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Flow injection potentiometric sensor for determination of phenylpropanolamine hydrochloride

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Abstract A new polymeric membrane electrode has been constructed for the determination of phenylpropanolamine hydrochloride. The electrode was prepared by solubilizing the phenylpropanolamine-phosphomolybdate ion associate into a polyvinyl chloride matrix plasticized by dibutylphthalate as a solvent mediator. The electrode showed near-Nernstian response over the concentration range of 1×10^{-5} – 1×10^{-2} M with low detection limit of 6.3×10^{-6} M. The electrode displays a good selectivity for phenylpropanolamine with respect to a number of common inorganic and organic species. The electrode was successfully applied to the potentiometric determination of phenylpropanolamine ion in its pure state and its pharmaceutical preparation in batch and flow injection conditions.

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1. Introduction

Phenylpropanolamine hydrochloride (PPACl), Benzenemethanol, α -(1-aminoethyl) hydrochloride, (R^* , S^*) ($\pm$) [154-41-6], belongs to the sympathomimetic amine class of drugs and is structurally related to ephedrine hydrochloride (USP

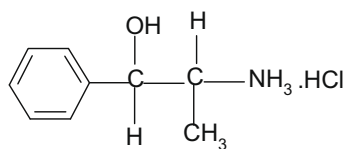
Dictionary of USAN and International Drug Names, 1996) (Scheme 1).

A number of analytical methods have been reported for the determination of PPACl. Among these are HPLC (Dowse et al., 2006; Kaddoumi et al., 2004; Nakashima et al., 2002; Rind et al., 2001; Zaater et al., 1999; Yamashita et al., 1990), gas chromatographic (Harsono et al., 2005; Van-Eenoo et al., 2001), capillary electrophoresis (Mateus-Avois et al., 2003; Suntornsuk, 2001; Wang et al., 2000), conductimetric (Issa et al., 2005) and spectrophotometric methods (Khuhawar et al., 2005; Ferreyra and Ortiz, 2002; Goicoechea and Olivieri, 1999; Le-Hazif et al., 1996; Ma et al., 1991; Onur and Acar, 1990). Potentiometric ion-selective electrodes based on phenylpropanolamine-tetraphenylborate or phenylpropanolamine-phosphotungstate have been reported (Badawy et al., 2004). Ion-selective membrane electrodes play an increasing role in pharmaceutical analysis with further use in FI (Vytras, 1989;

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Scheme 1

Vire and Kauffmann, 1994; Cosofret, 1991) offering advantages of simplicity, rapidity and accuracy. Liquid membrane electrodes using phosphotungstic and phosphomolybdic acids were previously described (Issa and Zayed, 2006).

The present work describes the construction and potentiometric characterization of new potentiometric sensor for PPA. The electrode is based on the incorporation of phenylpropanolamine-phosphomolybdate (PPA)₃-PM ion associate in a polyvinyl chloride (PVC) membrane plasticized with dibutylphthalate (DBP). Applications of the electrode for the determination of PPACl in pharmaceutical preparation for batch and FI analysis system were also described.

2. Experimental

2.1. Reagents and materials

All chemicals were of analytical grade. Double distilled water was used throughout all experiments. Pure grade phenylpropanolamine hydrochloride (PPACl) and the pharmaceutical preparation Contac 12 capsules were provided by Kahira pharmaceutical and Chemical Industries Co., Egypt, and Egyptian International Pharmaceutical Industries Co., (EIPICO), respectively. Phosphomolybdic acid (PMA), dioctyl sebacate (DOS), and tricresyl phosphate (TCP) were from Fluka, dibutyl phthalate (DBP), and dioctyl phthalate (DOP) from Merck. PVC of relatively high molecular weight was from Aldrich.

2.2. Apparatus

Potentiometric and pH measurements were carried out using a Seibold G-103 digital pH/mV meter (Vienna, Austria). A techne circulator thermostat Model C-100 was used to control the temperature of the test solutions. A saturated calomel electrode (SCE) was used as the external reference, while an Ag/AgCl wire as an internal electrode.

