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A Simple Potentiometric Sensor for *Rhodamine B*

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Abstract: The construction and performance characteristics of PVC electrodes for *Rhodamine B* (RB) are described. Different methods for electrode fabrication (modified with the ion-pair, ion pairing agent or soaking the plain electrode in the ion-pair suspension) have been used. Matrix compositions were optimized on the basis of effects of type and content of the modifier as well as influence of the plasticizers. The fabricated electrodes worked satisfactorily in the concentration range from 1×10^{-6} to 0.001 M with Nernstian cationic slopes, depending on the method of electrode fabrication. The ion-pair modified electrode showed the best performance (slope 56.3±2.0 mV decade^{-1}) compared with the plain electrodes or modified with sodium tetraphenylborate (NaTPB) and fast response time of about 8 sec and adequate lifetime (4 weeks). The developed electrodes have been successfully applied as well as end point indicator electrode for the potentiometric titration of RB with high accuracy and precision. The solubility products of different RB ion-pair were determined conductometrically.

Keywords: *Rhodamine B*; PVC electrode; Potentiometry; Solubility products.

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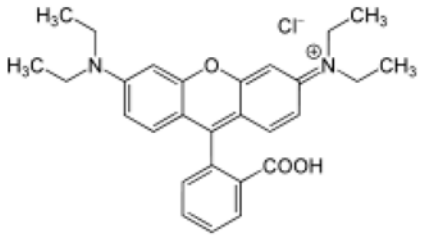
Introduction

Rhodamine B ($C_{28}H_{31}ClN_2O_3$, 9-(2-carboxyphenyl)-6-diethylamino-3-xanthen-yl-dene]-diethyl ammonium chloride, aka "*Basic Violet 10*"; see scheme 1) is usually listed as basic dye, having the overall positive charge. It is most commonly used as a fluorochrome, an example being in mixture with *Auramine O* to demonstrate acid fast organisms.



Scheme 1:

Rhodamin B

In analytical chemistry, RB is often used as a suitable ion-association reagent for heteropolymolybdate ion [1, 2], or a color reagent for spectrophotometric determination of different ions [3-5]. Catalytic methods are usually based on the oxidation of organic indicators with various oxidants. Among such indicators, RB is one of the most popular redox indicator applied for catalytic spectrophotometeric/ fluorimetric reactions [6-16].

The yield of RB from an initial commercial manufacturing synthesis is approximately 85% and there may be significant variations between batches. However, relatively little information on the analysis of such dyestuffs has been published; the book of Lastovskii and Vainshtein [17] is still a very useful manual. Application of spectro-photometeric methods is not possible since there is no pure standard dye for construction of the calibration curve. On the other hand, chromatographic methods require expensive apparatus with special columns or involve several manipulation steps before the final result of analysis. In contrast, electrochemical techniques are of choice since they possess the advantages of simplicity, accuracy and low cost without separation or pretreatment procedures. Concerning potentiometric methods for the dyes control [18, 19], simple indicator coated-wire type electrodes were also prepared and applied in potentiometric titrations of RB and other cationic dyes against NaTPB. Unjyo et al [20] applied the bis-(2-ethylhexyl) sulphosuccinate-RB ion-pair as electroactive material in liquid RB electrode; the proposed electrode showed Nernstian response in the concentration range 1×10^{-6}-10^{-3}M and was applied as an end-point indicator electrode in iodimetric titration. Ding prepared a coated glass electrode using a PVC membrane plasticized by dibutylphthalate containing RB-TPB as an electroactive ion-exchanger; the electrode was applicable in the concentration range 5×10^{-5}–5×10^{-3} M for RB with average recovery of 99.7% and showed a static response time about 1 min [21].

The present study is concerned with preparation, characterization and application of simple potentiometric sensors for rapid determination of RB. Electrodes were fabricated in plain and modified forms and then subjected to a series of tests to elect sensor possessing the most favorable analytical characteristics. The developed sensors were also applied as indicator electrode in the potentiometric titration of MB.

