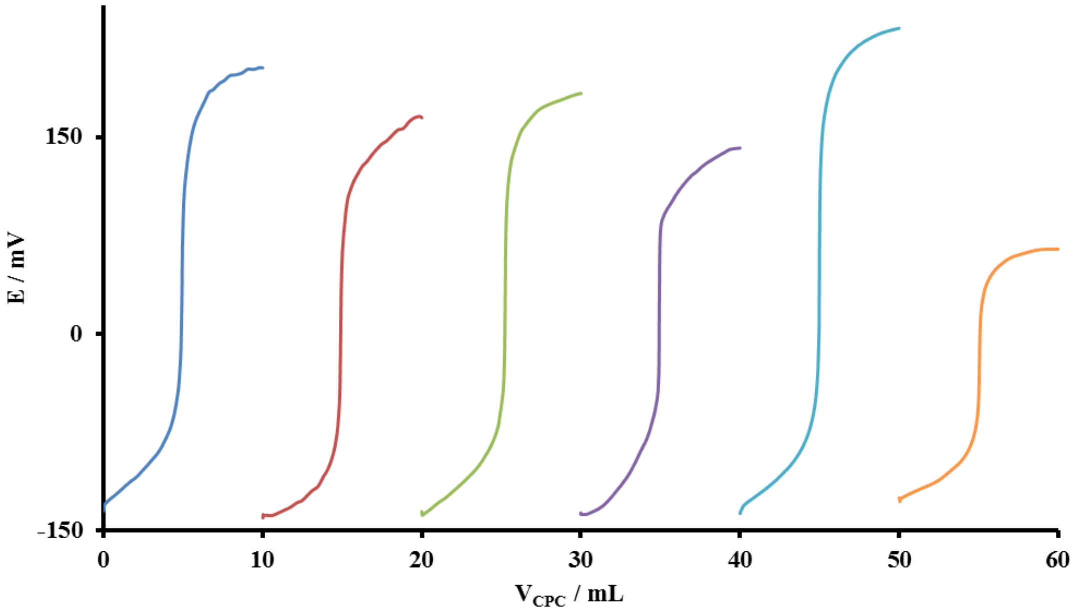
Table 3. Statistics of the response characteristics of surfactant sensor to DBS in deionised water for six different plasticisers: 2-nitrophenyl octyl ether (P1), bis(2-ethylhexyl) phthalate (P2), bis (2-ethylhexyl) sebacate (P3), 2-nitrophenyl phenyl ether (P4), dibutyl phthalate (P5) and dibutyl sebacate (P6); given with ± 95 % confidence limits.

Parameters	**PLASTICISER TYPE**					
	P1	**P2**	**P3**	**P4**	**P5**	**P6**
Slope / (mV/decade of activity)	-50.6 ± 0.7	-49.7 ± 0.2	-48.9 ± 0.8	-47.3 ± 0.5	-48.1 ± 0.6	-103.3 ± 2.2
Intercept (mV)	-110.4 ± 3.5	-153.4 ± 3.4	-205.2 ± 2.1	-256.6 ± 2.3	-312.2 ± 3.8	-587.7 ± 7.7
Standard error	1.2	1.1	1.3	1.1	1.1	2.3
Correlation coefficient (R2)	0.9991	0.9991	0.9988	0.9992	0.9991	0.9986
Detection limit (M)	3.2×10^{-6}	5.9×10^{-6}	3.9×10^{-6}	3.0×10^{-6}	3.9×10^{-6}	2.2×10^{-5}
Useful conc. range (M)	1.8×10^{-3} – 4.9×10^{-6}	1.8×10^{-3} – 9.8×10^{-6}	1.8×10^{-3} – 6.8×10^{-6}	1.8×10^{-3} – 4.9×10^{-6}	1.8×10^{-3} – 6.8×10^{-6}	1.2×10^{-3} – 3.6×10^{-5}

