Int. J. Electrochem. Sci., 6 (**2011**) 240 - 253

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

A New Anionic Surfactant-Sensitive Potentiometric Sensor with a Highly Lipophilic Electroactive Material

Dubravka Madunić-Čačić[1], *Milan Sak-Bosnar*[2,*], *Ružica Matešić-Puač*[2]

[1] Saponia Chemical, Pharmaceutical and Foodstuff Industry, M.Gupca 2, HR-31000 Osijek, Croatia
[2] Department of Chemistry, Josip Juraj Strossmayer University of Osijek, F. Kuhača 20, HR-31000 Osijek, Croatia
[*]E-mail: msbosnar@kemija.unios.hr

Received: 15 December 2010 / *Accepted:* 20 December 2010 / *Published:* 1 January 2011

A hexadecyltrioctadecylammonium-tetraphenylborate (HTA-TPB) ion pair, incorporated into a plasticized PVC membrane as a sensing material, was used for the preparation of a new anionic surfactant sensor. The sensor exhibited a Nernstian response (58.1 mV/decade of activity) between 3×10^{-7} - 3×10^{-3} M for dodecyl sulfate. The interfering effect of several inorganic and organic anions, most frequently used in formulated products, was investigated. The influence of pH on the sensor behavior at potentiometric titrations was also studied. The sensor was used for end-point detection in potentiometric titrations of anionic surfactants. The homologous series of C_7 – C_{12} alkane sulfonates and some commercial detergent products have been successfully titrated. The sensor and analyte parameters were estimated from the derivative curves and by multivariate analysis and the Solver optimization.

Keywords: Ion-sensitive sensor, PVC membrane, anionic surfactant, potentiometric titration, detergent products

1. INTRODUCTION

Synthetic surface-active substances (surfactants) are produced worldwide in large volumes. The total world consumption of surfactants in 2003 was estimated at approximately 9.2 million tons, 4.5 million tons of which was from the consumption of anionic surfactants [1]. The wide application of anionic surfactants in laundry detergents, domestic and industrial cleaning products, cosmetics and personal care products results in the increased pollution of surface waters.

Generally, analytical methods for the quantitative determination of surfactants must be fast, accurate and cost-effective for routine application. The most widely used technique for the industrial control of anionic surfactants of detergents in routine procedures is based on the two-phase titration method [2,3], which suffers from many drawbacks. They are time-consuming, tedious procedures that are not suitable for routine measurements, and they require the use of chloroform, which is restricted for environmental and toxicological reasons. Additionally, the numerous matrix interferences and the limited applications for strongly colored and turbid samples present additional problems.

Although most anionic surfactants in use today are biodegradable, the environmental impact of surfactants as serious pollutants of aquatic systems implies the importance of adequate analytical methods for their determination. The determination of the anionic surfactants in wastewater on the micromolar level is difficult because of the absence of functional groups with highly distinctive characteristics. Despite numerous interferences, the most widely used method for their determination is an extractive spectrophotometric procedure for the determination of methylene blue-active substances (MBAS) with sodium dodecylbenzene sulfonate as the standard [4-6].

Investigations of the potentiometry with surfactant-sensitive electrodes used as sensors for surfactant determination began in the 1970s [7-11]. The simple, rapid and inexpensive method for surfactant determination overcomes most of the limitations of the two-phase titration method and MBAS method.

A certain number of electrodes for anionic surfactants have been described [12-19]. A few excellent articles have reviewed the use of different types of sensors for surfactant analysis [20-24]. Several highly sensitive potentiometric sensors have been investigated also for the determination of anionic surfactants in industrial effluents and wastewater [10, 25-27] and as sensors in wastewater analysis via an automated procedure in a flow-injection analysis (FIA system) [28-30]. In a few investigations, an online solid-phase extraction (SPE) for sample pretreatment (purification and concentration) was included in an FIA system using potentiometry with tubular flow-through surfactant-sensitive electrodes [31-33].

In this paper, the hexadecyltrioctadecylammonium-tetraphenylborate (HTA-TPB) ion-pair as an electroactive material in PVC-plasticized liquid membrane electrode was investigated. This highly sensitive, fast responding sensor was characterized and tested for the potentiometric determination of anionic surfactants in pure anionic surfactants and commercial products.

2. EXPERIMENTAL

2.1. Reagents and Materials

The sensor response characteristics were investigated using sodium dodecyl sulfate (DS). The standard solution (*c* = 4 mM) of Hyamine 1622 (benzethonium chloride, diisobutylphenoxyethoxyethyldimethylbenzylammonium chloride), cetylpyridinium chloride (CPC), 1,3-didecyl-2-methylimidazolium chloride (DMIC), and hexadecyltrimethylammonium bromide (CTAB) were used as titrants. The homologous series of the following reagent-grade alkane sulfonates were used as the analytes: 1-heptane sulfonate, 1-octane sulfonate, 1-nonane sulfonate, 1-decane sulfonate, 1-undecane sulfonate, and 1-dodecane sulfonate (all sodium salts, supplied by Fluka). A few liquid and powdered commercial detergent products were used for the testing of the applicability of the sensor for the determination of anionic surfactant contents. Hexadecyltrioctadecylammonium bromide (HTAB), *o*-nitrophenyloctylether (*o*-NPOE), and high molecular-weight poly(vinyl chloride) (PVC), (all from Fluka, Switzerland) were used for the preparation of the sensor membrane.

