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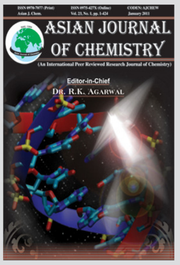

Potentiometric Behaviour of *p*-Nitroaniline and its Quantification in Environmental Samples

NASHWA M.H. RIZK

Department of Environmental Biotechnology, Genetic Engineering and Biotechnology Research Institute (GEBRI), Minufiya University, Sadat City, Egypt

Corresponding author: E-mail: nashwa05@yahoo.com

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The construction and electrochemical response characteristics of poly(vinyl chloride) membrane sensors for the determination of *p*-nitroaniline were described. The sensors are based on using of ethamsylate as an ionophore and *o*-nitrophenyl octyl ether as plasticizer in the poly(vinyl chloride) matrix. Conventional and graphite membrane sensors were prepared and the performance characteristics are evaluated according to IUPAC recommendations, reveal fast, stable and linear response for *p*-nitroaniline over the concentration range 1×10^{-5}-1×10^{-3} and 5×10^{-5}-1×10^{-3} M with cationic slopes of 51.5 and 50.6 mV per concentration decade at pH 5 for conventional and graphite membrane sensors, respectively. Sodium tetraphenylborate was used as ionic additive with ethamsylate. The potentiometric selectivity data revealed no interference from common cations. The direct potentiometric determination of *p*-nitroaniline using the proposed sensors gave average recoveries of 99.7 ± 1.1 and 101.4 ± 0.9 for the conventional and graphite sensors, respectively. The sensors are used for direct measurement of *p*-nitroaniline content in industrial waste water. The developed method was found to be simple, accurate and precise when compared with a published spectrophotometric method.

Key Words: *p*-Nitroaniline, Ethamsylate, Waste water, Graphite sensor.

INTRODUCTION

Electrochemical sensors are expected to play an increasing role in environmental monitoring. Significant technological advances are developed to facilitate the environmental applications of electrochemical devices. Electroanalytical chemistry can play an important role in the protection of our environment. In particular, electrochemical sensors and detectors are very attractive for on-site monitoring of priority pollutants, as well as for addressing other environmental needs. Such devices satisfy many requirements for on-site environmental analysis. They are inherently sensitive and selective towards electroactive species, fast and accurate, compact, portable and inexpensive. Such capabilities have already made a significant impact on decentralized clinical analysis.

p-Nitroaniline is commonly used as an intermediate in the synthesis of dyes, antioxidants, pharmaceuticals and gasoline, in gum inhibitors, poultry medicines and as a corrosion inhibitor. *p*-Nitroaniline is a starting material for the synthesis of Para Red, the first Azo dye[1]. The compound is toxic by way of inhalation, ingestion and absorption and should be handled with care. *p*-Nitroaniline is particularly harmful to all aquatic organisms and can cause long-term damage to the environment if released as a pollutant. Few methods were published for the determination of *p*-nitroaniline, *e.g.* spectrophotometry[2,3], double organic substrate oscillating chemical system using non-equilibrium stationary state[4], capillary zone electrophoresis with amperometric detection[5], thin-layer chromatography (TLC) and high performance liquid chromatography (HPLC)[6].

Because of the high potential for *p*-nitroaniline to cause methemoglobin formation, *p*-nitroaniline should be considered hazardous by all routes of exposure and the exposures should be tightly controlled.

Ethamsylate or cyclonamine (diethylammonium, 2,5-dihydroxybenzene-sulfonate) is a haemostatic agent commonly used in the prevention and control of haemorrhage from small blood vessels (Fig. 1)[7]. Recently, some drugs are used as carriers for the determination of some cations[8,9]. Because of the presences of some functional groups in the chemical structure of the drug which are valuable and attractive for the reaction with cations.

Although direct potentiometry with chemical sensor has found many applications in some analyses[10], no such methods are available, so far, for *p*-nitroaniline. In this work, preparation, characterization and application of simple potentiometric membrane sensor for fast determination of *p*-nitroaniline in pure form and environmental samples are described. The sensing membranes incorporate ethamsylate ionophore in poly(vinyl chloride) matrix and *o*-nitrophenyl octyl ether as plasticizer.

