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PORTABLE BIOSENSOR IN ANALYSIS OF SURFACTANTS

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Souhrn

Byl připraven citlivý potenciometrické enzymatický biosenzor, který byl použit k analýze povrchově aktivních látek na základě jejich inhibičního účinku na enzym acetylcholinesterázu (AChE). Enzymatická aktivita byla monitorována sledováním hydrolýzy acetylcholinu (ACh) tímto potenciometrickým čidlem. Na základě inhibičního účinku na acetylcholinesterázu byly stanoveny různé kationtové, aniontové a neiontové povrchově aktivní látky na v koncentračním rozmezí od 0 do 40 μg ml^{-1} s detekční limity až 0,07 μg ml^{-1} (v závislosti na charakteru povrchově aktivních látek). Stupeň inhibice AChE způsobený vlivem testovaných tenzidů se snižoval v pořadí chlorid cetylpyridinia (CPC) > chlorid benzyldimethylhexadecylamonia (BDHAC) > Hyamin (Hy) > bromid cetyltrimethylamonia (CTAB) > Triton X-100 (TX-100) > dodecylsíran sodný (SDS). Navržená metoda byla použita při stanovení povrchově aktivních látek ve farmaceutických a detergentových přípravcích i ve a vzorcích životního prostředí.

Abstract

Sensitive potentiometric enzymatic biosensor was constructed and applied for analysis surfactants based on their inhibitory effect on acetylcholinesterase enzyme (AChE). The enzymatic activity was measured through monitoring hydrolysis of acetylcholine (Ach) with a disposable acetylcholine potentiometric sensor. Based on inhibition of AChE, different

cationic, anionic and nonionic surfactants were determined in the concentration range from 0 to 40 μg mL^{-1} with detection limits reaching 0.07 μg mL^{-1} (depending on the nature of surfactants). The degree of AChE inhibition caused by different tested surfactants were as follows: cetylpyridinium chloride (CPC) > benzyldimethylhexadecyl ammonium chloride (BDHAC) > Hyamine (Hy) > cetyltrimethylammonium bromide (CTAB) > Triton X-100 (TX-100) > sodium dodecyl sulphate (SDS). The proposed method was applied for determination of surfactants in pharmaceutical formulation, detergents products and environmental samples.

Introduction

Surfactants form a unique class of organic compounds which are generally consist of a hydrophilic head group and a hydrophobic chain (or tail)[1]. The hydrophobic part is usually hydrocarbon chain (C_8–C_{18}), while the hydrophilic group may be carboxylates, sulfates, sulfonates (anionic), polyoxyethylenated chains (nonionic) or quaternary ammonium salts in case of cationic surfactants[1-3]. In 2008, the overal worldwide production of surfactants was about13 million metric tons; 70 % of them representing anionic ones. Surfactants are mainly employed in formulation of detergents, personal-care products, paints, pesticides and textile industry[4-6]. After application, surfactants are discharged into waste treatment units and then dispersed into the environment causing serious toxic effects on aquatic organisms when discharged with massive quantities[7-9].

Such widespread applications of surfactants and their environmental impacts were reflected on the development of reliable, rapid and accurate procedures for surfactant analysis[10-17], from them the so/called two-phase titration is still quite popular[18]. The target surfactant is extracted into organic solvent via formation of lipophilic ion-pair with suitable titrant in presence of an ionic dye which colors the organic layer differently at the end point. Formation of emulsion during titration, toxicity of the chlorinated organic solvent and lack of efficiency for short chain surfactant are the main drawbacks of such method[14]. Potentiometric approaches using ion selective electrodes (ISEs) are promising option for analysis of surfactants, offering simple measuring protocol and sample pre-treatment. Surfactant potentiometric sensors are usually used as titration end-point indicator electrodes; although some direct potentiometric surfactant sensors have also been reported[13,17,19,20]. Clasical polymeric liquid membranes electrodes[21,22] are convenient but measurements with them is sometimes complicated because of their high ohmic resistence. Solid-state electrodes were reported referring to a new type of ISEs in which the internal reference element was in direct

contact with the electroactive membrane[13,20,23-25]. Elimination of the internal reference solution leads to certain advantageous such as simplicity, miniaturization and ability to operate at higher pressure environment where the PVC membrane can be damaged. Carbon paste electrodes (CPEs) were introduced as end-point indicator electrode for potentiometric titration of surfactants[19,20] with very short response time in addition to the ease of fabrication and regeneration. However, designs and shapes of the aforementioned sensors were inconvenient for every purpose such as flow injection analysis or portable analyzers where the measuring units required sensors of special constructions and size.

