

Full Paper

Anions Selective Electrodes with Unusual Half Nernstian Response

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Abstract- Selective poly (vinylchloride) membrane electrodes based on a quaternary ammonium compound, malachite green as a novel ion exchanger for anionic species were prepared. The developed membrane electrodes were used successfully for the quantification of sulphadimethoxine, iodide ions and thiocyanate ions in their pure powdered forms, fish water and/or pharmaceutical formulation. Linear responses were obtained within a concentration range of 10^{-5} - 10^{-2} M for the three selected monovalent anionic species. The electrodes exhibited unusual half Nernstian slopes when the divalent cationic malachite green is used as a novel lipophilic ion exchanger in PVC based membranes for determination of monovalent anions. They have fast response times about 20 s, satisfactory reproducibility, and long life times.

Keywords- Anions selective electrodes, Fish water, Half Nernstian response, Malachite green, Novel ion exchanger

1. INTRODUCTION

Anions play fundamental roles in a wide range of biological, medicinal and environmental processes. The direct and rapid determination of minute quantities of ionic

Donnan failure at the upper detection limit, and responses to interfering ions or sample contamination (or depletion) by currentless transmembrane ion fluxes at the lower detection limit [5].

Some monovalent anions namely; Sulphadimethoxine as an organic anion, iodide and thiocyanate as inorganic anions were included in the study. At room temperature, a 10-fold increase in the activity of the anion X^- with the charge z results in a decrease in the emf of 59.2 mV/z, as predicted by Nernst equation (Eq. 1):

$$E = E^0 - \frac{0.592}{z} \text{Log}X^- \quad (1)$$

Surprisingly, those investigated monovalent anions were sensed as divalent ions giving the unusual half Nernstian response slopes.

Sulfadimethoxine (SDM), (Fig. 2), belongs to sulphonamides, which is commonly used in food-producing animals as growth promoters and as therapeutic and prophylactic drugs [6] that were used in combination with trimethoprim.

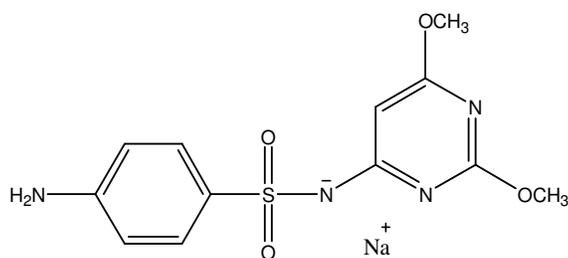


Fig. 2. Structural formula of Sulphadimethoxine sodium [$C_{12}H_{13}N_4NaO_4S$, formula weight 332.32 g/mol]

Thiocyanate finds in many industrial applications, though not toxic as cyanide, it is harmful to the aquatic life. Its determination at low levels in water and industrial effluents is therefore, important [7].

Iodine is an essential micronutrient and it is a key ion in many biological activities such as brain function, cell growth, neurological activities and thyroid function [8].

The concentrations of iodide and thiocyanate in aquatic fish water are sensitive to the surrounding conditions, for example biological activity and redox conditions. Iodide and thiocyanate are, therefore, regarded as important in studies of the marine environment.

The aim of this work was to develop anions-selective electrodes based on plasticized PVC membranes, containing malachite green as a novel cationic exchanger and application of these electrodes for the determination of the investigated anions in fish water. The selectivity for a variety of ions and effect of pH on the potentiometric response properties of the proposed electrodes were investigated.

2. EXPERIMENTAL

2.1. Instrument

A Jenway digital ion analyzer model 3505 (Essex, UK) with Ag/AgCl double junction reference electrode (Aldrich, Germany) was used for potential measurements. A Jenway 1000 hot plate and Magnetic stirrer (UK) was used. A Jenway pH glass electrode no. 924005-BO3-Q11C (Essex, UK) was used for pH adjustments. Membrane filter (sartoriusstedim biotech, 0.45 μm , Lot No. 16555 00867103).