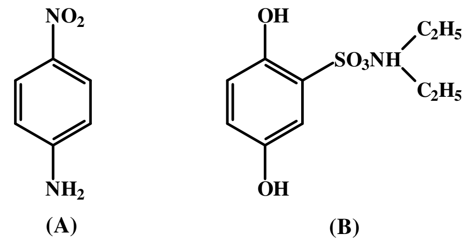

Fig. 1. Chemical structure of (A) *p*-nitroaniline and (B) ethamsylate

Conventional and graphite membrane sensors were prepared characterized and applied for the determination of *p*-nitroaniline in industrial waste water.

EXPERIMENTAL

Potentiometric measurements at 25 ± 1 ºC were made with an orion digital ion-analyser (model) 420A and *p*-nitroaniline conventional and graphite membrane sensors based on ethamsylate as ionophore. *p*-nitroaniline membranes were used in conjunction with an Orion 90-02 Ag-AgCl double-junction reference electrode containing a 10 % (w/v) KNO_3 solution in the outer compartment. Adjustment of the pH was made with an Orion 91-20 combination glass electrode.

All chemicals were of analytical-reagent grade, unless otherwise stated and bidistilled deionized water was used throughout. *p*-Nitroaniline and ethamsylate were obtained from Sigma Chem. Co. (St. Louis, MO., USA). *o*-Nitrophenyl octyl ether (*o*-NPOE) plasticizer and tetrahydrofuran (THF) (freshly distilled prior to use) were obtained from Aldrich Chemical Co. (Milwaukee, Wisconsin, USA). Sodium tetraphenylborate (NaTPB), was obtained from Fluka (Ronkonkoma, NY).

Conventional membrane sensor: The general procedure used for preparation of poly(vinyl chloride) membrane is similar to the previously described[11-13]. The membranes were prepared by dissolving 3 mg of ionophore, 0.2 mg of sodium tetraphenylborate, 68 mg of poly(vinyl chloride) and 124 mg of *o*-nitrophenyl octyl ether in about 5 mL of tetrahydrofuran. The solution mixture was poured into about 5 cm Petri dish and left to dry overnight at room temperature. A transparent master poly(vinyl chloride) membrane with an average thickness of *ca.* 0.1 mm was sectioned with a cork borer (10 mm diameter) and glued to polyethylene tube. The internal solution was a mixture of an equal volume of *p*-nitroaniline and KCl solutions (1×10^{-3} M). The prepared sensor was conditioned by soaking in *p*-nitroaniline solution (1×10^{-3} M) for 9 h and was stored in the same solution when not in use.

Graphite membrane sensor: Graphite poly(vinyl chloride) membrane was prepared as mentioned before. The resulting mixture was transferred into a glass dish of 5 cm diameter. Graphite electrodes (3 mm diameter and 10 mm long) were prepared from spectroscopic grade graphite. A shielded copper wire was glued to one end of the graphite rod with epoxy resin and the electrode was sealed into the end of a poly(vinyl chloride) tube of about the same diameter by epoxy resin. The working surface of the electrode was polished with fine alumina slurries on a polishing cloth, sonicated in distilled water and dried in air. The polished electrode was dipped into the membrane solution and the solvent was evaporated. A membrane was formed on the graphite surface and was allowed to set overnight. For a comparative study, a membrane containing no active component was also prepared. The electrode was finally conditioned for 9 h by soaking in a 1×10^{-3} M *p*-nitroaniline.

Sensor calibration: The sensors were calibrated by transferring 1.0 mL aliquots of 1×10^{-5}-1×10^{-3} M aqueous solution of *p*-nitroaniline to 25 mL beaker containing 9.0 mL of acetate buffer pH 5. The sensor is immersed in the solution inconjunction with a double junction Ag/AgCl reference electrode. The potential readings were recorded after stabilization to ± 0.2 mV and emf was plotted as a function of logarithm *p*-nitroaniline concentration. The calibration graphs (Fig. 2) were used for subsequent determination of unknown *p*-nitroaniline concentrations.