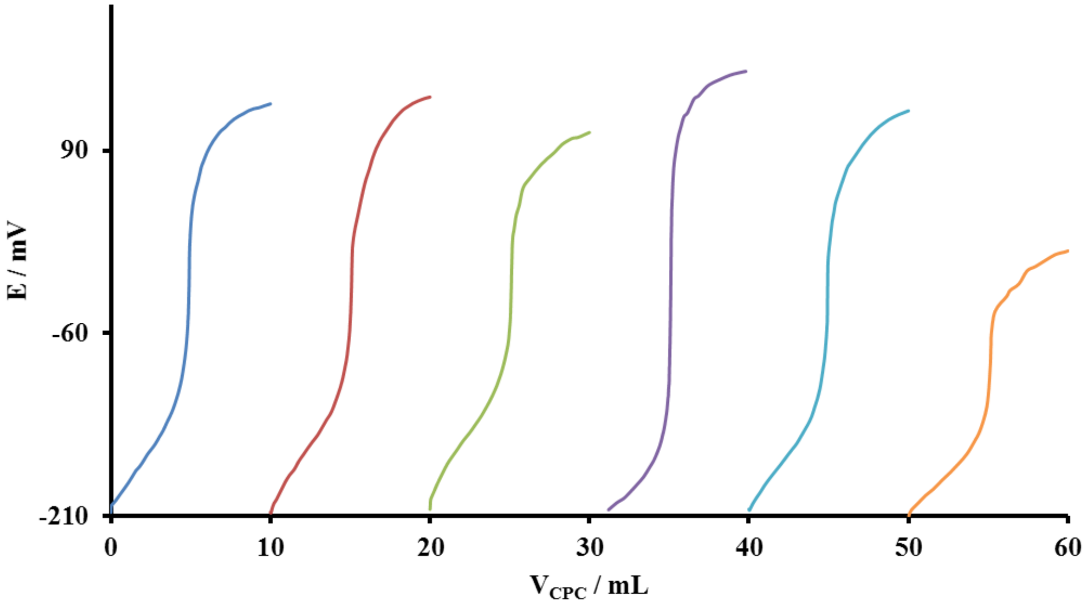
3.3. Titrations

3.3.1. Potentiometric titrations of SDS and DBS

The main applications of the surfactant sensors are end-point indications during surfactant potentiometric titrations. Two anionic surfactants (SDS and DBS) were determined by direct potentiometric titrations with DDA-TPB surfactant sensors containing six different plasticisers. The standard CPC solution (c = 4 × 10^{-3} M) was used for SDS (c = 4 × 10^{-3} M) and DBS (c = 4 × 10^{-3} M) potentiometric titrations. The resulting potentiometric titration curves were presented in Figure 2.



a)



b)

Figure 2. Potentiometric titration curves for a) SDS (c = 4 × 10^{-3} M) and b) DBS (c = 4 × 10^{-3} M) with CPC (c = 4 × 10^{-3} M) obtained by the use of DDA-TPB sensor and six different plasticisers, from left to right: 2-nitrophenyl octyl ether (P1), bis(2-ethylhexyl) phthalate (P2), bis (2-ethylhexyl) sebacate (P3), 2-nitrophenyl phenyl ether (P4), dibutyl phthalate (P5) and dibutyl sebacate (P6).

SDS titrations

The titration curves of SDS ($c = 4 \times 10^{-3}$ M) with CPC ($c = 4 \times 10^{-3}$ M), using DDA-TPB sensors containing six different plasticisers, exhibited well-defined and sharp inflexion points (Fig 2). The titration curve obtained by use of sensor containing P5 exhibited the highest potential jump, up to 359.8 mV, and the use of sensor containing P6 exhibited the lowest potential jump, up to 194.4 mV (Table 4). The highest value of potential change at the end-point was demonstrated by the sensor containing P5. The greatest accuracy of the determination was obtained by using P5 (99.6 %).

Table 4. Titration data and statistics of SDS ($c = 4 \times 10^{-3}$ M) and DBS ($c = 4 \times 10^{-3}$ M) determination with CPC ($c = 4 \times 10^{-3}$ M) using DDA-TPB sensor and six different plasticisers (ΔE/mV represents the difference between the end and the start potential of the titration curve; dE/dV represents the value of first derivative in the end-point of the titration). The statistics were based on five independent measurements.

				PLASTICISER TYPE		
Electrode	**P1**	**P2**	**P3**	**P4**	**P5**	**P6**
				SDS with CPC		
ΔE	343,2 ± 6.3	299,1 ± 8.3	316,58 ± 2.1	277,8 ± 4.3	359,8 ± 2.8	194,4 ± 5.3
dE / dV	67,2 ± 0.7	70,9 ± 0.2	75,7 ± 0.6	60,6 ± 0.5	77,4 ± 0.4	70,9 ± 0.4
Accuracy / %	98.4	97.9	104.8	98.6	99.6	100.9
SD	0,0238	0,0041	0,0068	0,0297	0,0069	0,0161
				DBS with CPC		
ΔE	340,3 ± 5.2	330,9 ± 11.3	326,1 ± 9.2	374,6 ± 4.1	344,1 ± 13.7	221,4 ± 2.1
dE / dV	66,02 ± 0.2	59,36 ± 1.1	69,66 ± 0.2	74,08 ± 0.3	63 ± 2.3	59,03 ± 1.3
Accuracy / %	98.6	102.2	102.3	101.3	99.3	103.7
SD	0,0445	0,0242	0,0089	0,0464	0,0172	0,0223

DBS titration

The titration curves of DBS ($c = 4 \times 10^{-3}$ M) with CPC ($c = 4 \times 10^{-3}$ M) using DDA-TPB sensors containing six different plasticisers, exhibited well-defined and sharp inflexion points (Figure 3). The titration curve obtained by use of sensor containing P4 exhibited the highest potential jump, up to 374.6 mV, and the sensor containing P6 exhibited the lowest potential jump, up to 221.4 mV (Table 4). The greatest accuracy of the determination was obtained by using P5 (99.3 %).

