Available online at www.sciencedirect.com

SCIENCE DIRECT®

Talanta 69 (2006) 1143–1148

Talanta

www.elsevier.com/locate/talanta

A bromide selective polymeric membrane electrode based on Zn(II) macrocyclic complex

A.K. Singh*, Sameena Mehtab, Puja Saxena

Department of Chemistry, Indian Institute of Technology-Roorkee, Roorkee 247667, India

Received 8 October 2005; received in revised form 9 December 2005; accepted 9 December 2005

Abstract

A novel bromide ion-selective PVC membrane sensor based on 2,3,10,11-tetraphenyl-1,4,9,12-tetraazacyclohexadeca-1,3,9,11-tetraene zinc(II)complex (**I**) as carrier has been developed. The electrode exhibited wide working concentration range 2.2×10^{-6} to 1.0×10^{-1} M and a limit of detection as 1.4×10^{-6} M with a Nernstian slope of 59.2 ± 0.5 mV per decade. The response time of electrode was 20 s over entire concentration range. The electrode possesses the advantages of low resistance, fast response and good selectivities for bromide over a variety of other anions and could be used in a pH range of 3.5–9.5. It was successfully used as an indicator electrode in the potentiometric titration of bromide ions with silver ion and also in the determination of bromide in real samples.

Keywords: Bromide-selective electrode; Zinc(II)complex; Potentiometry; PVC membrane sensor

1. Introduction

The quick determination of trace quantities of ionic species, by simple methods, is of special interest in analytical chemistry. Ion selective electrodes based on solvent polymeric membranes with incorporation of ion carriers are shown to be very useful tools for chemical, clinical and environmental analyses as well as in process monitoring [1–3]. In addition to the cation-selective electrodes, recently the design and synthesis of sensory molecules for anion-selective electrodes has become challenging subject [4]. The ion-selective electrodes usually reported have been mainly based on lipophilic cationic salts, quaternary ammoniums, organometallic compounds, Vitamin B_{12} derivatives and metalloporphyrins, Schiff base complexes.

Bromide ion has an important role in biological systems. Blood biochemistry shows interference of bromide ions with serum chloride resulted in spurious hyperchloremia with a negative anion gap and can cause epilepsy [5–7]. Bromide ion-selective electrode is used to determine bromide concentration in patient with epilepsy and hyperchloremia [8,9]. The use of bromide sensor is also useful for detecting low levels bromide concentration in wine samples [10].

A simple, cheaper and convenient method with fast response is required for analysis of large number of environmental and other samples. The analysis by ion-selective sensor provides such procedures. Efforts to develop bromide ion selective sensors were initiated but so far only few selective bromide ion sensors are reported [11–17], which suffers from various limitations. It is, therefore, still desirable to continue efforts to make available sufficiently selective and sensitive bromide ion sensor with low detection limit. The problem with regard to such development is non-availability of ionophores shows high affinity to bromide ion. Therefore, in this paper we employed a zinc complex of 2,3,10,11-tetraphenyl-1,4,9,12-tetraazacyclohexadeca-1,3,9,11-tetraene (**I**), as an excellent ion carrier to construct a highly selective electrode for potentiometric determination of bromide ion.

2. Experimental

2.1. Reagents

Reagent grade dibutyl phthalate (DBP), tri-*n*-butyl phosphate (TBP), benzil acetate (BA), *ortho*-nitrophenyloctyl ether (*o*-NPOE) from Aldrich and 1,4-diaminobutane, benzil, ethanol and Zn(II)acetate dihydrate, tetrahydrofuran (THF), high molecular weight PVC, hexadecyl trimethylammonium bromide

---

* Corresponding author. Tel.: +91 1332 285798.
E-mail address: akscyfcy@iitr.ernet.in (A.K. Singh).

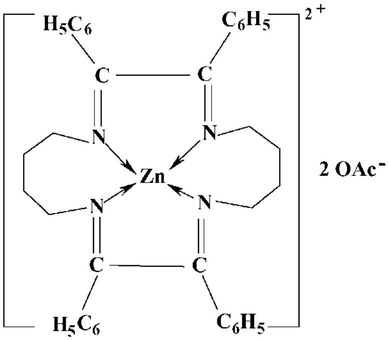
0039-9140/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2005.12.028

(HTAB), sodium salts of all anions from Merck were purchased and used without any further purification. Doubly distilled water was used throughout.