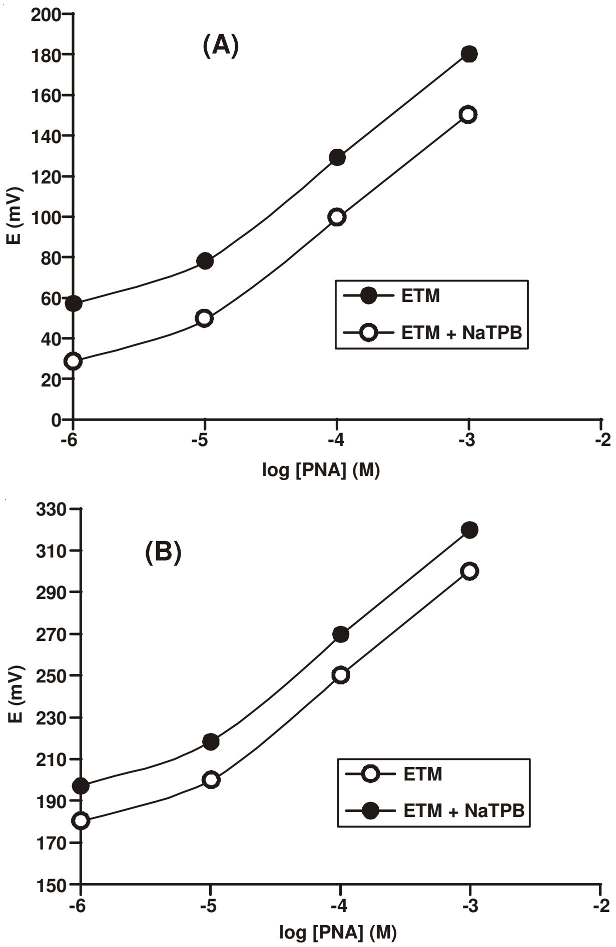

Fig. 2. Potentiometric response of of *p*-nitroaniline (A) conventional; and (B) graphite poly(vinyl chloride) membrane sensors

Sensor selectivity: The selectivity of *p*-nitroaniline sensors were measured using the separate solutions method (SSM)[14]. A 1.0 mL aliquot of 1×10^{-3} M of the *p*-nitroaniline solution was transferred into a 25 mL beaker containing 9.0 mL of acetate buffer pH 5. The *p*-nitroaniline sensor in conjunction with a double junction Ag-AgCl reference electrode was immersed in the solution and the potential was measured. In a separate run, a 1 mL of aliquot of 1×10^{-3} M of the interfering solution was transferred into 25 mL containing 9 mL of the same buffer and the potential reading was recorded. Selectivity coefficients were calculated from the following equation:

TABLE-1
RESPONSE CHARACTERISTICS OF *p*-NITROANILINE SENSORS

Parameter*	Convenential sensors		Graphite sensors	
	Ethamsylate	Ethamsylate + NaTPB	Ethamsylate	Ethamsylate + NaTPB
Slope, (mV per decade)	51.5 ± 0.6	52.1 ± 0.7	50.6 ± 0.5	51.4 ± 0.4
Correlation coefficient, (r)	0.997	0.998	0.997	0.998
Linear range, (M)	1×10^{-3}-2×10^{-5}	1×10^{-3}-1×10^{-5}	1×10^{-3}-2×10^{-5}	1×10^{-3}-1×10^{-5}
Lower limit of detection, (M)	9×10^{-6}	8×10^{-6}	9×10^{-6}	8×10^{-6}
Response time for 10^{-3} M, (s)	20 ± 2	20 ± 2	20 ± 2	20 ± 2
Recovery time for 10^{-3} M, (s)	30 ± 2	30 ± 2	30 ± 2	30 ± 2
Working range, (pH)	3-6	3-6	3-6	3-6
Life span, (week)	4	4	4	4
Accuracy (%)	99.5	99.6	99.4	99.6
Repeatability, CV_w (%)	0.7	0.9	0.8	0.9
Between day-variability, CV_b (%)	1.5	1.2	1.3	1.2
Relative standard deviation, RSD (%)	1.2	1.1	1.3	1.1