The practical and economic interests have been driven the development of various kinds of disposal electrochemical sensors based on screen-printing technology[26,27]. Recently, simple disposable potentiometric sensor for titration of surfactant was reported[28]. The cited sensors have been applied for determination of cationic and anionic surfactants in pharmaceutical formulations, detergents and water samples using a portable titration system.

Attention was also paid to applications of biosensors containing cholinesterases, which represent hydrolyzing enzymes present in vertebrates and insects converting the neurotransmitter acetylcholine into choline and acetic acid. Organophosphorous pesticides and some pharmaceutical compounds are powerful inhibitors of cholinesterase enzymes[29]. Based on this inhibition, cholinesterase (ChE) biosensors have been applied as efficient tool for toxicity assessment in environmental monitoring and food quality control[29-31]. Moreover, it was reported that surfactants can inhibit cholinesterase enzymatic activity in aquatic animals[32,33]. The enzymatic activity can be altered through binding or disrupting enzyme structure by surfactants[34].

This study deals with applications of disposable potentiometric cholinesterase biosensor for analysis of different surfactant categories in their pharmaceutical preparations, detergents formulations and environmental samples. Cholinesterase free in solution was incubated with the surfactant solutions and the relative inhabitation degree was estimated by measuring the residual AChE activity using a potentiometric biosensor. The achieved sensitivities were higher than those reported in literature. Thus, such potentiometric methods can be recommended as simple and direct screening techniques to monitore detoxification processes.

Experimental

Reagents and chemicals. All reagents were of the analytical grade and bidistilled water was used throughout the experiments. Butyrylcholine iodide (BuCh) and acetylcholine

chloride (ACh) were purchased from Fluka and used without further purification. Aqueous 10^{-2} M solutions of BuCh and ACh were prepared in phosphate buffer solution (pH 7.0). Stock solutions of butyrylcholinesterase and acetylcholinesterase enzymes (Sigma) were prepared by dissolving the vial in phosphate buffer solution (pH 7.0) andtheir specific enzyme activity was verified using Ellman's photometric method as modified by Gorun et al.[35]. Cetylpyridinium chloride (CPC, Fluka), cetyltrimethylammonium bromide (CTAB, Fluka), Hyamine 1622 (Hy, Fluka), benzyldimethyhexadecylammonium chloride (BDHAC, Sigma), sodium dodecylsulphate (SDS, Sigma) and Triton X-100 (TX-100, Sigma) were used without further purification. To eliminate the adsorption of surfactant on the inner surface of vessels, accurate amounts the surfactant (3.58, 3.64, 4.48, 3.96, 2.88 and 6.4 mg of the aforementioned compounds in the same order) were dissolved in water and filled up to the mark yielding 10^{-3} M solutions. Solutions were left standing for at least 24h to cover all internal adsorption centers of the vessel by surfactant molecules; then discarded and prepared again in the same manner without intermediate rinsing the flask. The exact surfactant concentration was estimated via potentiometric titration with sodium tetraphenylborate (NaTPB) using a disposable potentiometric sensor as indicator electrode[28].

Surfactant samples. CPC and its pharmaceutical preparation Ezaflour (mouth wash solution assigned 50 mg mL^{-1}, Kahira-Pharmaceuticals, Cairo, Egypt) was purchased from local drug stores. Commercial detergents samples (Fast, containing 5% cationic surfactants) sample was obtained from local market. Anionic surfactants in agricultural drainage water (Alazazia Sea, Sharkia Governorate) and tap water (National Research Centre, Giza Governorate) samples were analyzed. Aliquot of water sample was transferred to a 10.0 mL beaker containing 2.0 mL citrate buffer at pH 3.0.

Sensor preparation. The bielectrode potentiometric strips were fabricated by screen printing technique on 5 × 35 mm ceramic supports as described recently[36]. Ag/AgCl pseudo-reference electrodes were firstly printed using a homemade ink prepared from by mixing 0.9 g Ag/AgCl mixture (65:35%) with 0.8 g of 8% PVC solution (in acetone–cyclohexanon mixture), and cured at 60 ^{o}C for 30 min. The working electrodes were printed on graphite/PVC conducting track using ion-sensing cocktail containing 0.75 mg α-CD, 0.5 mg KTCPB, 360 mg *f*-PNPE, 6 mL THF, 30 mg MWCNTs and 240 mg PVC. The fabricated sensors were directly used in measurements after preconditioning for 10 min in 10^{-3} mol L^{-1} of ACh or BuCh solution, respectively.

