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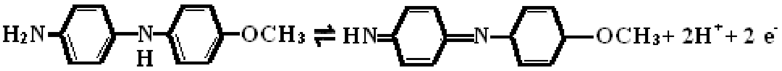
Novel Variamine Blue Potentiometric Sensor

E. Khaled[#], M.A. El-Ries[*], F.I. Zidane[**], S.A. Ibrahim[*] and M.S. Abd-Elmonem[*]
Microanalysis Laboratory, National Research Centre, Giza, [*]National Organization of Drug Control and Research and [**]Chemistry Department, Faculty of Science, Al-Azhar University, Cairo, Egypt .

NOVEL polyvinyl chloride (PVC) potentiometric sensors are constructed for determination of variamine blue (VB). Different methods for electrode fabrication including; modification with the VB-TPB ion pair, modification with sodium tetraphenylborate or soaking of the plain electrode in the ion-pair suspension, have been described. Electrode 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 10^{-6} to 10^{-2} M of VB. Electrodes modified with VB-TPB showed the best performance (Nernstian slope 62.0±0.7 mV decade^{-1}) with fast response time of about 8 sec and adequate lifetime (4 weeks). The developed electrodes have been successfully applied as end point indicator electrode for the potentiometric titration of 6.75-20.25 mg VB with high accuracy and precision. The solubility products of different VB ion-pair were determined conductometrically.

Keywords: Variamine blue, PVC electrode fabrication, Potentiometric titration, Ion pairs and Solubility products.

4-Amino 4'-methoxydiphenylamine, known as Variamine Blue (VB) was first suggested as a redox indicator by Erdey(1,2). This reagent is soluble in water and produces a colorless solution which turns blue violet meriquinone which absorbs at 570-610 nm upon oxidation(3).



VB Reduced, colorless   VB Oxidized, violet

VB was recommended as redox indicator for potentiometric and visual titrations with Fe (III)(3,4), bromamine-B(5) or bromate(6). More recently, Basavaiah and Charan used VB for the assay of methdilazine in bulk drug applying potassium iodate as oxidant(7).

[#] E-mail address: elmorsykhaled@yahoo.com

Heavy metals are important environmental pollutants, second only to pesticides in terms of environmental impact; therefore, monitoring of heavy metals at trace levels is usually an increasingly important issue. Simple, rapid and sensitive spectrophotometric methods utilizing VB as chromogenic reagent were suggested for determination of arsenic(8), chromium(9), vanadium(10) or selenium(11). Because of the growing need for high sensitive analytical methods, the catalytic kinetic method has become an attractive procedure as the trace determination can be achieved without the use of expensive or special equipment with lower probability to receive interferences(12,13). Catalytic methods are usually based on the oxidation of organic indicators with various oxidants. Among these organic indicators, VB was applied for catalytic spectrophotometeric determination of environmentally important species(14-17). Finally, the utility of VB as an analytical reagent has been well reviewed by Bishop(18).

The yield of VB from an initial commercial manufacturing synthesis is approximately 75% and there may be significant variations between batches. However, relatively little information on the analysis of such dyestuffs has been published; but the book of Lastovskii and Vainshtein(19) is still a very useful manual. Application of spectrophotometeric 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. Although ion- selective electrodes (ISEs) had found wide applications for dye analysis(20-24), no VB sensor was found in literature.

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 subjected to a series of tests to select sensor possessing the most favorable analytical characteristics. The developed sensors were also applied as indicator electrode in the potentiometric titration of VB.

Experimental

Apparatus

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 dye 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.

Reagents

All reagents were of the analytical grade and double distilled water was used throughout the experiments. Variamine Blue (10^{-2} M) stock solution was prepared by dissolving the appropriate weight of the VB. HCl ($C_{13}H_{14}N_2O$-HCl, BDH, UK) in hot water followed by filtration and complete the volume to 100 ml. o-Nitrophenyloctylether (o-NPOE) from Sigma was used for sensors fabrication. Other types of plasticizers, namely dibutylphthalate (DBP), dioctylphthalate (DOP), dioctylsebacate (DOS) and tricresylphosphate (TCP) were purchased from BDH, Sigma, AVOCADO and Fluka, respectively.

