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PVC MEMBRANE ELECTRODES FOR MANUAL AND FLOW-INJECTION DETERMINATION OF TETRAPHENYLBORATE: APPLICATIONS TO SEPARATE AND SEQUENTIAL TITRATIONS OF SOME METAL IONS

SAAD S. M. HASSAN* and IBRAHIM H. A. BADR
Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, Egypt

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Summary—Three novel poly (vinyl chloride) matrix membrane electrodes, highly sensitive and selective for tetraphenylborate anion (TPB), are developed and electrochemically evaluated. They are based on the use of iron(II) bathophenanthroline, nickel(II) bathophenanthroline–and nitron–TPB ion-pair complexes as electroactive materials with dioctylphthalate (DOP) and 2-nitrophenyl phenyl ether (NPPE) as plasticizing solvent mediators. The electrodes exhibit stable and rapid near-Nernstian response for 10^{-2}–$10^{-6}M$ TPB over the pH range 4–10. Use of these electrodes for direct potentiometric determination and potentiometric titration of as low as 1 μg of TPB/ml and 0.6 mg of TPB/ml give results with average recoveries of 99.3% (mean standard deviation 0.5%) and 99.4% (mean standard deviation 0.2%), respectively. Incorporation of nitron–TPB PVC sensor in a flow-through sandwich cell provides an efficient flow-injection detector for determining TPB with an input rate of at least 60 samples/hr. The limit of detection is 1.6 μg TPB/ml in a 20-μl sample. The electrodes are also used to monitor separate and sequential titrations of some metal ions with TPB. Alkaline earth and transition-metal ions upon reaction with polyethylene glycol and ethylenediamine, respectively, form cationic complexes readily titrated with TPB. Optimum conditions are outlined for sequential titrations of various combinations of metallic species.

Tetraphenylborate (TPB) has been extensively used in analytical chemistry as a reagent for the determination of monovalent cations including alkaloids, cationic surfactants, arenediazonium salts, quaternary ammonium compounds and amines.[1] It has also been utilized in solar batteries[2] and in the treatment of nuclear waste.[3] On the other hand, many ion pair complexes of TPB have been used as electroactive materials in liquid and polymeric membrane electrodes responsive for various basic drugs and related substances.[4,5]

Although many sensors of different nature have been suggested for monitoring titrations involving TPB,[1,6] few membrane electrode systems are available, for direct potentiometric measurement of low concentrations of TPB. Liquid and polymeric membranes consisting of tetrapentyl-ammonium-TPB in 4-nitro-*m*-xylene,[7] tetraalkyl ammonium-tetrakis (*m*-trifluoromethyl-phenyl) borates in ethyl nitrobenzene,[8] and hexadecyl-pyridinium-TPB in PVC matrix[9] have been suggested. Some of these membrane electrodes, however, have a narrow response range and poor selectivity, and suffer from rapid response deterioration and require special storage and regeneration.[7–9]

Recent studies have shown that perrhenate,[10] tetrachloroaurate(III),[11] thiocyanate[12] and azide[13] ion selective membrane electrodes can be prepared with nitron and metal bathophenanthroline as the counter cations. The results presented here demonstrate that nitron-, iron(II) bathophenanthroline-, and nickel (II) bathophenanthroline-tetraphenylborate ion pair complexes can be used as electroactive species in PVC membrane electrodes responsive for TPB ions. These electrodes display long term stability, high sensitivity, remarkable selectivity and applicability for manual and flow-injection mode of operations over a wide range of pH. Uses of the electrodes for direct potentiometry and potentiometric titration of TPB as well as for monitoring separate and sequential titrations of some mono-and di-valent metal ions with TPB titrant are outlined.

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*Author for correspondence.

EXPERIMENTAL

Apparatus

All potentiometric measurements were carried out at 25 ± 1°C with pH/mV meter (Orion 720), using the TPB-PVC matrix membrane electrodes in conjunction with a single-junction Ag/AgCl reference electrode (Orion 90-01). Ross glass electrode (Orion 81-02) was used for all pH measurements. The previously described laboratory-made flow-through sandwich cell[13,14] was equipped with nitron-TPB-PVC membrane and incorporated in a single FI system, with an Omnifit injection valve and a peristaltic pump (Manostat) cassette junior model. The potentiometric output was measured with an Orion SA 720 digital pH/millivoltmeter and recorded with a strip-chart recorder (Linear 1200).