Apparatus. All potentiometric measurements were carried out using Radio Shack Digital multimeter with PC interface. For pH measurements, Metrohm 692 pH meter equiped

with combined glass electrode was used.

Measurement of inhibition by surfactant. Aliquots of the surfactant solution were incubated with 0.4 U AChE for the appropriate incubation time. The residual enzymatic activity was measured by transferring the reaction mixture to electrochemical measuring cell containing 10 mL of 10^{-4} M ACh solution in phosphate buffer (pH7.0) at 25ºC. The change in ACh electrode potential within the reaction time was monitored to estimate the AChE activity by initial rate method ($\Delta E/\Delta t$, determined by drawing tangent of the first linear part of potential-time curve). For each concentration, 5 replicates were measured and the mean value of the inhibition degree was represented against the surfactant concentration[36].

Sample analysis. Aliquots of the sample solution were diluted to the suitable concentration and analyzed by the proposed enzymatic procedures in comparison to the official European Pharmacopoeia[37] and official spectrophotometric Ellman's method for acetylcholinesterase activity[38,39]. Standard spectrophotometer microplate reader was consequently filled with 400 µL of 10^{-3} M 5,5-dithiobis-(2-nitrobenzoic) acid, 100 µL of AChE solution,100 µl of tested compound or phosphate buffered and 300 µL of phosphate buffered. Reaction was started by adding 100 µL of 10^{-3} M acetyllthiocholine and absorbance was measured at 412 nm after 15 and 315 s, respectively. The difference of the absorbance was used for calculation of enzymatic activity.

Results and Discussion

Surfactants as cholinesterase inhibitors. The possible effects of surfactants on cholinesterase activity have been demonstrated[32,33,40]. Li studied the inhibitory effect of both ionic and nonionic surfactants on cholinesterase activity[41]. According to the reported results, Hyamine 1622 significantly inhibits AChE activities more than other tested surfactants in the concentration range from 0.1 to 1 mg L^{-1}. Cholinesterase inhibitors can bind into esteratic part of active site, anionic part of active site (α anionic site), aromatic gorge, and peripheral (or β in some sources) anionic site[42,43]. The action of surfactant on ChE can be mediated through binding of the inhibitor to the catalytic site or peripheral anionic site of the enzyme[44]. In contrast to the irreversible inhibitors, the chemical structure of surfactant is lack of the molecular interaction potential of the ester group of the enzyme. However, surfactants can alter ChE activity via binding to the anionic site or by changing allosteric interaction of the enzyme[45,46]. The toxicity of surfactants depends greatly upon their structure and the alkyl chain length in the hydrophobic group. Generally, cationic surfactants were more potent to aquatic organisms than anionic and/or nonionic surfactants[47]. The lethal dose (LD_{50}) of

different surfactant categories with rats were ranged from 1000 to 25000, from 700 to 15000 and from 300 to 600 mg kg^{-1} for nonionic, anionic and cationic surfactants, respectively[48]. According to cholinesterase enzymatic action, both BuCh and ACh substrates were hydrolyzed to Ch and the corresponding organic acids. Following the enzymatic action, the BuCh and ACh concentration at the phase boundary of sensing membrane is decreased and consequently the electrode potential decreased. An analytical protocol can be introduced by incubation of cholinesterase enzyme with surfactant solution for appropriate incubation period followed by measuring the residual enzymatic activity using the potentiometric biosensor. Factors affecting the sensitivity of sensitivity of the procedures were investigated including the effect of incubation time, type of cholinesterase enzyme and the working calibration ranges.

