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A novel chemically modified carbon paste electrode based on a new mercury(II) complex for selective potentiometric determination of bromide ion

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Abstract A new modified carbon paste electrode based on a recently synthesized mercury (II) complex of a pyridine containing proton transfer compound as a suitable carrier for Br^- ion is described. The electrode has a linear dynamic range between 3.00×10^{-2} and 1.0×10^{-5} M with a near-Nernstian slope of 61.0 ± 0.9 mV per decade and a detection limit of 4.0×10^{-6} M (0.32 ppm). The potentiometric response is independent of the pH of the solution in the pH range 4.0–8.3. The electrode possesses the advantages of low resistance, fast response and good over a variety of other anions. It was applied as an indicator electrode in potentiometric titration of bromide ions and for the recovery of Br^- from tap water.

Keywords Bromide ion-selective electrode · Carbon paste · Mercury(II) complex · Potentiometry

Introduction

Carbon paste electrodes (CPEs) are among the most popular types of carbon electrodes which have been widely used in electroanalysis, mainly due to such interesting properties as chemical inertness, low cost, wide potential window and suitability for a variety of sensing and detection applications [1–3]. The operation

mechanism of the CPEs depends on the properties of the modifier materials used to impart selectivity towards the target species [4]. Such chemically modified carbon paste electrodes (CMCPEs) possess several advantages over the polymeric membrane ion-selective electrodes, including ease of preparation, low ohmic resistance, low background contributions, renew ability, stable response and no need for an internal solution [5–7]. Since the first use of a CMCPE containing a co-precipitated silver halide-silver sulfide for potentiometric monitoring of halide and silver ions in 1973 [8], a number of potentiometric chemically modified carbon paste electrodes for the determination of different cations [9], anions [6, 10, 11] and biologically important molecules [7, 12, 13] have been reported.

Since the halide ion selective electrodes possess a wide variety of applications especially clinical chemistry [14, 15], in the past decade, a relatively large number of carrier-based ion-selective polymeric membranes for chloride [16–19] and iodide [20–25] ions have been reported in the literature. However, despite the urgent need for selective determination of bromide ion in different industrial, environmental and clinical samples, there are only a limited number of previous reports on the carrier-based ion-selective membrane sensors for bromide ion [26–30].

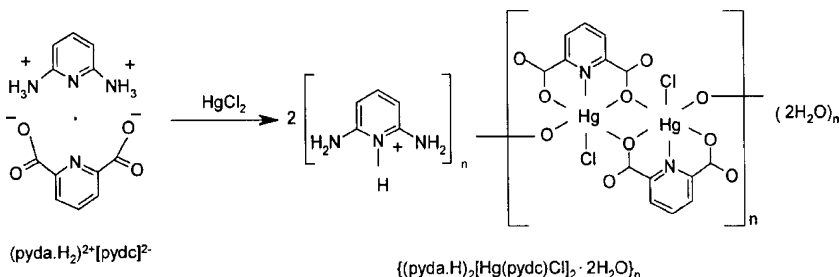
We have recently introduced a number of PVC-based potentiometric membrane sensors for different anionic species, some examples of which include Br^- [29, 30], I^- [22–25], I_3^- [31], SCN^- [32], ClO_4^- [33], NO_2^- [34], HPO_4^{2-} [35] and SO_4^{2-} [36] and an iodide-selective carbon paste electrode [11]. In this paper we employed a hexa-coordinated mercury(II) complex of a pyridine containing proton transfer compound $\{(\text{pyda.H})_2[\text{Hg}(\text{pydc})\text{Cl}]_2 \cdot 2\text{H}_2\text{O}\}_n$ (where $\text{pyda} = 2,6$ -pyridinediamine and $\text{pydc.H}_2 = 2,6$ -pyridinedicarboxylic acid), recently synthesized in our research laboratories [37], as an excellent ion-carrier to construct a highly selective CMCPE for potentiometric determination of Br^- ion. The synthetic pathway of the Hg(II) complex is shown in Scheme 1.

