

Selective Membrane Electrode for Bromide Ion Based on Aza Pirylium Ion Derivative as a new Ionophore.

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ABSTRACT

A highly selective electrode for Bromide ion based on aza pyrilium derivative as an excellent ionophore is described. The sensor exhibits a good linear response with a slope of (60 ± 1) mV per decade over the concentration range of $(1 \times 10^{-3} - 9 \times 10^{-6} \text{ M})$, and a detection limit of $(3 \times 10^{-6} \text{ M})$ of Bromide ions. The electrode response is independent of pH in the range of (4.0 - 9.5). Selectivity coefficients determined by the matched potential method (MPM). Indicate that the interference from inorganic and organic anions is negligible. The proposed sensor shows a fast response time of approximately (20 s). It has been used as an indicator electrode in titration of Bromide with Ag^+ .

Keywords: Bromide selective electrode; PVC membrane; Azapyrilium salt.

INTRODUCTION

It has been well documented that the selective complexation of anions by synthetic ionophores can be used to design anion selective electrodes that exhibit non-Hofmeister selectivity patterns, i.e., selectivities that are not based solely on the analyte lipophilicity. Most of these electrodes are based on vitamin B₁₂ derivatives [1,2], metalloporphyrins [3-5], organo mercury compounds [6], Schiff base complexes of metal ions [7], trialkyl Tin derivatives [8-12], phthalocyanines [13-15] and metal complexes of organophosphines [16-18]. In all of these cases, selective binding of the primary anion to the central metal ion is responsible for the observed selectivity pattern.

Due to the vital importance of Bromide determination, especially in food and biological samples there are several reports on the development of Bromide - selective membrane electrodes based on a variety of ion carriers [19-23].

Recently new cationic and anionic electrodes, for such ionic species as Pb^{2+} [24-28], Be^{2+} [29], Sr^{2+} [30], Ni^{2+} [31,32], Ce^{3+} [33], Br^- [34], I_3^- [35] and SCN^- [36] have been reported. In this work, we wish to report the utility of a plasticized (poly vinyl chloride) membrane sensor based on 4-(4-N,N diethyl phenyl)-2,6-diphenyl aza pyrilium perchlorate (I) (Fig.1) for the highly

selective detection of Bromide ion over a wide concentration range

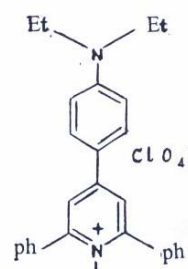


Fig.1. The structure of ligand (I).

EXPERIMENTAL

1. Reagents

Reagent grade dibutyl phthalate (DBP), acetophenone (AP), ortho-nitro Phenyl octyl ether (NPOE), hexa decyl tri methyl - ammonium bromide (HTAB), oleic acid (OA), benzyl acetate (BA), tetra hydro furan (THF) and high relative molecular weight PVC were purchased from Aldrich chemical company and used were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5 . Triply distilled deionized water was used throughout.

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N, N-diethyl amino phenyl) -3,5 - diphenyl aza pyrilium perchlorate [I] was synthesized and purified as described earlier [37].

2. Electrodes preparation and potential measurement

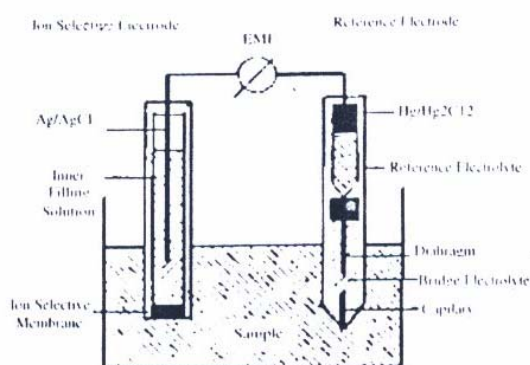
The general procedure to prepare the PVC membrane was to mix thoroughly 30 mg of powdered PVC, 5 mg of ionophore (I), 2 mg of cationic additive HTAB and 65 mg of -plasticizer DBP. Then the mixture was dissolved in 5 ml of dry THF, The resulting clear mixture was evaporated slowly until on oily concentrated mixture was obtained.