Determination of cetylpyridinium chloride (CPC). The inhibitory effect of CPC on cholinesterase enzymes was investigated via incubation of 0.14 µg CPC with 0.4 U AChE for different incubation periods. Increased inhibitory effect was recorded as the relative inhibition degree increased from about 2% at zero time to 9.89 % after 10 min and 14.04 % after 15 min. The inhibition curve tends to a stable value with further incubation time; therefore incubation for 20 min was selected to compromise between the sensitivity and analysis time (Fig.1a). Upon construction, the fabricated sensors were used for measuring the remained

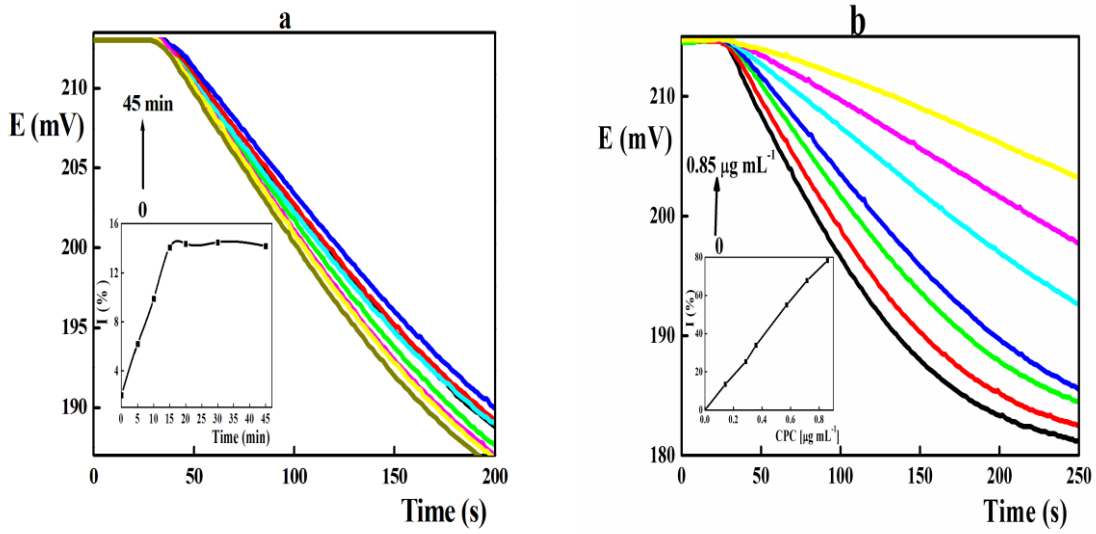

Fig. 1. (a) Effect of incubation time on the inhibitory action of CPC on AChE enzyme: measuring cell contain 10 mL of 10^{-4} M ACh solution and 0.14 µg mL^{-1} CPC incubated with 0.4 U enzyme; (b) inhibition of AChE enzymes by CPC after incubation period for 20 min at 25°C.

cholinesterase activities (either AChE or BuChE) after incubation with different CPC concentrations. The relative inhibition degree of BuChE was proportional to CPC in the

concentration range from 0 to 4 µg mL^{-1} with regression equation: I % = 3.77 + 15.86 CPC [µg mL^{-1}] and detection limit 0.5 µg mL^{-1}. On the other hand, more potent inhibitory effect of CPC on AChE (about 5.86 folds) was observed. The linear equation was I % = 0.15 + 92.94 CPC [µg mL^{-1}] with detection limit 0.07 µg mL^{-1}. For reproducibility measurement of the developed sensors, five runs were carried out on 4 different days; the average recoveries were 100.07±2.2 % (Table 1).

Determination of Hyamine (Hy). Similar to CPC, hyamine as cationic surfactant can inhibit cholinesterase enzymes. Faster inhibition process was observed as the relative inhibition degree of the enzyme was 23.31 % without incubation then increase to 40.00 and 42.02 % after 10 and 15 min, respectively (Fig.2 a). Consequently 15 min was selected as the proper incubation time. Constructing the calibration curve, different Hy concentrations were