2.2. Synthesis of macrocycle complex

The zinc complex of 2,3,10,11-tetraphenyl-1,4,9,12-tetraazacyclohexadeca-1,3,9,11-tetraene (**I**) was synthesized by dissolving 1,4-diaminobutane (5.025 ml, 0.05 mol), Zn(II)acetate dihydrate (2.24 ml, 0.025 mol) in 50 ml of distilled methanol in a 250 ml round bottom flask. The mixture was stirred and to this a solution of benzil (10.52 g, 0.05 mol) in 30 ml methanol was added drop wise over a period of 1 h. The reaction mixture was refluxed for 8 h. After reducing the volume of the solution the flask was kept at 0 °C for 24 h microcrystalline product was obtained, it was filtered, washed with diethyl ether and dried under vacuum:

Yield = 84%, mp = 214 °C, Anal. calcd. for [$C_{36}H_{36}N_4Zn$]%: C, 73.29; N, 9.50; Zn, 11.09; H, 6.12. Found, %: C, 73.12; H, 6.15; N, 9.89; Zn, 11.13. IR, cm^{-1}: >C=N (1620); –C=C– (1560); Ph ring vibr. (740, 1170, 1440); Zn–N (420); C–H (2860, 2740). ^1H NMR (δ); 7.7, singlet, 20H, due to phenyl proton; 2.04, triplet, 8H, (–C–N–CH_2–) methylene proton; 1.40, multiplet, 8H, (–C–CH_2–C–) methylene proton. FAB + MS (*m*/*e*) 589.39.



Zinc complex of 2,3,10,11-tetraphenyl-1,4,9,12-tetraazacyclohexadeca-1,3,9,11-tetraene (**I**)

2.3. Electrode preparation

Varying amount of the ion active phase (**I**) and cation excluder HTAB were dissolved with an appropriate amount of PVC in 3 ml THF. To these, solvent mediators viz. *o*-NPOE, DBP, BA, TBP were added to get membrane of different compositions. The mixture was shaken vigorously. When the solution became viscous it was poured in acrylic rings resting on smooth glass plate. The solution was then allowed to evaporate for 24 h at room temperature to get transparent membrane of about 0.2 mm thickness. Which was then cut to size and glued to one end of a pyrex glass tube with araldite.

The ratio of membrane ingredients, time of contact and concentration of equilibrating solution were optimized so that the membrane develops reproducible and stable potentials.

2.4. Equilibration of membranes and potential measurements

The membranes were equilibrated for 3 days in 1.0×10^{-1} M NaBr solution. The potentials were measured by varying the concentration of the test solution in the range 1.0×10^{-7} to 1.0×10^{-1} M. Standard NaBr solutions were obtained by gradual dilution of 0.1 M NaBr solution. The potential measurements were carried out at 25 ± 0.1 °C using saturated calomel electrode (SCE) as reference electrode with the following cell assembly:

$$\mathrm{Ag/AgCl|KCl(3\,M)|0.1\,MNaBr||PVCmembrane||testsolution}$$
$$\mathrm{|Hg/Hg_2Cl_2|KCl(saturated)}$$

3. Result and discussion

The ion carrier macrocyclic complex (**I**) was used as a potential carrier to prepare the plastized PVC-based membrane electrode for a large number of anions. The potential responses of these electrodes are shown in Fig. 1. As can be seen, the membrane sensor displayed a remarkable selectivity for bromide ion over other anions. The preferential response toward bromide ion is believed to be associated with the coordination of bromide with the central metal atom of the carrier. It is well known that the selectivity and sensitivity obtained for a given ionophore depends significantly on the membrane condition [18–22].

With UV–vis spectra, as illustrated in Fig. 2, it was possible to distinguish the interaction between the metal and bromide ions. The substantial increase in the absorbance at 264.0 nm after the contact with a carrier solution of the bromide-containing phase suggested that absorbing species had increases in size and the axial coordination might have taken place [23,24]. Beside the critical nature of an ionophore used in preparation of membrane; the amount of ionophore, the nature of solvent mediator, the plasticizer:PVC ratio and especially the nature of additive used, are also known to significantly influence the sensitivity and selectivity of an ion-selective electrode [25–27].