Experimental

Chemicals and Reagents

All reagents were of the analytical grade and double distilled water was used throughout the experiments. Rhodamine B (RB: $C_{16}H_{12}ClN_3S$, Merck) was used without further purification. o-Nitrophenyloctylether (o-NPOE) from Sigma was used for preparation of the sensors. Other types of plasticizers, namely dibutylphthalate (DBP), dioctylphthalate (DOP), dioctylsebacate (DOS), tricresylphosphate (TCP) and Tri (2-ethylhexyl) trimelliate (TOTM, S) were purchased from BDH, Sigma, AVOCADO and Fluka, respectively.

Sodium tetraphenylborate (NaTPB) solution (ca.0.01M) was prepared by dissolving a weighed amount of the substance (Fluka) in worm water, then adjusted to pH 9 by adding sodium hydroxide solution and completed to the desired volume with water. The resulting solution was standardized potentiometrically against standard 0.01M $TlNO_3$ solution [22]. Reineckate ammonium salt (RAS, Fluka), phosphotungstic acid (PTA, BDH), and phosphomolybdic acid (PMA, Fluka) were used for precipitation of different RB ion pairs.

Apparatus and Other Instrumentation

All potential measurements were performed using a 4310 Jenway digital pH meter with PC interface, equipped with silver-silver chloride double junction reference electrode in conjugation with the sensing drug ISE. A combined pH glass electrode was used for all pH measurements. Conductance was measured using 4310 Jenway Conductivity meter. Manual potentiometric titrations were performed using a Brand Digital Burette.

Construction of the Electrode

Ion-Pair Preparation. Ion-pairs synthesis protocol included drop wise addition of 10^{-2} M aqueous solution of ion pairing agents (NaTPB, RAS, PTA or PMA) to 50 ml of 10^{-2} M RB solution. The mixture was left to react for 5min under stirring at room temperature. The resulting precipitate was then filtered off on Whatman filter paper and washed several times with doubly distilled water. The compound was left to dry for 24h at 60ºC, washed with petroleum ether to remove any residual moisture, and then grinded to fine powder. Small sample portions were sent for elemental analysis.

Conductometric Determination of the Stoichiometric Ratios. A definite volume (5 ml) of 10^{-3} M RB was transferred to a 50 ml volumetric flask and made up to the mark with doubly distilled water. The dye solution was placed in a suitable titrating vessel and the conductivity cell was immersed, then a titrant of 10^{-3} M of TPB, RAS; 2.5×10^{-4} M of PMA, PTA was added from a digital burette. After each addition (0.2 ml), the solution was stirred for 1-2min and allowed to attain equilibrium; the conductance (μS) was measured. The cell is washed with doubly distilled water, immersed in 0.5 M H_2SO_4, electrolyzed with DC voltage using repeated polarity reversal to remove impurities, and finally washed and stored in doubly distilled water.

To eliminate the effect of dilution on the increase in conductance, the measured values were corrected for volume change by means of the following equation, assuming that conductivity is a linear function of dilution:

$$k_{corr} = k_{obs}[(v_o + v_{added}) / v_o]$$

Where, k_{obs}, the observed specific conductivity, v_o, the initial volume, and v_{added}, the added volume. The corrected conductivity was then plotted against the volume added of titrant and the first derivative was used to estimate the end point and the stoichiometric ratios (see [24-26]).

Conductometric Determination of the Solubility Products. Series of solutions of different concentrations were prepared for each of RB, TPB, RAS, PMA and PTA. The conductivities of these solutions were measured at 25°C and the specific conductivities (k), corrected for the effect of dilution were calculated and used to obtain the equivalent conductivities (λ) of these solutions.