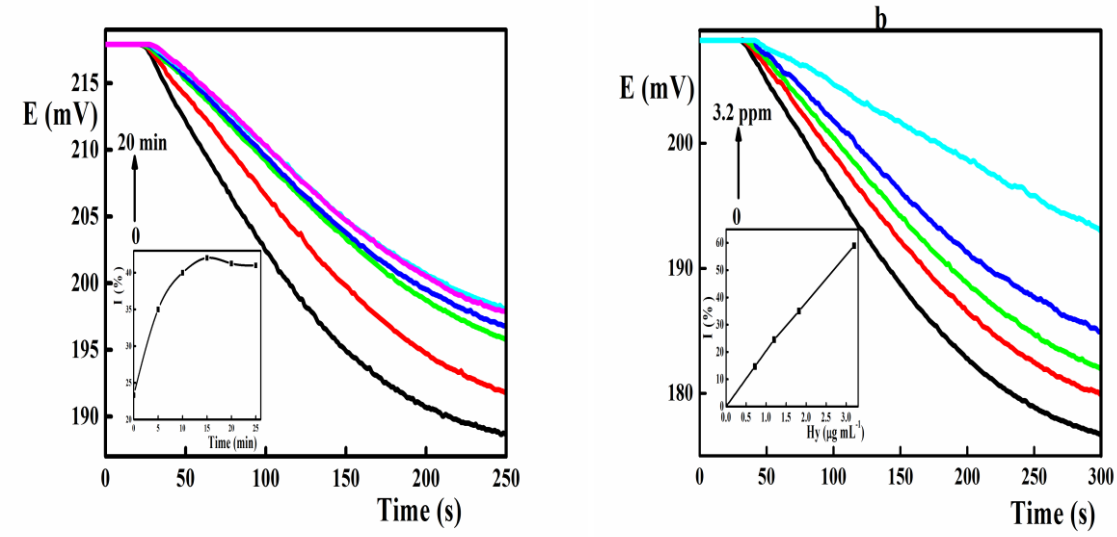

Fig. 2. (a) Effect of incubation time on the inhibitory action of Hyamine on AChE enzyme: measuring cell contain 10 mL of 10^{-4} M ACh solution and 0.96 µg mL^{-1} hyamine incubated with 0.4 U enzyme solution; (b) inhibition of AChE by hyamine after incubation period for 15 min at 25ºC.

incubated with AChE enzyme for 15 min and the residual enzymatic activities were measured. Calibration curves (Fig. 2b) were linear in the concentration range from 0 to 3.2 µg Hy (I % = 1.23 + 18.31 [µg mL^{-1}]) with detection limit 0.5 µg. The average recovery for 2.1 µg mL^{-1} was 103.4±3.5%.

Determination of benzyldimethyhexadecyammonium chloride (BDHAC). Benzyl-dimethylhexadecylammonium chloride inhibits cholinesterase enzyme, its inhibitory action was one of the potent between other tested surfactants. Inhibition of AChE by 0.22 µg BDHAC increased from 10 % at zero time to 16.6 % after 5 min and 20.4 % after 10 min.

Further incubation did not improve the inhibition of enzyme (Fig. 3a). Linear relationship was constructed in the concentration range from 0 to 0.8 µg surfactant, I % = -0.58 + 89.51 [µg mL^{-1}], with detection limit 0.1 µg (Fig. 3b). The average recovery for 0.25 µg mL^{-1} was 100.8±2.1%.