Sodium tetraphenylborate (NaTPB) solution (ca. 10^{-2} M) was prepared by dissolving a weighed amount of the substance (Fluka) in 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 10^{-2} M thallium (I) nitrate solution(25). Reineckate ammonium salt (RAS, Fluka), phosphotungstic acid (PTA, BDH), and phosphomolybdic acid (PMA, Fluka) were used for precipitation of different VB ion pairs.

Electrode construction

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 VB solution and the mixture was left to react for 5 min under stirring at room temperature. The resulting precipitate was then filtered off and left to dry for 24 hr at 60°C.

Conductometric determination of the stoichiometric ratios

A definite volume of 10^{-2} M VB was transferred to a 50 ml volumetric flask and made up to the mark with bidistilled water. The dye solution was placed in a suitable titrating vessel and the conductivity cell was immersed, then a titrant of 10^{-2} M of TPB, RAS; 2.5×10^{-3} M of PMA, PTA was added from a digital burette and the conductance (µS) was measured after 2 min to ensure the equilibrium. To eliminate the effect of dilution on 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.

Conductometric determination of the solubility products

Series of solutions of different concentrations (10^{-2}-10^{-4} M) were prepared for each of VB, TPB, RAS, PMA or 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 a finite concentration) and λ_o (at infinite dilution) can be related by the equation[(26)]:

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

Straight line plots of λ versus $C^{1/2}$, were constructed and the equivalent conductance values at infinite dilution ($\lambda_{\circ VB}$, $\lambda_{\circ TPB}$, $\lambda_{\circ RAS}$, $\lambda_{\circ PMA}$ 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[(27,28)].

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

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

where k_s, is the specific conductivity of a saturated solution of IP at 25°C and corrected for the effect of dilution.

Electrode fabrication

Matrices compositions composed of 7.5 mg of VB-TPB or 30 mg of NaTPB, were mixed with 240 mg o-NPOE, 6 ml THF and 240 mg PVC. The cocktail was stirred for 5 min and poured into a Petri dish “5 cm” diameter. After 24 hr of slow evaporation of solvent, a master membrane with 0.11 mm thickness was obtained. One end of a PVC tube was softened by immersion in THF for 1 min, a piece “2 cm diameter disk” of the PVC membrane was mounted on the softened end of the PVC tubing with the help of adhesive solution prepared by dissolving PVC in THF. The PVC closed tube with the membrane was filled with 10^{-2}M KCl and 10^{-2} M VB solution using Ag /AgCl as internal reference electrode. The fabricated electrodes were soaked in 10^{-2} M of VB for 24 hr before using. The plain electrode was prepared in the same manner using the plain membrane (without any modification) where the electrode was soaked in the suspended solution of VB-TPB ion pair for 24 hr before measurement.

Analytical procedure

Calibration of sensors

Sensors were calibrated by transferring 25 ml aliquots of 10^{-7}-10^{-2} M VB solutions into a 50 ml double jacket thermostated glass cell at 25°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 [VB]) and the sensors performances were evaluated according to IUPAC recommendation(29).

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 VB concentration from 10^{-6} to 10^{-3} M.

Effect of pH

The influence of pH on the electrode response was checked by recording the potential readings of the cell for solutions containing 10^{-3} M VB at different pH values (pH 2–6). Variation of pH value was done by adding very small volumes of HCl and/or NaOH solution (0.1−1 M of each) to the dye solution.

Potentiometric titration

Aliquots of the sample solution containing 6.75 – 20.25 mg VB was titrated with standardized NaTPB. The titration process was monitored using VB 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.

Results and Discussion

Preliminary IP identification studies

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

TABLE 1. Characterization of different VB-IPs.