*Average of five measurements.

$$\log\left(K^{Pot}_{PNA,M}\right) = \left(\frac{a_{PNA}}{(a_I)^{Z_{PNA}/Z_I}}\right)$$

where a_{PNA} and a_I are the activities of the primary ion *p*-nitroaniline and the interfering ion, respectively; z_{PNA} and z_I are the charges of the primary ion *p*-nitroaniline and the interfering ion, respectively.

Determination of *p*-nitroaniline in waste water: Several waste water samples (10 samples) were collected from dyes factories in Egypt. Each sample solution was then diluted using acetate buffer pH 5. Solutions were transferred to 50 mL volumetric flasks and diluted to the mark with 0.02 M acetate buffer pH 5 and measured using direct potentiometric method. Alternatively, standard addition technique was used by monitoring the potential of 50 mL sample test solution before and after addition of 0.50 mL of standard 1 x 10^{-3} M *p*-nitroaniline solution. The potentiometric results were compared with data obtained by spectrophotometric method[3].

RESULTS AND DISCUSSION

Conventional and graphite membrane sensors were prepared and the performance characteristics are evaluated according to IUPAC recommendations[15]. The conventional sensor incorporating membrane plasticized with (*o*-nitrophenyl octyl ether) was prepared with the composition of 1.5 wt. % ethamsylate (ETM), 34.8 wt. % poly(vinyl chloride), 63.5 wt. % *o*-nitrophenyl octyl ether and 0.1 wt % sodium tetraphenylborate. The sensors show linear potentiometric response over the concentration range of 1 × 10^{-3}-1 × 10^{-5} M with cationic slope of 51.5 and 52.1 mV per decade for sensor without and with additive, respectively. The response time of the sensors was 20-30 s and the life span of the sensors was about 4 weeks. Graphite sensor was prepared with the composition of 1.5 wt % ethamsylate and 0.1 wt % sodium tetraphenylborate, which exhibits the best performance, slope 50.6 and 51.4 mV per decade at 25 ºC, over concentration range 1 × 10^{-5}-1 × 10^{-3} M, for sensors without and with additive and response time 20-30 s and the life span of the sensors was about 4 weeks. The presence of very small amount of lipophilic negatively charged membrane additives improves the potentiometric behaviour of the sensors and enhances the selectivity[16], probably due to reducing their ohmic resistance and catalyzing the exchange kinetics at the sample/membrane interface[17]. Membranes with the composition of 0.1 wt % sodium tetraphenylborate as a membrane additive, 1.5 wt % ionophore, 34.8 wt % poly(vinyl chloride) and 63.5 wt % plasticizer, show a slight improvement. Table-1 shows the performance characteristics of both sensors in the presence and in the absence of sodium tetraphenylborate membrane additive.

Effect of pH: The influence of the pH on the potential response of *p*-nitroaniline based membrane sensors was tested using 1 × 10^{-4} and 1 × 10^{-3} M *p*-nitroaniline solutions over the pH range 2-10. Adjustment of pH was carried out using KOH and/or HCl. From pH-potential profiles, it is apparent that there is no change in potential response within the pH range 3-6. In these acidic solutions, *p*-nitroaniline is completely ionized, dissociated and sensed as monovalent cation. The potential reading over this range are constant within ± 0.3 mV.

Effect of interfering ions: The potentiometric selectivity coefficients ($K^{Pot}_{PNA,I}$) of *p*-nitroaniline sensors based on with and without sodium tetraphenylborate were determined using the separate solutions (SSM) method[14] at a concentration level ~ 10^{-4} M of both *p*-nitroaniline solution and interfering cations. The influences of 20 different organic and inorganic cations on the response of the sensors were evaluated by measuring the selectivity coefficients. The results are listed in Table-2. The results obtained show that these sensors display significantly high selectivity for *p*-nitroaniline over many common organic and inorganic cations. Sensors incorporating sodium tetraphenylborate in the membranes exhibit better selectivity compared with those without sodium tetraphenylborate.

