A NEW HIGH SENSITIVE POTENTIOMETRIC SENSOR FOR ANIONIC SURFACTANTS

R. Matešić-Puač[1], M. Sak-Bosnar[2], D. Madunić-Čačić[3], Z. Grabarić[4]

[1] Faculty of Food Technology, Josip Juraj Strossmayer University of Osijek,F. Kuhača 18, HR-31000 Osijek, Croatia
[2] Department of Chemistry, Josip Juraj Strossmayer University of Osijek, F. Kuhača 20, HR-31000 Osijek, Croatia
[3] Saponia Chemical, Pharmaceutical and Foodstuff Industry, M.Gupca 2, HR-31000 Osijek, Croatia
[4] Faculty of Food Technology and Biotechnology, University of Zagreb, Pierottijeva 6, HR-10000 Zagreb, Croatia

ABSTRACT

A new anionic surfactant sensor has been prepared, based on 1,3-didecyl-2-methyl-imidazolium-tetraphenylborate ion-exchange complex as sensing material incorporated into the plasticized PVC-membrane. The sensor exhibited Nernstian response (59.0 mV/decade) in the region between 2-10000 μmol/dm^3 for dodecylsulfate and 61.6 mV/decade between 1-2000 μmol/dm^3 for dodecylbenzen-sulfonate. The main application of the sensor described was indication of the end-point in ion-pair surfactant potentiometric titrations. The electrode showed satisfactory analytical performances within pH range 2.5 - 11. The potentiometric selectivity coefficients were determined by fixed interferent method. The sensor was also applied for potentiometric titration of some two-components mixtures.

INTRODUCTION

Synthetic surface-active substances (surfactants) (SAS) are produced worldwide in large amounts. The total world consumption was over 10 million tonnes in 2000 [1]. Surfactants as environmental pollutants are present in various materials, including natural and waste waters, process solutions of industrial enterprises, household consumer products, etc. Anionic surfactants (AS) account for about 50 % of surfactants use in Europe and about 60 % in United States.

Nowadays, SAS are determined by spectroscopic, chromatographic, and electrochemical methods, as well as by the methods based on measuring their colloidal and physical properties [2-4].

The most widely used technique in surfactant analysis is the so-called two-phase titration method, but this technique suffers from large number of drawbacks [5].

The potentiometry with selective electrodes (sensors) is a promising, simple, rapid available and inexpensive method for determining surfactants [6-11]. The electrode may be sensitive to the analyte or to the titrant. Basically, these electrodes have the same design : the electroactive part of an ISE membrane consists of an ion-pair (C^+A^-), where A^- is anion of an anionic surfactant (AS) and C^+ is positively charged counter ion, usually a cation of a cationic surfactant (CS). This kind of ISE is suitable for the detection of A^- and C^+.

In this paper a PVC plasticized liquid type anionic surfactant sensitive membrane has been prepared based on 1,3-didecyl-2-methylimidazolium-tetraphenylborate (TG-TPB) as sensing ion-pair element and o-nitrophenyloctylether (*o*-NPOE) as plasticizer. The sensor was applied for potentiometric determination of single pure and technical grade anionic surfactants and for some two-components mixtures.

EXPERIMENTAL

Electrode preparation

The electrode membrane was of the following composition: o-nitrophenyloctylether (o-NPOE) as plasticizer (66 %), PVC of high molecular mass (33 %) and 1,3-didecyl-2-methylimidazolium-tetraphenylborate (TG-TPB) ion-exchange complex as sensing material (1 %). The membrane was mounted in Philips electrode body IS-561 (Glasblaeserei Moeller, Zurich, Switzerland). Sodium dodecylsulfate solution ($c = 1x10^{-3}$ mol dm^{-3}) was employed as internal filling solution. Between measurements, the electrode was kept in distilled water. The lifetime of the electrode was several months in pure surfactant solutions, but decreased in more complex solutions. A silver/silver (I) chloride reference electrode (Metrohm, Switzerland), reference electrolyte c(KCl) = 3 mol dm^{-3} was used as reference one.

Reagents and solutions

The sodium dodecylsulfate and sodium dodecylbenzensulfonate were used for electrode response characteristics measurements and for potentiometric titration. The standard solutions of cetylpyridinium chloride (CPC), c = 4 mmol/dm^3 and 1,3-didecyl-2-methylimidazolium chloride (DDMICl), c = 2 mmol/dm^3 were used as titrants.