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Scheme 1 The synthetic scheme for the preparation of $\{(\text{pyda.H})_2[\text{Hg}(\text{pydc})\text{Cl}]_2 \cdot 2\text{H}_2\text{O}\}_n$



Experimental

Chemicals

Reagent grade paraffin oil and graphite powder (both from Fluka) were used as received. The sodium salts of all anions used (Merck) were of the highest purity available and used without any further purification except for vacuum drying. All other chemicals were purchased from Merck chemical company and used as received. Doubly distilled deionized water was used throughout.

The Hg(II) complex $\{(\text{pyda.H})_2[\text{Hg}(\text{pydc})\text{Cl}]_2 \cdot 2\text{H}_2\text{O}\}_n$ was synthesized based on Scheme 1, as follows [37]. To a solution of LH₂ (0.5 g, 1.8 mmol) in water (100 mL) was added a solution of HgCl₂ (0.245 g, 0.9 mmol) in water (20 mL) and the resulting yellow solution stirred for 1 min. After 2 weeks, golden crystals were obtained as needles. The crystals were collected, washed with fresh distilled water and dried. The pure golden crystalline Hg(II) complex (0.85 g) were prepared in 88.7% yield: mp: 260–262°C. Anal. Calcd: for C₂₄H₂₄Cl₂Hg₂N₈O₁₀: C, 27.20%; H, 2.27%; N, 10.58%; Cl, 6.70%; Hg, 37.89%. Found: C, 27.50%; H, 2.45%; N, 10.61%; Cl, 6.50%; Hg, 37.67%. ¹H NMR (DMSO-d₆) δH 6.001 (d, 4H, H3, 5 pyda.H), 7.273 (br, 8H, 4 NH₂), 7.590 (t, 2H, H4, pyda.H), 8.428 (m, 2H, H2, pydc), 8.592 (m, 4H, H3,5 pydc) ppm. ¹³C NMR (DMSO-d₆) δC 95.08 (C3, pyda.H), 127.00 (C3, pydc), 142.00 (C4, pydc), 144.66 (C4, pyda.H), 148 (C2, pyda.H), 152.7 (C2, pydc), 164 (C5, pydc) ppm. IR (KBr): 3520 (w), 3440 (s), 3320 (s), 3080 (s), 2760 (w), 1660 (s), 1640 (s), 1600 (s), 1570 (s), 1480 (w), 1420 (m), 1360 (s), 1340 (w), 1300 (w), 1275 (m), 1160 (m), 1080 (w), 1020 (m), 980 (w), 910 (m), 840 (w), 810 (w), 760 (w), 720 (m), 700 (w), 670 (w), 560 (w), 480 (w), 440–420 (w), 240 (w) cm⁻¹.

Electrode preparation

The Hg(II) complex containing carbon paste electrode was prepared by hand-mixing of 57.0 mg of graphite powder and 6.0 mg of the ionophore in a mortar for at least 10 min until the ionophore was uniformly dispersed throughout the graphite powder. Then 37.0 mg of paraffin oil was added and the mixture was mixed

until a uniform paste was obtained. The mixture was then packed in the end of a disposable polyethylene syringe (3 mm i.d., 1 mL), the end of which had been cut off with a razor blade. Electrical contact to the carbon passed was made with a copper wire. Fresh surface was obtained by applying mutual pressure to the piston. The resulting fresh surface was polished on a white paper until the surface had a shining surface. For activation, the electrode was immersed in water and 0.01 M NaBr solution prior to immersion in the sample solution.

Emf measurements

All emf measurements were carried out with the following cell assembly:

Ag-AgCl, KCl (satd.) || test solution | carbon paste electrode | Cu

The emf observations were made relative to a double junction silver/silver chloride electrode with the chamber filled with a potassium nitrate solution. Activity coefficients were calculated according to the Debye-Hckel procedure.

Apparatus

A Metrohm ion analyzer model 654 was used for the potential measurements of $25.0 \pm 0.1^\circ\text{C}$. All UV-Vis absorption spectra were recorded on a GBC 911 spectrophotometer at $24.0 \pm 0.1^\circ\text{C}$.

Results and discussion

The selective interaction of a given analyte anion and a lipophilic ionophore within the PVC-membrane is proven to be essential for the development of anion-selective membranes possessing anti-Hofmeister potentiometric selectivity patterns [17–36]. In the case of metalloporphyrin derivative, metal ion complexes with lipophilic macrocyclic ligand and Schiff's bases and organometallic compounds, it has been well established that the anion selectivity is mainly governed by specific interaction between central metal ion and anion of interest.