$$\lambda = 1000\ k / C$$

λ (at finite concentration) and λ_o (at infinite dilution) can be related by Onsanger equation [27]:

$$\lambda = \lambda_o - (a + b\ \lambda_o)\ C^{1/2}$$

Straight line plots of λ versus $C^{1/2}$, were constructed and the equivalent conductance values at infinite dilution ($\lambda_{\circ RB}$, $\lambda_{\circ TPB}$, $\lambda_{\circ RAS}$, $\lambda_{\circ PMA}$ and $\lambda_{\circ PTA}$) were determined from the intercept of the respective line with the λ axis. The equivalent conductance values of the IPs under complete dissociation condition ($\lambda_{\circ IP}$) were calculated from Kohlrausch's law of independent migration of the ions [28-30].

$$\lambda_{\circ IP} = n\,\lambda_{\circ RB} + \lambda_{\circ\ (\text{ion pairing agent})}$$

where; *n* is the stoichiometric ratio.

The solubility (*S*) and the solubility product (K_{sp}) of a particular ion associate were calculated using the following equations:

$$S = k_s \times 1000 / \lambda_{\circ IP}$$

$K_{sp} = S^2$ for 1: 1 ion associate;

$K_{sp} = 4S^3$ for 1: 2 ion associate;

$K_{sp} = 27S^4$ for 1: 3 ion associate;

where k_s, is the specific conductivity of a saturated solution of IP at 25^{o}C and corrected for the effect of dilution. The saturated IP solutions were prepared by stirring the IP suspensions in bidistilled water for 3h and then left for 24h before measurement.

PVC Electrode Construction. Matrices compositions composed of 10 mg of RB-TPB or 20 mg of NaTPB were mixed with 240 mg o-NPOE, 6 mL THF and 240 mg PVC for electrode fabricated by different methods were described elsewhere [30]. The internal filling solution (10^{-3} M RB and 10^{-2} M KCl) and Ag/AgCl internal reference electrode were used. The fabricated sensors were conditioned for 24 h in 10^{-3} M RB before use and soaked in the same solution. Plain electrode was prepared in the same manner using the plain PVC membrane and presoaked in freshly prepared RB-IPs suspension for 24h.

Analytical Procedure

Calibration of Sensors. Sensors were calibrated by transferring 25 ml aliquots of 10^{-7}-10^{-3} M RB solutions into a 50 mL double jacket thermostated glass cell at 25 ^{o}C followed by immersing the sensor in conjugation with Ag/AgCl double junction reference electrode in the solution. The potential readings were recorded after stabilization and plotted against dye concentration in logarithmic scale (–log [RB]). The sensors performances were evaluated according to IUPAC recommendation [31].

Electrode Response Time. The dynamic response time of the electrode was tested by measuring the time required to achieve a steady state potential (within ±1 mV) after sudden 10-fold increase in RB concentration from 10^{-6} to 10^{-3} M.

Effect of pH. The influence of pH on the response of PVC was checked by recording the potential readings of the cell for solutions containing 10^{-3} M RB at different pH values (pH 3–11). Variation of pH value was done by adding very small volumes of HCl and/or NaOH solution (0.1−1M of each) to the drug solution.

Potentiometric Titration. An aliquot of the sample solution containing 0.48 – 33.6 mg RB was titrated with standardized NaTPB. The titration process was monitored using RB sensor in conjugation with Ag/AgCl reference electrode where the emf values were plotted against the ml added from the titrant to estimate the end point.

Result and Discussion

Preliminary IP Identification Studies

RB is a tertiary amine cation which forms water insoluble ion- pair complexes with the oppositely charged anions such as TPB, RAS, PTA or PMA [1, 2, 21]. The resultant IPs can be used as ion exchangers for RB potentiometric sensors. From this point of view, different types of RB-IPs were prepared and their stoichiometric ratios were estimated from elemental analysis and conductometric titration data. The elemental analysis data (see Table I) revealed that RB forms 1:1 IPs with both TPB and RAS. Complexes of RB with PTA and PMA showed ratio 1:3.