IP	MWt_{cal}	C%		H%		N%		S%		Tentative Formula
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
VB-TPB	543.8	81.6	80.8	5.7	5. 8	7.7	7.9	-		$[C_{13}H_{14}N_2O][C_{24}H_{20}B]$
VB-Rn	543	37.6	37.2	3.1	3.0	23.2	23.2	23.6	23.2	$[C_{13}H_{14}N_2O][C_4H_6CrN_6S_4]$
VB-PMA	2497	18.7	18.1	0. 6	0.7	5.4	5.1	-		$[C_{13}H_{14}N_2O]_3[PMo_{12}O_{40}]$
VB-PTA	3552	13.2	13.1	0.4	0.2	3.5	3.6	-		$[C_{13}H_{14}N_2O]_3[PW_{12}O_{40}]$

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 (Fig. 1). By addition of the titrant to VB solution, the system showed a regular rise in conductance up to the equivalence point where a sudden change in the conductance was 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.

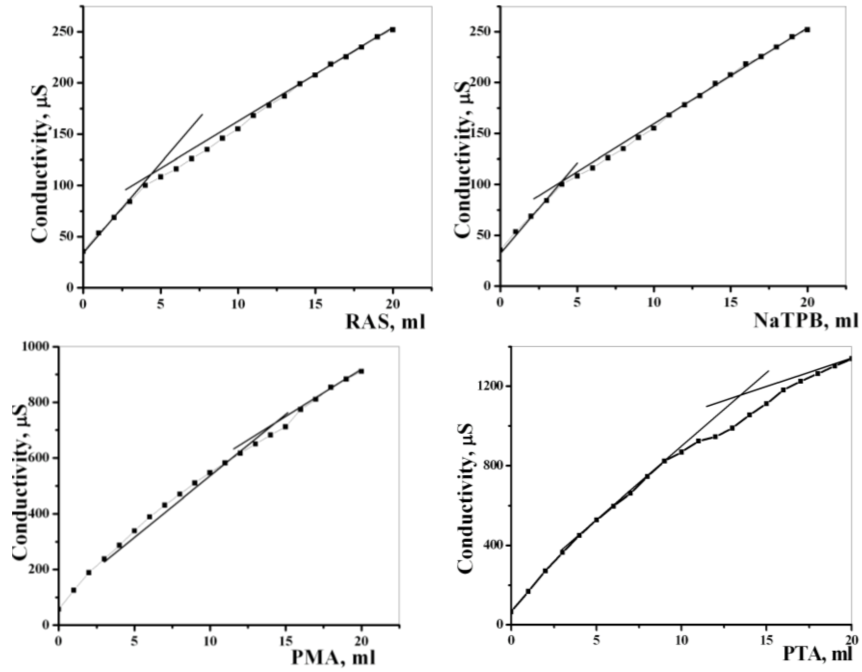


Fig. 1. Conductometric titration of VB with different ion pairing agents.

The solubility products of the ion associates were determined conductimetrically and found to be 5.74×10^{-7}, 1.72×10^{-8}, 1.89×10^{-10} and 1.11×10^{-11}, for VB-TPB, VB-RAS, VB-PTA and VB-PMA, 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 VB-IPs, or the ion pairing agents) were prepared and tested for nature and content of modifier, plasticizer, pH, response time and applications.

Electrodes modified with VB- 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[30-33]. Different VB-IPs were incorporated in the PVC matrix, and the fabricated electrodes were conditioned in 10^{-2} M of VB solution for 24 hr. Preliminary experiment declared that PVC electrodes contain no electroactive material and plasticized with o-NPOE showed no response towards the VB; while those incorporated with different VB-IPs gave Nernstian responses with slopes and sensitivities depend on the nature of ion pair used. The electrode incorporated with VB-TPB ion pair showed the best performance (slope 51.5±2.8 mV decade^{-1}) compared to electrodes modified with other VB ion pairs. This behavior may be attributed to the poor solubility of these ion pairs in the membrane matrix.