The flow injection setup as previously reported (Issa and Zayed, 2006). Fig. 1 represents the schematic diagram of the flow injection system used in the measurements.

2.3. Preparation of the ion associate

The ion associate (PPA)₃-PM, was prepared by mixing 150 ml of 10⁻² M PPACl solution with 50 ml of 10⁻² M phosphomolybdic acid. The formed precipitate was filtered, washed thoroughly with bidistilled water until chloride free and dried at room temperature. The composition of the ion-associate was found to be 3:1 as confirmed by elemental analysis data done at microanalytical research laboratory in National Research Centre (Dokki, Cairo, Egypt). The percentages values found are 14.20, 1.91 and 1.82 and the calculated values are 14.24, 1.73 and 1.84 for C, H and N, respectively.

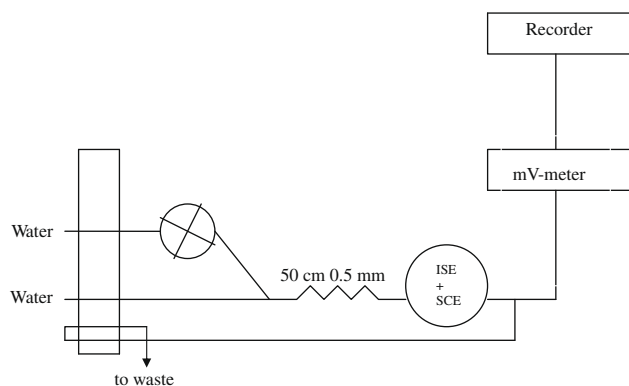


Figure 1 Schematic diagram of the flow injection system used in the measurements.

2.4. Electrode preparation

The electrode was constructed as previously described (Issa and Zayed, 2006). The membranes were prepared by dissolving the required amount of the ion associate, PVC and DBP, in about 10 ml of THF. The solution mixture was poured into a 6.0 cm Petri dish and left to dry in air. To obtain a uniform membrane thickness, the amount of THF was kept constant, and its evaporation was fixed for 24 h. The thickness of the membrane was about 0.2 mm.

A 12 mm diameter disk was cut out from the prepared membrane and glued using PVC-THF paste to the polished end of a plastic cap attached to a glass tube. The electrode body was filled with a solution of 1 × 10⁻¹ M NaCl and 1 × 10⁻² M PPACl. The electrode was pre-conditioned before use by soaking in a 1 × 10⁻³ M PPACl solution.

2.5. Potentiometric determination of PPACl

The standard addition method (Baumann, 1986) was applied, in which small increments of the standard solution (10⁻¹ M) of PPACl were added to 50 ml aliquot samples of various concentrations from pure drug or pharmaceutical preparations. The change in millivolt reading was recorded for each increment and used to calculate the concentration of PPACl sample solution using the following equation:

$$C_x = C_s \left(\frac{V_s}{V_x + V_s} \right) \left(10^{n(\Delta E/S)} - \frac{V_x}{V_x + V_s} \right)^{-1},$$

where C_x and V_x are the concentration and the volume of the unknown, respectively, C_s and V_s the concentration and the volume of the standard solution, respectively, s the slope of the calibration graph and ΔE is the change in millivolt due to the addition of the standard solution.

2.6. Determination of phenylpropanolamine hydrochloride in Contac 12 capsules

Twenty capsules were accurately weighed and powdered in a mortar, the required amount from the capsules powder was dissolved in chloroform to separate phenylpropanolamine hydrochloride from the capsules matrix (chloroform dissolves isopropamide iodide only).

The separated phenylpropanolamine hydrochloride was dried and then dissolved in about 30 ml bidistilled water and

filtered in a 50 ml measuring flask. The residue was washed three times with bidistilled water, the volume was completed to the mark by the same solvent, the contents of the measuring flask were transferred into a 100 ml beaker and subjected to a potentiometric determination of PPACl.