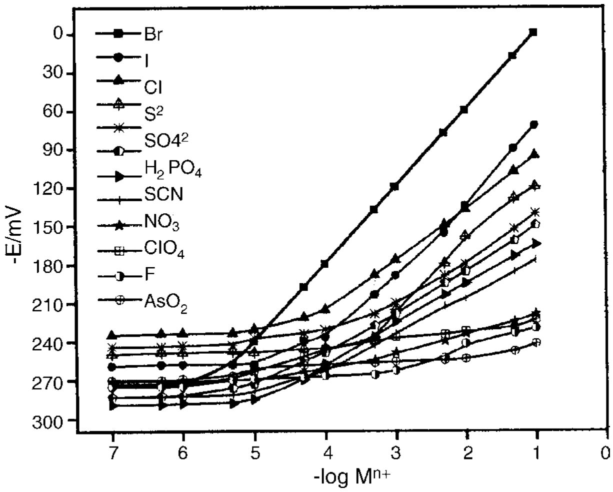


Fig. 1. The potential responses of anion-selective electrodes based on Zn[Ph_4(16)tetraeneN_4] for various anions.

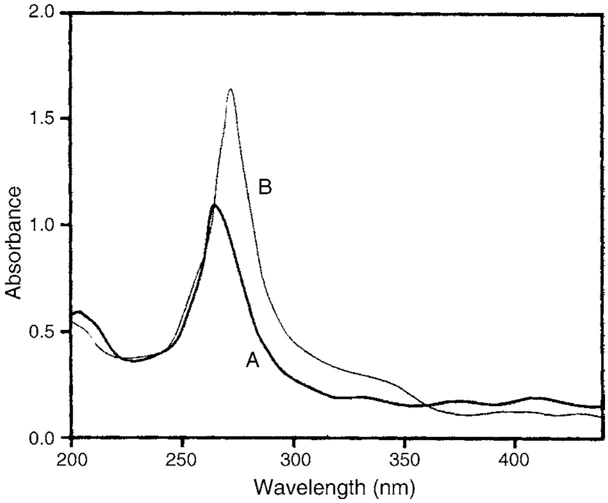


Fig. 2. UV–vis absorption spectra of 1.0×10^{-4} M solution of Zn(II) complex in the absence (A) and presence (B) of equimolar amount of sodium bromide in DMSO solution.

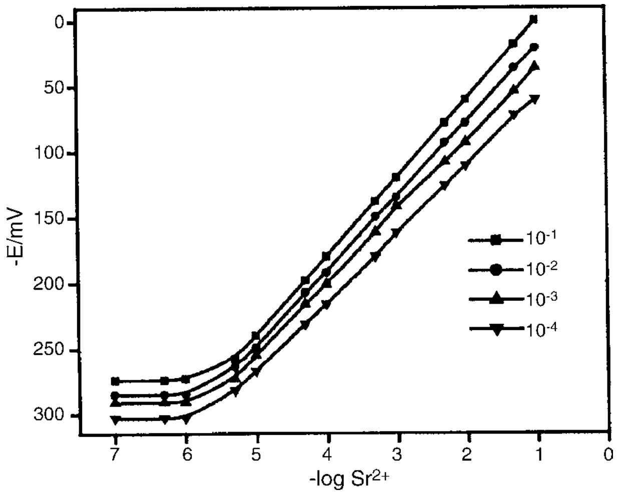


Fig. 3. Effect of internal filling solution on the potential response of the electrode.

The composition of membrane with different plasticizers and additive, performing best is given along with their characteristics in Table 1. Among the four different plasticizers (NPOE, DBP, BA, TBA) used NPOE is a more effective solvent mediator in preparing the bromide selective membrane electrode. It should be noted that the nature of the plasticizers influence both the dielectric constant of the membrane and as well as the mobility of ionophore and its complex.

The amount of ionophore was also found to affect the response of membrane electrode (Table 1). The sensitivity of the electrode response increased with increase in the ionophore content till the value of 5 mg. Further, addition of ionophore will however resulted in diminishing the response of the electrode, which may be due to some inhomogenities and possible saturation of the membrane [28]. The presence of 3 mg of HTAB as a cationic additive improved the sensitivity of bromide sensor considerably (no. 4). As can be seen from Table 1 that the membrane having composition PVC:NPOE:**I**:HTAB as 150:345:5:3 (w/w/w/w) exhibits the best results with Nernstian slope and limit of detection 1.4×10^{-6} M. This sensor no. 4 having this composition gave response to bromide ion over a wide concentration range (1.0×10^{-1} to 2.2×10^{-6} M).