A Pyrex tube (5 mm I.d.) [25, 36] was dipped into the mixture for approximately 15s so that a non - transported membrane of approximately 0.3 mm thickness was formed.

The tube was then pulled out from the mixture and kept at room temperature for approximately 1h. The tube was then filled with an internal solution (1.0×10^{-3} M KBr). The electrode was finally conditioned for 12h by soaking in a (1.0×10^{-2} M KBr) solution. A silver / silver chloride electrode was used as an internal reference electrode.

All emf measurements were carried out with the following assembly (scheme.1):

(Hg / Hg₂ Cl₂, (satd) KCl: KCl (3 M)/Test solution // PVC membrane/ internal solution /Ag/AgCl)



Scheme 1. Assembly for emf measurements.

A corning ion analyzer 250 - pH meter was used for the potential measurement at ($25 \pm 0.1^\circ$ C). The emf observations were made relative to the double junction saturated calomel electrode

(SCE, Philips) .With the chamber filled with an ammonium nitrate solution. Activities were calculated according to the Debye-Huckel procedure [38].

RESULTS AND DISCUSSION

In case of anion selective sensors reported in the literature , the strong binding of the primary anion with the central metal ion of given metal - ligand complexes was found to be responsible for their selective behavior . In preliminary experiments, it was found that the plasticized PVC - based membrane electrodes containing ionophore (I) generate stable - potential responses in solutions containing Bromide ion after conditioning for approximately 12 h .

The membrane without ionophore displayed insignificant selectivity towards Bromide and several other anions. The preferential response has selective interaction with the highly lipophilic positive aza pyrilium ion derivative (I) .

With the aid of UV/VIS spectra as illustrated in Fig.2, it was possible to distinguish such an interaction between the cationic ionophore and Bromide ion. The substantial increase in absorbance at 244.2 nm after the contact of the carrier solution with an Bromide -containing phase suggested that the absorbing species had increased in size and the selective interaction was thought to take place .

At the same time , the effects of other anions on the spectrum of the carrier were investigated and no detectable change in the UV/VIS spectra were noted . Beside the critical role of the nature of ionophore in preparing membrane selective electrodes, Some other important features of the PVC membrane such as the amount of ionophore , the nature of the solvent mediator, the plasticizer: PVC-ratton and especially the nature of additives used are known to significantly influence the sensitivity and selectivity of ion-selective electrodes[25,39- 41] .

Thus, different aspects of the developed membrane based on ionophore (I) for bromide ion were optimized and results are given in Table 1. As can be seen from Table 1, among -three different plasticizer used, DBP was found to be more effective solvent mediator in preparing the Bromide - selective electrodes. It should be noted that the nature of the plasticizer influences both the dielectric constant of the membrane and the mobility of the ionophore and its complexes (NOS1-4). The sensitivity of the electrode response increases with increasing ionophore content until a value of (6 %) is reached.

Table 1. Optimization of membrane ingredient

NO	composition							I	SLOPE
	PVC	OA	HTAB	BA	DBP	NPOE	I		
1	30	—	—	—	67	—	2	21	
2	30	—	—	65	—	—	2	32	
3	30	—	—	63	—	—	6	31	
4	30	—	—	66	—	—	5	31.5	
5	30	10	—	—	65	—	5	36	
6	30	—	—	—	—	64	5	34	
7	30	—	—	—	55	—	5	4	
8	30	—	1	—	65	—	5	52	
9	30	—	2	—	65	—	5	60.5	
10	30	—	3	—	63	—	5	54	
11	30	—	2	63	—	—	5	37	
12	30	—	2	—	—	63	5	48	