Table I. *Characterization of different RB-IPs*

IP	MWt_{cal}	C%		H%		N%		S%		Tentative Formula
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
RB-TPB	797.3	78.3	78.0	6.4	6. 5	3.5	3.4	-	-	$[C_{28}H_{31}ClN_2O_3][C_{24}H_{20}B]$
RB-RN	796.5	48.2	48.1	4.6	4.4	14.1	14.0	16.0	17.1	$[C_{28}H_{31}ClN_2O_3][C_4H_{10}CrN_7S_4]$
RB-PMA	3257.5	30.9	30.7	1.0	0.9	2.6	2.6	-	-	$[C_{28}H_{31}ClN_2O_3]_3[PMo_{12}O_{40}]$
RB-PTA	4312.5	23.4	23.2	0.7	0.7	1.9	1 9	-	-	$[C_{28}H_{31}ClN_2O_3]_3[PW_{12}O_{40}]$

The stoichiometric ratios of the IPs formed can be estimated from the conductometric titration curve, obtained by plotting the change in conductance versus volume of titrant added (see Fig. 1). By addition of the titrant to RB solution, the system showed a regular rise in conductance up to the equivalence point where a sudden change in the conductance observed. Intersect of the two straight lines determine the stoichiometric ratio of the complexes formed. The obtained results sustained the elemental analysis data for the complex formation ratios.