The influence of concentration of internal solution on the potential response of the membrane electrode was also studied. It was found that the variation of the concentration 1.0×10^{-1} to 1.0×10^{-4} M of the internal solution (Fig. 3) does not cause any significant difference in the corresponding potential response; except for a change in the intercept of resulting Nernstian plot. A 1.0×10^{-2} M concentration of internal solution is appropriate for smooth functioning of the sensors since it provide a Nernstian slope.

The optimum equilibration time for the membrane electrode in the presence of 1.0×10^{-1} M NaBr solution was 3 days; it generated stable potentials in contact with bromide solution. The electrode showed a linear response to the concentration of bromide ion in the range of 2.2×10^{-6} to 1.0×10^{-1} (Fig. 1). The slope of the calibration graph was 59.2 ± 0.2 mV per decade. The limit of detection, as determined from the intersection of the two extrapolated segments of calibration graph was 1.4×10^{-6} M. The membrane sensor prepared could be used for at least 12 weeks without any divergence in potentials. The response time of the electrode was determines by measuring the time required to achieve a 90% of the steady potential. The static response time thus obtained was 20 s over the entire concentration range.

Table 1
Optimized membrane compositions and their potentiometric response as in bromide ion-selective electrodes

Membrane no.	Composition of membrane (mg)				Slope mV/decade (± 0.5)	Linear range (M)
	PVC	Plasticizer	Ionophore	HTAB		
1	150	277 (NPOE)	1	–	32.7	7.9×10^{-4} to 1.0×10^{-1}
2	150	301 (NPOE)	1	2	48.7	1.5×10^{-4} to 1.0×10^{-1}
3	150	343 (NPOE)	3	3	52.0	8.7×10^{-6} to 1.0×10^{-1}
4	150	345 (NPOE)	5	3	59.2	2.2×10^{-6} to 1.0×10^{-1}
5	150	333 (DBP)	5	3	37.1	1.9×10^{-4} to 1.0×10^{-1}
6	150	346 (DBP)	5	3	49.2	3.2×10^{-5} to 1.0×10^{-1}
7	150	310 (BA)	5	3	43.2	8.6×10^{-4} to 1.0×10^{-1}
8	150	339 (BA)	5	3	48.7	2.5×10^{-5} to 1.0×10^{-1}
9	150	348 (TBP)	5	3	50.1	7.8×10^{-4} to 1.0×10^{-1}
10	150	348 (NPOE)	7	3	68.7	8.9×10^{-5} to 1.0×10^{-1}

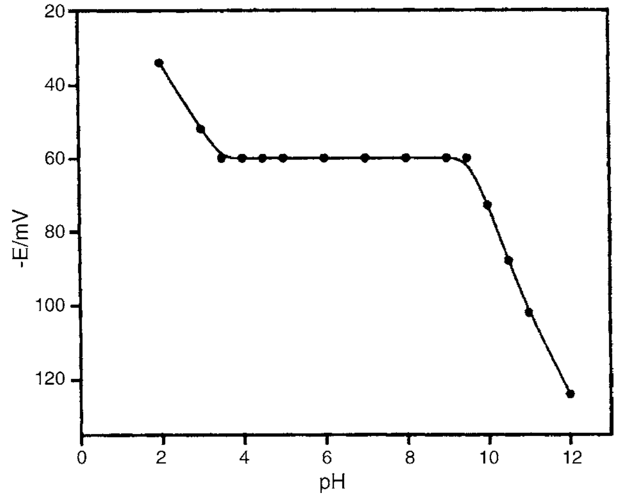


Fig. 4. Effect of pH on potential response of the Br^- ion-selective electrode using 1.0×10^{-2} M of Br^- solution.

The potentiometric response of the bromide sensor was found to be sensitive to pH changes. Thus, pH dependence of the potential of the proposed electrode for 1.0×10^{-2} M bromide was determined over the pH range 2–12. pH was adjusted by the addition of dilute nitric acid and sodium hydroxide. The results given in Fig. 4 show that the potential response remains constant over the pH range 3.0–9.5 and the same can be taken as the working pH range of the electrode. The significant change in potential response observed at a deviation at pH values <3.5, can be due to simultaneous response of the electrode to the oppositely charged H_3O^+ and Br^- ions. The contribution of H_3O^+ to potential response counteracts that of Br^- ions. The observed potential drift at high pH values could be due to response of sensor to OH^- and bromide Br^- ions.