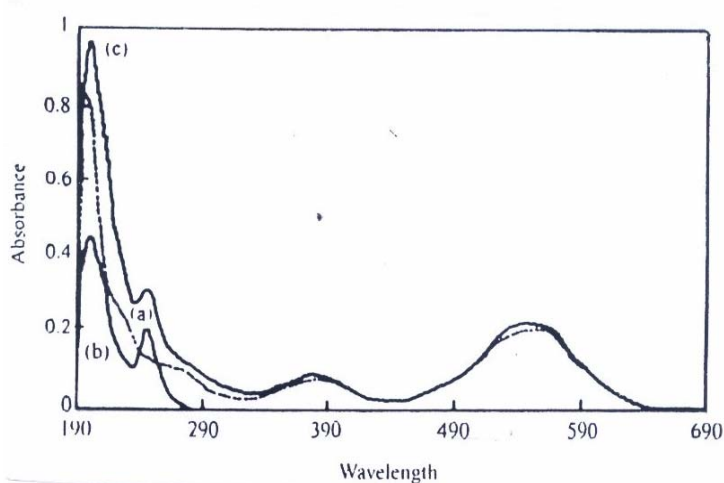


Fig.2. UV/VIS absorption spectra of acetonitril solution of the ionophore (I) (a); acetonitril Solution of 0.1 M KBr (b); ionophore (I) treated with 0.1 M KBr solution(c).

Further addition of ionophore, however, results in diminished response of the electrode most probably due to some inhomogenities and possible saturation of the membrane [42]. The data given in Table 1 show that in the absence of a cationic additive (Nos.1-6) or in the presence of an anionic additive (Nos.7,8), the sensitivity of the PVC membrane based on (I) is quite low, however, the presence of 2 % of HTAB as a suitable (No.9) cationic additive will improve the sensitivity of Br^- sensor considerably as seen, membrane No.9 with a PVC/DBP/I/ HTAB percent ratio (30:65:5:2) results in a Nernstian behavior of the membrane electrode over a wide concentration range. The concentration of internal KBr solution in the electrode was changed from 1.0×10^{-2} to 1.0×10^{-5} M, and the results showed that the concentration of internal solution does not cause any significant difference in the potential response of the electrodes, except for an expected change at the intercept of the resulting Nernstian plots. A 1.0×10^{-3} M concentration of the internal solution is quite appropriate for smooth functioning of the electrode system.

The optimum equilibration time for the membrane electrode in the presence of a 1.0×10^{-2} M KBr solution was 12 h, after which it would generate stable potential in contact with Bromide solution. The electrode shows a linear response to the concentration of the Bromide ion in the range of 1.0×10^{-1} to 9.0×10^{-6} M. The slope of calibration curve was 60 ± 1 mV per decay (Fig.3). The limit of detection, as determined from the intersection of the two extrapolated segments (i.e. the linear part of the graph at low concentration levels) of the calibration graph, was 3.0×10^{-6} M (25.4 nag/ml). Dynamic response time is an important factor for a Bromide sensitive electrode. In this study, the practical response time was recorded by changing solution with different low-to-high Br^- concentrations. The actual potential vs. time traces is shown in (Fig.4). As can be seen, in whole concentration range, the electrode reaches the equilibrium response in a very short time (approx. 20 s). To evaluate the reversibility of the electrode, a similar procedure at the opposite direction was adopted. This time, measurements were performed in the sequence of high – to – low sample concentrations and the results are shown in (Fig.5).

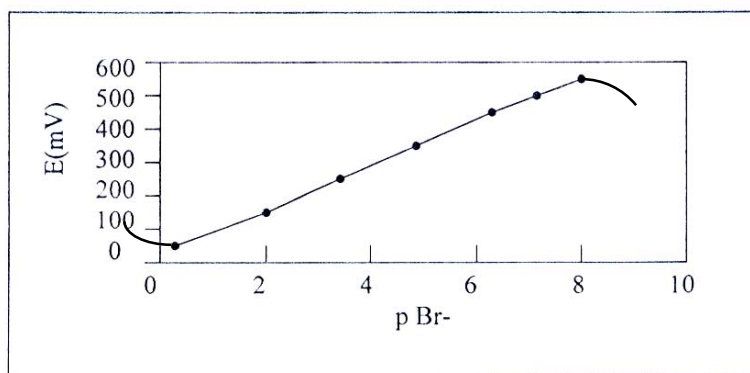


Fig.3. Calibration graph of Bromide ion-selective electrode.