2.2. Apparatus and Measurements

The all-purpose titrator 808 Titrando (Metrohm, Switzerland) combined with a Metrohm 806 Exchange unit (Metrohm, Switzerland) and controlled by Tiamo software was used as a dosing element to perform potentiometric titrations. During the titrations and measurements, the solutions were magnetically stirred using a 727 Ti Stand (Metrohm, Switzerland).

The Titronic Basic piston burette combined with Handylab pH12 (both manufactured by Schott Geraete GmbH, Germany) was controlled by a PC and was employed for the measurements of the response characteristics, dynamic response time, and interferences by means of self-programmed software.

2.3. Preparing the PVC-Plasticized Liquid Membrane Electrode

2.3.1. Preparation of the HTA-TPB ion pair and PVC-plasticized liquid mebrane

The HTA-TPB ion pair was prepared by dissolving an equimolar amount of HTAB and sodium tetraphenylborate in 50 mL of dichloromethane. The solution was washed with three portions of water, 50 mL each, and dried with anhydrous sodium sulfate. The solvent was evaporated at room temperature, and the precipitate was dissolved in 10 mL of a mixture of diethylether:methanol (1:1) by use of an ultrasonic bath. The solvent was evaporated at -18°C, and the isolated precipitate was used as a sensing material for the membrane preparation.

The sensor membrane was composed of *o*-NPOE as the plasticizer, high molecular-weight PVC and an isolated HTA-TPB ion pair as the sensing material (1.0%). The tested plasticizer:PVC ratio was 3:2. The mixture of the PVC, plasticizer and sensing material (total of 180 mg) was dissolved in 2 mL of tetrahydrofuran and carefully poured into a glass ring (i.d.=24 mm), which was fixed tightly on a glass plate. After curing, small disks (i.d.=7 mm) were punched from the cast film and used for the sensor preparation.

2.3.2. Sensor Preparation

The membrane was mounted on a Philips electrode body IS-561 (Glasblaeserei Moeller, Zurich, Switzerland). Sodium chloride (c = 1 M) was employed as the internal filling solution. Between measurements, the sensor was kept in deionized water.

The sensor showed a lifetime of longer than four months.A silver/silver (I) chloride electrode (Metrohm, Switzerland) with a potassium chloride solution (c = 2 M) as the reference electrolyte was used as the external reference electrode.

2.4. Emf measurements

The PVC-plasticized liquid-membrane electrode and the external reference electrode were used for all the *Emf* (electromotive force) measurements. The potentiometric measurements were obtained by using the following cell assembly:

Ag/AgCl (KCl, c=2 M) ǁ test solution ǁ membrane | (NaCl, c=1 M) Ag/AgCl

The calibration curve was constructed by plotting the potential *E* versus the logarithm of the DS activity. The potentiometric selectivity coefficients were determined according to the fixed interference method proposed by IUPAC [34] using 0.01 M solutions of the interfering ion. The activity coefficients were calculated according to the Debye-Hückel approximation.

3. RESULTS AND DISCUSSION

3.1. Response Characteristics

The *Emf* of the membrane sensor assembly dipped in the solution of the anionic surfactant (AS) investigated is given by the Nernst equation:

$$E = E^0 - S \times \log a_{\mathrm{An}^-} \tag{1}$$

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

The response characteristics of the HTA-TPB surfactant sensor in solutions of sodium dodecyl sulfate are shown in Figure 1.

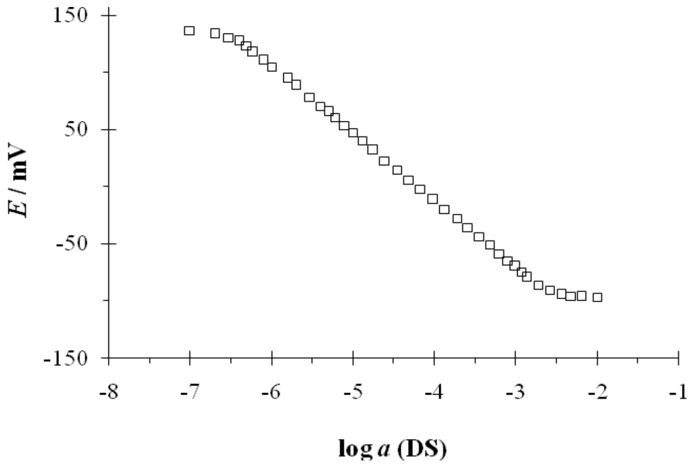

Figure 1. Response characteristics of HTA-TPB - based liquid-membrane surfactant sensitive electrode toward dodecyl sulfate.

The activity coefficients were calculated according to the Davies equation, an extended form of the Debye-Hückel equation. The statistical evaluation of the sensor characteristics, compared to those of the 1,3-didecyl-2-methylimidazolium-tetraphenylborate (DMI-TPB) sensor [18], is given in Table 1.

Table 1. Response characteristics of HTA-TPB liquid membrane surfactant sensitive electrode to dodecyl sulfate, given together with ± 95 % confidence limits.