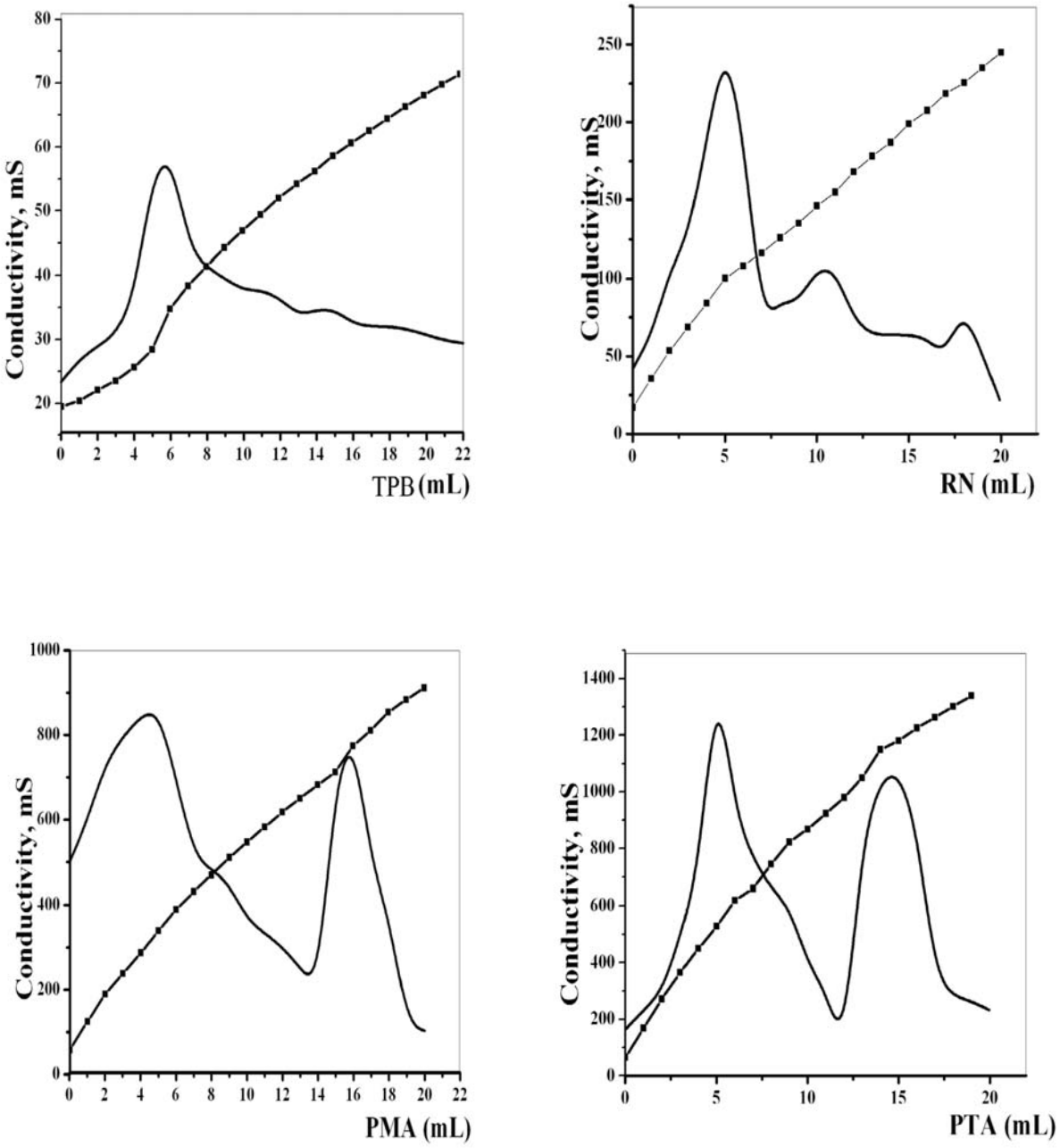


Figure 1: *Conductometric titration of RB with different ion pairing agents*

Solubility product of the IPs is important since its reciprocal is approximately equal to its formation constant, which in turns is tightly related to the degree of hydrophobicity of the ion exchanger and its solubility in the electrode matrix. The solubility products of the ion associates were determined conductimetrically, and found to be 2.56×10^{-7}, 1.34×10^{-8}, 1.18×10^{-11}, and 4.67×10^{-12}, for RB-TPB, RB-RN, RB-PMA, and RB-PTA, respectively.

Optimization of the Electrode Performance

For quantitative and qualitative composition optimization of the developed PVC sensors, an election scheme was followed. Both unmodified (plain) and modified electrodes (either with the RB-IPs, or the ion pairing agents) electrodes were prepared and tested for nature and content of modifier, type of plasticizer, pH effect, response time and applications.

Electrodes Modified with RB- Ion Pairs

The customary type of ion selective electrode is one in which the membrane is composed of a water-immiscible organic solvent containing the ion in question, usually in the form of an ion-pair with some anionic ion pairing agents such as NaTPB, TPA, TSA, flavianate, Reinickate or PMA in the electrode matrixes. Different RB-IPs were incorporated in the PVC matrix, and the fabricated electrodes were conditioned in 10^{-3}M of RB solution for 24 h. Preliminary experiment declared that PVC electrodes that contain no electroactive material, and plasticized with *o*-NPOE showed no response towards the RB; while those modified with different ion pairs gave Nernstian responses with different slopes, and sensitivities depend on the nature of the ion pair used. Electrode incorporated with RB-TPB showed the best performance slope (55.6±3.5 mV/decade in the concentration range 3×10^{-7}-10^{-3}M) compared to those modified with other RB ion pairs.

Constructing ion selective electrode, the amount of ion pair in the electrode matrix should be sufficient to obtain reasonable ionic exchange and equilibrium at the membrane gel layer–test solution interface that is responsible for the membrane potential. If such salt is present in excess, over saturation occur in the network of the membrane hindering the ionic exchange process and leading to unsatisfactory result; therefore, the influence of the RB-TPB concentration in the PVC matrix was investigated. For this purpose, 8 electrodes were prepared containing different amounts of the ion-pair (2.5-20mg). Incorporation of 10 mg in the membrane matrix was sufficient for the ionic exchange at membrane interface, the corresponding slope 56.3±5.4 mV/decade in the tested concentration range, above this value the slope of the electrode decreased to reach 50.0mV/decade with 20mg IP.

Electrode Modified with the Ion-Pairing Agents (*In Situ*)

Incorporation of a suitable ion pairing agent in the electrode matrix followed by soaking in the dye solution may led to the formation of an ion exchanger at the electrode surface being subsequently extracted by plasticizer into the electrode bulk. Such an approach will reduce the time required for electrode fabrication as there is no need for IP precipitation.