Reagents and materials

All chemicals were of analytical reagent grade unless otherwise stated, and doubly distilled deionised water was used throughout. Poly (vinyl chloride) powder (PVC), dioctylphthalate (DOP), tetrahydrofuran (THF), bathophenanthroline (4,7-diphenyl 1,10 phenanthroline), nitron (4,5-dihydro-1,4-diphenyl-3,5-(phenylimino)-1,2,4-triazole, polyethylene glycol (PEG-6000) and zephiramine (tetradecyldimethylbenzyl ammonium chloride) were obtained from Aldrich Chemical Company, Inc. (Milwaukee, Wisconsin, U.S.A.). Sodium tetraphenylborate (NaTPB) and all metal salts (purity not less than 99%) were obtained from the British Drug Houses (B.D.H., Poole, England). 2-Nitrophenyl phenyl ether (NPPE) was purchased from Kodak (Eastman Kodak, Rochester, NY, U.S.A.). A standard $10^{-1}M$ tetraphenylborate solution was prepared and standardized by titration with $10^{-2}M$ of either aqueous zephiramine or thallium(I) sulphate solution using nitron-TPB PVC membrane electrode in conjunction with a double junction Ag/AgCl reference electrode. Dilute solutions (10^{-2}–$10^{-7}M$) were prepared by appropriate dilutions. Aqueous solution of ethylenediamine and polyethylene glycol 20% w/v were freshly prepared.

Electroactive TPB–ion pair complexes

Iron(II)- and nickel(II)–bathophenanthroline tetraphenylborate ion-pair complexes were prepared by dissolving 100-mg portions of bathophenanthroline (b.phen) in 20 ml of 60% v/v ethanol–water mixture followed by addition of 5 ml of either 0.02M iron(II) ammonium sulphate or 0.02M nickel(II) chloride. A few drops of either ethanol or water were added to the reaction solution to maintain the solution clear. A 5-ml aliquot of $5 \times 10^{-2}M$ aqueous sodium tetraphenylborate solution was added to the bathophenanthroline complexes. The precipitates were filtered off through a Whatman filter paper No. 42, washed with cold water several times, dried at room temperature and ground to fine powder. Infrared and elemental analysis data of the precipitates agreed with the formation of $[Fe(b.phen)_3]$ $[TPB]_2$ and $[Ni(b.phen)_3]$ $[TPB]_2$ ion-pair complexes.

Nitron-tetraphenylborate ion-pair complex was prepared by mixing 20 ml of $10^{-2}M$ NaTPB solution with 30 ml of $10^{-2}M$ nitron reagent (prepared in 20% v/v acetic acid–water mixture). The precipitate formed was filtered off through a Whatman filter paper No. 42, washed thoroughly with distilled water, dried at room temperature and ground to fine powder. Infrared and elemental analysis data of the precipitate agreed with the composition [nitron] [TPB] ion-pair complex. The solubility of the ion pair complexes of TPB in various solvent mediators was examined to select the most suitable plasticizer. Metal bathophenanthroline and nitron derivatives of TPB display almost complete solubility in 2-nitrophenyl phenyl ether and dioctylphthalate plasticizers, respectively.

Tetraphenylborate poly(vinyl chloride) membrane electrodes

A 10-mg portion of either $[Fe(b.phen)_3]$ $[TPB]_2$ or $[Ni(b.phen)_3]$ $[TPB]_2$ ion-pair complex was mixed in a glass Petri dish (5-cm diameter) with 0.35 ml of 2-nitrophenyl phenyl ether (NPPE) plasticizer and 0.19 g of poly(vinyl chloride) powder. Nitron-tetraphenylborate membrane was similarly prepared using a 10-mg portion of nitron- tetraphenylborate ion-pair complex and 0.45 g of dioctylphthalate (DOP) as plasticizer. The sensor cocktail was dissolved in 5 ml of tetrahydrofuran, the Petri dish covered with a filter paper, and left to stand for 20 hr to allow slow evaporation of the solvent at room temperature. A master PVC membrane (*ca.* 0.1 mm thick) was obtained, sectioned with a cork borer (10 mm diameter) and glued to a polyethylene tubing as previously described.[15] The electrode was filled with mixture of an equal volume of aqueous $10^{-2}M$ sodium tetraphenylborate and $10^{-2}M$ sodium chloride solutions. A