PARAMETERS	HTA-TPB SENSOR	DMI-TPB SENSOR*
Slope / (mV/decade of activity)	58.12 ± 0.3	59.3± 0.6
Correlation coefficient (R^2)	0.9998	0.9994
Detection limit (M)	2×10^{-7}	6×10^{-7}
Useful conc. range (M)	3×10^{-7} - 3×10^{-3}	8×10^{-7} - 6×10^{-3}

* Data from [18].

The slope values and correlation coefficients were calculated from the linear region of the calibration graph on a series of five measurements, using linear regression analysis. The detection limits were estimated according to the IUPAC recommendations [35].

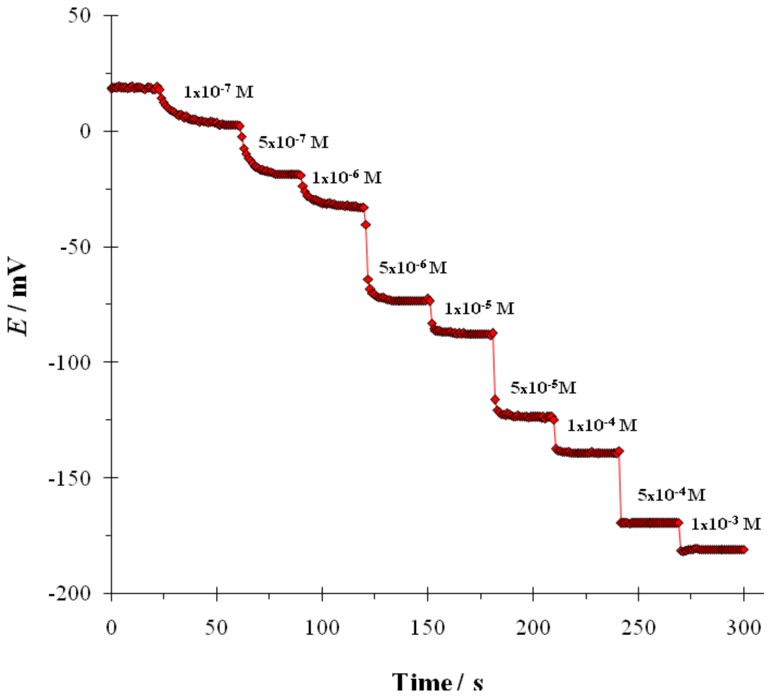

Figure 2. Dynamic response characteristics of HTA-TPB surfactant sensor in dodecyl sulfate solutions.

The investigated sensor showed a Nernstian response (58.1 mV/decade of activity) between 3 x 10^{-7} - 3 x 10^{-3} M for dodecyl sulfate. It is apparent that the sensor exhibits linear responses for dodecyl sulfate even below 10^{-6} M.

The dynamic response of the HTA-TPB surfactant sensor was also evaluated. As shown in Figure 2, the sensor responded in only a few seconds for each ten-fold concentration change in the range of 1 x 10^{-6} M - 1 x 10^{-3} M.

3.2. Potentiometric titration

3.2.1. Titrant selection

The following cationic surfactants have been employed as titrants for the potentiometric titration of anionic surfactants: 1,3-didecyl-2-methylimidazolium chloride (DMIC), Hyamine 1622 (benzethonium chloride, diisobutylphenoxyethoxyethyldimethylbenzyl-ammonium chloride), cetylpyridinium chloride (CPC) and hexadecyltrimethylammonium bromide (CTAB). Their standard solutions (c = 4 mM) were tested for the titration of the sodium dodecyl sulfate solution (c = 4 mM), and the resulting titration curves exhibited sharp inflections (Figure 3).

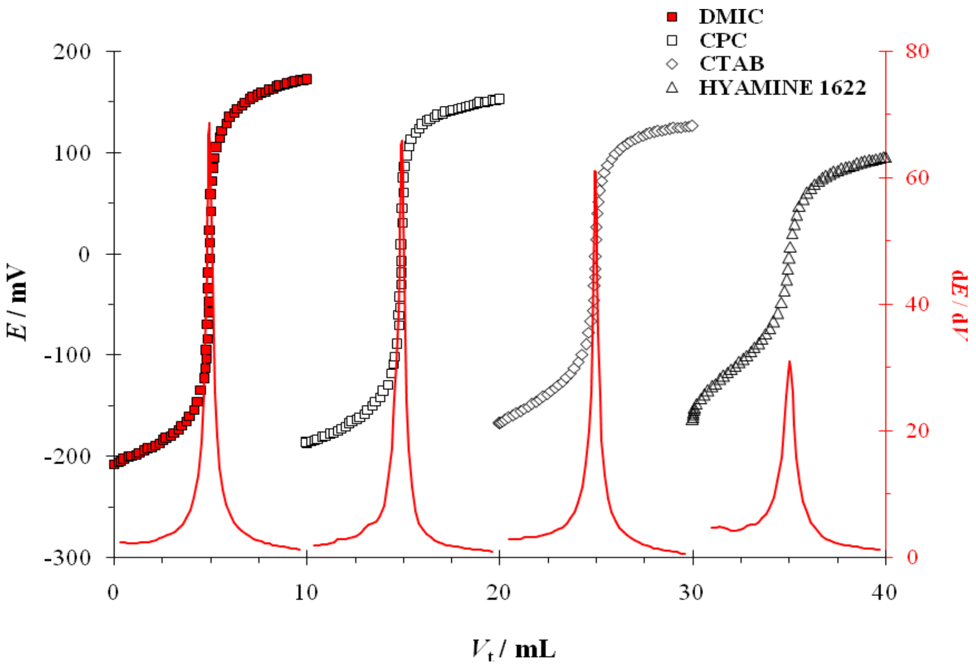

Figure 3. Potentiometric titration of sodium dodecyl sulfate solution (c = 4 mM) with several cationic surfactants using the HTA-TPB surfactant electrode as the indicator.