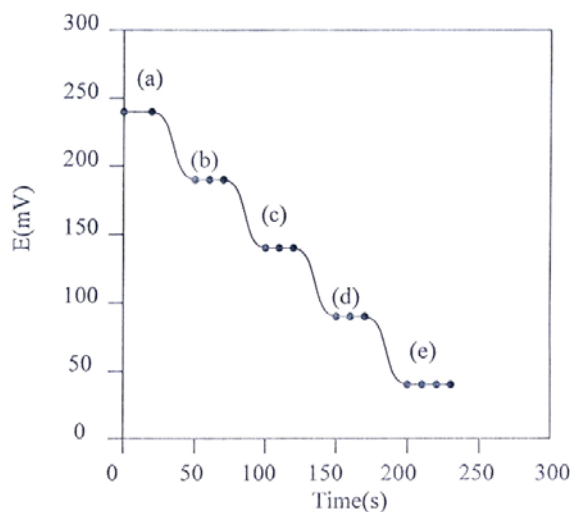


Fig.4. Dynamic response of Bromide sensor for step change in concentration of Bromide.

ion: (a) 1.0×10^{-5} M , (b) 1.0×10^{-4} M , (c) 1.0×10^{-3} M , (d) 1.0×10^{-2} M , (e) 1.0×10^{-1} M .

Fig.5. Shows that the potentiometric response of the sensor was reversible, although the time needed to reach equilibrium values were some with longer than that of the low – to -high order of sample concentration. The influence of pH of the test solution on the potential response of the membrane sensor was tested in the pH range 2.0 –10.0 (by using NaOH and $H_3 PO_4$) and the results are shown in Fig6. As can be seen, potential remains constant from pH 4.0-9.5, beyond which the potential change considerably. The diminished electrodes potential at lower and higher pH value could be most probably due to the simultaneous response of the electrode to phosphate and hydroxide ions, respectively.

It should be noted that the estimated selectivity coefficient values for phosphate and hydroxide ions are 7.0×10^{-3} and 1.0×10^{-2} M respectively .

Life time studies were carried out based on monitoring the change in the slope and detection limit

of the electrode with time and the results of the studies revealed a very slight gradual decrease in the slope and detection limit of the electrode (58.7 ± 0.3 mV per decay and 4.0×10^{-6} M respectively) after 3 months . The influence of interfering ions on the response behavior of ion –selective membrane electrodes is usually described in terms of selectivity coefficient ($K_A, BPOT$). The methods based on the Nicolsky – Eisenman equation for the determination of potentiometric selectivity coefficient (e.g. the fixed interference method and the mixed solution method) are among the most commonly used methods [43] . However, it has been shown that these methods suffer some limitation in terms of values for ions of unequal charge non -Nernstian behavior of interfering ions and activity dependence of values [44-46]. Thus , in this work , the recommended matched potential method (MPM) [44,45,46] which is totally independent of the Nicolsky – Eisenman equation , was used to overcome the above mentioned difficulties .

According to the MPM, a specified activity [concentration] of primary ions is added to a reference solution and the potential is measured. In a separate experiment, interfering ions (B) are successively added to an identical reference solution, until the measured potential matches the one obtained before by adding primary ions. The MPM selectivity coefficient, $K_{A,B}^{MPM}$, is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K_{A,B}^{Pot} = a_A/a_B$. The experimental conditions employed and the resulting values are summarized in Table 2. As seen, the $K_{A,B}^{MPM}$ values are in the order 2×10^{-3} and lower, indicating negligible interfering effect of diverse anions on the potentiometric response of the proposed bromide ion – selective electrode.