2.2. Chemicals and reagents

Sulphadimethoxine sodium was kindly supplied from Pharma Swede- Egypt and its purity was certificated to be 99.7%. Trimethoxin[®] was manufactured by Chemifarma and was purchased from Egyptian local market. Each 1 mL was claimed to contain 200 mg sulphadimethoxine and 40 mg trimethoprim, Batch number (BN.): A120009.

All chemicals and reagents used throughout this work were of analytical grade: Polyvinyl chloride (PVC), 2-Nitrophenyl octyl ether (NPOE), Tetrahydrofuran (THF) and Malachite green oxalate salt were used as received from Aldrich (Steinheim, Germany). Potassium or ammonium salts of all anions were of highest purity available from Prolabo (Pennsylvania, USA) and were used without further purification. All of the solutions were prepared using bi-distilled deionized water. The pH adjustments were made with dilute hydrochloric acid and sodium hydroxide solutions as required. A stock solution of each anion was prepared by dissolving an appropriate amount of its corresponding salt in 100 mL of double distilled water. Working solutions were prepared by successive dilutions with the same solvent. All solutions were kept in tight closed containers and protected from light.

2.3. Procedures

2.3.1. Fabrication of membrane sensors

In a glass Petri dish (5 cm diameter), 10 mg of MG-Oxalate ion exchanger was thoroughly mixed with 0.4 mL of NOPE and 0.19 g of PVC. The mixture was dissolved in 5 mL of THF. The Petri dish was covered with a filter paper and left to stand overnight to allow solvent evaporation at room temperature. A master membrane with a thickness of 0.1 mm was obtained.

2.3.2. Electrode assembly

From the master membrane, three discs (8 mm diameter) were cut using a cork borer and pasted using THF, to two interchangeable PVC tips that were clipped into the end of the three electrodes glass bodies to construct sensor 1, 2 and 3.

Sensor 1 was then filled with an internal solution of equal volumes of 10^{-2} mol L⁻¹ SDM and 10^{-2} mol L⁻¹ KCl, sensor 2 was filled with equal volumes of 10^{-2} M KI and 10^{-2} mol L⁻¹ KCl, whereas sensor 3 was filled with equal volumes of 10^{-2} mol L⁻¹ NH₄SCN and 10^{-2} mol L⁻¹ KCl. Ag/AgCl wire (1mm diameter) was used as an internal reference electrode. Each sensor was conditioned by soaking in 10^{-2} mol L⁻¹ of its corresponding aqueous solution for 24 h, and then stored in the same solution when not in use.

2.3.3. Effect of pH

The effect of pH on the potential values of the three sensors were studied over a pH range of 3-10 using 10^{-4} M and 10^{-3} M aqueous solutions of each corresponding anionic species. The pH was gradually increased or decreased by adding aliquots of dilute sodium hydroxide or dilute hydrochloric acid solutions. The potential obtained at each pH value was recorded.

2.3.4. Sensors calibration

Each sensor and the double junction Ag/AgCl was immersed in its corresponding aqueous solutions in the range of 1×10^{-7} to 1×10^{-2} mol L⁻¹. They were allowed to equilibrate whilst stirring and recording the emf readings within ± 2 mV. The membrane sensors were washed between measurements with water. The mV-concentration profiles were plotted. The regression equations for the linear part of the curves were computed and used for subsequent determination of the corresponding anion unknown concentrations.

2.3.5. Sensors selectivity

The potentiometric selectivity coefficient $\log K^{\text{pot}}_{(\text{Primary ion, interferent})}$ was used to evaluate the extent to which a foreign ion would interfere with the response of an electrode to its primary ion.

Selectivity coefficients were calculated by the separate solutions method [9], where potentials were measured for 10^{-3} mol L⁻¹ aqueous solutions for sensor 1, 2 and 3 and then for 10^{-3} M aqueous interferent solution separately, then potentiometric selectivity coefficients were calculated using the following equation (Eq. 2):

$$\text{Log } K^{\text{pot}}_{\text{A, B}} = (E_{\text{B}} - E_{\text{A}}) / S \quad (2)$$

Where $K^{\text{pot}}_{\text{A, B}}$ is the selectivity coefficient, E_{A} and E_{B} are the potentials of the drug and the interferent solutions respectively, S is the slope of the calibration plot.