The most important characteristic of any ion-selective electrode, is its relative response for the primary ion over other ions present in the solution, which is expressed in terms of potentiometric selectivity coefficients, $K^{\text{pot}}_{\text{A,B}}$, describing the preference of the membrane for an interfering ion relative to bromide ion. The selectivity coefficient for an interfering ion, B, relative to bromide ion, A, were determined by Match Potential Method (MPM) [29]. According to MPM, when the activity of the primary ion a_A increases to a'_A, the change in potential measured. Then the interfering ion is added if activity a_B to the primary ion solution of activity a_A and the same change in potential occurs [30]. $K^{\text{pot}}_{\text{A,B}}$ is determined from the following equation:

$$K^{\text{pot}}_{\text{A,B}} = \frac{\Delta a_A}{a_B} = \frac{a'_A - a_A}{a_B}$$

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^{-2} M. The resulting values thus obtained for the proposed Br^- ion-selective electrode are given in Table 2. The selectivity coefficients are in the order of 6.4×10^{-2} or smaller, which seems to indicate that these anions have negligible disturbance on the functioning of the bromide electrode.

Table 2
Selectivity coefficients of various Interfering anions for membrane no. 4

Interfering anions	$K^{\text{pot}}_{\text{Br}^-,\text{B}}$
I^-	6.4×10^{-2}
SCN^-	1.0×10^{-3}
S^{2-}	2.5×10^{-3}
$NO_3{}^-$	8.4×10^{-4}
$H_2PO_4{}^-$	5.5×10^{-4}
$NO_2{}^-$	1.2×10^{-5}
$ClO_4{}^-$	2.6×10^{-5}
$AsO_2{}^-$	8.2×10^{-5}
Cl^-	8.6×10^{-2}
F^-	4.2×10^{-5}
$SO_4{}^{2-}$	3.2×10^{-4}

The selectivity coefficients and detection limit of the proposed sensor based on Zn[Ph_4(16)tetraeneN_4] (**I**) are compared with the previously reported bromide membrane electrodes (Table 3). As can be seen, the proposed bromide selective electrode show superiority over them in terms of wide concentration range (2.2×10^{-6} to 1.0×10^{-1} M), detection limit (1.4×10^{-6}) and response time (20 s). Thus, the sensor prepared is advancement over the reported systems.

3.1. Analytical application

The use of bromide ion-selective electrode for the determination of bromide ion in wine sample has been found to be rapid and reliable. For the analysis of bromide in, the sample was prepared as reported in literature [31]. According to this method, a 50 ml aliquot of wine was treated with 2 ml each of 3.75 M H_3PO_4, saturated KNO_3 and 1 M $CuSO_4$. After 10 min the electrode was immersed in the sample and potential response was obtained. In coulometric titration of bromide with electrolytically generated silver(I) is an accurate and precise method. The supporting electrolytes 0.5 M $HClO_4$ and 2.0 M KNO_3 were used for the studies. The electrochemical reaction $Ag + Br^- \rightarrow AgBr + e^-$ supports the cell current during early stages of the titrations, i.e. when limiting current of Br^- is greater than the cell current [32]. The coulometric end point was determined quite satisfactorily by potentiometrically. The results of four replicate measurements are given in Table 4. As can be seen from the table that the result obtained from ISE agreed reasonably well with those obtained from coulometric method.

The proposed electrode was also used for the recovery of Br^- ion from tap water samples. The direct potentiometric measurement was carried out using standard addition technique. The result obtained for the determination of bromide ion at several concentrations is in close agreement with the known bromide content as given in Table 5.

The practical utility of the proposed membrane sensor was evaluated using as an indicator electrode by carrying out the titration of 15 ml of 1.0×10^{-2} M NaBr solution with a 0.02 M $AgNO_3$ solution. The titration plot shown in Fig. 5 is of sigmoid shape that is also an indication of selectivity of electrode. The inflexion of the end point of the plot corresponds to silver bromide formation in the ratio 1:1. As can be seen from the

Table 3
Comparison of the performance of the proposed bromide selective electrode with the reported electrodes