Furthermore, the amount of the electroactive material in the electrode matrix should be sufficient to achieve reasonable ionic exchange and chemical equilibrium at the membrane/solution interface that is responsible for the electrode potential. If such material is present in excess, over saturation occurs in the membrane network, hindering the ionic exchange process and leading to unsatisfactory performance. Thus, the influence of the VB-TPB content in the PVC matrix was investigated by varying the IP content in the electrode matrix from 1 to 10 mg (Fig. 2). Addition of 7.5 mg VB-TPB to the membrane matrix was sufficient for the ionic exchange at membrane interface; the corresponding slope was 56.3±2.4 mV/decade in the tested concentration range (from 10^{-6} to 10^{-2} M), above this value the slope of the electrode decreased to reach 48.0 mV/decade with 10 mg IP.

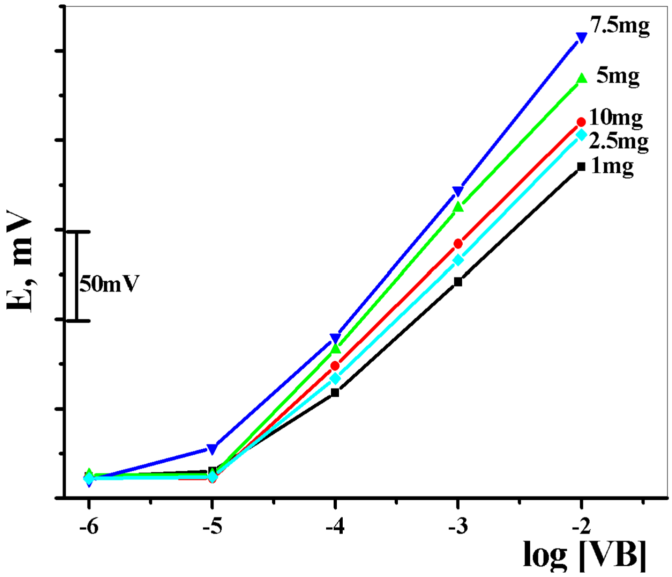


Fig. 2. Effect of the VB-TPB IP content on electrode performance.

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 lead to the formation of an ion exchanger at the electrode surface which subsequently extracted by the plasticizer into the electrode bulk. Such technique will reduce the time required for the electrode fabrication as there is no need for IP precipitation.

The effect of the ion pairing agent nature on the electrode performance was tested as the electrode matrices containing different ion pairing agents (NaTPB, RAS, PTA and PMA) were prepared and presoaked in 10^{-2} M VB solution for 24 hr. The obtained results indicated the priority of the incorporation of NaTPB indicated by the highest slope (60±1.3 mV decade^{-1}) compared to other ion pairing agents that gave relative lower slopes (Fig. 3); which may be explained from the point of view of the difference in the extraction of the formed ion-pairs into the electrode matrices. The content of Na-TPB within the electrode matrices was varied from 10 to 50 mg and incorporation of 30 mg of Na-TPB gave the highest slope (64.6±1.1mV decade^{-1}).

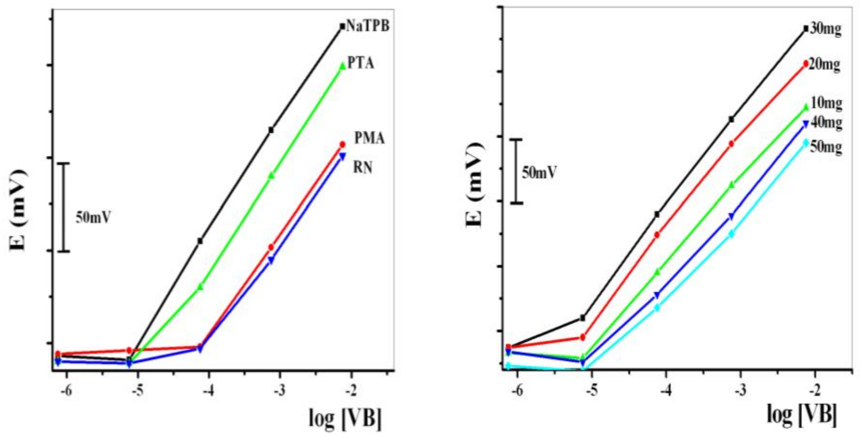


Fig. 3. Effect of the nature and content of the ion pairing agents on the performance of VB-PVC electrodes.

Soaked 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 (fabricated without any modification) in the aqueous suspension of the lipophilic VB-IPs 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(34, 35).

Calibration graphs of electrodes soaked in different VB ion pair suspensions showed that the electrodes soaked in the VB-TPB had the best sensitivity indicated by the highest slope (57.9±2.8 mV decade^{-1}) when compared with other IPs which may be directly related to the solubility products and extraction of the different ion-pairs in the membrane plasticizer.

Effect of membrane plasticizer

Plasticizers play an important role in the behavior of ISEs since they improve the solubility of the sensing material and lower the overall bulk resistance of the electrode due to their polarity characteristics(36, 37).

The effect of membrane plasticizer on the electrode performance has been studied. The electrode plasticized with *o*-NPOE was compared with those plasticized with TCP, DOS, DOP and DBP. The obtained calibration graphs (Fig. 4) clarified that the membrane plasticized with *o*-NPOE showed the highest sensitivity indicated by the highest slope values, which may be related to its high dielectric constant (**ε**=24, 17.6, 3.88, 5.2 and 4.7 for the tested plasticizers in the same order).

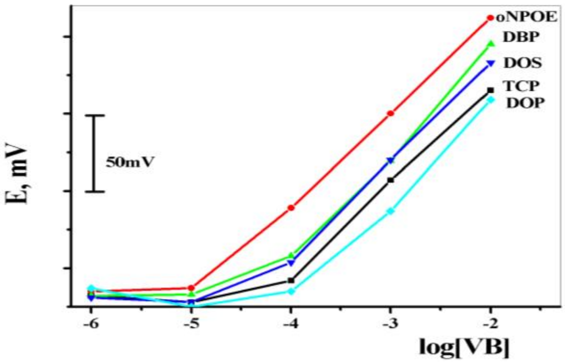


Fig. 4. Effect of the plasticizer on the performance of soaked VB electrodes.

Sensors performance

The potentiometric response characteristics of different VB-PVC sensors prepared with different methods (modification with VB-TPB ion pair, modification with NaTPB or plain) were evaluated according to IUPAC recommendations(27). Data obtained (Table 2) indicated that the developed sensors can be successfully applied for the potentiometric determination of VB in the concentration range from 10^{-6} to 10^{-2} M with Nernstian cationic slopes depend on the method of fabrication. The electrodes modified with NaTPB showed relatively higher slope (64.6±1.1 mV decade^{-1}) compared with those modified with VB-TPB ion-pair or plain electrodes. The limit of detection varies with the electrode type as it reached 4.6×10^{-7} M with the VB-TPB modified electrode.

TABLE 2. Performance characteristics* of VB sensors fabricated with different techniques.

Sensor	Modified with VB-TPB	Modified with NaTPB	Soaked
Concentration range (M)	10^{-6}-10^{-2}	10^{-5}-10^{-2}	10^{-5}-10^{-2}
Intercept (mV)	193.2±3.3	159.0±5.2	264.7±3.8
Slope (mV/ decade)	62.0±0.7	64.6±1.1	54.8±1.2
r	0.9945	0.9994	0.9993
LOD (M)	4.6×10^{-7}	5.2×10^{-6}	2.5×10^{-6}
Response time (s)	8	12	8
Lifetime (day)	28	21	14
pH range	3-5	3-5	3-5

*Average of five calibration graphs

For analytical applications, the response time of a new fabricated sensor was of critical importance. The response times of the fabricated electrodes were measured according to IUPAC recommendation. The average response time is defined as the time required for the electrode to reach a stable potential (within ±1 mV of the final equilibrium value) after sudden 10-fold increase in concentration by addition of small increments of 10^{-2} M VB solution. For the modified and soaked electrodes, the response time was found to be 8s for concentration of $\geq 1\times10^{-4}$ M and 10s for lower concentrations while that modified with NaTPB showed longer response time of 12 and 14s, respectively.