In order to obtain a clue about the possibility of use of the mercury complex $\{[\text{pyda.H}]_2[\text{Hg}(\text{pydc})\text{Cl}]_2 \cdot 2\text{H}_2\text{O}\}_n$ as a suitable anion-carrier, in preliminary studies, its

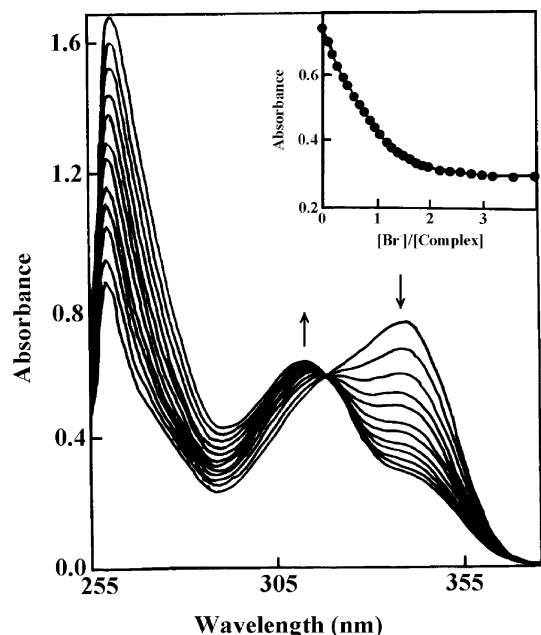


Fig. 1 Absorption spectra of a 1.0×10^{-4} M of Hg(II) complex in DMSO solution in the presence of increasing amount of bromide ion. Inset shows the corresponding absorbance-mole ratio plot at 340 nm

complexation with a variety of common anionic species was studied in DMSO solution spectrophotometrically. It was found that, with the exception of Br^- ion, the presence of anionic species resulted in negligible influence on the UV-Vis spectrum of the mercury complex. However, as it is obvious from Fig. 1, the titration of mercury complex with NaBr in DMSO revealed a gradual decrease in the complex's absorption band at 339.3 nm at the expense of the appearance of a new band at 312.1 nm, while passing through a sharp isosbestic point at 319.6 nm. The resulting absorbance-bromide ion concentration shown in the inset of Fig. 1 clearly indicates the formation of a 1:1 Hg complex- Br^- adduct in DMSO solution, the stability constant of which being evaluated as $\log K_s = 4.26 \pm 0.03$.

Moreover, in preliminary studies, the potential responses of the CPE modified with the mercury complex were obtained for a variety of anions and the results are shown in Fig. 2. As seen, except for Br^- and Cl^- ions, all other anions tested show a negligible response over the wide concentration ranges studied, due to their very weak interaction with the mercury complex. However, the CMCPE was found to possess much better response time, sensitivity and linear range for Br^- ion than for Cl^- ion. Thus, the properties of the CMCPE were studied in detail for bromide ion.

As it is obvious from Fig. 2, the selectivity sequence of the mercury complex used as an ionophore for anions differs from the Hofmeister selectivity pattern of the classical liquid ion-exchange type ionophores [38]. It is well established that, in the case of ionophores based on different metal ion complexes, the selectivity sequence is dominated by both electrostatic and coordination forces

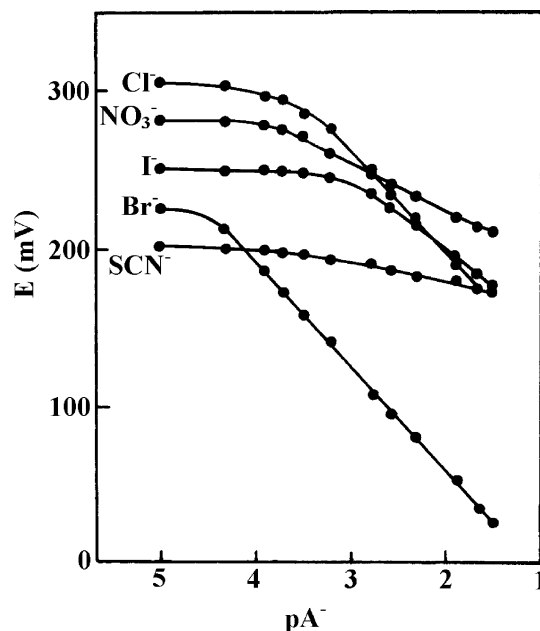


Fig. 2 Potential responses of various anion-selective electrodes based on ionophore $\{(\text{pyda.H})_2[\text{Hg}(\text{pydc})\text{Cl}]_2 \cdot 2\text{H}_2\text{O}\}_n$

