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Calixarene-doped PVC polymeric films as size-selective optical sensors: Monitoring of salicylate in real samples

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ABSTRACT

Preparation of novel salicylate-selective optical sensors (bulk optodes) was performed and applied successfully for salicylate determination in pharmaceutical formulations, Aspirin® and Aspocid®. t-butyl calix[4]arene ionophore was incorporated in a plasticized poly (vinyl-chloride) membrane containing the chromoionophore ETH5294 (O_1) or ETH7075 (O_5). The optical response to salicylate was due to size-selective extraction of salicylate from the aqueous solution to the optode bulk through formation of hydrogen bond accompanied by chromoionophore protonation, that resulted in the optical response at 680 or 540 nm for O_1 or O_5, respectively. Reliable size-selectivity was measured for salicylate over other anions; The calculated selectivity coefficients of O_5 optode were found to be: −4.4, −2.0 and − 3.7 for iodide, benzoate and perchlorate, respectively. The hydrogen bonding mechanism and selectivity pattern were ensured and explained by IR and ^{1}H NMR spectroscopy. For the same purpose, a molecular recognition constant of $\beta_{sal}=10^{0.043}$ was calculated using sandwich membrane method, and its small value ensured that hydrogen bonding interaction is responsible for the optode response. The detection limits of O_1 and O_5 in salicylate buffered solutions were 9.0×10^{-5} and 8.9×10^{-5} M with response times of 5 and 3 min, respectively, and with very good reversibility. The practical utility of the developed sensors was ensured by salicylate determination in Aspirin® and Aspocid®. Beyond the observed analytical performance, the present work aims not only to effectively apply Calixarene without derivatization, but also to estimate the strength of the size-dependent hydrogen bonding and comprehensively study the interaction mechanism.

1. Introduction

Membrane ion-selective bulk optodes are plastic optical sensors that can be considered as the other coin side of the PVC ion selective sensors (ISEs) and their sensor selectivity is due to the presence of a selective ionophore [1]. They offer a simpler signal transduction mechanism between the optical signal output and the recognition of the target ion due to the incorporation of a distinct chromoionophore. Interesting advantages are also provided by bulk optodes including: pH cross sensitivity, low cost, absence of internal solution which causes lower detection limit than their counterpart ISEs, excellent selectivity with extended library of the available ionophores, and high ability to be combined with other assays [1].

Although many bulk optodes were established for the different cations [2], lower number of anion selective optodes are reported due to shortage in specific guest (ionophore) species that can interact with the desired anions in a selective fashion.

Salicylate is an important molecule, as a metabolite resulting from the hydrolysis of acetylsalicylate and its derivatives, and known for prophylactic effect for heart attack in numerous medical formulations [3–5]. High levels of salicylate (>2.2 mM) are considered poisonous for patients [5,6]. Therefore, salicylate quantitation is very important in the different human-related samples.

Many techniques were previously reported for salicylate determination including: UV spectrophotometry [7,8], high performance liquid chromatography [9,10], voltammetry [11], and fluorimetry [12]. The literature reported also different ion-selective electrodes for the determination of salicylate [13–16]; some of these electrodes depend on the weak hydrogen bonding interaction that is controlled directly to size capability of the host-guest (anion-ionophore) interaction [15]. Three optodes were constructed for salicylate estimation [17–19]; yet, the used ionophores were expensive and exhibited low selectivity and high limit of detection.

Calix[4]arenes were previously used in the construction of different sensors after their derivatization or complexation [20–22]. In this work, we report for the first time, the use of the simply available t-butyl calix [4]arene as a hydrogen bonding establishing ionophore, for the construction of innovative membrane optodes with very good selectivity for salicylate. Two chromoionphores, ETH5294 and ETH7075 were used as the optical transducing element with or without the incorporation of the cationic additive tridodecyl methyl ammonium chloride (TDMAC), that is necessary for the ionophores of neutral charge [23].

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Compared to the previously reported ones, the current presented optodes exhibit improvement in the working concentration range, response time, and better selectivity over lipophilic species (perchlorate) and hydrogen bonding species (sulphate).

2. Experimental

2.1. Reagents, Materials and Instrumentation

All chemicals were of analytical grade, and doubly distilled water was used. 5,11,17,23-Tetrakis(2-methyl-2-propanyl)pentacyclo [19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa 1(25), 3(28), 4, 6, 9(27), 10,12,15 (26),16,18,21,23-dodecaene-25,26,27,28-tetrol ionophore (t- butyl Calix[4]arene; Fig. 1), Tridodecyl methyl ammonium chloride (TDMAC), the chromoionophore VI (ETH7075) 4,5-dibromofluorescein octadecyl ester (Fig. 1), 2-nitrophenyl octylether (o-NPOE), the chromoionophore I (ETH 5294) 3-Octadecanoylimino-7-(diethylamino)-1,2-benzophenoxazine, 9-(Diethylamino)-5-(octadecanoylimino)-5*H*-benzo[*a*] phenoxazine, *N*-Octadecanoyl-Nile blue (Fig. 1), dioctyl phthalate (DOP), and graphite were obtained from Sigma-Aldrich (Germany). tetrahydrofuran (THF), ferric nitrate, glacial acetic acid, sodium hydroxide, sodium salts of sulphate, chloride, bromide, salicylate, iodide, nitrite, perchlorate monohydrate, benzoate, nitrate, thiocyanate and acetate were got from ADWIC (Egypt). 5×10^{-2} mol L^{-1} Acetate (pH 4.5 and 5.5) buffers were used for the subsequent preparations and dilutions of all other anions solutions.