2.3.6. Direct potentiometric determination of SDM in its pharmaceutical formulation (Sensor1)

From Trimethoxin[®] bottle, Suitable dilutions were taken using bi-distilled water to obtain serial of 10^{-4} to 10^{-3} mol L⁻¹ SDM. Procedure was then completed as under Section 2.3.4. From the recorded potential calculate the concentration of SDM from its corresponding regression equation.

2.3.7. Application to fish water

The collected fish water samples were filtered through whatman filter paper to eliminate suspended matter and then filtered through 0.45 μ m nylon membrane filter to eliminate fine particulate matter. Samples were stored at 4 $^{\circ}$ C in order to avoid any degradation or deterioration. In volumetric flasks 25 mL, the filtered fish water was spiked with each standard anion solution and the volume was completed to the mark with the fish water. Then the emf values of these spiked water samples were recorded using the corresponding sensor and the concentration of SDM, iodide and thiocyanate ions were calculated each from its corresponding regression equation.

3. RESULTS AND DISCUSSION

It is well known that the performance characteristics of ISEs based on ion-exchangers depend to a large extent on the nature of these ion-exchangers and their lipophilicities. The novelty of this work arises from the use of malachite green as a bulky, highly lipophilic cationic exchanger that allows its minimal leaching and longer life time of the membrane.

In the past, there were only two well-documented reasons for super-Nernstian slopes, i.e., ion fluxes [10–13] and the presence of more than one type of ions in the ISE membrane, with one distinct stoichiometry for each ion. Apparently twice-Nernstian responses were the first examples of super-Nernstian responses that could be explained by phase boundary equilibria alone [14–18]. This present work shows another cause for non-Nernstian responses, i.e., half-Nernstian responses as discussed in this contribution.

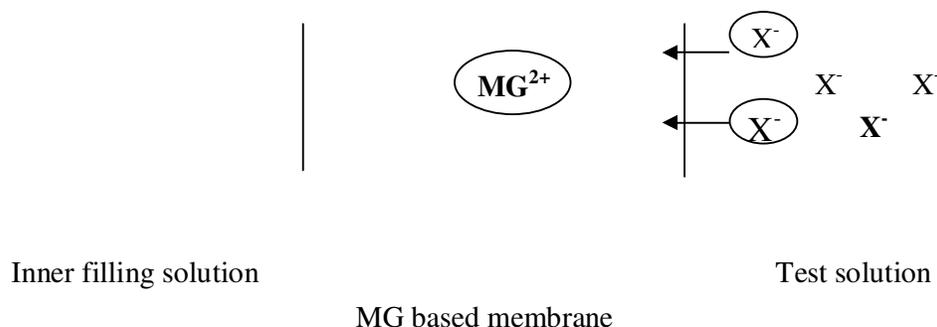


Fig. 3. Figure showing potentiometric monovalent anions (X^-) responses in presence of divalent MG ionic site

When the malachite green based membrane is exposed to solutions of a monovalent anionic species (X^-), loading the membrane bulk with X^- (whose concentration, for reasons of bulk electroneutrality [19-21] is equivalent with the concentration of the ion exchanger sites provided by malachite green) so X^- (SDM^- , I^- or SCN^-) is detected as a divalent anion (Fig. 3). A finding that is supported by the unusual half Nernstian response for each of the studied monovalent anions.

For reasons of bulk electroneutrality explained by the phase boundary model, X^- (SDM^- , I^- or SCN^-) is detected as a divalent anion result in an unusual half-Nernstian response slope.

3.1. Performance characteristics of the sensors

The electrochemical performance characteristics of the three investigated sensors were systematically evaluated according to the IUPAC standards in Table 1.