Ag/AgCl internal reference wire electrode (~ 1.0 mm diameter) was immersed in the internal solution. The electrode was conditioned by soaking into $10^{-2}M$ NaTPB solution for 2 hr, stored in the same solution when not in use and calibrated. All TPB test solutions were prepared in $5 \times 10^{-2}M$ NaCl background and their pH values were adjusted to 6–8.

Potentiometric determination of TPB

A 10-ml portion of TPB test solution (3–50 μg/ml) was transferred to a 50-ml beaker. The TPB membrane electrode in conjunction with an Orion double junction Ag/AgCl reference electrode was immersed in the solution. The emf was recorded after stabilization to ±0.5 mV and compared with the calibration graph. Alternatively, the standard known addition (spiking) technique was used by recording the emf of the test solution before and after the addition of 1 ml of a standard aqueous $10^{-2}M$ NaTPB solution. The change in the potential reading was recorded and used for calculation of the TPB content. Aqueous test solutions (~ 10 ml) containing 3–30 mg of TPB are also titrated with a standard $10^{-2}M$ zephiramine solution using the same electrode system. The titration curves was recorded and equivalence points were calculated from the maximum slope ($\Delta E/\Delta V$).

Flow-injection determination of TPB

A laboratory-made flow-through sandwich potentiometric cell, equipped with nitron-TPB-PVC membrane, was fabricated and used in a single-stream FI system. The TPB sensor was prepared and conditioned as described previously.[13,14] The cell was assembled and connected to the flow injection system. The cell and the single-junction Ag/AgCl reference electrode were placed in a Petri dish filled with the electrolyte carrier solution. A carrier solution consisting of $5 \times 10^{-2}M$ NaCl was propelled through the cell, by means of a peristaltic pump and PTFE tubing (0.8 mm id.), at a flow rate of 0.4 ml/min. An Omnifit injection valve was used for successive injections of 20 μl aliquots of TPB sample solutions into the flowing stream. The tubing distance between the injection valve and the detector was about 10 cm. Both the TPB sensor and the reference electrode were connected to an Orion 720 pH/mV meter, which was attached to a strip-chart recorder to record the FI signals. The waste from the Petri-dish was continuously removed by the peristaltic pump.

Potentiometric titration of monovalent metal ions with TPB

A 5-ml aqueous solution containing Ag^+, Tl^+, K^+ or NH_4^+ ion (≡0.05–1 mmole) was directly titrated with a standard $10^{-2}M$ sodium tetraphenylborate, using a nitron-TPB-PVC membrane electrode in conjunction with a Ag/AgCl single junction reference electrode. The electrode potential was monitored as a function of the titrant volume. Titration end points were calculated from the first and second derivative titration curves.

Separate and sequential potentiometric titrations of transition metal ions

A 5-ml aqueous solution containing Cd^{2+}, Pb^{2+}, Pd^{2+}, Ni^{2+} or Zn^{2+} (≡0.05–0.1 mmole) was treated with 1 ml of 5% v/v ethylenediamine, followed by titration with $5 \times 10^{-2}M$ standard NaTPB, using a nitron-TPB-PVC membrane electrode in conjunction with a single junction Ag/AgCl reference electrode. Binary mixtures of Cd^{2+}–Zn^{2+}, Cd^{2+}–Pd^{2+}, Cd^{2+}–Ni^{2+}, Pb^{2+}–Zn^{2+} as well as binary mixtures of transition metal ions with mono valent cations are similarly titrated. Mixtures of alkaline earth and transition metal ions are titrated in the presence of PEG-6000 for the alkaline earth metal, in one run, and in the presence of ethylenediamine for the transition metal ion in a second run.