The magnitudes of the potential jumps at the equivalence points were in the range of 160 mV (CTAB) to 240 mV (DMIC), where DMIC > CPC > CTAB > Hyamine. DMIC revealed superior characteristics, which enabled the titration of micromolar amounts of anionic surfactants, even for those with shorter alkyl hydrophobic chains (C_8 and C_{10}) that are usually heavily titratable with other cationic titrants. Therefore, DMIC was used in further investigations.

3.2.2. Titration of pure anionic surfactants

The sensor described was used as the end-point indicator in ion-pair surfactant potentiometric titrations. The anionic surfactant (An^- = analyte) reacts during the titration with the cationic surfactant (Cat^+ = titrant), forming a water insoluble (1:1) ion-pair, Cat^+An^-, of which the solubility product is defined as shown in Eq. (2):

$$K_{\mathrm{sp}} = a(\mathrm{Cat}^+) \cdot a(\mathrm{An}^-) \tag{2}$$

where $a(\mathrm{Cat}^+)$ and $a(\mathrm{An}^-)$ are the activities of the corresponding surfactant ions.

From Eq. (2), $a(\mathrm{An}^-) = K_{\mathrm{sp}} / a(\mathrm{Cat}^+)$, and after insertion into Eq. (1) and a subsequent rearrangement yields:

$$E = E^{0'} + S \times \log a(\mathrm{Cat}^+) \tag{3}$$

where $E^{0'} = E^0 - S \times \log K_{\mathrm{sp}}$.

Eq. (3) defines the sensor response after the equivalence point (cationic response). It can be seen from Eq. (3) that the magnitude of the inflection at the equivalence point is dependent on the solubility product value. The lower K_{sp} value causes a higher potential change at the equivalence point, resulting in a more sensitive surfactant determination.

A homologous series of the six sodium salts of analytical-grade alkane sulfonates (C_7 - C_{12}) have been titrated potentiometrically using the new HTA-TPB surfactant sensitive electrode as the end-point detector. The surfactant solutions were titrated with a standard solution of DMIC as the titrant. The resulting potentiometric titration curves are shown in Figure 4.

The shorter hydrocarbon chain in the anionic surfactants, due to higher solubility, are usually more difficult to titrate.

The use of the HTA-TPB - based surfactant sensor as an indicator enables the successful potentiometric titration even of those anionic surfactants (e.g., heptane sulfonate, octane sulfonate, nonane sulfonate, and decane sulfonate). The analyte concentration level of all the anionic surfactants investigated was $c = 4 \times 10^{-4}$ M. The titration curves obtained exhibited regular, defined and sharp inflection points with a potential jump of over 200 mV at the equivalence point, except for the smaller hydrocarbon members of the homologous series (C_7 - C_{10}), in which the potential jump was somewhat lower but analytically still usable.

The equivalence points by all the titrations have been calculated from the derivative curves.

The initial *Emf* values of the analyte solutions of homologous series investigated increase with the decline in *lipophilicity* and the number of the carbon atoms in the hydrocarbon chain of the molecular structure.

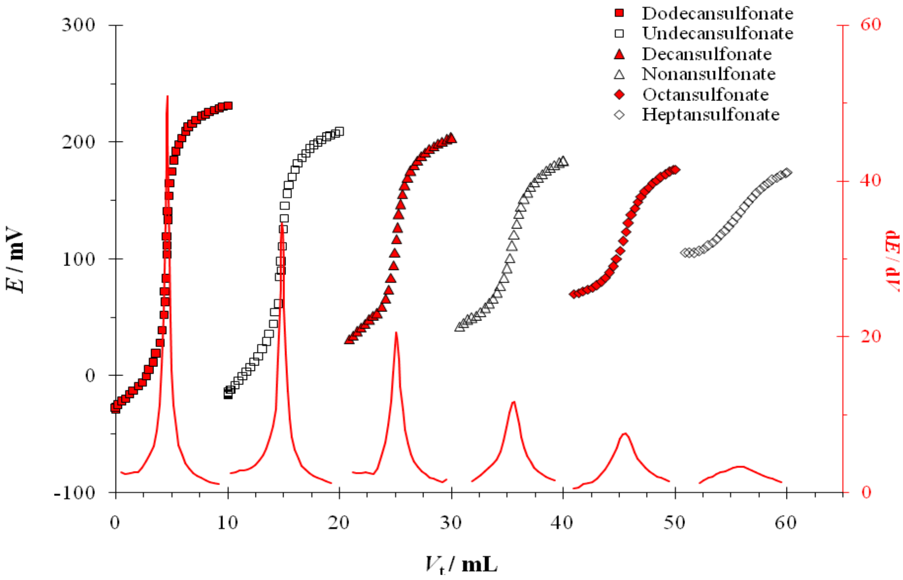

Figure 4. Titration curves and their corresponding first derivatives of a homologous series of alkane sulfonates (C_7 - C_{12}) using the HTA-TPB surfactant sensitive electrode and DMIC (c = 4 mM) as a titrant.