The useful lifetimes of different fabricated electrodes were tested by performing day-to-day calibrations; the fabricated electrodes showed useful lifetime of about 4 weeks during which the Nernstian slopes did not change significantly (±2 mV decade^{-1}).

The influence of pH on the electrode potential was studied by measuring the calibration graphs at different pH values (from 2 to 6) as higher pH values cause precipitation of the VB base with sharp decrease in the electrode potential. The electrode showed a stable potential reading in the pH range from 3 to 5.

The selectivity of the prepared VB sensors was tested towards different interfering ions using Separate Solution Method (SSM). The potential of the cell comprising an VB and a RE is measured with two separate solutions, one containing the ion *102-M VB*, the other one containing the 10-2M the interfering ion. If the measured values are E_A and E_B, respectively, the value of is calculated from the equation:

$$\log K_{A,B} = [(E_B - E_A)\, z_A F/RT \ln 10] + (1 - z_A/z_B) \log a_A$$

which is equivalent to:

$$K_{A,B} = a_A^{(1 - z_A/z_B)} e^{(E_B - E_A) z_A F/(RT)}$$

The developed sensors were highly selective; organic compounds (glycine, caffeine, citrate, maltose, sucrose, and starch) as well as inorganic cations (Na^+, K^+, Li^+, Ca^{2+}, Mg^{2+}, and $NH_4{}^+$) did not show significant interference.

Potentiometric titration

In contrast to direct potentiometric measurements requiring careful calibrations of measuring cells, the potentiometric titration techniques offer the advantage of high accuracy and precision; although the cost of increased time and consumption of reagents used as titrants. In the potentiometric titration of VB, different titrants and electrodes were investigated. Application of NaTPB as titrant gave the best titration curve with the highest potential break at the end point and a well defined reaction sticiochiometry (1:1) while other titrants (PTA, PMA) gave a poor titration curves.

When ISEs are used to monitor titration based on IP formation, the magnitude of both potential break and sharpness at the inflexion point of the titration curve is predetermined by the solubility of the corresponding IP in membrane plasticizer and also related to the extractability of the IP into the membrane mediator(20,21,25,34-36). The influence of the membrane plasticizer on the titration performance was investigated by performing the titration using electrodes plasticized with different plasticizer namely *o*-NPOE, TCP, DOP or DOS. Generally, the electrodes plasticized with *o*-NPOE gave the highest total potential change ($\Delta E = 200$ mV) compared with those plasticized with TCP, DOP or DOS (ΔE were 150, 140 and 120 mV for the plasticizers in the same order) which can be explained by higher extractability of the VB-TPB ion pairs into the membrane plasticizer due to the relative higher dielectric constant of *o*-NPOE.

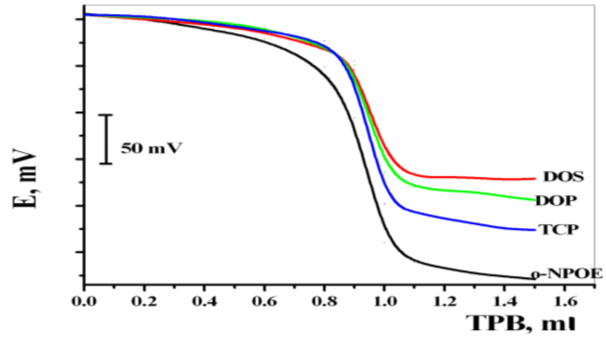


Fig. 5. Effect of the electrode plasticizer on the potentiometric titration of VB with NaTPB.

The effect of the electrode fabrication method on the titration process was also investigated. The plain electrodes showed the best titration curve compared with the modified with either the VB-TPB ion-pair or with the ion-pairing agent regarding the total potential change and the potential break at the end point.