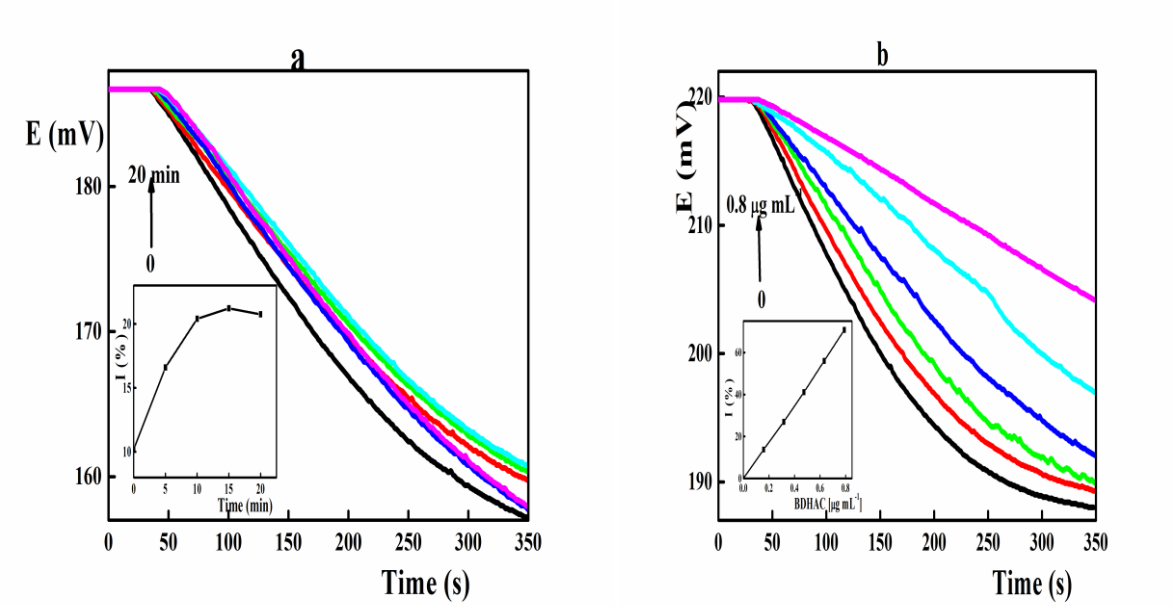

Fig. 3. (a) Effect of incubation time on the inhibitory action of BDHAC on AChE enzyme: measuring cell contain 10 mL of 10^{-4} M ACh solution and 0.22 µg mL^{-1} BDHAC incubated with 0.4 U enzyme. (b) Inhibition of AChE by BDHAC. Incubation was conducted for 10 min at 25°C.

Determination of cetyltrimethylammonium bromide (CTAB). In addition to the afore-mentioned cationic surfactants, CTAB showed less inhibition of cholinesterase enzymes. Via incubation of 2.0 µg mL^{-1} CTAB, the relative inhibition degree increased from 2 % at zero

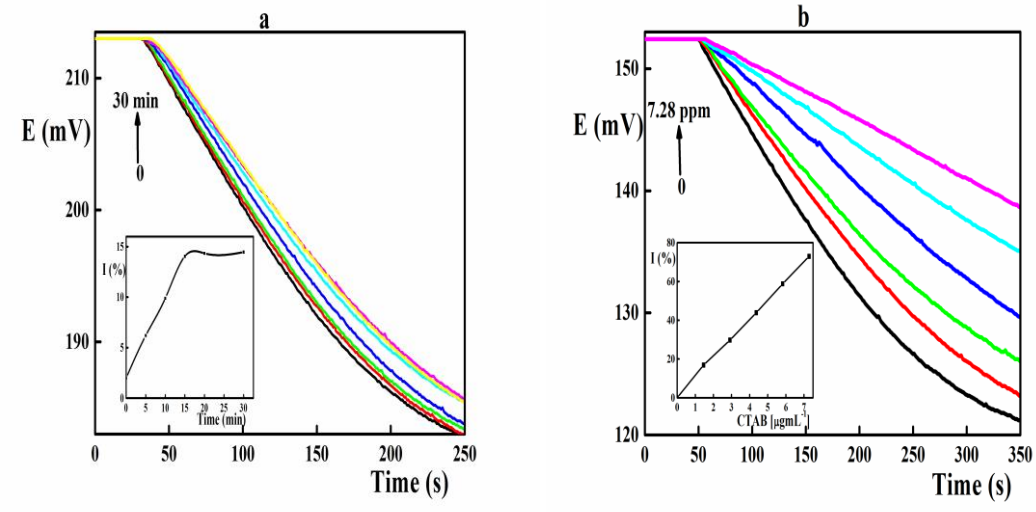

Fig. 4 (a) Effect of incubation time on the inhibitory action of CTAB on AChE enzyme: measuring cell contain 10 mL of 10^{-4} M ACh solution and 2.0 µgmL^{-1} CTAB incubated with 0.4U enzyme. (b) Inhibition of AChE by CTAB. Incubation was conducted for 15 min at 25°C.

time to 6.2 % after 5 min and to 14.4 % after 15 min (Fig. 4a). Calibration curve after 15 min incubation were linear in the concentration range from 0 to 7.28 µg CTAB, I % = 0.687 + 9.95 [µg mL^{-1}], with detection limit 1 µg (Fig. 4b).

Determination of anionic surfactant sodium dodecyl sulphate (SDS). To little extents, anionic surfactants such as SDS can also inhibit the enzyme through disturbing the soluble AChE conformation after interaction with surfactant micelles[41,47]. Anionic surfactant showed a noticeable inhibition on AChE compared with the BuChE enzyme (about three folds). After 20 min incubation time of SDS with acetylcholinesterase enzyme, the corresponding calibration curves were linear in the concentration range from 0 to 40 µg for AChE with regression I % = 0.53+ 2.05 [µg mL^{-1}] with detection limit 5 µg. For BuChE enzyme, the working range was from 0 to 80 µg with regression equation I % = -1.68+ 0.669 [µg mL^{-1}] and detection limit 10 µg (Fig. 5).