Separate and sequential titrations of alkaline earth metal ions

A 5-ml aqueous solution containing Ba^{2+}, Ca^{2+} and Sr^{2+} either singly or in their binary or ternary mixtures (≡0.05–0.1 mmole) was treated with ~0.3 ml of 20% w/v PEG-6000, diluted to ~25 ml with doubly distilled deionized water and potentiometrically titrated with $5 \times 10^{-2}M$ NaTPB, using nitron-TPB-PVC membrane electrode in conjunction with Ag/AgCl reference electrode. Mixtures containing alkaline earth metals and mono valent cations were similarly titrated.

RESULTS AND DISCUSSION

Tetraphenylborate–PVC membrane electrodes

Performance characteristics. Tetraphenylborate anion reacts with nitron, nickel(II)–tris bathophenanthroline and iron(II)–tris bathophenanthroline cations to form water insoluble ion-association complexes. The complexes were

Table 1. Response characteristics of PVC-TPB membrane electrode systems

Parameter	[Nitron][TPB]	[Fe(b.phen)$_3$][TPB]$_2$	[Ni(b.phen)$_3$][(TPB)]$_2$
Slope, (mV/decade)	−59.3	−56.6	−56.1
Intercept, (m V)	301.3	335.7	334.7
Correlation coefficient, (r)	0.9998	0.9999	0.9999
Lower limit of linear range, (M).	1.2×10^{-6}	5.3×10^{-6}	7.9×10^{-6}
Lower limit of detection, (M).	9.2×10^{-7}	2.2×10^{-6}	3.6×10^{-6}
Response time for $10^{-3}M$, (s)	20	25	20
Recovery time, (s)	20	20	20
Working range, pH	4–9.5	4–9	5.5–10

prepared, identified and examined as ion-exchange sites in PVC membrane electrodes responsive for tetraphenylborate (TPB) anion. The electrochemical performance characteristics of the electrode systems were systematically evaluated according to IUPAC recommendations,[16] and the results are given in Table 1. The calibration plots of the three tetraphenylborate PVC membrane electrodes are almost identical in terms of slope, linear range and detection limit. The electrode systems show near-Nernstian response for at least four orders of magnitude of tetraphenylborate concentration (10^{-6}–$10^{-2}M$) with calibration slopes of 59.3, 56.6, and 56.1 mV per decade change in concentration for electrodes based on nitron, iron(II)-tris bathophenanthroline and nickel(II)-tris bathophenanthroline, respectively.

The potentials displayed by the tetraphenylborate PVC membrane electrodes for consecutive measurements of 10^{-6}–$10^{-2}M$ standard TPB solution in the same day did not vary by more than ±1.0 mV ($n = 10$). Changes in the calibration slopes did not exceed ±0.5 mV per decade change of concentration. The long term reproducibility and stability of the potential was evaluated by determining replicate calibration graphs ($n = 10$) for each electrode over a period of 6 weeks. During this period, the electrodes were stored and conditioned in $10^{-2}M$ NaTPB solution and thoroughly washed with water between measurements. Although a slight positive shift of the absolute potentials (+3 mV) was noticed, the slopes of the calibration graphs remained practically constant within ± 1–2 mV/decade over this period. The detection limit, linear range, response time and selectivity values were almost constant for the three electrode systems for at least 5 weeks.

Effects of pH and foreign ions. The effect of pH of 10^{-3}–$10^{-5}M$ TPB test solutions on the electrode potential was investigated by following the variation of the potential with the change in pH. The responses of the electrodes are practically unaffected over the pH range 4–10. The increase of potential below pH 4 may be attributed to precipitation of HTPB as indicated by solution turbidity. On the other hand, the performances of the electrode systems in the presence of 25 different inorganic and organic anions were assessed by measuring the selectivity coefficient values ($K^{\text{pot}}_{\text{TPB,B}}$) using the separate solutions method,[4,16] with a fixed concentration of the interferent ($10^{-3}M$). The results obtained show high selectivity by the three electrode systems for TPB ion, due to its higher lipophilicity, in the presence of many foreign ions. Nitron-TPB membrane electrode was used for all subsequent measurements.