Ref. no.	Slope (mV)	Linear range (M)	Detection limit (M)	pH range	Selectivity coefficients $K_{A,B}^{pot}$										
					I^-	SCN^-	S^{2-}	NO_3^-	$H_2PO_4^-$	NO_2^-	ClO_4^-	AsO_2^-	Cl^-	F^-	SO_4^{2-}
[11]	61	10^{-5} to 10^{-2}	4.0×10^{-6}	4.2–8.3	1.8×10^{-3}	6.0×10^{-5}	–	–	–	1.6×10^{-5}	1.0×10^{-4}	–	1.2×10^{-2}	2.0×10^{-5}	1.5×10^{-5}
[15]	61	3.2×10^{-5} to 10^{-1}	2.0×10^{-5}	4.5–8.5	2.0×10^{-2}	6.9×10^{-2}	–	8.9×10^{-2}	–	6.0×10^{-3}	1.0×10^{-3}	–	7.9×10^{-2}	–	3.0×10^{-3}
[16]	59.1	10^{-5} to 10^{-1}	5.0×10^{-6}	4.0–9.5	1.0×10^{-3}	3.0×10^{-3}	–	8.0×10^{-3}	–	1.0×10^{-3}	4.0×10^{-4}	–	9.0×10^{-5}	2.6×10^{-5}	2.0×10^{-4}
[17]	59	7.0×10^{-6} to 10^{-1}	6.0×10^{-6}	3.0–9.0	5.5×10^{-3}	7.5×10^{-3}	–	8.5×10^{-4}	–	8.2×10^{-4}	4.7×10^{-4}	–	1.4×10^{-5}	7.5×10^{-4}	3.0×10^{-5}
This work	59.2	2.2×10^{-6} to 10^{-1}	1.4×10^{-6}	3.5–9.5	6.4×10^{-2}	1.0×10^{-3}	2.5×10^{-3}	8.4×10^{-4}	5.5×10^{-4}	1.2×10^{-5}	2.6×10^{-5}	8.2×10^{-5}	8.6×10^{-2}	4.2×10^{-5}	3.2×10^{-4}

Table 4
Bromide determination in wine samples ($n = 4$)

Sample no.	Coulometric method (meq/l)	Present sensor (meq/l)
1	44.2 ± 0.2	44.6 ± 0.3
2	45.5 ± 0.3	45.8 ± 0.4
3	48.5 ± 0.2	48.6 ± 0.6
4	51.4 ± 0.3	51.7 ± 0.8

Table 5
Potentiometric determination of Br^- ion in tap water sample

Sample no.	Added (μM)	Found (μM)
1	25	24.6
2	50	48.2
3	100	102.3

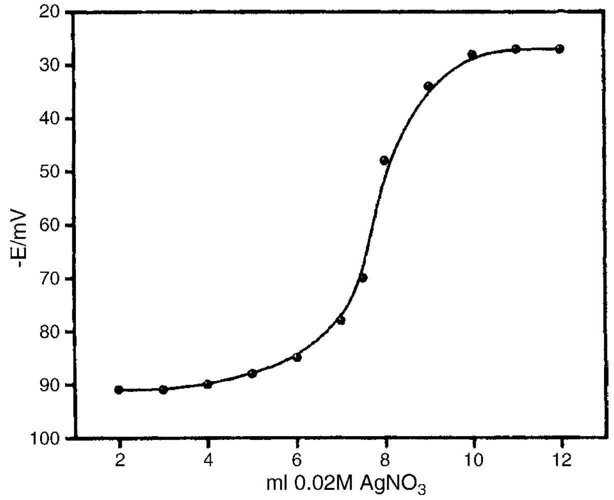


Fig. 5. Potentiometric titration curve for 15 ml of 1.0×10^{-2} M Br^- with 2.0×10^{-2} M of Ag^+, using the proposed sensor.

figure, the amount of bromide ions in solution can be accurately determined from the titration curve providing a sharp end point.

4. Conclusion

Based on the results discussed in this manuscript, the macrocyclic zinc complex, $Zn[Ph_4(16)tetraeneN_4]$ is considered to be a neutral carrier for constructing a PVC-based membrane electrode to determine concentration of bromide ion. The proposed electrode has been shown to have good operating characteristics (sensitivity, stability, life-time, response time and a wide concentration range). The proposed sensor can be used successfully for bromide ion determination both by direct potentiometry and potentiometric titration. It can also be used in determination of bromide ions in wine and tap water samples.

Acknowledgement

Ms. Sameena Mehtab is grateful to University Grant Commission (UGC) New Delhi, India for providing financial assistance for this work.