Under the optimum conditions, the titration curves were symmetrical in the concentration range 6.75-20.25 mg VB with a very well defined potential jump indicating the high sensitivity of the electrode (Fig. 6).

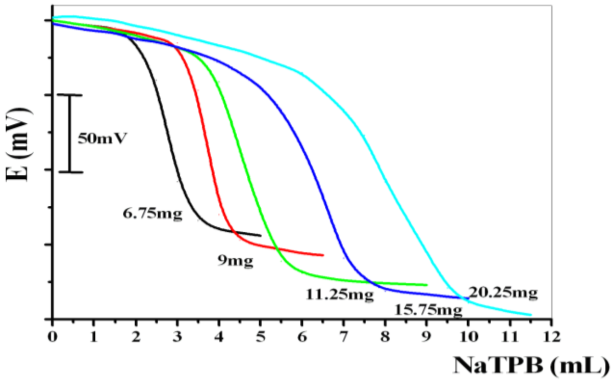


Fig. 6. Potentiometric titration of VB with 10^{-2}M NaTPB using PVC electrode modified with VB-TPB.

Analytical application

The proposed electrode was successfully employed for the assay of VB applying potentiometric titration method. The data given (Table 3) clearly indicated satisfactory agreement between the VB contents in different samples determined by the proposed sensor and elemental analysis method as there is no official methods for VB.

Conclusion

The present work has successfully demonstrated the fabrication of novel VB-PVC electrodes utilizing different preparation methods as no electrodes have been published for potentiometric determination of VB. The fabricated electrodes showed Nernstian slopes in the concentration range from 10^{-6} to 10^{-2} 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 VB with NaTPB offering good accuracy and sensitivity. It should be mentioned that the fabricated electrodes were suitable in kinetic catalytic determination of trace iodide based on the oxidation of VB with hydrogen peroxide due to their high sensitivity and fast response to the change in VB concentration.

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أقطاب جهدية جديدة لازرق الفاريامين

المرسى خالد، محمد عبد النبى الريس* ، فاروق إسماعيل زيدان ، سامى عبد المعطى إبراهيم* ، محمود سيد عبد المنعم***
معمل التحليلات الدقيقة-المركز القومى للبحوث - الجيزة ،*الهيئة القومية للرقابة والبحوث الدوائية و**قسم الكيمياء-كلية العلوم-جامعة الأزهر- القاهرة – مصر.

تم تصميم أقطاب جهدية جديدة لتقدير صبغة أزرق الفاريامين حيث تم تطبيق طرق مختلفة لتحضير الأقطاب تشمل التدعيم بالزوج الأيونى لأزرق الفاريامين مع رابع فينيل بورات الصوديوم، التدعيم برابع فينيل بورات الصوديوم أو نقع الأقطاب فى معلق الزوج الأيونى لأزرق الفاريامين مع رابع فينيل بورات الصوديوم. تم ضبط تركيبة الأقطاب على أساس تأثير نوع وتركيز مادة التدعيم وكذلك المادة الملدنه. عملت الأقطاب بنجاح فى مدى تركيزات من $١٠^{-٦}$ الى $١٠^{-٢}$ عيارى من أزرق الفاريامين وكانت الأقطاب المدعمة بالزوج الأيونى لأزرق الفاريامين مع رابع فينيل بورات الصوديوم هى الأعلى كفاءة حيث أعطت ميل خطى ٧، ٠ ± ٠، ٦٢ ملى فولت/تركيزمع وقت إستجابه سريع يصل الى ٨ ثوانى وفترة عمر تصل الى ٤ أسابيع. تم تطبيق الأقطاب المقترحة بنجاح كقطب دليل فى المعايرة الجهدية لأزرق الفاريامين فى مدى تركيزات ٦,٧٥-٢٢,٠٥ ملى جرام بدقة عالية. كما تم أيضا تقدير ناتج الذوبانية للأزواج الأيونية المختلفة بطرق توصيلية.