The effect of the ion pairing agent type was tested with the electrode matrices prepared and incorporated via different ion pairing agents (NaTPB, RNS, PTA or PMA) soaked in 0.001M RB solution. The results obtained indicated the superiority of the incorporation of NaTPB indicated by the lowest detection limit (5×10^{-7} M). The content of NaTPB in the electrode matrix varied within 5-30 mg, being found that the incorporating 20 mg of NaTPB in the PVC matrix gave the highest slope (53.3±4.0mV decade).

The Plain Electrodes

In addition to the aforementioned methods for the electrode fabrication, a simple and reliable suggested procedure could be applied by soaking the plain electrodes in the aqueous suspension of the lipophilic IP solutions. The electrode mediator (plasticizer) extracts IPs and becomes gradually saturated with this IP and hence, there is no need to incorporate neither the IPs nor the ion pairing agents into the electrode matrix. The IP concentration in the organic phase increases with increasing both the extractability and the solubility product of the IP formed [33, 34].

The plain electrodes were soaked in the aqueous suspensions of different RB-IPs for 24 h before potentiometric measurements. The results obtained showed that the electrodes soaked in the RB-TPB had the best sensitivity indicated by the highest slope (55.3±5.5 mV $decade^{-1}$) when compared with other IPs (44.5±10.1, 40±0.9 and 42.7±2.6 for PVC soaked in RB-RAS, RB-PTA and RB-PMA, respectively) which is directly related to the solubility products of these IPs and the extent of their extraction into the electrode matrix.

Sensors Performance

The potentiometric response characteristics of different rhodamine B sensors prepared with different methods of preparation (modification with RB-TPB, modification with NaTPB or plain) were evaluated according to IUPAC recommendations. The data obtained (Figure 2) indicated that the developed sensors can be successfully applied for the potentiometric determination of RB in concentration range 10^{-6} to 10^{-3} M with Nernstian cationic slopes depend on the method of electrode fabrication. The modified electrode showed the best performance compared with the plain electrodes or modified with the ion pairing agent (slope values were 56.3, 53.3 and 54.7 mV/decade for the electrodes modified with RB-TPB, NaTPB or plain electrode, respectively) with detection limit about 3×10^{-7} M.

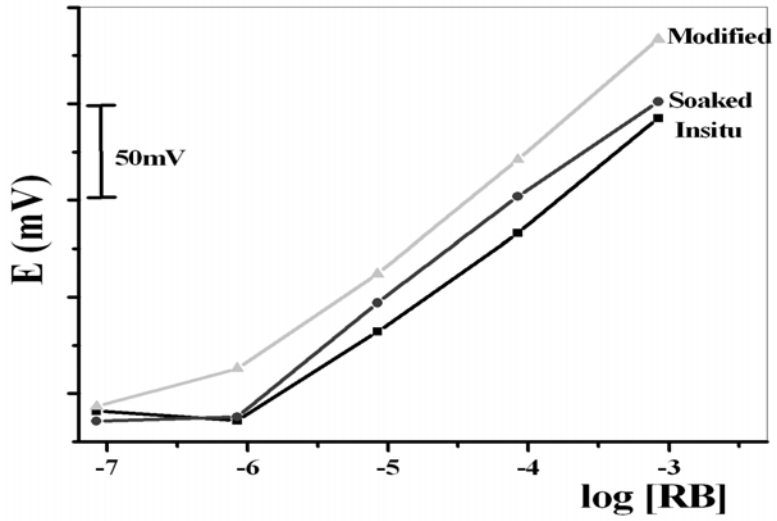


Figure. 2: *Potentiometric determination of RB using different PVC electrodes*.

The response times of all fabricated electrodes were measured according to the IUPAC recommendation. Fast and stable potentials were achieved as the response times were 8, 13 and 10s for electrodes modified with RB-TPB, NaTPB, or plain electrode respectively. The useful lifetimes of different fabricated electrodes were tested via day-to-day calibrations and the fabricated electrodes showed useful lifetime of about 4 weeks during which the Nernstian slopes did not change significantly (±2 mV/decade).