3.2.3. *Titration of commercial products*

Three commercial liquid detergent products with different contents of anionic surfactants have been potentiometrically titrated using the new HTA-TPB sensor as an indicator. The resulting potentiometric titration curves, shown in Figure 5, exhibited strong and well-defined inflections.

The pH values of samples was varied between 8 and 11. No pH or ionic strength adjustment was made.

Additionally, a heavy-duty powder detergent containing polycarboxylate has been potentiometrically titrated using the new HTA-TPB sensor. The two titrations were performed in strong acidic and alkaline solutions (Figure 6). A significant potential jump in the acidic solution corresponded to the anionic surfactant consumption and was used for the anionic surfactant quantification.

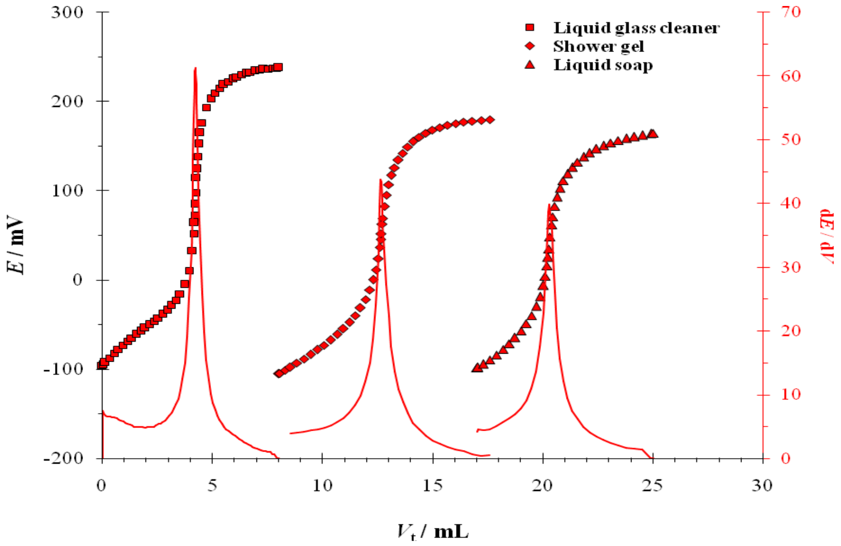

Figure 5. Titration curves of three commercial liquid detergent products containing anionic surfactants, using the HTA-TPB sensor as the end-point indicator and DMIC (c = 4 mM) as a titrant.

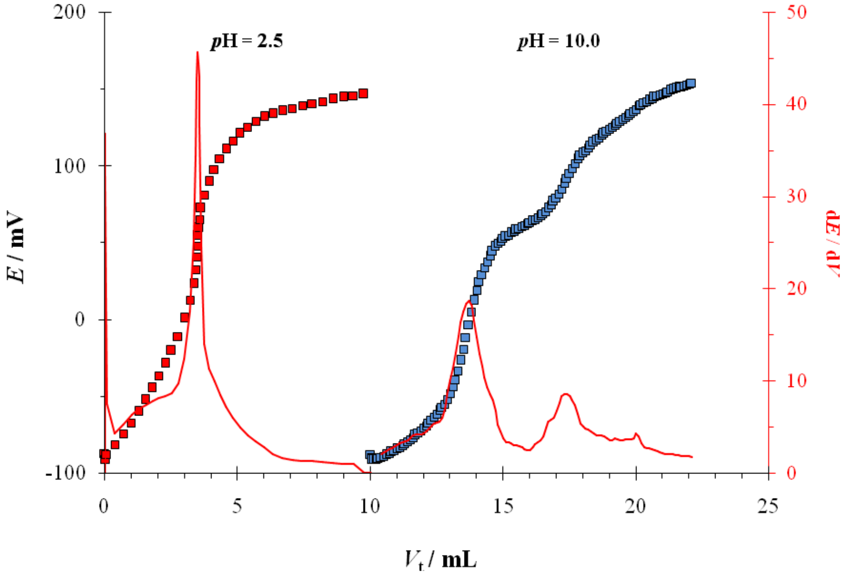

Figure 6. Titration curves of the heavy-duty powder detergent containing polycarboxylate using the HTA-TPB sensor as the end-point indicator and DMIC as a titrant (c = 4 mM).

The results of all the commercial detergent products (Table 2) were compared to those obtained with the commercial surfactant electrode (Metrohm), and the standard two-phase titration method exhibited satisfactory mutual agreement.

Table 2. Results of potentiometric titrations of four commercial products containing anionic surfactants using DMIC (*c* = 4 mM) as a titrant and HTA-TPB surfactant sensor as an indicator, in comparison with the results obtained with commercial potentiometric sensor and standard two-phase titration method (NaDBS – Sodium dodecylbenzensulfonate, NaLS – Sodium lauryl sulfate, NaLES – Sodium laurylether sulfate).