3. Results and discussion

3.1. Optimization of the ISE response in batch conditions

Four membrane compositions were prepared by varying the percentages of the ion associate, while keeping the percentages of the PVC and the plasticizer equal 1:1 (Table 1).

The results showed that the electrode made of membrane with 5% PPA-PM ion associate exhibits the best performance characteristics [slope 54.88 mV concentration decade⁻¹ at 25 °C, usable concentration range 1×10^{-5} – 1×10^{-2} M and detection limit (Buck and Cosofret, 1993) 6.31×10^{-6} M PPACl] (Table 2). The role of the membrane liquid is significant because the nature of the selected organic solvent determines the extraction parameters of the ion associates and consequently, the electrode selectivity towards the ion of interest (Vytras, 1989).

Four plasticizers were tested to evaluate the effect of the plasticizer on the response of PPA electrode (Table 2). The results indicate that DBP is the best plasticizer tested. Poor sensitivities for the electrodes plasticized using DOP, DOS and TCP are due to low solubilities or low distributions of (PPA)₃-PM ion associates in these solvents (Armstrong and Horvoi, 1990). The electrode using DBP as a plasticizer provides not only higher Nernstian slope but also a wide response range more stable potential reading and lower detection limit. It seems that DBP, as a low polarity compound, provides more appropriate conditions for incorporation of the highly lipophilic PPA⁺ ion into the membrane prior to its exchange with the soft ion exchanger. Therefore, we used DBP as a suitable plasticizer for further studies.

The effect of temperature on the electrode response was studied at different temperatures. The electrode gave good

Nernstian response over the temperature range 25–60 °C. The standard electrode potentials, E^0 , were determined at different temperatures and used to calculate the thermal coefficient of the electrode (Oesch et al., 1996), which were found to be -0.0020 V/°C and of the cell to be 0.0014 V/°C. These values indicate fairly good thermal stability of the electrodes.

The life time of the electrode was investigated by performing the calibration graphs after the electrode was soaked continuously in 10^{-3} M PPACl periodically till 28 days and calculating the response slopes. The results indicate that during the first day the slope remains constant at about 55.0 mV/concentration decade, then slightly decreased reaching 54.0, 53.0 and 52.0 mV/concentration decade after 12, 18 and 22 days, respectively. A further decrease reaching 49.0, 46.0 and 43.0 mV/concentration decade was observed after 24, 26 and 28 days, respectively. This decrease in the slope of the electrode may be due to the leaching of the lipophilic salts from the gel layer at the electrode surface.

3.2. Optimization of FI parameters

FI parameters were optimized in order to obtain the best signal sensitivity and sampling rate under low dispersion. The dispersion coefficient was 1.23, i.e., limited dispersion that aids optimum sensitivity and fast response of the electrode (Trojanowicz and Matuszewski, 1982). The influence of the injected volume was assessed for sample volumes from 4.7 to 500.0 µl. In general, the higher the sample volume, the higher the peak heights and residence time of the sample at the electrode surface, requiring a longer time to reach a steady state and greater consumption of sample (Yang et al., 1998). A sample loop of size 150 µl was used throughout this work, giving maximum peak height, less consumption of reagents, and a short time to reach the base line.

The effect of the flow rate was evaluated using different flow rates (4.15, 5.35, 7.50, 9.70, 12.50, 17.85, 23.25, 25.00, 27.00 and 30.00 ml/min) at a constant sample loop of size 150 µl. It was found that, as the flow rate increased, the peaks became higher and narrower until a flow rate of 7.50 ml/min.

Table 1 Composition of the membrane and the slope of the calibration graphs at 25 ± 1 °C and 30 min of soaking in 10^{-3} M PPACl.

Membrane	Composition% (W/W)			Slope mV/decade	RDS%
	Ion associate	PVC	DBP		
I	3.0	48.5	48.5	53.53	0.62
II	5.0	47.5	47.5	54.88	0.68
III	7.0	46.5	46.5	54.31	0.61
VI	10.0	45.0	45.0	50.78	0.54

RSD: relative standard deviation (four determinations).

