Materials Science and Engineering C 58 (2016) 504–509

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Development of a novel carbon paste sensor for determination of micromolar amounts of sulfaquinoxaline in pharmaceutical and biological samples

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ARTICLE INFO

Article history:
Received 21 June 2015
Received in revised form 3 August 2015
Accepted 21 August 2015
Available online 28 August 2015

Keywords:
Sulfaquinoxaline
Carbon paste electrode
Potentiometry
Triphenyltetrazolium chloride
Sensor

ABSTRACT

A potentiometric carbon paste sensor was fabricated for determination of sulfaquinoxaline (SQX) based on the use of ion-association complex of sulfaquinoxaline sodium with 2,3,5-triphenyltetrazolium chloride. The proposed sensor exhibited Nernstian slope of 58.4 ± 0.3 mV per decade for sulfaquinoxaline over a wide concentration range of 5.0×10^{-6} to 1.0×10^{-2} M, with a low detection limit of 3.0×10^{-6} M. The sensor manifested advantages of fast response time, satisfactory reproducibility, long life time, high thermal stability and, most importantly, excellent selectivities for sulfaquinoxaline relative to a wide variety of common foreign inorganic cations, anions, sugars and amino acids. The sensor was successfully used for determination of sulfaquinoxaline in pharmaceutical solution, blood serum, urine and milk samples. The isothermal coefficient of the electrode was calculated by the investigation of temperature effects on the electrode potential response.

1. Introduction

Sulfonamides (SAs) are an important group of synthetic antimicrobials which have been widely used in medicine and veterinary over 60 years. These drugs are commonly used in veterinary practice to prevent infections in livestock, treat diseases and promote growth [1,2]. The extensive use of sulfonamides in animal husbandry has been associated with the presence of sulfonamide residue in eggs, milk, meat and meat products. Therefore, the sulfonamide drugs can be extensively introduced in food production and their residues are a great concern, due to the possibility of risk to human health [3,4]. It has been reported that some evidences on the toxicity of sulfonamides on the thyroid gland have been presented [5]. Moreover, sulfonamides and their derivatives can cause extensive kidney damage, diminish blood sugar level and destroy red blood cells [6,7]. In milk, their presence may cause allergic reactions in sensitive individuals and interfere with starter cultures for cheese and other dairy products [8,9].

Sulfaquinoxaline (SQX), 4-Amino-N-2-quinoxalinylbenzene sulfonamide (Fig. 1), is one of the most important members of sulfonamide antimicrobial group which has been greatly used by veterinarians for therapeutic, prophylactic or growth-promoting purposes in laying hens [10]. It has high anticoccidial and anti-leucocytozoon effects which have been used to treat coccidiosis diseases in birds and animals [11]. This drug was designated as one of the feed additives in 1976 (60 g/t sulfaquinoxaline), and is used to promote the effective use of nutrient components in feeds for starting chicks, growing chicks and broiler chickens. High performance liquid chromatography (HPLC) is the main reported method for the determination of sulfaquinoxaline in different samples [4,10,12–16]. Some spectroscopic methods have been also reported for the determination of sulfaquinoxaline [17–19]. In spite of the high sensitivity of the chromatographic methods, time consuming, inherently expensive or complicated instruments, use of organic solvents and some complex sample preparation procedures are some of disadvantageous of these methods.

Electrochemical methods in the field of pharmaceutical and biological analysis have been used and attracted enormous interest due to their high sensitivity, selectivity and accurate analytical tools. Moreover, in comparison with other analysis techniques, because of the less sensitivity of electroanalytical methods to the matrix effects, derivatization or time-consuming extraction steps are not necessary. Thus, electrochemical sensors and biosensors have been widely used as sensitive and selective analytical tools for the environmental, clinical and biotechnical analysis over the past two decades [20–25]. They are composed of an electrode as transduction element which covered with a biological or chemical recognition layer. The specific recognition properties of this layer led to the development of highly selective sensor. The poor response of bare

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http://dx.doi.org/10.1016/j.msec.2015.08.034
0928-4931/

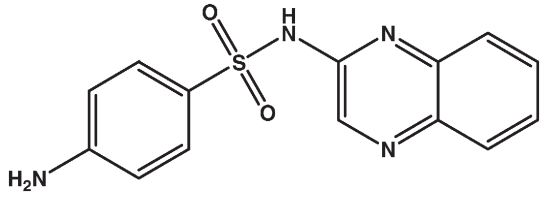

Fig. 1. Chemical structure of sulfaquinoxaline (SQX).

electrodes in direct analysis of electroactive species has led to use of mediators and modified electrodes to enhance the electrochemical response [26–29].