A typical selectivity pattern for a series of anions showed by the electrode is as follows:

$Br^- > CN^- > S_2O_3^{2-} > SCN^- > SO_3^{2-} > CrO_4^{2-} > NO_2^- > CO_3^{2-} > HCO_3^- > ClO_4^- > IO_3^- > Ascorbate > Salicylate > NO_3^- > I^- > Cl^- > Acetate > Citrate > SO_4^{2-}$

It is interesting to note that the observed selectivity pattern for the proposed sensor significantly differs from the so-called Hofmeister selectivity sequence (i.e. selectivity based solely on lipophilicity of anions). In Table 3 the most interfering ions (with selectivity coefficients $> 2 \times 10^{-3}$) for different Bromide – selective electrodes based on Nickel (II) tetraaza anilene macrocyclic complex [19], Silver (I) thio urea complex [20], Silver (I) complex of n-thio carbamyl imine – derivative [21], transitional metal chelates of bis-furfural – semi – O – tolidine [23]. As can be seen, none of the diverse ions studied show an interfering effect on the response of the proposed sensor, while the previously reported electrodes suffer the interfering effect from anions such as thio cyanate, nitrite, perchlorate and Bromide. The sensor was successfully applied as an indicator electrode for the potentiometric titration of Silver ion with Bromide solution.

(Fig.7) as it is seen, the amount of Ag^+ ion can be accurately determined by the electrode.

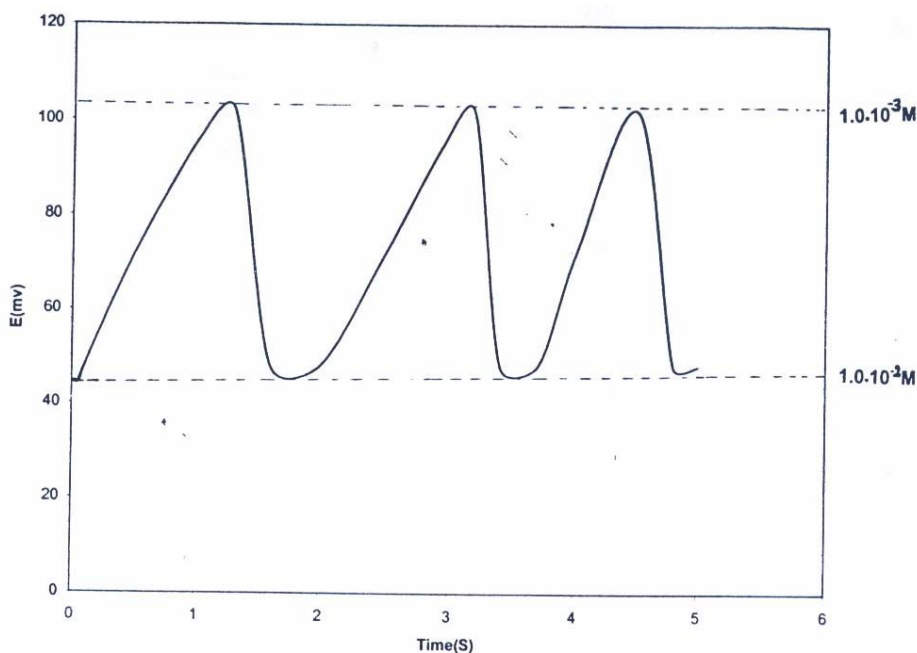


Fig.5. Dynamic response characteristics of the Bromide electrode for several high – to – low sample cycle.

Table 2. Selectivity coefficients of various interfering anions

Anion	$K_{i,A}^{pot}(MPM)$
Cl ⁻	$5 \cdot 10^{-4}$
SCN ⁻	$5.5 \cdot 10^{-4}$
HCO ₃ ⁻	$3.5 \cdot 10^{-3}$
CO ₃ ²⁻	$4 \cdot 10^{-3}$
NO ₂ ⁻	$4.8 \cdot 10^{-3}$
NO ₃ ⁻	$7 \cdot 10^{-4}$
S ₂ O ₃ ²⁻	$9.2 \cdot 10^{-5}$
SO ₃ ²⁻	$9.5 \cdot 10^{-5}$
SO ₄ ²⁻	$2 \cdot 10^{-5}$
CN ⁻	$2 \cdot 10^{-3}$
ClO ₄ ⁻	$5 \cdot 10^{-4}$
CrO ₄ ²⁻	$1 \cdot 10^{-4}$
IO ₃ ⁻	$2 \cdot 10^{-5}$
Citrate ⁻	$9 \cdot 10^{-5}$
Salicylate ⁻	$7 \cdot 10^{-5}$
Ascorbate ⁻	$8 \cdot 10^{-5}$
I ⁻	$4 \cdot 10^{-5}$

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(Fig.7)As it is seen, the amount of Ag⁺ ion can be accurately determined by the electrode.