Table 2 Effect of plasticizers on PPA responsive membranes and slopes of the corresponding calibration graphs at 25 ± 1 °C and 30 min of soaking in 10^{-3} M PPACl.

Plasticizer	Slope mV/decade	Usable concentration range (M)	Detection limit (Buck and Cosofret, 1993)
DBP	54.9	1.00×10^{-5} – 1.00×10^{-2}	6.31×10^{-6}
DOP	44.0	1.00×10^{-5} – 1.00×10^{-2}	7.94×10^{-6}
DOS	50.1	3.98×10^{-5} – 1.00×10^{-2}	1.12×10^{-5}
TCP	50.2	3.98×10^{-5} – 1.00×10^{-2}	1.41×10^{-5}

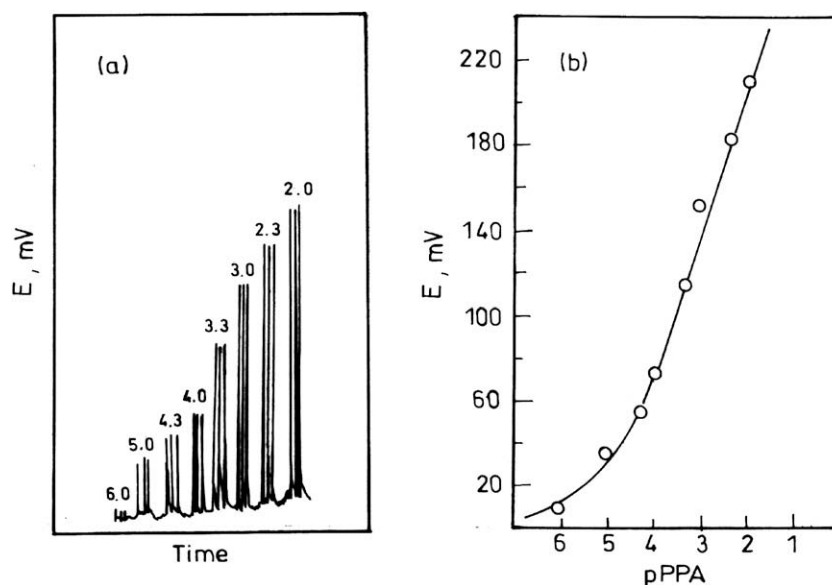


Figure 2 Recording (a) and its corresponding calibration graph (b) for PPA-PM electrode under FI conditions.

Then the peaks obtained above this flow rate was nearly the same. Therefore this flow rate was used throughout this work providing the maximum peak height, a shorter time to reach line and less consumption of the carrier solution. Under these conditions the electrode presented detection limit of 1.12×10^{-5} and a linear range of 5.0×10^{-5} – 1×10^{-2} M PPACl. Fig. 2a represents the recorded peaks and Fig. 2b, shows the calibration graph for the electrode at the optimum conditions.

The effect of the pH of the test solution on the electrode potentials was studied in batch and FI conditions. In batch measurements the effect of pH of the test solution (10^{-4} , 10^{-3} and 10^{-2} M PPACl) on the electrode potential was investigated by following the variation in potential with the change in pH by adding of very small volumes of hydrochloric acid and sodium hydroxide (each 0.1–1.0 M). The results indicated that the electrode did not respond to the pH change in the range 2.8–6.8 (Fig. 3). In this pH range, the electrode can be used safely for the respective determination of PPACl in the pharmaceutical preparations. The increase in mV reading at pH less than 2.8 may be due to the penetration of H^+ into the membrane surface. While the decrease in the potential reading after pH 6.8 most probably attributed to the formation of the free phenylpropanolamine base in the solution, leading to a decrease in the concentration of phenylpropanolamine cation. In FI a series of solutions of concentration that are 10^{-3} M PPACl and have pH values ranging from 1 to 12 were injected in the flow stream adjusted to the same pH, then the peak heights representing the variation of potential with pH were measured. No variation in the peak height was observed in the same pH ranges registered in the steady state mode for the electrode. This indicates that the electrode do not respond to pH changes in these ranges under FI conditions.