Determination of *p*-nitroaniline in wastewater: The proposed *p*-nitroaniline sensors were used for direct potentiometric determination of *p*-nitroaniline in some industrial wastewater samples obtained from local dyes factories. The samples were collected, kept and measured. The results were compared with data obtained by spectrophotometry[3]. The wastewater samples were diazotized with orcinol on a silica gel plate. Quantitative evaluation of *p*-nitroaniline is made by visual comparison of intensities of colour by spectrophotometry at 400 nm. The results complied in Table-3 clearly indicate good agreement.

TABLE-3
DETERMINATION OF *p*-NITROANILINE IN WASTE WATER

Sample No.	Conventional sensors (mg/L)*		Graphite sensors (mg/L)*		UV-VIS^3
	Ethamsylate	Ethamsylate + NaTPB	Ethamsylate	Ethamsylate + NaTPB	
1	190.4 ± 0.7	191.3 ± 0.6	190.8 ± 0.2	191.9 ± 0.8	189.8 ± 0.5
2	250.6 ± 0.9	250.9 ± 0.5	250.2 ± 0.6	251.5 ± 0.3	249.2 ± 0.7
3	265.5 ± 0.8	264.7 ± 0.9	265.2 ± 0.9	266.1 ± 0.8	263.6 ± 1.1
4	279.5 ± 0.4	278.9 ± 0.8	279.8 ± 0.7	280.2 ± 0.6	277.5 ± 0.9

*Average of five measurements.

TABLE-2
POTENTIOMETRIC SELECTIVITY COEFFICIENTS
OF PNA MEMBRANE SENSORS

Interferent (I)	$\log (K^{Pot}_{PNA,I})$*			
	Conventional sensors		Graphite sensors	
	ETM	ETM + NaTPB	ETM	ETM+NaTPB
p-Aminophenol	-3.0	-3.2	-3.1	-3.4
p-Aminobenzoate	-2.9	-3.1	-3.0	-3.5
Glycinate	-2.5	-2.8	-2.6	-3.1
Alaninate	-3.0	-3.2	-3.0	-3.3
Aspartate	-2.6	-3.0	-2.5	-2.7
Urea	-2.8	-3.1	-2.7	-2.9
Thiourea	-3.1	-3.4	-3.0	-3.2
Glucose	-3.5	-4.1	-3.6	-3.8
Fractose	-3.8	-4.3	-3.6	-4.1
Maltose	-3.6	-4.2	-3.6	-4.3
Tartarate	-3.2	-3.5	-3.0	-3.3
Oxalate	-2.7	-3.1	-2.9	-3.3
Citrate	-3.1	-3.3	-3.0	-3.4
Acetate	-3.2	-3.4	-3.1	-3.3
Na^+	-3.5	-3.6	-3.2	-3.7
K^+	-3.0	-3.1	-3.0	-3.5
NH_4^+	-3.4	-3.6	-3.2	-3.6
Ca^{2+}	-3.0	-3.2	-3.1	-3.5
Mg^{2+}	-3.1	-3.5	-3.0	-3.7
Ag^+	-3.2	-3.4	-3.2	-3.3

*Average of five measurements, ETM = Ethamsylate.

Conclusion

Potentiometric *p*-nitroaniline-selective membrane sensors based on ethamsylate as ionophore plasticized in *o*-nitrophenyl octyl ether and poly(vinyl chloride) as a polymeric matrix show fast, stable, reproducible and selective characteristics toward *p*-nitroaniline ions with a reasonable linear range, lower detection limit and good selectivity. Conventional and graphite sensors are prepared and characterized. Applications to the determination of *p*-nitroaniline in wastewater are demonstrated and the results compare favorably with data obtained with spectrophotometric method.

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