so that both the nature of the complexed metal ion and the coordination ligand properties play important roles in determining the selectivity of the ionophore towards a specific anion [22–36].

It is well known that, in the CMCPEs, the sensitivity and linearity for a given anion depend significantly on the percentage of ionophore in carbon paste composition [6–13]. Thus, the influence of percent ionophore in the paste composition was investigated. The results revealed that, while, in the absence of ionophore, the CPE possesses a negligible response for Br^- ions, the increasing amount of the mercury complex caused the increasing response slope towards bromide ions, until an optimum amount of 6% is reached. However, further increase in the amount of ionophore in paste composition resulted in the diminished response slope of the CPE, most probably due to some inhomogeneities and possible saturation of the electrode. Thus, an optimum past composition of 57% graphite powder, 37% paraffin oil and 6% ionophore was used for further studies.

The critical response characteristics of the proposed Br^- -selective CMCPE were assessed according to IUPAC recommendations [39]. The emf values of the electrode at varying concentrations of bromide ion (Fig. 3) indicate a rectilinear range from 1.0×10^{-5} to 3.0×10^{-2} M. The slopes of the calibration curves were 61.0 ± 0.9 mV per decade of Br^- ion concentration. The limit of detection (LOD), as determined from the intersection of the two extrapolated segments of the calibration graph was 4.0×10^{-6} M (0.32 ppm).

The average time required for the proposed CMCPE to reach 90% of the potential response after successive immersions in a series of Br^- solutions, each having a

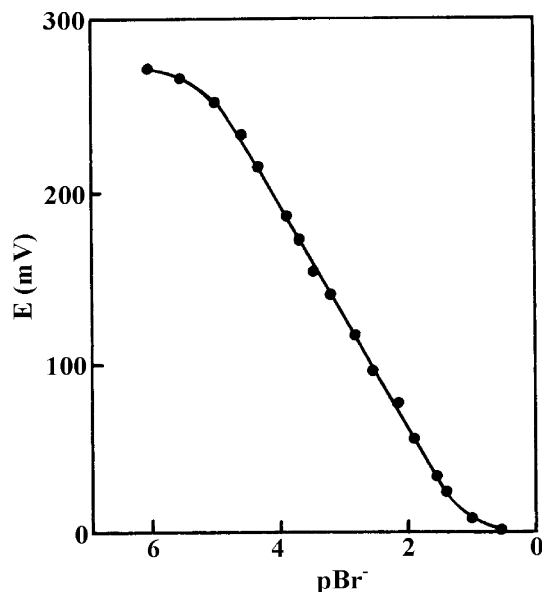


Fig. 3 Calibration graph for the bromide ion-selective electrode

10-fold difference in concentration, was less than 30 s over entire concentration range studied. The standard deviation of potential responses in a 1.0×10^{-3} M solution of Br^- was 1 mV ($n=6$). The proposed electrodes could be used for at least 3 months without any measurable divergence in potential.

The potentiometric response of the proposed CPE was found to be sensitive to pH changes of test solutions. Thus, the pH dependence of the potentials of the electrode for 1.0×10^{-3} M bromide ion was tested in a pH range of 3.0–11.0 (adjusted with either HNO_3 or NaOH) and the results are shown in Fig. 4. As it can be seen, the potential response remains constant over the pH range 4.0–8.3, which can be taken as the working pH range of the electrode. The observed significant emf deviations at pH values < 4.0 and > 8.3 could be possible due to simultaneous response of the electrode to H_3O^+ and Br^- and the strong competition of OH^- with Br^- ion for the ionophore, respectively.