The effect of pH on the RB electrode potential was investigated by observing the changes in the potential with pH of the solution after the addition of small volumes of HCl and/or NaOH (0.1 or 1M). The investigated electrode gave a useful pH range from 3.0–7.0.

Potentiometric Titration

In contrast to direct potentiometric measurements requiring careful calibrations of measuring cells, the potentiometric titration techniques offers the advantage of high accuracy and precision; although the cost of increased time and consumption of reagents used as titrants. Parallel to the studying of the factors affecting the electrodes performance under the batch conditions, the effect of these factors was also investigated under the conditions of potentiometric titration of MB with NaTPB.

When ISEs are used to monitor the titration based on IP formation, the magnitude of both the potential break and sharpness at the inflexion point of the titration curve is predetermined by the solubility of the corresponding IP in membrane solvent (IP modified mode) and connected also with the extractability of the IP into the membrane mediator (insitu and plain mode). The effect of the electrode plasticizer on the titration process was investigated using membranes plasticized with different plasticizers (see Fig. 3). Generally, the electrodes plasticized with *o*-NPOE gave the highest total potential change (ΔE=562mV) compared with those plasticized with TCP, DOP, DOS, DBS, DBP or TTOM (ΔE= 528, 500, 510, 457, 472 and 230 mV for the plasticizers in the same order).

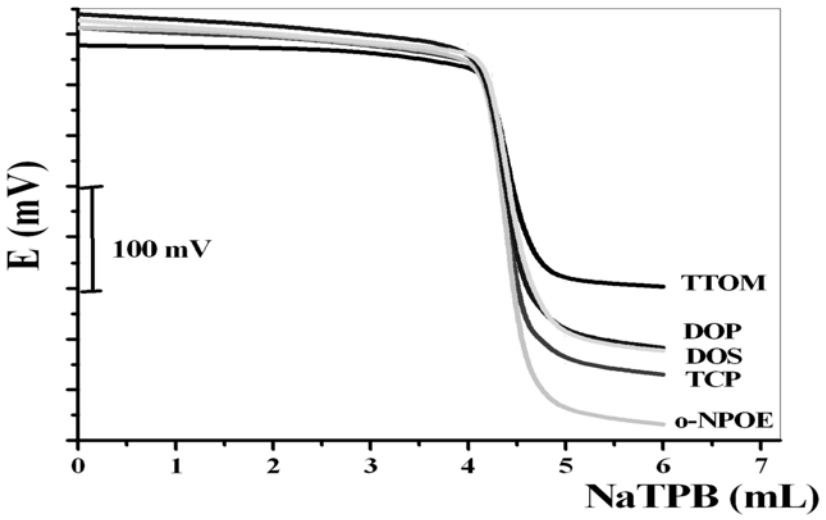


Figure 3: *Effect of the plasticizer on the potentiometric titration of RB with NaTPB.*

The effect of the electrode fabrication techniques on the titration process was investigated. The plain electrodes showed the best titration curve compared with the modified with either the RB-TPB ion pair or with the ion pairing agent regarding the total potential change or the potential break at the end point (see Fig. 4).

Under the optimum conditions, the titration curves were symmetrical with a very well defined potential jump indicating the high sensitivity of the electrode. Concerning the titration process, the total potential changes and the potential breaks at the end point were large (ΔE=560mV) allowing the application of the electrode to determine RB reaching down to 0.48 mg (Fig. 5). The titration process was highly reproducible, when the average recovery was 84.0±1.6%.