3.4. Plasticiser selection and real sample measurements

3.4.1. Dynamic response measurements

The dynamic response time of the sensor was determined by measuring the time needed for the sensor to attain a stable potential value after an abrupt change (increase) of surfactant concentration.

Figure 3 presents the dynamic response of the selected DDA-TPB sensor containing plasticiser P5. The use of the selected plasticiser demonstrated the best response characteristics (Table 2), and titration parameters (Table 4). Additionally, the price of P5 is much lower than that of the o-NPOE used for surfactant sensor membrane fabrication in our previous investigations [5,28].

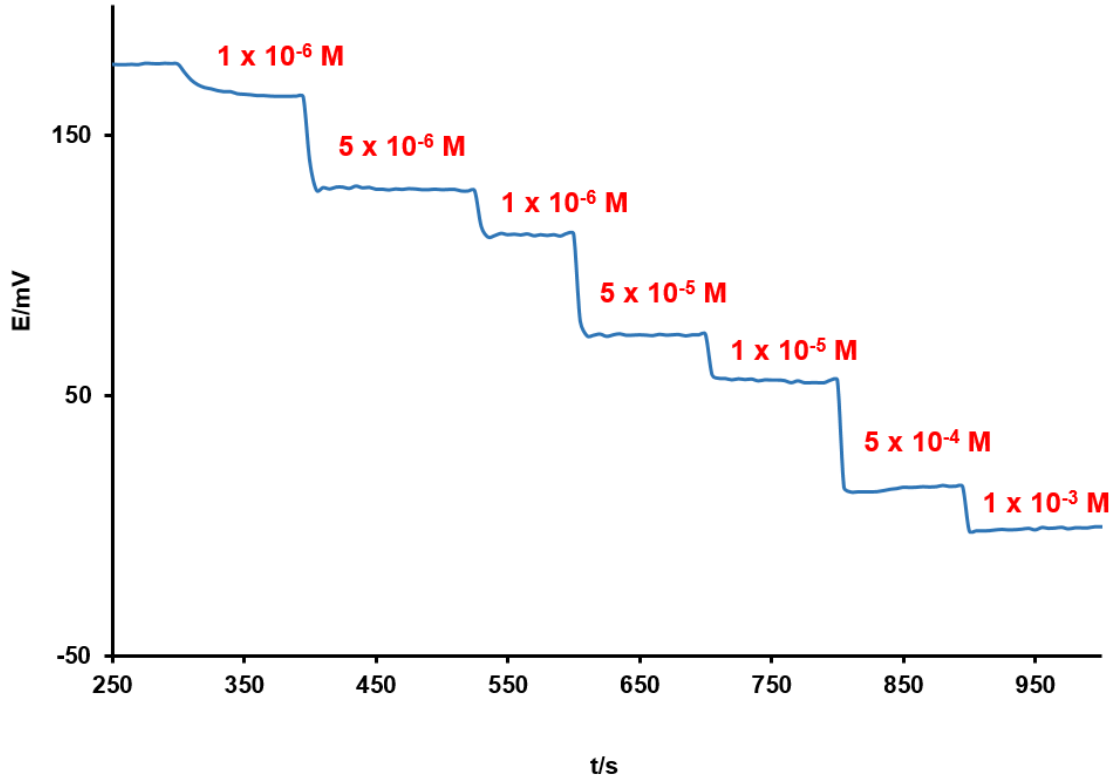


Figure 3. Dynamic response characteristics of the selected DDA-TPB sensor containing plasticiser P5 (dibutyl phthalate) towards SDS.

3.4.2. Interferences

The influence of some interfering anions on the response of the selected DDA-TPB sensor containing plasticiser P5 was defined by the Nikolskii-Eisenman equation:

$$E = E^0_{An^-_{\mathrm{det}}} - \frac{RT}{F} \times \ln\left[a_{An^-_{\mathrm{det}}} + K^{pot}_{An^-_{\mathrm{det}} An^-_{\mathrm{int}}} \cdot a_{An^-_{\mathrm{int}}} \right] \qquad (1)$$

where $K^{pot}_{An^-_{\mathrm{det}} An^-_{\mathrm{int}}}$ = potentiometric selectivity coefficient, $a_{An^-_{\mathrm{det}}}$ is the analyte activity and $a_{An^-_{\mathrm{int}}}$ is the activity of the interfering agent.