The potentiometric selectivity coefficients, which reflect the relative response of a membrane sensor for the primary ion over other ions present in solution, is perhaps the most important characteristic of an ion-selective electrode [40–42]. In this work, the potential response of the proposed Br^- ion-selective sensor to ten common anions were investigated by the matched potential method (MPM) [41, 42]. This is a recently recommended method [42] which gets rid of the limitations of the corresponding methods based on Nicolskii-Eiseman equation for the determination of potentiometric selectivity coefficients (including the fixed interference and the mixed solution methods) [40–42]. These limitations include non-Nernstian behavior of interfering ions and inequality of charges of primary and interfering ions.

According to the MPM [42], the selectivity coefficient is defined as the activity ratio of the primary ion (A) and

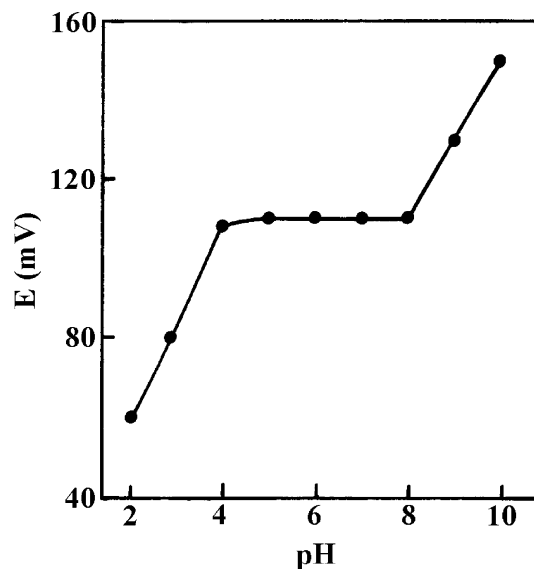


Fig. 4 Effect of pH of test solution (1.0×10^{-3} M of Br^-) on the potential response of the bromide ion-selective electrode

the interfering ion (B) that gives the same potential change in a reference solution. Thus, one should measure the change in potential upon changing the primary ion activity. Then the interfering ion would be added to an identical reference solution until the same potential change is obtained. The selectivity coefficient, $K_{A,B}^{\text{Pot}}$, is determined as

$$K_{A,B}^{\text{Pot}} = \frac{\Delta A}{a_B}$$

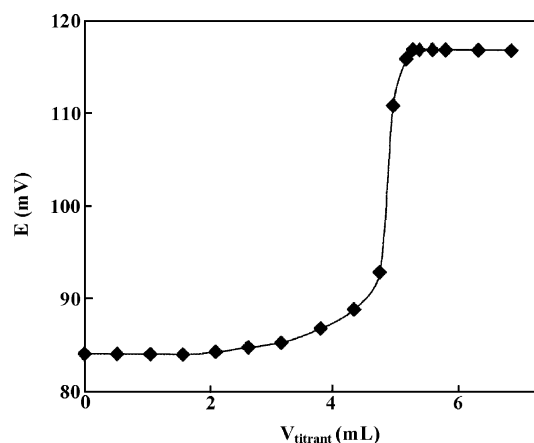
where $\Delta A = a'_A - a_A$, a_A is the initial primary ion activity and a'_A the activity of A in the presence of interfering ion, B. It should be noted that the concentration of Br^- used as a primary ion in this study was 1.0×10^{-4} M. The resulting $K_{A,B}^{\text{Pot}}$ values thus obtained for the proposed Br^- ion-selective electrode are summarized in Table 1. As seen, none of the interfering ions tested can disturb the functioning of the Br^- ion-selective membrane electrode significantly. It is interesting to note that the observed selectivity pattern ($\text{Br}^- > \text{Cl}^- > \text{I}^- > \text{IO}_3^- > \text{ClO}_4^- \cong \text{NO}_3^- > \text{SCN}^- \text{F}^- \sim \text{SO}_3^{2-} > \text{NO}_2^- > \text{SO}_4^{2-}$) significantly

