

A chloride ion-selective potentiometric sensor based on a polymeric schiff base complex

K Girish Kumar*^a, K Saji John^a & C J Indira^b

^aDepartment of Applied Chemistry, Cochin University of Science and Technology, Kochi 682 022, India

^bElectroanalytical Section, Central Electro Chemical Research Institute, Karaikudi 636 006, India

Email: giri@cusat.ac.in

Received 4 April 2005; revised received 6 July 2005; accepted 18 November 2005

This paper describes the fabrication of an ion-selective electrode in which a polymeric schiff base complex of cobalt(II) is used as the ionophore. The main advantage of the electrode is that it is mechanically stable upto 3 months. The electrode shows a linear response in the range of 2.5×10^{-5} - 0.5×10^{-1} mol dm⁻³. The response time of the electrode is 30 s. The pH range at which the electrode works is 3.8 to 6.8. The electrode was found to be selective towards chloride ion in the presence of ions like Na⁺, Ca²⁺, Mn²⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, CH₃COO⁻, NO₃⁻, SO₄²⁻, Br⁻ and NO₂⁻.

Keywords: Ion selective electrodes, Chloride ion, Amino methylated polystyrene

IPC Code: Int. Cl.⁷ C07C251/02

Ion-selective electrodes (ISEs) provide a convenient and quick analytical procedure for the estimation of ions in solutions which may be turbid, coloured and contain additives^{1,2}. ISEs for many species ranging from simple cations to large organic molecules have been constructed in a fashion from an appropriate cocktail based on either ion-exchangers or neutral carriers^{3,5}. Because of their simplicity, low cost, improved accuracy, applicability to unusual or extreme conditions, and timeliness ISEs are recognized as novel analytical tools^{6,7}. Their properties and characteristics make them suitable for diverse fields of analysis such as pharmaceutical analysis, plant and vegetable analysis, seawater analysis, etc.⁸⁻¹².

Ion-selective electrodes of different types are reported in the literature¹³⁻¹⁴. Polymeric membrane ISEs provide one of the most powerful sensing methods as it is possible to select various sensory elements according to the shape and size of the target ion¹⁵. Most membranes in polymer membrane ion-selective electrodes are based on a polyvinylchloride matrix^{16,17}. Polyvinylchloride, whilst being a very successful matrix material, poses certain difficulties in the manufacture of the membrane, which arise from the need for a solvent to dissolve the polymer, which is then to be evaporated to cast the membrane. This procedure is relatively slow, requiring several days to

make an electrode. Recently polystyrene based electrodes were prepared and are found to be inert, mechanically stable with long life and low response time^{18,19}. The need for ionophores having anion binding functionalities in the field of anion-selective electrodes is increasing²⁰⁻²². An ISE for acetate has been recently developed based on free base porphyrins having anion binding functionalities²³. There is also a report on anion-selective electrodes prepared with polymeric membranes doped with gallium(III), indium(III) and thallium(III) metalloporphyrins²⁴. These group XIII metals, when inserted into either octaethyl- or tetraphenylporphyrin derivatives and subsequently incorporated into plasticized poly(vinyl chloride) membranes, serve as anion-selective ionophores towards chloride and fluoride ions. A number of attempts have been made to develop chloride ion selective electrodes which are based on conducting polymers^{25,26}, polyvinyl chloride²⁷, etc. In the present investigation, a sensitive electrode, selective to chloride ion has been developed. The fabricated electrode has a stable shelf life of about three months and is inert towards most of the transition metal ions and a variety of anions. Cobalt complex of amino methylated polystyrene-salicylaldehyde schiff base has been developed as the ionophore in the fabrication of the electrode.

Experimental Procedure

Reagents

All reagents used were of analytical reagent grade and were used without further purification. Amino methylated polystyrene (2% cross-linked with divinyl benzene) was obtained from Thermax India Ltd., Mumbai, as a gift sample. Salicylaldehyde, cobalt chloride and the organic solvents like dimethylformamide (DMF), methanol, etc., were all products of Merck.