Solver (MS Excel) was used to fit the experimental data to the Nikolskii-Eisenman equation, and the fixed interference method was used [26] to determine the potentiometric selectivity coefficient (Table 5).

Table 5. Potentiometric selectivity coefficients for anions used in commercial detergents calculated by the fixed interference method for the selected DDA-TPB sensor containing plasticiser P5 (dibutyl phthalate).

Interference	$\mathbf{K_{ij}^{pot}}$
Acetate	5.2×10^{-5}
Ethylenediaminetetraacetate	9.3×10^{-6}
Citrate	5.8×10^{-6}
Benzoate	4.5×10^{-5}
Toluensulfonate	1.3×10^{-4}
Xylensulfonate	1.8×10^{-4}
Hydrogenphosphate	4.8×10^{-5}
Hydrogencarbonate	4.8×10^{-5}
Nitrate	5.2×10^{-5}
Borate	1.5×10^{-5}
Sulfate	9.3×10^{-6}
Dodecylbenzenesulfonate	3.7×10^{-1}
Hydrogensulfate	4.6×10^{-5}
Carbonate	2.7×10^{-5}
Dihydrogenphosphate	3.1×10^{-5}

3.4.3. Titration of the real samples

Everyday use products in the household detergents, cosmetics, etc.; contain anionic surfactants. The DDA-TPB sensor containing P5 plasticiser was employed as an end-point indicator in potentiometric titration for determination of anionic surfactants in three samples of dishwashing detergents. The standard solution of CPC ($c = 4 \times 10^{-3}$ M) was used as a titrant. A known addition method was employed to check the accuracy and precision of the determination. For known addition method, a standard SDS solution was employed. Table 6 presents the results and statistics for the determination of anionic surfactants in three commercial products. The accuracy of the determination was in the range of 98.2 to 102.4 %.

Table 6. Results of determination of the anionic surfactants in commercial dishwashing detergent sample with the known addition method using SDS. As an end-point indicator, the selected DDA-TPB sensor containing plasticiser P5 was used.

Dishwashing detergent	**Anionic surfactant content / %**	**SDS taken / mol**	**SDS found / mol**	**Recovery / %**
A	8.21	5×10^{-6}	5.07×10^{-6}	101.4
B	13.86	5×10^{-6}	4.91×10^{-6}	98.2
C	9.15	5×10^{-6}	5.12×10^{-6}	102.4

No significant differences were observed (for four independent commercial detergent samples containing anionic surfactants) between the means of both the DDA-TPB sensor containing plasticiser P5 and the PVC liquid membrane surfactant sensor (PLMSS) at the 95% confidence level. A sufficient well agreement was observed for all results (Table 7).

Table 7. The results of potentiometric titrations of anionic surfactants in commercial dishwashing detergent samples using SDS (c = 4 mM) as titrant and a DDA-TPB sensor containing plasticiser P5 as an indicator, in comparison with the results obtained with a PVC liquid membrane surfactant sensor (PLMSS).

Product	**ANIONIC SURFACTANT CONTENT***			
	DDA-TPB sensor with P5		**PLMSS****	
	%	**RSD (%)**	**%**	**RSD (%)**
A	8.21	0.74	8.32	0.69
B	13.86	0.62	13.89	0.75
C	9.15	0.72	9.07	0.85
D	9.25	0.88	9.32	0.91

* average of 5 determinations
** described in ref. [28]

4. CONCLUSION

Six different plasticisers were incorporated into the membrane of a PVC-based surfactant sensors and their response characteristics were investigated. Dimethyldioctadecylammonium-tetraphenylborate (DDA-TPB) was used as an ion pair. Potentiometric response curves using plasticisers 2-nitrophenyl octyl ether (P1) and bis(2-ethylhexyl) phthalate (P2), both used for sodium laurylsulfate (SDS), and P1 and 2-nitrophenyl phenyl ether (P4), both used for dodecylbenzenesulfonate (DBS), exhibited the broadest useful concentration range. Titration curves for SDS and DBS with CPC revealed well defined and sharp inflexion points, whereas sensors using dibutyl phthalate (P5), for SDS and P4, for DBS, exhibited the highest potential jumps. It can be concluded that the PVC membrane containing plasticiser P5 exhibited the best analytical performances and it was used for further characterisation; in addition, its price is much lower than that of commonly used plasticisers. The sensor responded rapidly and it was successfully tested in anionic surfactant determination of commercial dishwashing detergents. No significant influence on potentiometric measurements was observed from anions commonly present in commercial formulations. A satisfactory agreement was observed between the results obtained with the DDA-TPB sensor containing plasticiser P5 and a conventional polymeric PVC liquid membrane surfactant sensor.

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