Table 1. General characteristics of the three investigated sensors

Parameter	Sensor 1	Sensor 2	Sensor 3
Slope (mV/decade) ^a	28.1	29.6	30.4
Intercept (mV)	4.4	-58.1	-86.9
LOD (mol L ⁻¹) ^b	9.80×10 ⁻⁶	9.75×10 ⁻⁶	9.60×10 ⁻⁶
Response time (s)	20	25	25
Working pH range	5-8	4-7	4-8
Concentration range (mol L ⁻¹)	10 ⁻⁵ - 10 ⁻²	10 ⁻⁵ - 10 ⁻²	10 ⁻⁵ - 10 ⁻²
Stability (Months)	>3	>3	>3
Average recovery (%)±S.D ^a	100.02 ±0.36	100.05 ±1.01	99.98 ±0.33
Correlation coefficient (r)	0.9999	0.9996	0.9999
Precision (%) ^c	99.87	99.67	100.28

^aResult of five determinations.

^bLimit of detection (measured by interception of the extrapolated arms of Fig. 3).

^cAverage recovery percent of determining 10⁻³ and 10⁻⁴ mol L⁻¹ SDM, iodide ions and thiocyanate ions for the studied sensors using different runs.

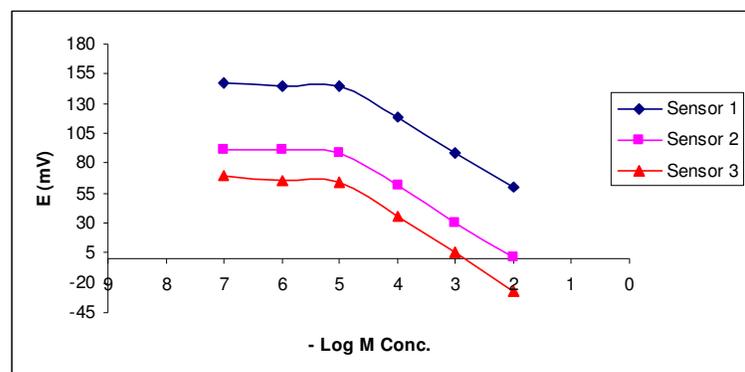


Fig. 4. Profile of the potential in (mV) versus -log concentration of the corresponding anion in mol/L

The slope of the calibration plots were typically 28.1, 29.6 and 30.4 mV/concentration decade for sensors 1, 2 and 3 respectively. Typical calibration plots for the three sensors are shown in Fig. 4.

3.2. Dynamic response time

Dynamic response time is an important factor for analytical applications of ion selective electrodes. In this study, practical response time was recorded by increasing the SDM, iodide and thiocyanate ions concentrations by up to 10- folds. The required time for sensors to reach values within ± 1 mV of the final equilibrium potential was nearly 20 s for sensor 1 and about 25 s for sensors 2 and 3.

3.3 Effect of pH

Studies were carried out to reach the optimum experimental conditions. The potential obtained at each pH value was recorded. It was apparent from the potential–pH profile (Fig. 5A) that the response is fairly constant over the pH range 5-8 for sensor 1, while the response is constant over a pH range 4-7 for sensor 2 (Fig. 5B) and 4-8 for sensor 3 (Fig. 5C).

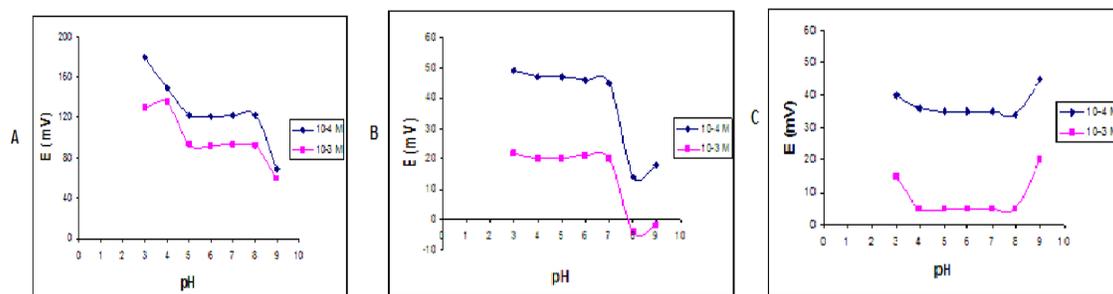


Fig. 5. Effect of pH on Sensor 1 (A), sensor 2 (B) and sensor 3 (C)

3.4. Sensors selectivity

The potentiometric selectivity coefficients of the proposed sensors (1, 2&3) were evaluated in the presence of co-formulated drug (trimethoprim) , organic neutral additives and some Inorganic metals (K^+ , Na^+ , Ca^{++} , NO_3^- , NO_2^- , F^-) that are usually present in pharmaceutical dosage forms, in biological fluids or in fish water as shown in Table 2 .