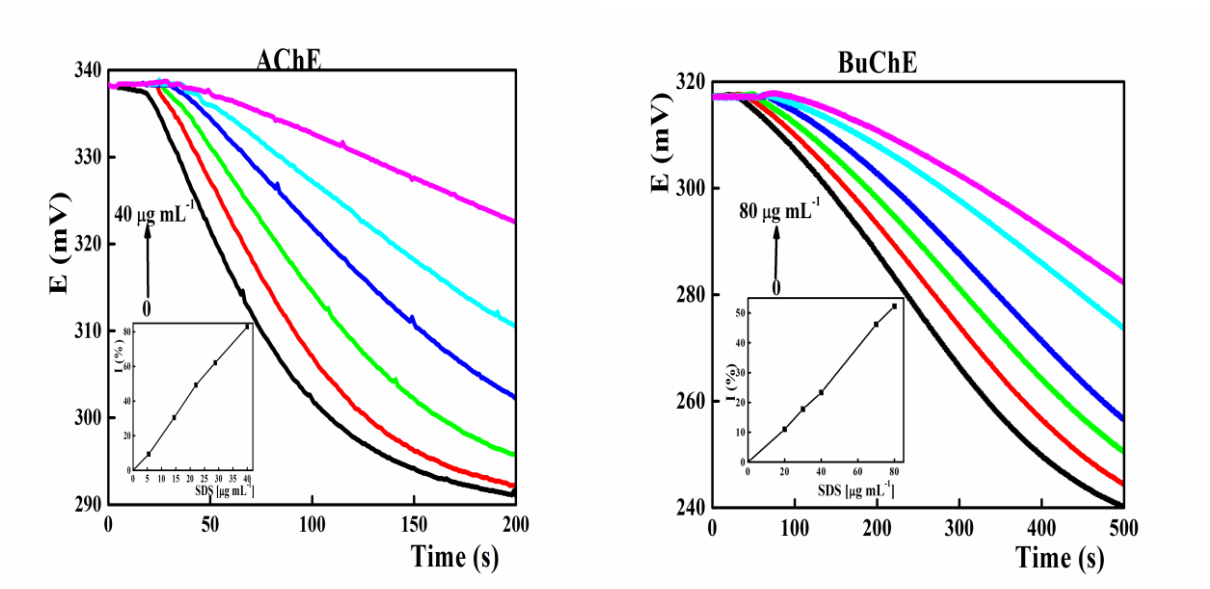

Fig. 5. Inhibition of cholinesterase enzymes by SDS. Experimental conditions: measuring cell contain 10 mL of 10^{-4} M ACh and BuCh, respectively. Incubation was conducted for 20 min at 25°C.

Determination of nonionic surfactant Triton X-100. In addition to the ionic surfactant, nonionic surfactant can also inhibit cholinesterase enzymes. Comparing the inhibitory effect of TX-100 on cholinesterase, the susceptibility of BuChE to inhibition was about two fold more than that of AChE (Fig. 6). Calibration curves were linear in the concentration range from 0 to 15 µg with regression equations I % = -1.52 + 4.62 [µg mL^{-1}] and I % = -0.92+ 2.75 [µg mL^{-1}] for BuChE and AChE, respectively.