Commercial product	AS	M_r	ANIONIC SURFACTANT CONTENT			
			HTA-TPB sensor*		Commercial sensor	Two-phase titration
			%	RSD (%)	%	%
Heavy duty powder detergent	NaDBS	344	4.87	0.70	4.93	4.75
Liquid glass cleaner	NaLS	297	0.268	0.22	0.280	0.273
Shower gel	NaLES	384	11.29	0.57	11.37	11.25
Liquid soap	NaLES	384	9.22	0.76	9.16	9.36

* average of 5 determinations

3.3. Interferences

3.3.1. The influence of pH

The sensor potential stability has been investigated over a wide pH range, simulating the practical titration conditions of different, more or less acidic or alkaline formulated products. The investigations were performed in solutions of sodium dodecyl sulfate and at two concentration levels: 0.4 mM and 4 mM. The pH values were adjusted with solutions of NaOH and H_2SO_4 (c = 1 M, 0.1 M and 0.01 M, respectively). The surfactant solutions investigated contained 0.1 M Na_2SO_4, providing the measurements a constant ionic strength. The sensor potential readings were maintained within ± 1 mV. There was no significant sensor potential deviations within the pH range of 2 to 11, which enabled the applicability of the sensor in strongly acidic and alkaline conditions (Figure 7).

The shapes of the titration curves and the magnitude of the potential change at the inflection point, at different pH values, additionally supported the above statement (data not shown).

3.3.2. The influence of polycarboxylates

Polycarboxylates were used in low-phosphate and phosphate-free detergents for avoiding incrustation and soil redeposition. Their influence on the potentiometric titration of anionic surfactants has been investigated. For that purpose, Sokalan CP5 (BASF, Germany) maleic acid/acrylic acid copolymer sodium salt was titrated in a modeled solution containing sodium DBS using DMIC (c = 4 mM) as the titrant (Fig. 8). It can be seen that in the strong acidic medium, only DBS was titrated, whereas in alkaline solution, both DBS and polycarboxylate were differentially titrated. The first slightly distorted inflection corresponds to the anionic surfactant titration, whereas the second significantly weaker inflection relates to the carboxylate titration. Hence, the anionic surfactant determination in detergent formulations containing carboxylate should be performed in strong acidic solutions, preventing polycarboxylate dissociation.

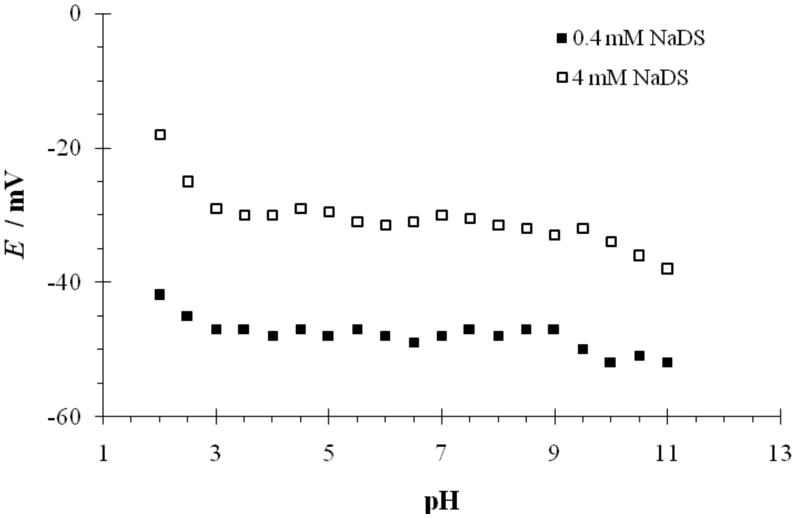

Figure 7. The influence of the pH value on the potentiometric response of the HTA-TPB surfactant electrode in the solutions of dodecyl sulfate.

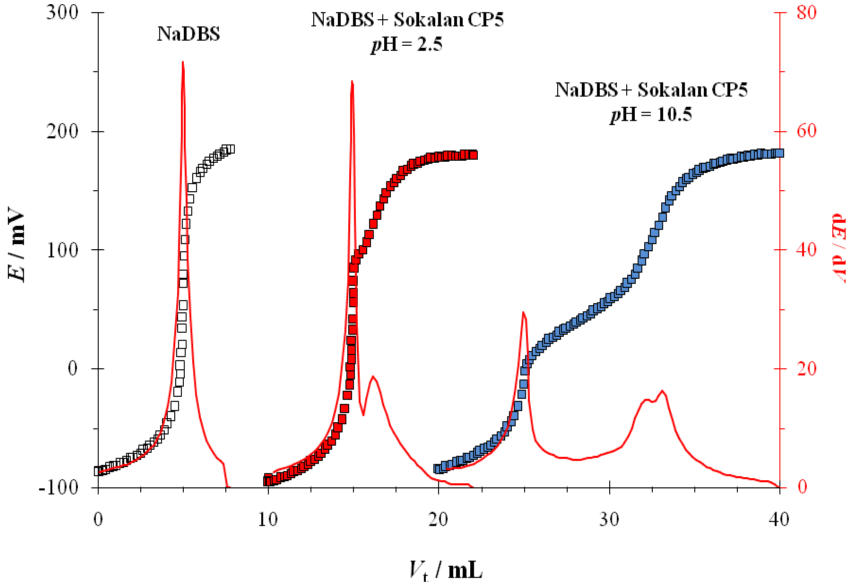

Figure 8. Titration curves and their corresponding first derivatives of a mixture of Sokalan CP5 and sodium DBS at different pH values using the HTA-TPB surfactant-sensitive electrode and DMIC (c = 4 mM) as a titrant. The titration of pure DBS was used as a reference.