Aspirin® (320 mg tablet) and Aspocid® (75 mg tablet) solutions were prepared by dissolution of 10 tablets in acetate buffer (pH 4.5), warming the solution, cooling followed by filtration, and finally completing the solution to 500 mL; this stock was used for other serial dilutions [19] whenever required. Although both Aspirin® and Aspocid® contain the same active ingredients, the solution of Aspirin® is colorless and that of Aspocid® is red (mainly due to colored coating of the dosage form).

UV–VIS OPTIZEN POP automated spectrophotometer (Korea) was used for getting different spectra. SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), Netherlands was used to evaluate the membrane morphology. ^{1}H NMR was performed in Cairo University using mercury-300BB "NMR300" where both Calixarene and its complex with different anions were prepared in deurated DMSO. IR was performed in the central lab of Cairo University using SHIMADZU IR spectrometer by recording the spectra of Calixarene containing membrane before and after soaking in 0.01 M salicylate for one hour.

2.2. Preparation of Potentiometric Sensors and Sandwich Membrane Method

The PVC and carbon paste electrodes were prepared as described elsewhere [24]. The binding strength between Calixarene and salicylate was estimated by the determination of their complex formation constants in the membrane phase; Sandwich Membrane Method (SMM) is very useful for this purpose [25]. Two membranes, one incorporating both the ion-exchanger together with the ionophore (M1) and the other membrane incorporating only the ion-exchanger (M2), were prepared. M1 was then placed on top of M2, and the potential across the sandwich was measured at pH 4.5 [25].

2.3. Optode Preparation and Measurement System

The bulk optodes membranes were manually cast as described elsewhere [19]; in brief, the optode different constituents were dissolved in ~2 mL THF (Table 1), followed by casting onto 1.0 mm thickness dust-free quartz slides (0.9×4 cm^2), dried in air for about 10 min to form an optode of thickness 6–9 μm [17,19]. The absorbance was measured by placing the optode in a quartz cuvette ($1 \times 1 \times 4$ cm^3) that containing the target anion, and absorbance was measured using UV–VIS OPTIZEN POP automated spectrophotometer. Optodes were conditioned in acetate buffer solution (pH = 4.5) for 20 min before the first measurement [23]. For correcting response in the background, the absorbance of a blank sensor prepared without chromoionophore was recorded. For calculating α, the absorbance readings of the fully protonated and deprotonated chromoionophores were recorded for optodes conditioned in 10^{-1} M HCl and 10^{-1} M NaOH, respectively.

3. Results and Discussion

3.1. Elucidation of Response Mechanism

The ionophore and host-guest interaction are the main factors in both electrodes and optodes. Calixarene ionophore and different chromoionophores (Fig. 1) were used in primary potentiometric (not shown) and spectroscopic studies (Fig. 2).

The H-NMR spectroscopy for the Calixarene showed that the chemical shift of OH and aromatic hydrogens (9.90, 7.13) was changed to (9.91, 7.18) in case of salicylate-Calixarene complex, Fig. S1; this weak upfield shift confirms that OH is partially involved in the hydrogen bonding to the salicylate [26]. The weak shift and weak OH signals may be understood in terms of the weakness of the hydrogen bonding, the low solubility of the Calixarene and the presence of different isomers of Calixarene [26,27].

The IR spectroscopy showed different peak shifts (Fig. S2) [27]; peak at 3113 cm^{-1} assigned to OH is shifted to 3120 cm^{-1} with peak broadening, peak at 3074 cm^{-1} assigned to aromatic CH is shifted to 3078 cm^{-1}. Peaks at 1465, 1519 and 1580 cm^{-1} assigned to C=C stretching, where C-OH bending were shifted to 1469, 1523 and 1600 cm^{-1}, which confirms the existence of hydrogen bonding.

The use of optode O_1 (Table 1) exhibited new peaks at 615 and 680 nm in presence of 10^{-3} M salicylate, Fig. 2; accordingly, it can be concluded that size-dependent hydrogen bonding is responsible for

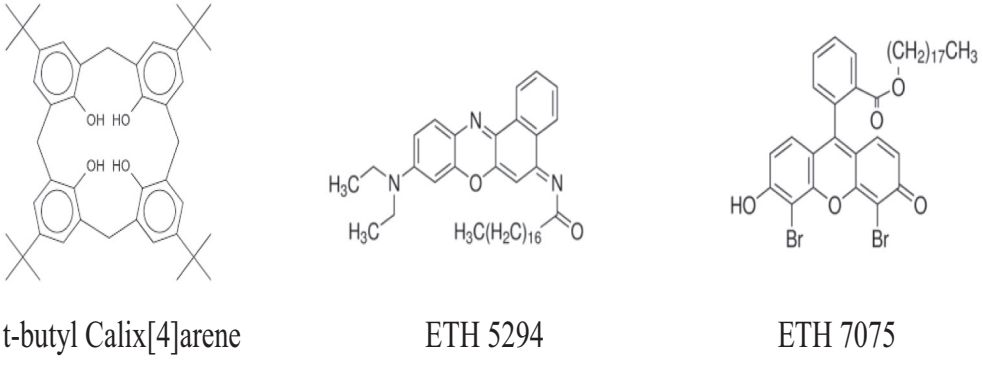

Fig. 1. Structure of the Calixarene ionophore, chromoionophore ETH5294, and the chromoionophore ETH7075.