3.3. Selectivity of the electrode

The effect of some inorganic cations, sugars, amino acids and vitamins on the response of phenylpropanolamine ion selective electrode was investigated. The selectivity coefficients were

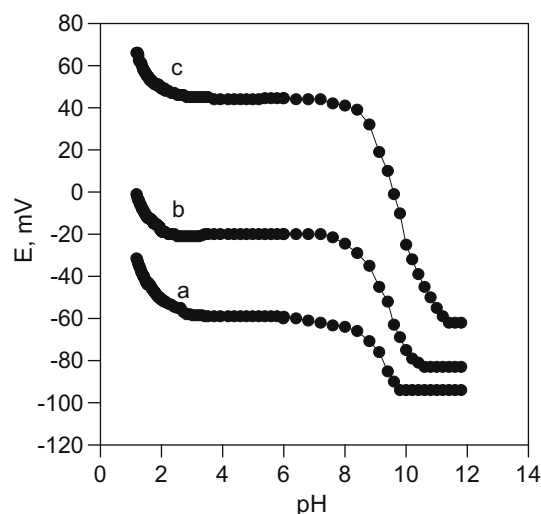


Figure 3 Effect of the test solution on the potential response of the PPAFM electrode (a) 1×10^{-4} , (b) 1×10^{-3} and (c) 1×10^{-2} .

determined using two methods, the separate solution method (SSM) (Guibault et al., 1976) and the matched potential method (MPM) (Umezawa et al., 2000, 1995). In the separate solution method, the Nicolsky–Eisenman equation was used:

$$\log K_{PPA,J}^{pot} = (E_2 - E_1)/S + \log[PPACl] - \log[J^{z+}]^{1/z},$$

where E_1 and E_2 are the electrode potentials in a 1×10^{-3} M solutions of PPACl and interfering ions J^{z+} , respectively, and S is the slope of the calibration graphs in mV concentration decade $^{-1}$.

In matched potential method, the potentiometric selectivity coefficient is defined as the activity ratio of primary ions and interfering ions that give the same potential change under identical conditions. At first, a known activity of phenylpropanolamine ion solution is added into a reference solution that contains a fixed activity of phenylpropanolamine α_{PPA} ,

Table 3 Selectivity coefficients for PPA-PM responsive electrode.

Interferent	$K_{PPA,J^{Z+}}^{pot}$		FI
	Batch		
	SSM	MPM	
Na ⁺	2.41×10^{-3}	7.44×10^{-4}	1.90×10^{-2}
K ⁺	1.53×10^{-2}	6.53×10^{-4}	1.83×10^{-2}
Mg ²⁺	9.78×10^{-4}	4.87×10^{-4}	2.24×10^{-4}
Ca ²⁺	1.19×10^{-4}	7.75×10^{-4}	4.69×10^{-4}
Ba ²⁺	1.99×10^{-4}	7.57×10^{-4}	1.47×10^{-4}
Sr ²⁺	4.88×10^{-4}	6.45×10^{-4}	7.93×10^{-4}
Co ²⁺	2.13×10^{-4}	7.24×10^{-4}	1.32×10^{-4}
Zn ²⁺	1.82×10^{-4}	8.77×10^{-4}	3.42×10^{-4}
Cu ²⁺	2.23×10^{-5}	6.80×10^{-4}	2.24×10^{-4}
Vitamin B ₁	1.05×10^{-2}	1.44×10^{-3}	2.51×10^{-2}
Vitamin B ₆	8.97×10^{-2}	3.28×10^{-3}	4.72×10^{-2}
Glucose	—	2.85×10^{-4}	—
Fructose	—	2.69×10^{-4}	—
Maltose	—	3.03×10^{-4}	—
Lactose	—	2.92×10^{-4}	—
Alanine	—	2.40×10^{-4}	—
Glycine	—	2.45×10^{-4}	—

Table 4 Determination of PPACl in pure form and in pharmaceutical preparation by applying standard additions method and under FI conditions ($n = 4$).