Developments in pharmaceutical analysis with potentiometric sensor have enabled the direct and selective measurement of the activity of various pharmaceutical compounds, in most instances without prior separation of the active substance from the formulation matrix. Furthermore, potentiometric detection based on ion-selective electrodes (ISEs), offers several advantages such as speed, ease of electrode preparation, simple instrumentation, relatively fast response time, wide dynamic range, reasonable selectivity and low cost [30].These advantages make potentiometric sensors as very attractive alternative tool for pharmaceutical analysis [31,32]. Carbon paste electrodes (CPEs) are one of the categories of potentiometric sensors which have unique characteristics as analytical tool. Compared to other types of potentiometric sensors, CPEs possess advantages of facility to prepare, simple surface renewal process, stable potentiometric response and very low ohmic resistance [33]. The operation mechanism of the CPEs depends on the properties of the modifier materials used to import selectivity towards the target species [34]. So, by application of appropriate ionophore into the composition of the CPEs, these electrodes exhibit high selectivities which the primary species can be measured without any interferences and separation steps [35]. In the case of pharmaceutical compounds, incorporation of ion association complexes (Q^+X^-), cyclodextrins (CDs) and also different ionic additives in the carbon paste matrix have led to construct the sensors which can selectively respond to a target drug [30,32]. Thus, chemically modified carbon paste electrodes (CMCPEs) have been successfully applied as potentiometric sensors for determination of various pharmaceutical species [30,32,36].

In recent years, we have successfully reported the construction of sensitive and selective chemical sensors for a variety of species such as SO_4^{2-} [37], $C_2O_4^{2-}$ [38], H^+ [39], phenylephrine [40] and carvedilol [41] drugs. With respect to the importance of the determination of sulfaquinoxaline in pharmaceutical and clinical analysis, development of a potentiometric selective CPE with wide linear range and good selectivity for easy, fast and selective determination of sulfaquinoxaline in different media can be very valuable. However, to the best of our knowledge, there is no previous report on the potentiometric sensor for the determination of sulfaquinoxaline. In this paper, the preparation, characterization and analytical application of a new carbon paste sensor in pharmaceutical preparations and also biological matrices have been described. The proposed CPE was made based on sulfaquinoxaline-triphenyltetrazolium (SQX-TT) ion association complex as an ion exchanger. The obtained results showed that the constructed CPE exhibited low detection limit and also excellent selectivity to sulfaquinoxaline, features which permit the direct determination of this drug concentration in different media without prior separation steps.

2. Experimental

2.1. Reagents

All of the chemical used were of highest purity available and used without any further purification except for vacuum drying. Reagent grade, dioctyl phthalate (DOP), dibutyl phthalate (DBP), dioctylsebacate (DOS), tetraoctylamonium bromide (TOA-Br), tridodecylmethylammonium chloride (TDMA-Cl), cetyltrimethylammonium bromide (CTA-Br), cetylpyridinium chloride (CP-Cl), paraffin oil (PO), graphite powder, nitrate salts of all cations and also potassium salts of all anions (all from Merck, Germany) were used as received. Sulfaquinoxaline sodium salt (SQXNa) and 2,3,5-triphenyltetrazolium chloride (TTC) were obtained from Aldrich (Germany) and used as received. Pharmaceutical oral solution of sulfaquinoxaline, Sulfaverdine Forte, was obtained from Kimia Faam Pharm. Co., Tehran, Iran. Doubly distilled water was used throughout for preparation of all aqueous solutions. A working SQXNa standard solution of 0.2 M was prepared in water in a 10 cm^3 calibrated volumetric flask. More diluted solutions were prepared by further dilution of the appropriate volumes of this standard solution.

The ion-association complex (SQX-TT) was prepared by the mixing an equal volume of a 1.0×10^{-2} M aqueous solution of SQXNa and TTC. The resulting precipitate was filtered through a filter paper, thoroughly washed with distilled water and dried under a vacuum over P_2O_5. This precipitate was grounded to fine powders before using as carbon paste ingredient.

2.2. Preparation of the sensor

The modified carbon paste sensors containing SQX-TT were generally prepared by hand-mixing various amounts of graphite powder and ion exchanger (SQX-TT) in a mortar for at least 10 min until the ion exchanger was uniformly dispersed through the graphite powder. Then, pasting liquid was added to this mixture and the mixture was mixed again until a uniform paste was obtained which was used for sensor construction. The paste was packed in the end of a disposable polyethylene syringe (3 mm i.d.), the tip of which had been cut off with a razor blade. Electrical contact to the carbon paste was made with a copper wire. Fresh surface was obtained by applying manual pressure to the piston. The resulting fresh surface was polished on a white paper until the surface had a shiny surface. The unmodified carbon paste sensor was also prepared using the same procedure except that ion-exchanger complex did not exist in the paste mixture.

2.3. Emf measurements

All potentiometric measurements with the modified CPE were carried out with the following cell assembly.

Ag/AgCl (satd) || sample solution | carbon paste | Cu

A Metrohmion analyzer model 654 (Switzerland) was used for the potential measurements. The emf observations were made relative to a double-junction Ag/AgCl electrode (Metrohm, Switzerland) containing a saturated solution of KCl with the chamber filled with potassium nitrate solution. Suitable increments of SQXNa solution were added to 20 mL of 0.05 M Britton–Robinson buffer solution (pH = 9.0) to cover the concentration range 5.0×10^{-7} to 5.0×10^{-2} M and the emf values were recorded after each addition. Calibration graphs were then constructed by plotting the recorded potentials versus log [SQX]. The obtained graphs were then employed for the characterization of the modified CPE (slope and linear range of determination).

2.4. Potentiometric assay of pharmaceutical preparation

5.9 mL of sulfaquinoxaline pharmaceutical oral solution (25.6 $mg.mL^{-1}$) was transferred into a 100 mL calibrated flask. The solution was diluted to the mark with buffer (pH = 9), shaken for 5 min and then 20 mL of the obtained solution was transferred into a 50 mL beaker. The sulfaquinoxaline content of the solution was