Table 2. Potentiometric selectivity coefficients of sensor 1, 2 and 3 by separate selectivity method (SSM)

Selectivity coefficient			
Interferent ^a	Sensor 1	Sensor 2	Sensor 3
KCl	1.5×10^{-2}	8.2×10^{-2}	4.0×10^{-2}
Lactose	1.3×10^{-2}	7.7×10^{-2}	1.4×10^{-2}
Glucose	8.5×10^{-3}	5.7×10^{-2}	1.0×10^{-2}
Urea	1.8×10^{-1}	8.9×10^{-2}	1.3×10^{-1}
NaCl	4.3×10^{-2}	5.7×10^{-2}	5.4×10^{-2}
CaCl ₂	4.6×10^{-2}	7.1×10^{-2}	7.2×10^{-2}
NaNO ₃	3.1×10^{-2}	1.8×10^{-1}	2.8×10^{-2}
NaNO ₂	2.8×10^{-2}	8.3×10^{-2}	3.7×10^{-2}
NaF	1.5×10^{-2}	5.3×10^{-2}	3.0×10^{-2}
KI	2.3×10^{-2}	-----	1.9×10^{-1}
NH ₄ SCN	2.9×10^{-2}	1.97	-----
Trimethoprim ^b	1.2×10^{-1}	-----	-----
Sulphadiazine Sodium	7.5×10^{-2}	-----	-----

^a aqueous solutions of 1×10^{-3} M were used.

^b was dissolved in least amount of Methanol and the volume was then completed with bi-distilled water

3.5. Potentiometric determination of SDM in its pharmaceutical formulation

Sensor 1 was successfully applied for the selective analysis of SDM in its pharmaceutical formulation with fairly no interference from trimethoprim or excepients. The results proved the applicability of the sensor for the determination of the studied drug in pharmaceutical formulation as shown in Table 3.

Table 3. Determination of sulphadimethoxine sodium in pharmaceutical formulation by the suggested potentiometric procedures (Sensor 1)

Pharmaceutical preparation	Taken Concentration (mol L ⁻¹)	Recovery %±RSD*
Trimethoxin B.N. (A120009)	10^{-4}	97.62±0.54
	10^{-3}	101.13±1.15

* Average of five determinations

3.6. Application to spiked fish water

For the application to fish water, it was found that the three sensors are reliable and give stable results with high accuracy and precision without preliminary extraction procedures,

which is shown in Tables 4. The pH of these samples were measured before spiking and was found to be 6.5 ± 0.5 , which is within the pH working range of the three proposed sensors.

Table 4. Determination of each anion in spiked fish water samples by its corresponding sensor

Measured conc. in fish water samples	R% \pm RSD*		
	Sensor 1	Sensor 2	Sensor 3
1×10^{-4} M	100.01 \pm 0.54	104.12 \pm 1.98	97.03 \pm 0.41
1×10^{-3} M	103.89 \pm 0.78	101.77 \pm 1.56	100.35 \pm 0.26

* Average of three determinations

4. CONCLUSION

The novelty of these fabricated sensors was raised from that, MG was used for the first time as a cationic exchanger for electrochemical determination of different anionic species such as SDM, iodide and thiocyanate ions. The very high lipophilicity and cationic structure of malachite green suggests its use as a novel electroactive material in PVC membrane sensors. The developed membrane was used for determination of SDM, iodide and thiocyanate ions, selectively in fish water. The electrodes have shown good operating characteristics (unusual half-Nernstian response; reasonable detection limit; relatively high selectivity, especially with respect to the highly lipophilic anions; wide dynamic range; fast response; applicability over a wide pH range; remarkable long lifetime). These characteristics and the typical applications made these electrodes suitable for measuring the concentration of the selected anions in a wide variety of samples without the need for pretreatment steps and without significant interference from other anionic or cationic species present in the aquatic environment.

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