	Taken, mg	Mean recovery, %	RSD, %
Pure solution	1.0×10^{-4}	99.73	0.732
Standard additions method	2.0×10^{-4}	99.39	1.475
	3.0×10^{-4}	98.72	0.650
	5.0×10^{-4}	98.48	1.156
	1.0×10^{-4}	100.52	0.422
Capsules (Contac 12)	1.0×10^{-4}	100.52	0.422
Standard additions method	2.0×10^{-4}	100.78	0.537
	3.0×10^{-4}	100.50	0.717
	5.0×10^{-4}	101.46	0.742
	5.0×10^{-5}	100.86	0.984
FI	1.0×10^{-4}	100.68	0.836
	5.0×10^{-4}	100.72	0.477
	1.0×10^{-3}	100.62	0.802
	1.0×10^{-3}	100.62	0.802

($\alpha'_{PPA} - \alpha_{PPA}$ is the change in activity), and the corresponding potential change ΔE is recorded. The change in potential produced at the constant background of the primary ion must be the same in both cases:

$$K_{PPA,J^{Z+}}^{pot} = \frac{a'_{PPA} - a_{PPA}}{a_J},$$

where a_J is the activity of the added interferent.

In FI, a series of standard PPACl solutions between 5×10^{-6} and 1×10^{-2} M was prepared; their corresponding heights were measured and used to determine the slope of the calibration graph. Solutions that are 1×10^{-3} M of interfering ions were prepared; and their corresponding peak heights were also measured. The selectivity coefficients were calculated using the separate solution method. The selectivity coefficients values $K_{PPA,J^{Z+}}^{pot}$ of the electrode listed in Table 3 reflect a high selectivity of this electrode towards phenylpropanolamine cation. The inorganic cations do not interfere

owing to the differences in ionic size and consequently in their mobilities and permeabilities as compared with PPA⁺. In case of non ionic species, the high selectivity is due to the difference in polarity and to the lipophilic nature of their molecules relative to PPA cation.

3.4. Analytical applications

In order to assess the applicability of the proposed selective electrode, the method was applied for the determination of PPACl in pure solutions and in the pharmaceutical preparation Contac 12 Capsules (phenylpropanolamine HCl, 50 mg and isopropamide, 3.4 mg under batch and FI conditions. The mean recovery and the relative standard deviation values are summarized in Table 4. The interference resulted from the other drug, isopropamide was prevented by dissolving the capsules powder in chloroform, that dissolve only isopropamide, the data indicated that there is no interference

Table 5 Statistical comparison between the results of determination of the pharmaceutical preparation Contac 12 capsules applying the proposed and official methods ($n = 4$).

Parameter	Standard additions	FI	Official method (United states Pharmacopeia, 2002)
Mean recovery, %	100.81	100.72	101.72
SD	0.609	0.780	0.655
RSD	0.604	0.774	0.644
F -ratio (9.28) ^a	1.157	1.418	
t -test (2.447) ^b	2.036	1.964	

SD: standard deviation.

RSD: relative standard deviation.

^a Tabulated F -value at 95% confidence level.^b Tabulated t -value at 95% confidence level and six degrees of freedom.

from the other excipients used in the formulations of the capsules.

The results obtained were compared with the official method (United states Pharmacopeia, 2002) (Table 5) and found to be in good agreement with those obtained from the official method. Student's t - and F -tests (at 95% confidence level) were applied (Miller and Miller, 1993) and the results show that the calculated t - and F -values did not exceed the theoretical values.

4. Conclusion

The proposed sensor based on (PPA)₃-PM ion associate as the electroactive compounds might be a useful detector for the determination of PPACl in pharmaceutical preparations, in batch and FI system. The inherent advantages of the proposed techniques are their high selectivity, rapid response, simple operation, precise results and low cost.

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