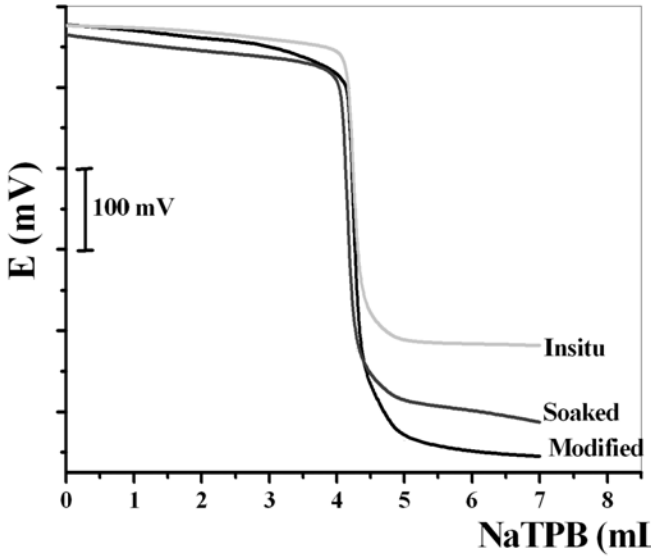


Figure 4: *Potentiometric titration of RB with NaTPB using different RB electrodes*

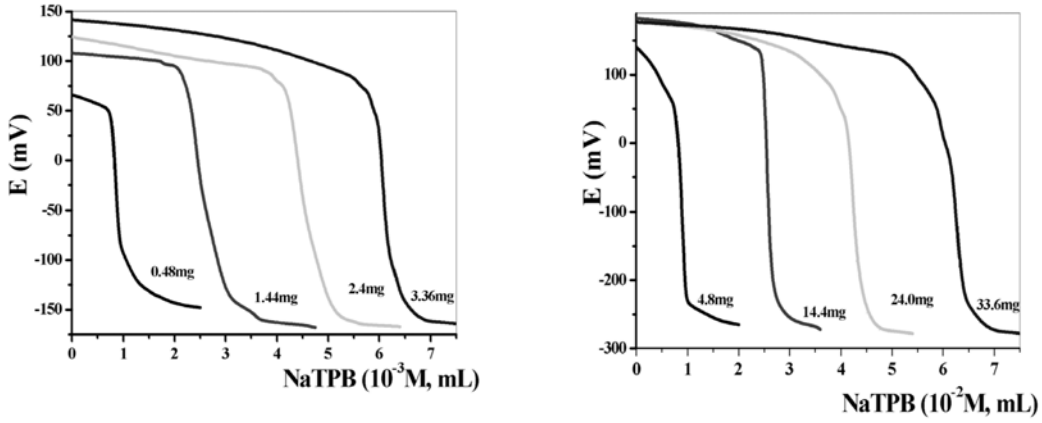


Figure 5: *Potentiometric titration of RB with NaTPB using RB PVC electrode*

Analytical Applications

The proposed electrode was successfully employed for the assay of RB in their authentic samples applying potentiometric titration method. The data given in Table II clearly indicate satisfactory agreement between the RB content in different samples determined by the proposed sensor and elemental analysis as there is no official method.

Table II: *Determination of RB in pure form, and in pharmaceutical preparations via potentiometric titration with NaTPB*

Taken [mg]	**Found** [mg]	Recovery [%]	SD* (n = 5)
0.48	0.41	85.42	2.20
1.44	1.25	86.81	2.10
2.40	2.00	83.33	2.00
3.36	2.72	81.09	1.90
4.80	4.00	83.33	1.10
14.40	12.12	84.16	1.65
24.00	20.12	83.83	1.20
33.60	28.38	84.46	1.00
Average recovery		84.4±1.6	

Note: *) Average of five replicates (titrations) performed.

Conclusions

The present work demonstrated the fabrication of novel RB-PVC electrode utilizing different preparation methods. The fabricated electrodes showed Nernstian slopes in the concentration range from 10^{-6} to 10^{-3}M with fast response time (8 s) and long operational lifetime. The fabricated electrodes were successfully applied as end point indicator electrode for potentiometric titration of RB with NaTPB in the concentration range 0.48-33.6 mg with good accuracy and sensitivity. The fabricated electrode possessed shorter response time compared with Ding electrode [21]; and they are more suitable for following the catalytic determination of trace iodide based on the oxidation of RB with hydrogen peroxide.

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