NEW POTENTIOMETRIC SURFACTANT SENSOR FOR ANIONIC SURFACTANTS DETERMINATION IN REAL SYSTEMS CONTAINING AMPHOTERIC SURFACTANTS

Nikola SAKAČ[1], Dubravka MADUNIĆ-ČAČIĆ[2], Dean MARKOVIĆ[3] and Marija JOZANOVIĆ[4]

[1]**FACULTY OF GEOTECHNICAL ENGINEERING**, University of Zagreb, 42000 Varaždin, Croatia; nsakac@gfv.unizg.hr
[2]**SAPONIA**, Chemical, Pharmaceutical and Foodstuff Industry, Inc., 31000 Osijek, Croatia; dubravka.madunic-cacic@saponia.hr
DEPARTMENT OF BIOTECHNOLOGY, University of Rijeka, 51000 Rijeka, Croatia
[4]**DEPARTMENT OF CHEMISTRY**, Josip Juraj Strossmayer University of Osijek, 31000 Osijek, Croatia

Potentiometric sensor based on 1,3-dihexadecyl-1*H*-benzo[d]imidazol-3-ium-tetraphenylborate sensor used as ionophore (DHBI-TPB sensor) was used for anionic surfactants determination in real systems containing amphotheric surfactants. Potentiometric response measurements showed excellent response characteristics with a Nernstian slope in the linear response region for investigated surfactants. The sensor showed high stability, reproducibility and long-lifetime.

Recently DHBI-TPB sensor was used for the detection of cationic surfactants in personal care products and disinfectants[1]. In this paper we investigated performances of proposed DHBI-TPB surfactant sensor for anionic surfactants determination in model solutions and in detergents and household care product. Some of them contained amphoteric surfactants betaine or amine oxide. These determinations were performed with prior pH adjustment and showed excellent performances and good recoveries (Madunić-Čačić et al., 2011).

EXPERIMENTAL

Reagents and materials

Potentiometric sensor based on 1,3-dihexadecyl-1*H*-benzo[d]imidazol-3-ium - tetraphenylborate sensor as ionophore (DHBI-TPB sensor) was used for anionic surfactants determination in real systems containing amphotheric surfactants.

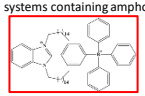

Figure 1. 1,3-dihexadecyl-1H-benzo[d]imidazol-3-ium tetraphenylborate (DHBI–TPB ion-pair)

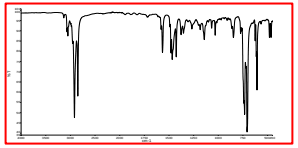

Figure 2. ATR - FT-IR spectrum of the 1,3-dihexadecyl–1H-benzo[d]imidazol–3-ium tetraphenylborate, newly synthesized ion-pair used as ionophore for the ionic surfactant ion-selective electode (DHBI-TPB sensor).

Analytical grade :

o-nitrophenyloctylether (*o*-NPOE), high molecular-weight PVC (Selectophore™ quality; Fluka, Switzerland), and newly sintesised ion-par DHBI-TPB were used for the preparation of the sensor membrane.

1,3-didecyl-2-methylimidazolium chloride (DMIC; TegoTRANT, Mr=399,1; Metrohm, Switzerland), Hyamine 1622 (M_r=448,08; Sigma-Aldrich, Switzerland), Cetylpyridinium chloride (CPC, M_r=358,07; Merck, Germany) and Hexadecyltrimethylammonium bromide (CTAB, M_r=364,45; Sigma-Aldrich, Sigma-Aldrich, Switzerland) were used in titrant selection titrations (**Figure 3**).

Technical grade: sodium dodecyl sulphate (Na DDS; Empicol LX 28/Z, M_r=296; Huntsman, Holland), sodium alkylbenzene sulphonate (Na ABS; Nansa HS 85 S, M_r=344; Huntsman, Holland), sodium lauryl ether sulphate, (Na LES, M_r=384; Empicol ESB 70, Huntsman, Holland) and sodium secondary alkane sulphonate (Na SAS, M_r=328; Hostapur SAS 60; Clariant, Germany) were used for accuracy and precision determination.

Apparatus and measurements

- The all-purpose titrator 808 Titrando (Metrohm, Switzerland)
- Metrohm 806 Exchange unit (Metrohm, Switzerland)
- Tiamo software was used for the titrator control
- Magnetic stirrer 727 Ti Stand (Metrohm, Switzerland).
- A silver/silver (I) chloride reference electrode (Metrohm, Switzerland), reference electrolyte sodium chloride solution (*c* = 2 mol/l), was used as one reference.

RESULTS AND DISCUSSION

Table 1
Calculated response characteristics of DHBI-TPB surfactant sensor to anionic surfactants SDS and DBS measured in H_2O and Na_2SO_4, at wide concentration range, with mean values at ± 95% confidence limits.

PARAMETERS	ANIONIC SURFACTANT			
	SDS		DBS	
	in H_2O	in SO_4^{2-}	in H_2O	in SO_4^{2-}
Slope (mV/decade)	60,1 ± 0,5	59,7 ± 0,4	58,4 ± 0,6	58,7 ± 0,5
Correlation coefficient (R^2)	0,9993	0,9994	0,9995	0;9995
Limit of detection (M)	$3,2 \times 10^{-7}$	$2,6 \times 10^{-7}$	$6,1 \times 10^{-7}$	$5,9 \times 10^{-7}$
Useful linear concentration range (M)	$4,6 \times 10^{-7}$ to $5,1 \times 10^{-3}$	$3,9 \times 10^{-7}$ to $5,1 \times 10^{-3}$	$8,9 \times 10^{-7}$ to $4,1 \times 10^{-3}$	$8,8 \times 10^{-7}$ to $4,1 \times 10^{-3}$

Table2
Potentiometric titration results of some technical grade anionic surfactants with DMIC (*c*=4 mM) as a titrant and the DHBI-TPB surfactant sensor as an end-point indicator.

TECHNICAL GRADE ANIONIC SURFACTANT	w (surfactant)* %	n (added) µmol	n (found)** µmol	Recovery %	RSD %
Dodecyl sulfate	92,51 ± 0,54	30	30,12 ± 0,07	100,4	0,22
Alkyl benzene sulfonate	47,73 ± 0,21	30	30,22 ± 0,05	101,0	0,31
Lauryl ether sulfate	27,12 ± 0,09	30	29,85 ± 0,11	99,5	0,54
Secondary alkane sulfonate	67,41 ± 0,48	30	30,38 ± 0,11	101,3	0,76

* Average on 5 determinations
** Average on 3 determinations

Table 3
Results for potentiometric titration of commercial products containing anionic surfactants compared with results obtained with two-phase titration method*.

COMMERCIAL PRODUCTS	Sample No.	ANIONIC SURFACTANT (%)		
		DHBI-TPB sensor*	Two-phase titration**	Recovery (%)
Liquid detergents Without amphoteric surfactants	1	15,6 ± 0,09	15,35	101,5
	2	10,52 ± 0,15	10,48	101,5
	3	8,65 ± 0,06	8,73	100,8
Liquid detergents containing *Cocoamidopropyl Betaine* as amphotric surfactant	1	12,7 ± 0,15	11,05	87,0
	2	9,24 ± 0,37	8,17	88,4
	3	6,22 ± 0,22	5,75	92,4
Liquid detergents containing Amine Oxide as amphotric surfactant	1	18,55 ± 0,59	13,95	75,2
	2	12,75 ± 0,61	9,27	72,7
	3	15,42 ± 0,25	12,73	82,6

* Average on 3 determinations
** ISO 2271:1989 Surface active agents — Detergents — Determination of anionic-active matter by manual or mechanical direct two-phase titration procedure (Referece method)

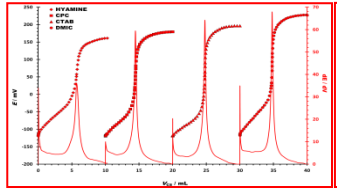

Figure 3. Potentiometric titration curves for titrations of NaDDS with four different cationic surfactants used as a titrant (*c*= 4 mM) and DHBI-TPB sensor for end-point detection.

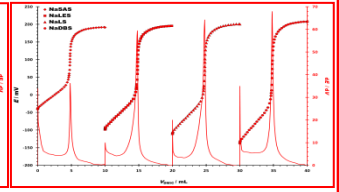

Figure 4. Titration curves of four technical grade anionic surfactants with DMIC as a titrant (*c*= 4 mM) and DHBI-TPB sensor for end point detection.

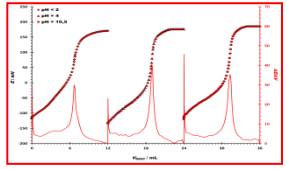

Figure 5. Titration curves of commercial liquid detergent containing anionic surfactant NaLES and amphoteric surfactant *Cocoamidopropyl Betaine*, using DMIC as a titrant (*c*=4 mM) and DHBI-TPB surfactant sensor for end-point detection.

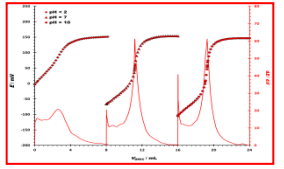

Figure 6. Titration curves of commercial liquid detergent containing anionic surfactant NaLES and amphoteric surfactant *Amine Oxide*, using DMIC as a titrant (*c*=4 mM) and DHBI-TPB surfactant sensor for end-point detection.

DHBI-TPB surfactant sensor with 1,3-dihexadecyl-1*H*-benzo[d]imidazol-3-ium-tetraphenylborate as an electroactive material in PVC-plasticized liquid membrane electrode was used in all here presented investigations.
Response characteristics of the sensor are given in **Table 1**. The slope values and correlation coefficients were calculated from the linear region of the calibration graph using linear regression analysis. The detection limits were estimated according to the IUPAC recommendations[2]
Accuracy and precission of the sensor were tested on dodecyl sulfate, dodecyl alkyl benzene sulfonate, lauril ether sulfate and secondary alkane sulfonate, all sodium salts. Results and titration curves are presented in **Table 3** and **Figure 4**.
Cocoamydopropyl betaine exhibit properties of cationic surfactants at low pH, and anionic surfactants at high pH values. Therefore, the exact titrimetric determination of anionic surfactants in the presence of betaine is strongly pH dependent and should be performed at pH 4 (izoelectric point). The same situation is with *Amin-oxide* with only difference in pH value izoelectric point (pH 7).

References

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