Table 1 Selectivity coefficient of various interfering anions

Anion	$K_{A,B}^{\text{Pot}}$
I^-	1.8×10^{-3}
SCN^-	6.0×10^{-5}
SO_3^{2-}	2.0×10^{-5}
SO_4^{2-}	1.5×10^{-5}
F^-	2.0×10^{-5}
NO_3^-	1.0×10^{-4}
NO_2^-	1.6×10^{-5}
ClO_4^-	1.0×10^{-4}
IO_3^-	5.0×10^{-4}
Cl^-	1.2×10^{-2}

Table 2 Response characteristics and selectivity coefficients of interfering ions for different bromide ion-selective electrodes

Reference	Slope (mV decade ⁻¹)	Linear range (M)	LOD (M)	Selectivity coefficient									
				F ⁻	Cl ⁻	I ⁻	ClO ₄ ⁻	IO ₃ ⁻	SCN ⁻	NO ₂ ⁻	NO ₃ ⁻	SO ₃ ²⁻	SO ₄ ²⁻
This work	61.0	1.0×10 ⁻⁵ –1.0×10 ⁻²	4.0×10 ⁻⁶	2.0×10 ⁻⁵	1.2×10 ⁻⁵	1.8×10 ⁻³	1.0×10 ⁻⁴	5.0×10 ⁻⁴	6.0×10 ⁻⁵	1.6×10 ⁻⁵	1.0×10 ⁻⁴	2.0×10 ⁻⁵	1.5×10 ⁻⁵
28	59.2–60.4	1.0×10 ⁻⁶ –1.0×10 ⁻¹	3.0×10 ⁻⁷	–	1.7×10 ⁻³	2.5×10 ⁺³	1.3×10 ⁻⁵	–	2.5×10 ⁻¹	–	1.2×10 ⁻⁶	9.2×10 ⁻³	8.0×10 ⁻⁷
29	61	3.2×10 ⁻⁵ –1.0×10 ⁻¹	2.0×10 ⁻⁵	–	7.9×10 ⁻²	2.0×10 ⁻²	1.0×10 ⁻³	–	6.9×10 ⁻²	6.0×10 ⁻³	8.9×10 ⁻²	–	3.0×10 ⁻³
30	59.1	1.0×10 ⁻⁵ –1.0×10 ⁻¹	5.0×10 ⁻⁶	2.6×10 ⁻⁵	9.0×10 ⁻⁵	1.0×10 ⁻³	4.0×10 ⁻⁴	–	3.0×10 ⁻³	4.0×10 ⁻³	8.0×10 ⁻³	–	2.0×10 ⁻⁴

**Fig. 5** Potentiometric titration curve for 50 mL of 1.0×10⁻³ M NaBr solution with 1.0×10⁻² M of AgNO₃, using the proposed sensor as an indicator electrode

differs from the so-called Hofmeister selectivity sequence (i.e., selectivity based solely on lipophilicity of anions) [38].

In Table 2, the slopes, linear ranges, LODs and selectivity coefficients over diverse anions are compared for the best of the previously reported Br⁻ ion-selective electrodes [28–30] and the proposed CMCE. A comparison of the selectivity coefficients obtained with the proposed sensor along with those reported before [28–30] clearly indicated a considerable improvement in the selectivity behavior of the proposed electrode for Br⁻ ion. It is interesting to note that, in the case of electrode introduced in reference [28], despite its Nernstian slope and wide linear range for bromide ion, the electrode strongly suffers from the severe interfering effect of iodide ion with a highly positive selectivity coefficient of 2.5×10⁺³. Meanwhile, the linear range and LOD of the proposed bromide sensor are also improved in comparison with those reported in references [29, 30].

The practical utility of the proposed membrane sensor was tested by its use as an indicator electrode for the titration of 50 ml of 1.0×10⁻³ M KBr solution with a 1.0×10⁻² M AgNO₃ solution and the results are shown in Fig. 5. As seen, the amount of bromide ions in solution can be accurately determined from the titration curve providing a sharp end-point.

The proposed electrode was also used for the recovery of Br⁻ ion from a tap water sample, and the results

Table 3 Potentiometric determination of Br⁻ ion in tap water sample

Sample no.	Added (μM)	Found (μM)	% Recovery
1	20	19.5	97.5
2	50	52.0	104.0
3	100	103.2	103.2
4	300	305.5	101.8
5	500	506.0	101.2

are given in Table 3. As seen, in all cases, the recovery of bromide ion is almost quantitative.

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