Determination of TPB. The reliability of nitron-TPB membrane electrode for quantification of TPB was assessed by determining 1–160 μg/ml standard NaTPB (5 replicates each) using the standard addition method. The

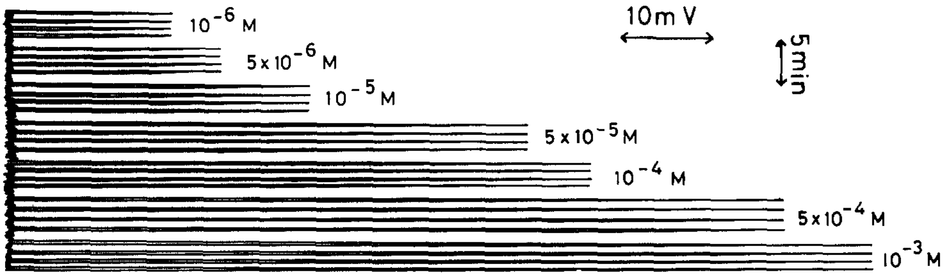

Fig. 1. Typical FIA recorder peaks produced by injection of 20 μl of standard TPB solutions in a flow through sandwich detector with nitron-TPB PVC membrane sensor.

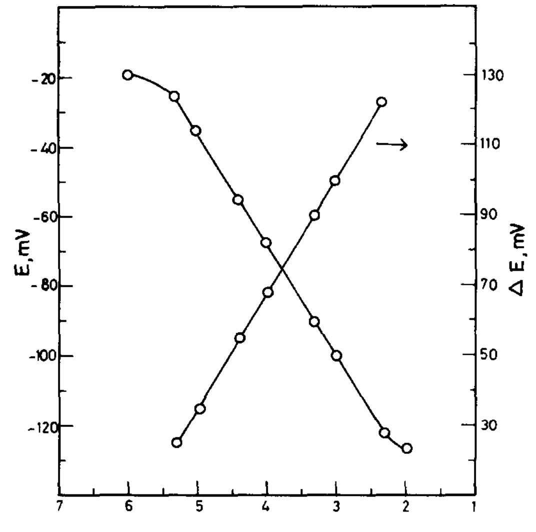

Fig. 2. Potentiometric response of the flow-through sandwich TPB detector with nitron-TPB PVC membrane sensor.

results show an average recovery of 99.3% and a mean standard deviation of 0.5% ($n = 5$). TPB was also determined by potentiometric titration with standard thallium(I) and zephiramine solutions using the same electrode system. It may be noticed that with the most commonly recommended titrant for TPB[1] (*i.e.*, Tl^+), the inflection break at the equivalence point for $10^{-2}M$ solution is only 260 mV compared to 400 mV obtained with zephiramine titrant. The results obtained for determination of 3–35 mg TPB by potentiometric titration with zephiramine show an average recovery of 99.4% and a mean standard deviation of 0.2% ($n = 5$).

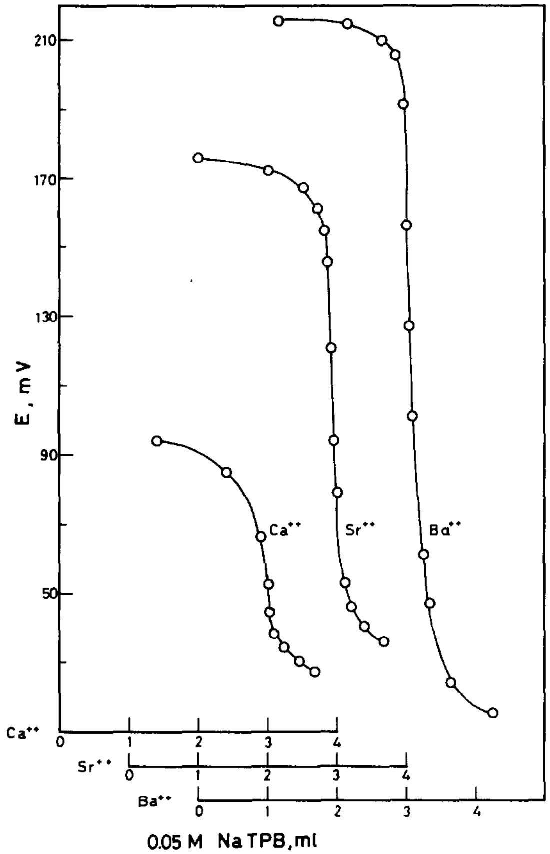

Fig. 3. Typical potentiometric titration curves of Ca^{2+}, Sr^{2+} and Ba^{2+} in the presence of polyethylene glycol with standard TPB using nitron-TPB PVC membrane electrode.