Fabrication of the chloride ion-selective electrode

Co(II) complex of amino methylated polystyrene salicylaldehyde schiff base was developed as the electro active material (ionophore) for the fabrication of the chloride ion-selective electrode. The ionophore was prepared as reported in the literature²⁸, by soaking the salicylaldehyde schiff base of amino methylated polystyrene (1×10^{-3} mol dm⁻³) in DMF for 1 h and refluxing with a DMF solution (10 mL) of CoCl₂.6H₂O (1×10^{-3} mol dm⁻³) for 15 h. The resulting solution was allowed to cool and then filtered. It was then washed with DMF, methanol, distilled water and diethyl ether and finally dried *in vacuo*. The complex formation can be represented as



where PS-LH is the polymeric schiff base and PS-LCoCl.DMF is the complex formed.

About 100 mg of dried electro active material was mixed with 400 mg of araldite and the paste was spread over a Whatman No. 41 filter paper to 0.1 mm thickness and air-dried for 48 h. It was then separated from the membrane by dipping it in a solution of CoCl₂. It was then cut to size and attached to one end of a glass tube with araldite. The tube was filled with 0.1 mol dm⁻³ CoCl₂ solution and kept immersed in the CoCl₂ solution of same strength for 24 h. Potentials were determined by direct potentiometry at room temperature. A saturated calomel electrode (SCE) was used as the reference electrode. The cell set-up was as follows:

Hg, Hg₂Cl₂/satd KCl//testsolution/ionophore/0.1 mol dm⁻³CoCl₂/.

The emf of the cell so set-up was measured using an Aplab Digital Multimeter at room temperature. Response behaviour of the electrode was studied by measuring the potential of the electrode at different concentrations of chloride ion. The pH dependence of

the electrode potential was studied by varying the pH of the chloride solution of fixed concentration with buffer solutions. Interference studies were also carried out by mixing the chloride solution of fixed concentration (0.05 mol dm⁻³) with solutions of different concentrations of foreign ions like Na⁺, Ca(II), Mn(II), Co(II), Fe(III), Ni(II), Cu(II), Zn(II), CH₃COO⁻, NO₃⁻, SO₄²⁻, Br⁻ and NO₂⁻ and measuring the potentials one after another.

Results and Discussion

Response behaviour of the electrode

Electrodes were constructed with different proportions of the ionophore and the binder; it was found that stability and slope are highly favouring a proportion of 1:4. Hence, further work was carried out using an electrode of this composition.

Stable potentials were developed within a time span of 30 s, when the developed sensor is placed in chloride solution. The mechanism may be a smooth exchange of Cl⁻ ions between the complex and the solution. The electrode potentials show a linear response in the range of 2.5×10^{-5} – 0.5×10^{-1} mol dm⁻³ of Cl⁻ concentration. The slope of E versus $-\log \text{Cl}^-$ is 57.7 mV (Fig. 1), which indicates the Nernstian nature of the electrode. The slope remained constant for about four weeks even after continuous use and the linear response was maintained for about three months, although absolute potential values changed slightly (<5 mV), as is commonly observed with ISEs¹⁸. The response time of the membrane was measured at various concentrations of test solutions. Stable potential was obtained within 30s which remained unaltered upto 7 min. Potentials were

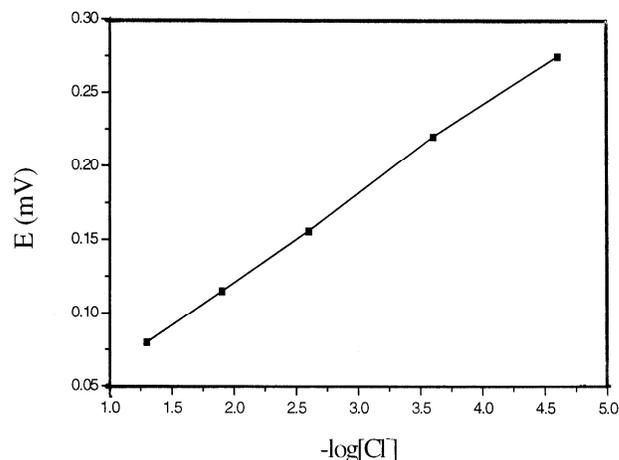


Fig. 1—Potentiometric responses of the membrane towards different concentrations of chloride ion.

Table 1 — Determination of chloride

Chloride taken				Chloride found			
[Cl ⁻] (mol dm ