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Poly(4-vinylpyridine)isopentyl bromide based selective electrode with PVC matrix in aqueous media

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ABSTRACT

A selective PVC-membrane based on "poly(4-vinylpyridine)isopentyl bromide" as a carrier is tested as an ion sensor. This sensor reveals a linear response towards Br^-, Cl^-, I^-, IO_3^- *and* NO_3^- *ions in the concentration range* (10^{-4} - 10^{-1} *M. The potentiometric behaviour of the electrode is independent of the pH in test solutions with a slope near 59 mV per decade in middle in the range* $4 < pH < 9$. *The electrode possesses a satisfactory reproducibility and a fast response time.*

Keywords: Br^-, Cl^-, I^-, NO_3^-; poly(4-vinylpyridine); PVC-membrane; Ion-selective electrode.

INTRODUCTION

Ion selective electrodes (ISEs) find large applications in chemical, clinical, environmental and industrial analysis. Their fast response, good stability with time and temperature and their easy preparation make them a versatile tool in chemical sensing. A series of anion selective electrodes based on classical ion exchangers such as quaternary ammonium salts, phosphonium salts, metalloporphyrin, calixarene and other complexing agents were realised [1-7]. The choice of an ionophore is essentially based on their complexation properties and their application for separation. The nature of the central active atoms plays an important role in the realisation of the selectivity pattern. It also reported that the values of ISEs can be more reproducible and stable by incorporating a ionophore and its complex within the polymeric sensing film [7]. It's well known that the sensitivity, linearity and selectivity of an ionophore depend essentially on the membrane composition and the nature of the plasticizer and additive used [8]. Furthermore in recent work, it is shown that the concentration of internal solution on the potential response of the ion-selective electrode does not cause any significant difference in the potential response except for an expected change in the intercept of the resulting nernstian plots [9].

Potentiometric ion-selective electrodes offer several advantages such as reasonable selectivity, relatively fast response, wide dynamic range, simple instrumentation and low cost. Therefore, they have been widely applied in diverse fields [10-13].

We have been recently involved in the preparation of new ion-selective electrode based on catigen for some iodide and other halides [14].

The force field of poly(4-vinylpyridine) to form complexes and to inhibit iron and copper corrosion in acidic solutions has been mentioned [15,16]. Spectroscopic and structural studies on metal halide complexes of 4-vinylpyridine are made [17]. An iron(III) selective electrode based on poly(Fe-4-vinylpyridine) modified composite graphite paste was also investigated [18].

The aim of this work is to describe the construction and to study the response of a selective PVC membrane based on “poly(4-vinylpyridine)isopentyl bromide” for bromide, chloride, iodide, iodate and nitrate anions. The slopes and the concentration and pH ranges are also determined.

2. Experimental

2.1. *Reagents*

“poly(4-vinylpyridine)isopentyl bromide”, plant-carbon powder, dioctylphtalate (DOP), tetrahydrofuran (THF) and PVC. Potassium salts of all anions used (from Merck, G.P.R, and Panreac Quimica).

Career synthesis

Poly (4-vinypyridine) (P4VP) was prepared by radical polymerisation of 4-vinylpyridine in methanol, under vacuum, with azobisisobutyl nitrile (ANBN) as initiation, as described elsewhere [18]. The polymer was fractionated by partial precipitation from methanol solution with ethyl petrol. P4VPIPBr has been obtained by mixing P4VP to isopentyl bromide (IPBr) in chloroforme ($CHCl_3$) in a thermostatic bath (70°C). The structure was checked by NMR and IR spectra. The molecular weight was estimated by the viscosity technique using methanol as solvent [19]. P4VPIPBr has an average molecular weight of $7.16\ 10^5$g/mol.

The molecular structure of the synthesised Poly (4-vinylpyridine isopentyl bromide) (P4VPIPBr) is shown in Fig. 1.

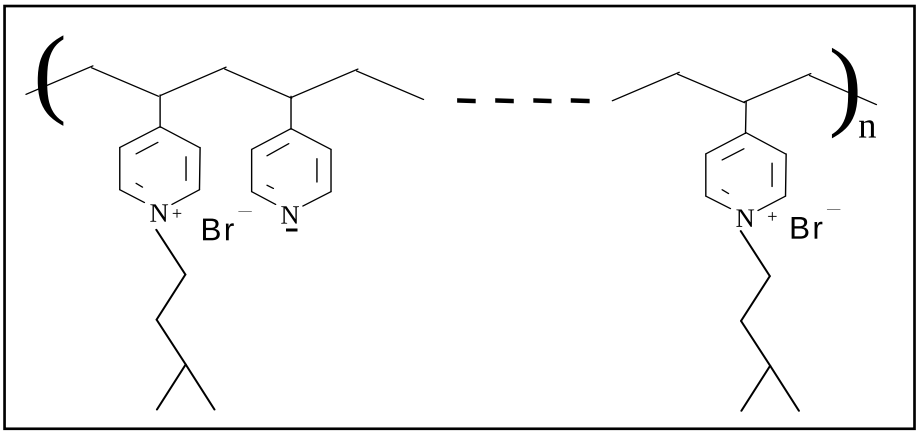

Fig. 1. The molecular structure of P4VPIPBr.

2.2. *Electrode preparation*:

The electrode was prepared by the following procedure: 25 mg poly(4-vinylpyridine) isopentylbromide, 100 mg plant-carbon powder, 100 mg PVC and one or two drops of DOP were dissolved in THF, and the mixture was shaken until total dissolution was obtained. The preparation of the electrode is made as described in figure 2. After 24 hours, the well dried membrane will be stuck (with no reagent glue) on a Pyrex glass-tube (figure 2-c).

Finally, the electrode was conditioned for at least 24 hours in 0.001M potassium bromide. The same solution was used for storing the electrode between determinations.

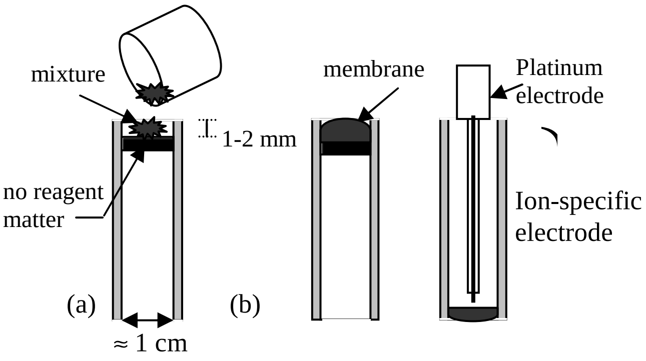

Fig. 2. Preparation of selective electrode

2.3. *The emf measurements*

All emf measurements were carried out with the following assembly (electrochemical chain):
Pt│internal solution, 0.1M KBr ││PVC membrane││ test solution│Hg-Hg_2Cl_2, KCl (satd).
A Heito high impedance pH/mV meter, model PSD5, was used for the potential measurement at 25 ± 1 °C.

RESULTS AND DISCUSSION

3.1. Time response.

The electrode is conditioned in 0.1 M Br^- solution for one day. After that equilibrium potentials of P(4-VP)iPBr electrode are achieved quickly and the time response which leads to stable values is less than ten seconds. Values are easily reproducible.

3.2. Response of p(4-VP)iPBr electrode towards bromide at different pH values

The potential-response characteristics of the tested electrode at various concentrations of Br^- at pH 7.0, 4.6, 8.3 and 2.9 are regrouped in Fig.3. The concentration domain studied is 10^{-6}-10^{-1} M. The internal and external solutions are at the same pH. We notice that the conditioned electrode gives best results with a wide concentration range of 10^{-5}-10^{-1} M with a slope of 59 mV per decade and a limit concentration of 10^{-5} M. The limit of detection is determined from the intersection of the two extrapolated segments of the calibration graph. The electrode seems to response to bromide ion at wide range of pH. The nernstian plots obtained between pH 4.6 and 8.3 shows that the electrode response is pH independent. A decrease of slope (51.6) is observed at pH 2.9. (Table1).

Table 1 Slope values at different pH values

pH	2.9	4.6	7.0	8.3
Slope	51.6	58.5	58.7	57.9

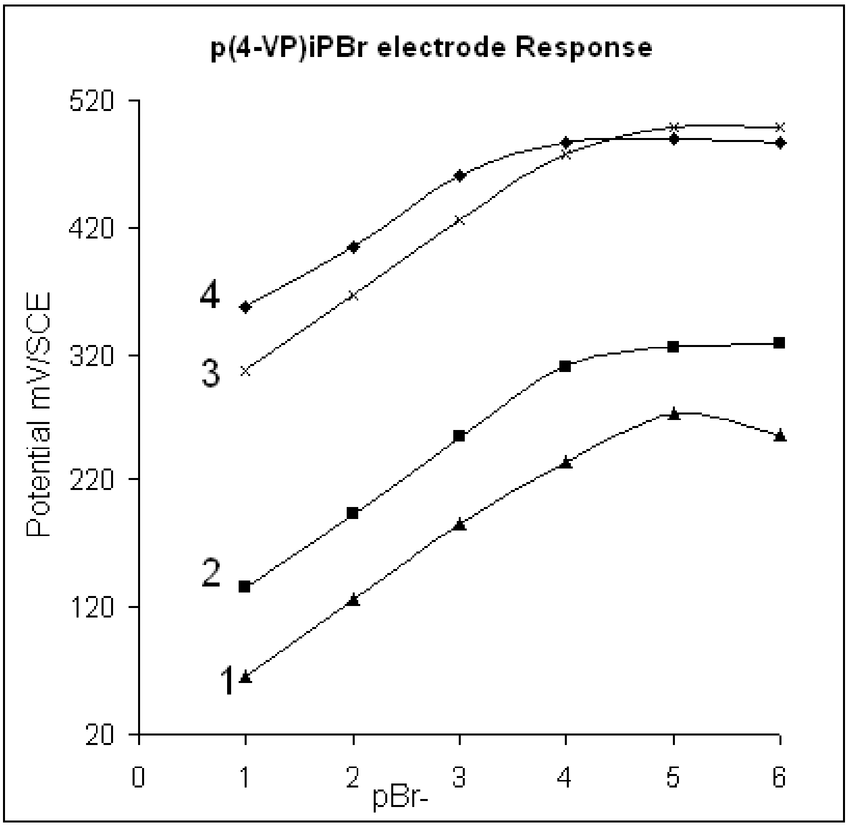

Fig.3. Response electrode in bromide solution at various pH
(1) pH = 7.0 ; (2) pH = 4.6 ; (3) pH = 8.3 ; (4) pH = 2.9.

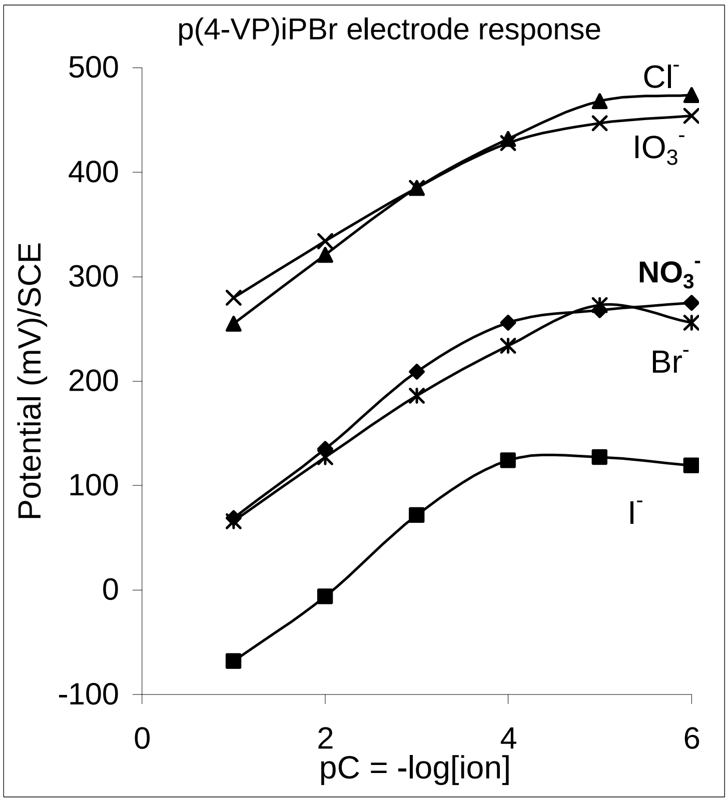

Fig.4. Electrode response towards other anions
(1) ion I^- ; (2) ion Br^- ; (3) ion NO_3^- ; (4) ion IO_3^- ; (5) Cl^- .

3.3. Response of p(4-VP)iPBr electrode towards other ions at pH = 7.0

The polymer containing bromide ion is responsible for this selective behaviour. Moreover it is very stable in acidic media since P(4-VP)iPBr is an excellent inhibitor for iron in molar sulphuric acid [20].

The encouraging results obtained above have incited us to test the prepared electrode in other anions such Cl^-, I^-, NO_3^- and IO_3^-. The domain studied is $10^{-6} – 10^{-1}$ M. The obtained results reported in Fig. 4 show that the electrode response is also linear in the range $10^{-4} – 10^{-1}$ M for the tested anions with, generally, a Nernstian behaviour, the deduced slope values are given in Table 2.

Table 2 Slope values at pH = 7

Ion	Cl^-	IO_3^-	NO_3^-	I^-
Slope	59.5	49.4	63.5	65.4

CONCLUSION

We have demonstrated that the poly(4-vinylpyridine)isopentylbromide doping the electrode can be used as ion-selective electrode for Br^-, Cl^-, IO_3^- and NO_3^-. This sensor shows a good Nernstian behaviour to changing tested ions concentrations in the range $10^{-5} – 10^{-1}$ M. It exhibits a short time response and good stability versus time. This electrode can be used successfully as monitor electrode for Br^-, Cl^-, IO_3^- and NO_3^- in potentiometry.

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