Standard NaTPB solutions (1–160 μg/ml) were determined by FI analysis. The results show an average recovery of 99.3% and a mean standard deviation of 0.5% ($n = 5$) using a laboratory-made flow through sandwich potentiometric cell equipped with nitron-TPB PVC-membrane and $5 \times 10^{-2}M$ NaCl solution as a carrier electrolyte reagent in a single stream FI system. Typical FIA recorder signals are shown in Fig. 1. It can be seen that the dynamic linear response range under hydrodynamic mode of operation is slightly less than that obtained under the static conditions probably due to sample dilution. The detection limit defined as the μg concentration for which the signal to noise ratio = 5 is $10^{-6}M$. A working concentration range of 5×10^{-2}–$5 \times 10^{-6}M$ TPB is easily achieved under FI mode (Fig. 2).

Separate and sequential titrations of metal ions with TPB

Monovalent metals. Nitron-TPB PVC-membrane electrode was used to monitor direct titrations of some metal cations with TPB. Monovalent cations such as Ag^+, Tl^+, K^+ and NH_4^+ display sharp inflection breaks at the equivalent points ranging from 100 to 280 mV at 1:1 (metal:TPB) reaction. These potential breaks are much greater and significantly sharper than those obtained by using other monitoring potentiometric sensors.[1] Determination of Tl^+, K^+ and NH_4^+ (3–30 mg/ml) shows an average recovery of 98.9% and a mean standard deviation of 0.7% ($n = 5$).

Alkaline earth metals. Potentiometric titrations of some alkaline earth metals with TPB after conversion of the cations into cationic complexes with polyethylene glycol have been previously suggested.[17] Oxonium cations formed by alkaline earth metals with polyethylene glycol (PEG) were potentiometrically titrated with TPB using nitron-TPB PVC membrane electrode. In the presence of 20-fold excess by weight of PEG-6000, calcium, strontium and

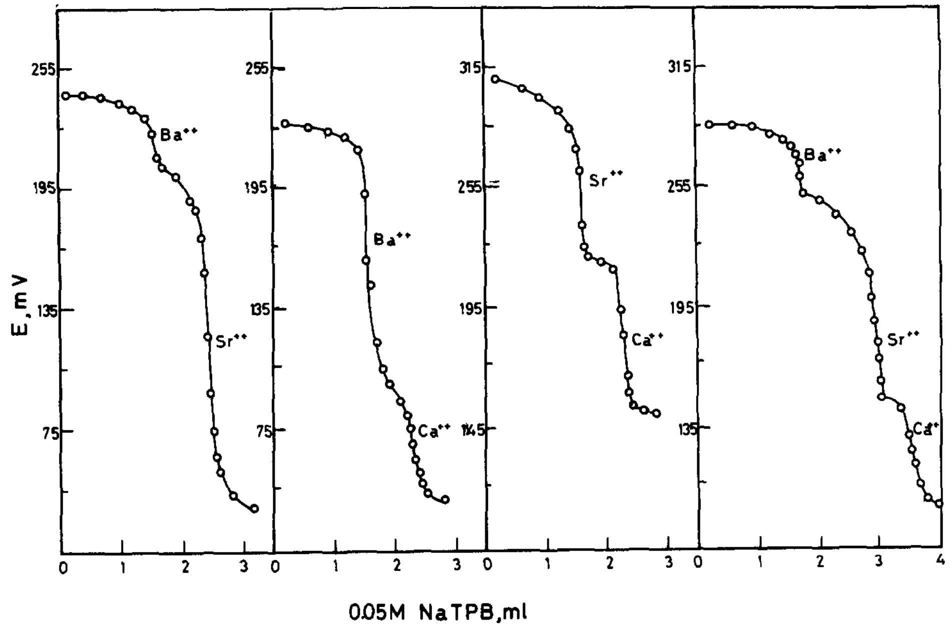

Fig. 4. Typical potentiometric titration curves for sequential titrations of binary and ternary mixtures of Ca^{2+}, Sr^{2+} and Ba^{2+} in the presence of polyethylene glycol with standard TPB using nitron-TPB PVC membrane electrode.