Apparatus

The 751 GPD Titrino and 794 Basic Titrino (Metrohm, Switzerland), the all-purpose titrators combined with Metrohm 806 Exchange units (Metrohm, Switzerland) as dosing element were used for performing of the potentiometric titrations. The solutions during titrations were magnetically stirred using the 727 Ti Stand (Metrohm, Switzerland). The Titronic Basic piston burette combined with Handylab pH12 (both manufactured by Schott Geraete GmbH, Germany) and controlled by PC, were employed for the measurements of response characteristics and interferences by means of self-programmed software.

Procedure

The electrode has been calibrated with standard solutions of sodium dodecylsulfate and sodium dodecylbenzensulfonate in the range of $10^{-2} - 10^{-6}$ mol/dm^3. The volume of solution used for titration was 20 cm^3. All measurements and titrations were performed at $(25.0 \pm 0.2)^0$ C. The titrator was programmed to work in MET (Monotonic Equivalent point Titration) Mode with dosing increments of 0.1 cm^3, equilibrium time 30 s and signal drift 5 mV/min and DET (Dynamic Equivalent point Titration) Mode with signal drift 5 mV/min and equilibrium time 60 s.

RESULTS AND DISCUSSION

3.1. Response characteristics

Electromotive force of the membrane electrode assembly dipped into a solution of anionic surfactant investigated is given by Nernst equation:

$$E = E^0 - S \log a(SAn^-) \qquad (1)$$

Where E^o = formal potential, S = Nernst slope = *2.3 RT/zF,* $a(\mathrm{SAn}^-)$ = activity of surfactant anion.

The response characteristics of TG-TPB surfactant sensor in solutions of sodium dodecylsulfate and sodium dodecylbenzensulfonate are shown in Fig.1. The activity coefficients were calculated

according to the Davies equation. Statistical evaluation of the electrode characteristics is given in Table 1. The slope values and correlation coefficients were calculated from the linear region of the calibration graphs on the five series of measurements using linear regression analysis.

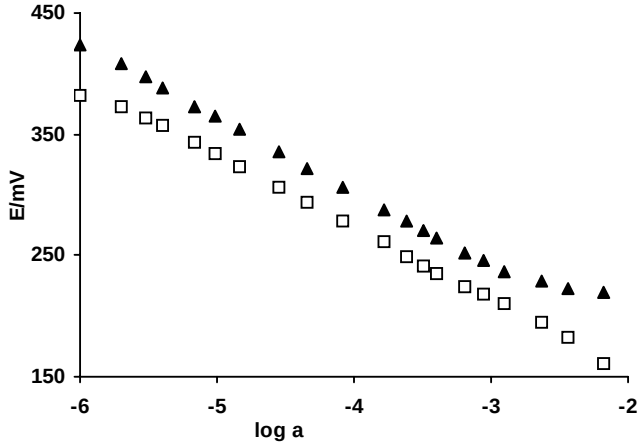

Figure 1. Dodecylsulfate (□ = DS) and dodecylbenzensulfonate (▲ = DBS) response of TG-TPB ion-pair-based surfactant sensor.

Parameters	Anionic surfactants	
	Dodecylsulfate	**Dodecylbenzensulfonate**
Slope (mV/decade)	59.0 ± 0.7	61.6 ± 0.5
Correlation coefficients (r)	0.9995	0.9998
Detection limit (μmol/dm^3)	1.6	0.5
Useful conc. range (μmol/dm^3)	2 – 10000	1 - 2000

Table 1 Response characteristics of TG-TPB based membrane selective to the anionic surfactants given together with ± 95% confidence limits.

3.2 Interferences

Determination of selectivity coefficients

Potentiometric selectivity coefficients, ($K_{I,J}^{pot}$), of the sensor against several anions were determined by fitting of Nikolskii-Eisenman equation to the experimental data obtained by fixed interferent method (FIM). As it can be seen in Table 2, the TG-TPB sensor exhibited high selectivity towards DS^- over many common anions. The selectivity order obtained is: $DS^- > DBS^- > XS^- > HCO_3^- > H_2PO_4^- > NO_3^- > CH_3COO^- > C_6H_5COO^- > Cl^- > CO_3^{2-} > B_4O_7^{2-} > SO_4^{2-} > EDTA^{2-}$.

Interferent, J	log $K_{I,J}^{pot}$	Interferent, J	log $K_{I,J}^{pot}$
$EDTA^{2-}$	-4.97	CH_3COO^-	-3.77
SO_4^{2-}	-4.89	NO_3^-	-3.74
$B_4O_7^{2-}$	-4.43	$H_2PO_4^-$	-3.71
CO_3^{2-}	-4.33	HCO_3^-	-3.38
Cl^-	-3.95	XS^-	-3.38
$C_6H_5COO^-$	-3.79	DBS^-	-0.11

Table 2 Potentiometric selectivity coefficients for different inorganic and organic anions used in commercial formulated products measured with TG-TPB surfactant electrode (XS^- = xylensulfonate; $EDTA^{2-}$ = ethylendiamintetraacetate, DBS^- = dodecylbenzensulfonate). Dodecylsulfate was used as the primary (analyte) ion, concentration of the interfering anion was c = 0.01 mol/dm^3.

3.3. Potentiometric titration of pure and technical grade anionic surfactants

The main application of the electrode described was for indication of the end-point in ion-pair surfactant potentiometric titrations. Anionic surfactant (SAn^- = analyte determined) reacts during titration with cationic surfactant ($SCat^+$ = titrant) accompanied by forming a water insoluble (1:1) ion-pair $SCat^+SAn^-$ (ion-exchange or ion-pair complex):

$$SCat^+SAn^- \rightleftharpoons SCat^+ + SAn^- \quad (2)$$

For the above equilibrium solubility product is defined as

$$K_{sp} = a(SCat^+) \cdot a(SAn^-) \quad (3)$$

where $a(SCat^+)$ and $a(SAn^-)$ are activities of the corresponding surfactant ions.
Before the equivalence point, the change (increase) of electrode potential responded to the change of anionic surfactant concentration as followed by the Eq. (1). After the equivalence point (all the anionic surfactant is precipitated), the increase of cationic surfactant concentration in solution is evident.
From Eq. (3) $a(SAn^-) = Ksp/a(SCat^+)$, and after inserting it into Eq. (1), the following electrode response is obtained:

$$E = E^0 - S \log K_{sp} / a(SCat^+) \quad (4)$$

which after rearrangement gives:

$$E = const + S \log a(SCat^+) \quad (5)$$

where $const = E^0 - S \log K_{sp}$

From Eq. (5) it follows, that after equivalence point the electrode responds to the change of cationic titrant (cationic response). Further addition of cationic titrant after equivalence point causes further increase of electrode potential *E*. The standard solutions of CPC and DDMICl were used as titrants in the determination of anionic surfactants forming the water insoluble (1:1) complexes. The four sodium salts of analytical grade anionic surfactants (dodecylsulfate, dodecylbenzensulfonate, *n*-octylsulfate and decansulfonate), three technical grade anionic surfactants in form of their sodium salts (dodecylethersulfate, *sec*-alkansulfonate, diisooctylsulfo-succinate) and sodium tetraphenylborate have been titrated potentiometrically using the new TG-TPB membrane electrode as surfactant sensor for end-point determination. The resulting potentiometric titration curves are shown in Fig. 2. The shorter hydrocarbon chain in anionic surfactants, due to higher solubility, are usually more dificult to titrate (by both potentiometric and by two-phase titration method).

The use of TG-TPB based surfactant electrode as indicating one enables the successful potentiometric titration even of those anionic surfactants (e.g. *n*-octyl-sulfate, decansulfonate). The titrand (analyte) concentration level of all the anionic surfactants investigated was $c = 0.4$ mmol/dm^3, except for *n*-octylsulfate (OS) and decansulfonate (DES), where it was 4 mmol/dm^3. The titration curves obtained with the both titrants, DDMICl and CPC exhibited regular defined and sharp inflexion points enabling a reliable equivalence point location. The equivalence points by all titrations have been calculated from the derivative curves. The sensor was also applied for potentiometric titration of some two-components mixtures.

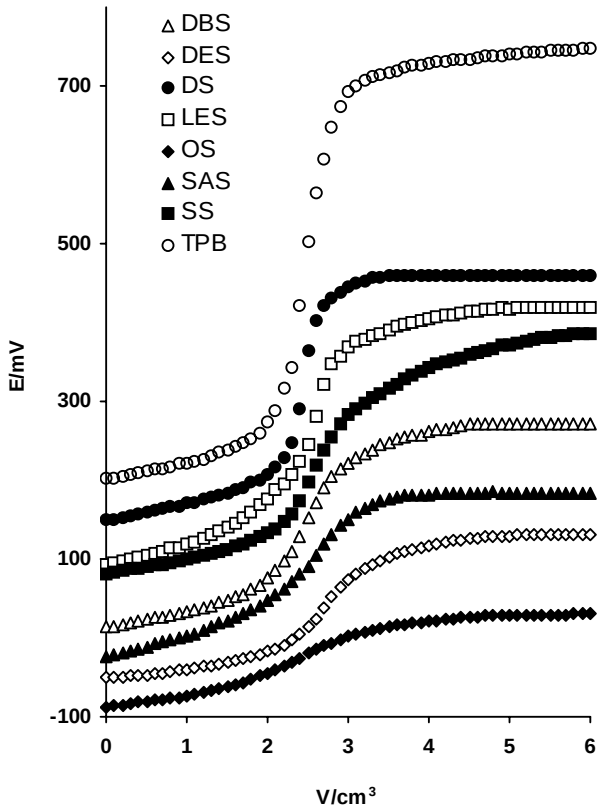

Figure 2. Titration curves of analytical and technical grade anionic surfactants using TG-TPB sensor and CPC as titrant (OS = n-octylsulfate; DES = decansulfonate; SAS = sec-alkansulfonate; DBS = dodecylbenzensulfonate; DS = dodecylsulfate; SS = diisooctylsulfosuccinate; LES = laurylethersulfate; TPB = tetraphenylborate).

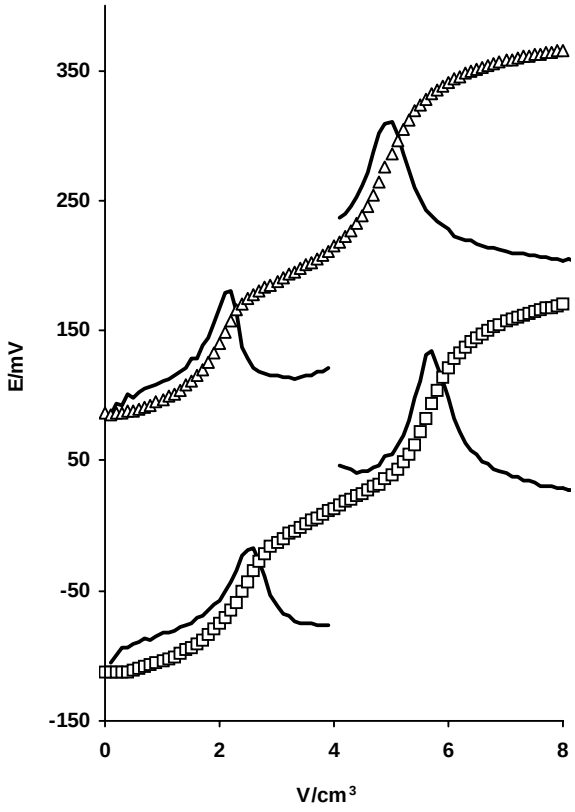

Figure 3. Titration curves of two-components surfactant mixtures with TG-TPB sensor and DDMICl as titrant [Δ = dodecylsulfate + n-octylsulfate (DS + OS); □ = dodecylsulfate + decansulfonate (DS + DES)].

CONCLUSION

A new liquid membrane anionic surfactant sensitive electrode has been prepared. The new synthesized ion-pair based on a highly lipophylic 1,3-didecyl-2-methyl-imidazolium cation and tetraphenylborate as antagonist ion, has been used as sensing material and incorporated into the plasticized PVC-membrane. The electrode exhibited Nernstian response (59.0 mV/decade) in the region between 2-10000 μmol/dm^3 for dodecylsulfate and 61.6 mV/decade between 1-2000 μmol/dm^3 for dodecylbenzensulfonate.

The main application of the electrode described was indication of the end-point in ion-pair surfactant potentiometric titrations. The electrode showed satisfactory analytical performances within pH range 2.5 - 11. The selectivity coefficients were determined by fitting of Nikolskii-Eisenman equation to the experimental data obtained by fixed interferent method (FIM). The sensor was also applied for potentiometric titration of some two-components mixtures. By all the investigations the resulting potentiometric titration curves revealed an analytically usable inflexion, enabling the reliable equivalence point detection using first derivative method.

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