Table 3. Comparison of interfering ions of different Bromide ion –selective electrodes

Reference	Interfering ion
19	SCN ⁻ , ClO ₄ ⁻ , NO ₂ ⁻
20	SCN ⁻
21	I ⁻ , SCN ⁻ , ClO ₄ ⁻
23	I ⁻ , SCN ⁻ , ClO ₄ ⁻ , NO ₂ ⁻
This work	—

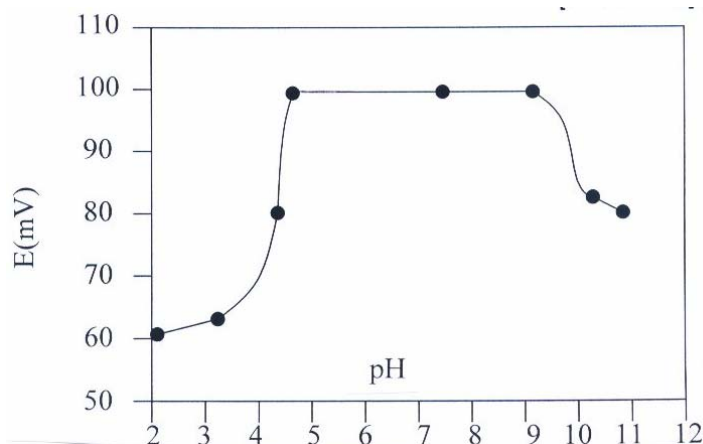


Fig.6. Effect of pH of the test solution (1.0×10^{-3} M) on the potential response of the Bromide sensor.

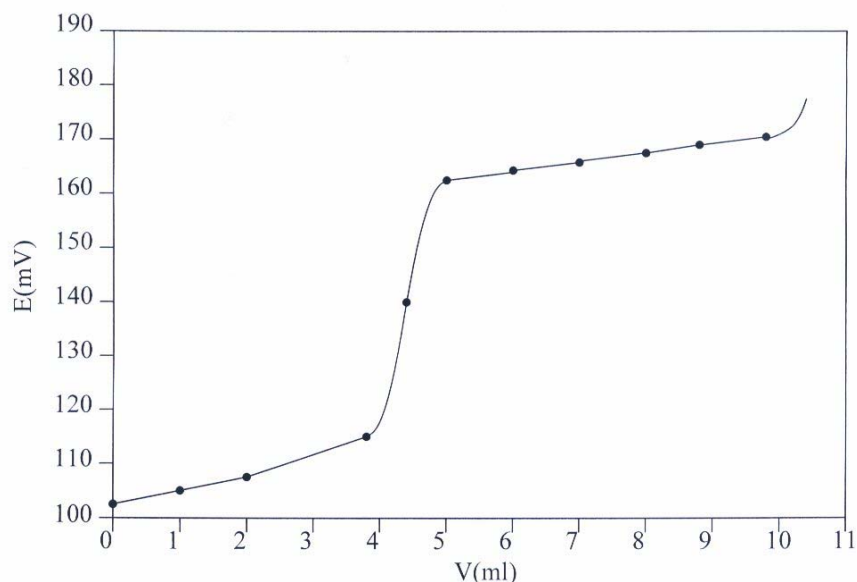


Fig.7. Potentiometric titration curves of 50 ml (1.0×10^{-3} M) KBr with (1.0×10^{-2} M) AgNO_3 . Using the proposed sensor as an indicator electrode.

CONCLUSIONS

The potentiometric method based on (I) membrane may provide an alternative for the direct determination of Bromide ion. This electrode is very easy to prepare, shows high selectivity and sensitivity, wide dynamic range, low detection limit and very fast response time. These properties make this electrode suitable for measuring the concentration of Bromide in a wide

variety of samples including water and salt samples, without the from need of pre - concentration or pre - treatment steps , and without significant interferences other anionic species present samples .The authors express their thanks to the university of Islamic Azad University - Science and Research Campus.

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