References

[1] D. Ammann, W.E. Morf, P. Anker, P.C. Meier, E. Pretsch, W. Simon, Sel. Electrode Rev. 5 (1983) 3.
[2] G.J. Moody, B.B. Saad, J.D.R. Thomas, Sel. Electrode Rev. 10 (1988) 71.
[3] M.E. Mayerhoff, M.N. Opdyche, Adv. Clin. Chem. 26 (1986) 1.
[4] M. Rothmaier, W. Simon, Anal. Chim. Acta 271 (1993) 135.
[5] P.S. Heckerling, K.A. Ammar, Am. J. Nephrol. 16 (1996) 537.
[6] Y.M. Hung, Hum. Exp. Toxicol. 22 (2003) 459.
[7] S. Vasuyattakul, N. Lertpattanasuwan, K. Vereesangthip, S. Nimmannit, S. Nilwarangkur, Nephron 69 (1995) 311.
[8] T. Katsu, Y. Mori, N. Matsuka, Y. Gomita, J. Pharm. Biomed. Anal. 15 (1997) 1892.
[9] T. Katsu, K. Furuno, S. Yamashita, H. Kawasaki, Y. Gomita, Y. Ohtsuka, S. Ohtahara, Clin. Chim. Acta 234 (1995) 157.
[10] J.E. Graf, T.E. Vaughn, W.H. Kipp, J. Assoc. Anal. Chem. 59 (1976) 53.
[11] M. Shamsipur, S. Ershad, N. Samadi, A. Moghimi, H. Aghabozorg, J. Solid State Electrochem. 9 (2005) 788.
[12] H. James, G. Carmack, H. Freiser, Anal. Chem. 44 (1972) 856.
[13] P.K.C. Tseng, Anal. Lett. 9 (1976) 795.
[14] Y.G. Viaso, L.N. Moskin, E.A. Bychkov, D.V. Glikov, Analyst 114 (1989) 185.
[15] M. Shamsipur, S. Rauhani, A. Mohajeri, M.R. Ganjali, P.R. Rashidi, Anal. Chim. Acta 418 (2000) 177.
[16] M.R. Ganjali, M. Tahami, T. Poursaberi, A.R. Pazoukian, M. Javanbakht, M.R. Baezat, Anal. Lett. 36 (2003) 347.
[17] M.R. Ganjali, P. Norouzi, M. Golmohammadi, M. Rezapour, M.S. Niasari, Electroanalysis 16 (2004) 910.
[18] M.K. Amini, S. Shahrokhian, S. Tangestaninejad, Anal. Chim. Acta 402 (1999) 137.
[19] M. Shamsipur, M. Yousefi, M.R. Ganjali, Anal. Chem. 72 (2000) 2391.
[20] P.C. Hauser, Anal. Chim. Acta 278 (1993) 227.
[21] S. Nomura, Analyst 120 (1995) 1503.
[22] A.R. Fakhari, M.R. Ganjali, M. Shamsipur, Anal. Chem. 69 (1997) 3693.
[23] D. Gao, J. Gu, R.-Q. Yu, G.-D. Zheng, Analyst 12 (1995) 499.
[24] E. Malinowska, M.E. Meyerhoff, Anal. Chim. Acta 300 (1995) 33.
[25] M.R. Ganjali, M. Yousefi, M. Javabankht, T. Poursaberi, M.S. Niasari, L.H. Babaei, E. Latifi, M. Shamsipur, Anal. Sci. 18 (2002) 887.
[26] M.R. Ganjali, T. Poursaberi, F. Basiripour, M.S. Niasari, M. Yousefi, M. Shamsipur, J. Fresenius Anal. Chem. 370 (2001) 1091.
[27] M.R. Ganjali, T. Poursaberi, M. Hosseini, M.S. Niasari, M. Yousefi, M. Shamsipur, Anal. Sci. 18 (2002) 289.
[28] X. Yang, N. Kumar, H. Chi, D.B. Hibbert, P.W. Alexander, Electroanalysis 9 (1997) 549.
[29] Y. Umezawa, K. Umezawa, H. Sato, Pure Appl. Chem. 67 (1995) 507.
[30] V.P. Gadzepko, G.D. Christian, Anal. Chim. Acta 164 (1984) 279.
[31] J.E. Graf, T.E. Vaughn, W.H. Kipp, J. Assoc. Anal. Chem. 59 (1976) 53.
[32] G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denney, Vogel's Textbook of Quantitative Chemical Analysis, fifth ed., Longman Groups, England, 1994, 529 pp.