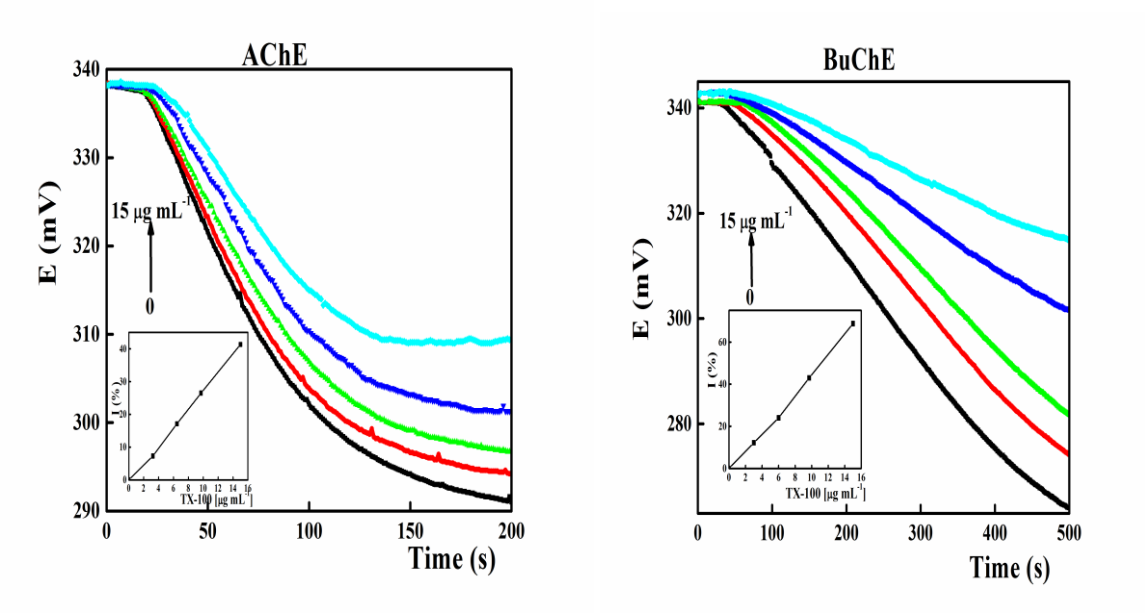

Fig. 6. Inhibition of cholinesterase enzymes by Trion X-100. Experimental conditions: measuring cell contained 10 mL of 10^{-4} M cholinesterase solution, incubation was conducted for 20 min.

Table 1. Coefficients of calibration curves (I % = a + b × [Surfactant]), detection limits and surfactant concentration range determined with acetylcholinesterase screen printed biosensor

Surfactant	CPC	Hyamine	BDHAC	CTAB	SDS	TX-100
Linear range, µg mL^{-1}	0-0.85	0-3.2	0-0.80	0-7.28	0-40.0	0-15.0
Incubation period, min	20	15	10	15	20	20
Slope, b	92.94±1.78	18.31±0.48	89.51 ±1.03	9.95±0.10	2.05±0.09	4.62±0.14
Intercept, a	0.15±0.09	1.23± 0.85	-0.58±0.49	0.69 ±0.09	0.53 ± 0.2	-1.52±0.52
R	0.9991	0.9982	0.9980	0.9998	0.9975	0.9986
Detection limit, µg mL^{-1}	0.07	0.50	0.10	1.00	5.00	1.50
Average recovery, µg mL^{-1}	100.1±2.2%	103.4±3.5	100.8±2.1	98.8±3.5 %	96.1±3.0	97.3±2.2%

Sample analysis. To demonstrate applicability of the proposed method, different ionic surfactants in their pharmaceutical, industrial formulations and environmental samples were analyzed. The obtained results (Table 2) were in agreement with the previous potentiometric and official methods[28,37]. In addition, the proposed potentiometric method showed average recoveries comparable with Ellman's spectrophotometric method for acetylcholinesterase[38,39] activity with the advantages of simple, inexpensive analysis protocol can be applied in field measurement with portable systems.

Table 2. Potentiometric enzymatic determination of cationic surfactants in their pharmaceutical preparations, industrial and environmental samples

Sample	Taken (μg)	Recovery (%) [a]	
		Present procedure	Gorun method
Ezaflour[b]	0.20	96.2±3.2	93.0±4.0
	0.45	98.6±3.6	95.6±3.9
	0.65	103.4±2.2	101.0±3.3
Detergent[c]	0.50	95.4±6.5	94.1±5.3
	0.70	97.4±±4.2	94.6±±4.8
Tape water	15.0	96.6±2.7	93.3±3.8
	30.0	98.2±2.1	96.0±1.9
Drainage swater	15.0	98.1±3.6	94.3±4.1
	30.0	101.7±3.8	99.0±2.4

[a]Mean recoveries and relative standard deviations of five determinations
[b] Recovery was calculated according to Ref. 37.
[c] Recovery was calculated according to Refs. 38, 39.

Conclusions

This study suggests the application of disposable potentiometric biosensor for surfactant analysis. Based on relative inhibition degree of cholinesterase enzyme, the proposed procedure can be applied for detection of different cationic, anionic and nonionic surfactants. The achieved sensitivities were higher than that reported in literature for potentiometric determination of surfactants. Different sensitivities were recorded depending on the inhibitory effect of the tested surfactant on cholinesterase activity. Generally, the cationic surfactants showed potent inhibition than nonionic and anionic surfactants. Even from the same family, the inhibition caused by cationic surfactant was controlled by its structure. This was in agreement with the reported ld_{50} values of surfactants[48]. The proposed procedures are attractive for their potential use as simple and direct screening technique for monitoring detoxification processes available to unskilled users with significant decrease in cost and time of analysis to complement or replace the classical analytical methods.

Acknowledgements

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