barium ions undergo stoichiometric reaction and reproducible consumption of 2.0 ± 0.01 mole of TPB per mole of the alkaline earth metal cation. The potential inflection breaks at the equivalence points (Fig. 3) for $10^{-2}M$ metal solutions (80–200 mV) are at least 3 times greater than those obtained by other sensors.[1,17] Determination of as little as (0.5–1.5) mg/ml of Ca^{2+}, Sr^{2+} and Ba^{2+} shows an average recovery of 99.7% and a mean standard deviation of 0.5% ($n = 5$). No interferences are caused by Mg^{2+}, Zn^{2+}, Co^{2+} and Fe^{2+} ions.

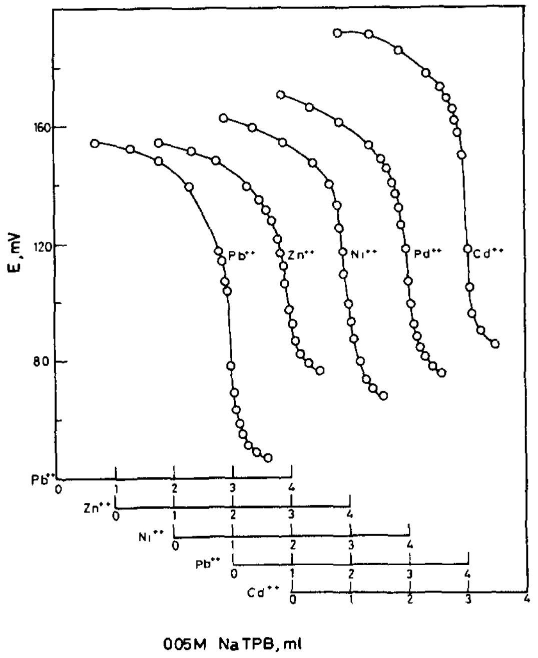

Fig. 5. Typical potentiometric titration curves of some transition metal ions in the presence of ethylenediamine with standard TPB using nitron-TPB PVC membrane electrode.

Binary and ternary mixtures containing Ca^{2+}, Sr^{2+} and Ba^{2+} are titrated with TPB under similar conditions. Potentiometric titration curves with consecutive sharp inflection breaks at the equivalence points of the constituent elements of these mixtures are obtained (Fig. 4). The sequence of the inflections is in the order: Ba, Sr and Ca which is the same as the sequence of the radius of these ions (Ba = 1.43 Å, Sr = 1.27 Å, Ca = 1.06 Å).[18] Binary mixtures containing alkaline earth and monovalent cations (*e.g.*, Ba^{2+}–Tl^{+}, Ba^{2+}–K^{+}) are sequentially titrated under the same conditions.

Transition metals. Direct titration of di-valent transition metal ions with TPB has never been reported, except for mercury(II) and copper(II) after a prior reduction into Cu(I). We have found that a number of transition metal cations and lead form stable water soluble cationic complexes with ethylenediamine which react stoichiometrically and reproducibly with TPB to form water insoluble 1:2 metal $(amine)_3$: TPB ion pair complexes as confirmed by elemental analysis. A preliminary investigation shows that nitron-TPB-PVC membrane elec-