3.3.3. Determination of selectivity coefficients

The influence of the interferents on the response of the surfactant sensors described is defined by the Nikolskii-Eisenman equation:

$$E = E^0_{\mathrm{An}^-_{\mathrm{det}}} - \frac{RT}{F} \times \ln\left[a_{\mathrm{An}^-_{\mathrm{det}}} + K^{\mathrm{pot}}_{\mathrm{An}^-_{\mathrm{det}}\mathrm{An}^-_{\mathrm{int}}} \cdot a_{\mathrm{An}^-_{\mathrm{int}}} \right] \qquad (4)$$

where $K^{\mathrm{pot}}_{\mathrm{An}^-_{\mathrm{det}}\mathrm{An}^-_{\mathrm{int}}}$ = selectivity coefficient, $a_{\mathrm{An}^-_{\mathrm{det}}}$ and $a_{\mathrm{An}^-_{\mathrm{int}}}$ are the activities of analyte ion (det) and interfering ion (int), respectively.

The mixed-solution method [36] has been used for the measurement of the selectivity coefficients. The sensor response has been measured in a series of solutions of varying primary (determined) ion activity $a_{\mathrm{An}^-_{\mathrm{det}}}$ and fixed interfering ion activity $a_{\mathrm{An}^-_{\mathrm{int}}}$. The selectivity coefficients are then estimated graphically, but more a reliable method involves fitting the Nikolskii-Eisenman equation (used as a model) to the experimental data obtained by the mixed-solution method. By using *Solver*, an analysis tool incorporated into Microsoft Excel, the minimal sum of the squared residuals was calculated by varying the values of E^0, S and $K^{\mathrm{pot}}_{\mathrm{An}^-_{\mathrm{det}}\mathrm{An}^-_{\mathrm{int}}}$.

Table 3. Potentiometric selectivity coefficients for different inorganic and organic anions used in commercial formulated products measured with HTA-TPB surfactant sensor. Dodecyl sulfate was used as the primary (analyte) ion, concentration of the interfering anion was c = 10 mM.

Interference, *X*	$K^{\mathrm{pot}}_{\mathrm{DS},X}$
Carbonate	3.98×10^{-5}
Hydrogencarbonate	3.84×10^{-4}
Nitrate	1.74×10^{-4}
Nitrite	2.90×10^{-5}
Sulfate	1.24×10^{-5}
Hydrogensulfate	9.22×10^{-6}
Borate	3.19×10^{-5}
Dihydrogenphosphate	1.40×10^{-4}
Chloride	9.94×10^{-5}
Acetate	1.84×10^{-4}
Benzoate	1.14×10^{-4}
EDTA	2.98×10^{-4}
Toluensulfonate	9.70×10^{-5}
Xylensulfonate	2.24×10^{-4}
Citrate	1.21×10^{-4}
Amidosulfonate	4.88×10^{-5}
Dodecylbenzen sulfonate	8.22×10^{-1}

The selectivity coefficients of some potentially interfering products, inorganic and organic anions that are typically present, were determined for the HTA-TPB ion pair-based sensor (Table 3). In all the selectivity measurements, dodecyl sulfate was used as the primary ion in the range of 10 µM to 10 mM, whereas the concentration of the interfering ion was 10 mM.

The new HTA-TPB - based sensor exhibits excellent selectivity performances for DS over almost all the organic and inorganic anions investigated. Toluene sulfonate and xylene sulfonate do not interfere, whereas dodecylbenzene sulfonate and other surfactant anions, as expected, interfere strongly.

4. CONCLUSIONS

A new liquid-membrane anionic surfactant-sensitive sensor based on a highly lipophilic hexadecyltrioctadecylammonium tetraphenylborate as a sensing material was prepared and incorporated into a plasticized PVC membrane. The sensor exhibited a Nernstian response (58.1 mV/decade of activity) between 3×10^{-7} - 3×10^{-3} M for dodecyl sulfate. The sensor responded in only a few seconds for each ten-fold concentration change in the range of 1×10^{-6} M - 1×10^{-3} M. The sensor described was used as the end-point detector in the ionic surfactant potentiometric titrations by using DMIC as the titrant. The sensor also enabled the titration of shorter hydrocarbon chain (C_7 - C_{10}) anionic surfactants, which are usually hardly titratable by other methods. A few liquid and powdered commercial detergents of various formulation complexity were also tested. The results were compared to those obtained with the commercial surfactant electrode and with the standard two-phase titration method, and they exhibited satisfactory mutual agreement. The resulting potentiometric titration curves revealed clearly defined inflection points in all the investigations, enabling the reliable equivalence point detection using the first derivative method. The sensor showed satisfactory analytical performances within a pH range of 2 to 11. The selectivity coefficients were determined by fitting the Nikolskii-Eisenman equation to the experimental data obtained by the mixed-solution method. The sensor exhibits excellent selectivity performances for DS over almost all the organic and inorganic anions investigated.

ACKNOWLEDGEMENT
This study is based on the work financed by the Croatian Science Foundation and Saponia Chemical, Pharmaceutical and Foodstuff Industry, Osijek.

References

1. B. Brackmann and C. D. Hager, CD Proceedings, 6th World Surfactant Congres CESIO, Berlin,Germany, 2004.
2. URL:http://www.firp.ula.ve/archivos/material_web_4xx/04_CESIO_Brackmann_112.pdf
3. S. R. Epton, *Trans. Faraday Soc.* 44 (1948) 226.
4. ISO 2271:1989 Surface active agents - Detergents - Determination of anionic-active matter by manual or mechanical direct two-phase titration procedure, International Organization for Standardization, Geneva, Switzerland.

5. D. C. Abbott, *Analyst*, 87 (1962) 286.
6. ISO 7875-1:1996 Water quality - Determination of surfactants - Part 1: Determination of anionic surfactants by measurement of the methylene blue index (MBAS) International Organization for Standardization, Geneva, Switzerland.
7. ISO 16265:2009 Water quality - Determination of the methylene blue active substances (MBAS) index - Method using continuous flow analysis (CFA), International Organization for Standardization, Geneva, Switzerland.
8. T. C. Gavach and C. Bertrand, *Anal. Chim. Acta*, 55 (1971) 385.
9. H. James, G. Carmack and H. Freiser, *Anal. Chem.*, 44 (1972) 856.
10. B. J. Birch and D. E. Clarke, *Anal. Chim. Acta*, 67 (1973) 387.
11. T. Fujinaga, S. Okazaki and H. Freiser, *Anal. Chem.*, 46 (1974) 1842.
12. N. Ciocan and D. F. Anghel, *Anal. Lett.*, 9 (1976) 705.
13. J. Baró-Romà, J. Sánchez, M. del Valle, J. Alonso and J. Bartrolí, *Sens. Actuat. B*, 15 (1993) 179.
14. M. Gerlache, Z. Senturk, J. C. Vire and J. M. Kauffmann, *Anal. Chim. Acta*, 349 (1997) 59.
15. J. Sanchez and M. del Valle, *Electroanalysis*, 13 (2001) 471.
16. R. Matesic-Puac, M. Sak-Bosnar, M. Bilic and B. S. Grabaric, *Sens. Actuat. B*, 106 (2005) 221.
17. I. Varga, R. Meszaros, Z. Szakacs and T. Gilanyi, *Langmuir*, 21 (2005) 6154.
18. J. Segui, J. Lizondo-Sabater , A. Benito, R. Martinez-Manez, T. Pardo, F. Sancenona and J. Soto, *Talanta*, 71 (2007) 333.
19. D. Madunić-Čačić, M. Sak-Bosnar, R. Matešić-Puač and Z. Grabarić, Sensor Lett., 6 (2008) 339.
20. J. Lizondo-Sabater, R. Martinez-Manez, F. Sancenon, M. J. Segu and J. Soto, *Talanta*, 75 (2008) 317.
21. B. J. Birch and R. N. Cockcroft, *Ion Sel. Electrode Rev.*, 4 (1981) 1.
22. K. Vytras, *Ion Sel. Electrode Rev.*, 7 (1985) 77.
23. N. Buschmann and R. Schultz, *Jorn. Com. Esp. Deterg.*, 23 (1992) 323.
24. M. Gerlache, J. M. Kauffmann, G. Quarin, J. C. Vire, G. A. Bryant and J. M. Talbot, *Talanta*, 43 (1996) 507.
25. J. Sanchez and M. del Valle, *Crit. Rev. Anal. Chem.*, 35 (2005) 15.
26. Lj. Zelenka, M. Sak-Bosnar , N. Marek and B. Kovacs, *Anal. Lett.*, 22 (1989) 2791.
27. M. Sak-Bosnar , R. Matesic-Puac, D. Madunic-Cacic and Z. Grabaric, *Tenside Surf. Det.*, 43 (2006) 82.
28. D. Madunić- Čačić, M. Sak-Bosnar, M. Samardžić and Z. Grabarić, *Sensor Lett.*, 7 (2009) 50.
29. G. A. Alvarez-Romero, A. Morales-Perez, A. Rojas-Hernandez, M. Palomar-Pardave and M. T.Ramirez-Silva, *Electroanalysis*, 16 (2004) 1236.
30. S. S. M. Hassan, I. H. A. Badr and H. S. M. Abd-Rabboh, *Microchim. Acta*, 144 (2004) 263.
31. M. Cortina, C. Ecker, D. Calvo and M. del Valle, *J. Pharmaceut. Biomed.*, 46 (2008) 213.
32. J. Alonso, J. Baró, J. Bartrolí, J. Sànchez and M. del Valle, *Anal. Chim. Acta*, 308 (1995) 115.
33. S. Martinez-Barrachina, J. Alonso, L. Matia, R. Prats and M. del Valle, *Anal. Chem.*, 71 (1999) 3684.
34. S. Martinez-Barrachina and M. del Valle, *Microchem. J.*, 83 (2006) 48.
35. Y. Umezawa, P. Bühlmann, K. Umezawa, K. Tohda and S. Amemiya, *Pure Appl. Chem.*, 72 (2000) 1851.
36. G. G. Guilbault, R. A. Durst, M. S. Frant, H. Freiser , E. H. Hansen,T. S. Light, E. Pungor , G.Rechnitz, N. M. Rice, J. J. Rohm, W. Simon and J. D. R.Thomas, *Pure Appl. Chem.*, 48 (1976) 127.
37. S. H. Hoke, A. G. Collins and C. A. Reynolds, *Anal. Chem.*, 51 (1979) 85