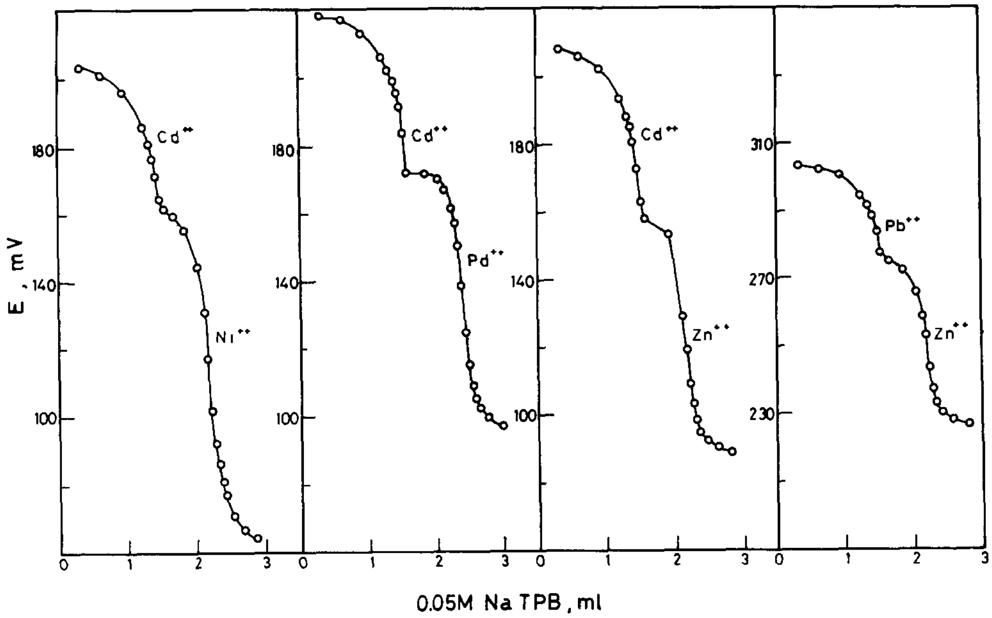

Fig. 6. Typical potentiometric titration curves for sequential titrations of some binary mixtures of transition metal ions in the presence ethylenediamine with standard TPB using nitron-TPB PVC membrane electrode.

trode does not respond to high concentrations of ethylenediamine (up to 20%) over the pH range 2–11. Titration of Zn^{2+}, Ni^{2+}, Pb^{2+}. Cd^{2+} and Pd^{2+} by addition of excess ethylenediamine followed by titration with TPB, shows titration curves with sharp inflection breaks (60–100 mV) at points equivalent to the consumption of 2.0 ± 0.02 mole of TPB per mole of the metal cation (Fig. 5).

Sequential titration of binary mixtures of Cd^{2+}–Ni^{2+}, Cd^{2+}–Pd^{2+}, Cd^{2+}–Zn^{2+} and Pb^{2+}–Zn^{2+} shows potentiometric curves with two consecutive inflection breaks due to the constituent metal ions of these mixtures (Fig. 6). The average recovery of the metals at the concentration levels of 3–10 mg/ml is better than 99% with a mean standard deviation of 0.4% ($n = 5$). However binary mixtures containing Cd^{2+}–Pb^{2+}, Pb^{2+}–Ni^{2+}, Ni^{2+}–Pd^{2+}, Zn^{2+}–Pd^{2+}, Ni^{2+}–Zn^{2+}, and Pb^{2+}–Pd^{2+} give only one unresolved inflection break at exactly their total titers. On the other hand, binary mixtures containing some mono- and di-valent metal ions such as Tl^{+}–Cd^{2+} are titrated in the presence of excess ethylenediamine. Two inflection breaks at 1:1 and 1:2 (metal:TPB) are obtained for the mono- and di-valent metal ions, respectively. Binary mixtures containing alkaline earth and transition metals such as Ba^{2+}–Cd^{2+} are satisfactorily determined by addition of excess polyethylene glycol and ethylenediamine in two separate runs followed by potentiometric titrations with TPB for Ba^{2+} and Cd^{2+}, respectively. The average recovery of both metal ions is 98.8% and the mean standard deviation is 0.4% ($n = 5$). These data reveal that the sequence of inflections of the titration curves of all the metal examined agree with the order of their ionic radii: (Tl > Ba > Sr > Ca > Cd > Pb > Zn > Pd > Ni).[18] Ions having higher ionic radii values are titrated before those of lower values in their mixtures.

In conclusion, the three TPB membrane electrodes described in the present work, offer the advantages of simplicity, sensitivity, long term stability, reliability, automation feasibility, and fast provision of analytical data. The electrode systems respond to 10^{-2}–$10^{-6}M$ TPB over a wide pH range with a near-Nernstian response and without any significant interference form many common anions. These sensors are suitable for use in FIA and for monitoring accurate separate and sequential titrations of some mono- and di-valent metal cations.

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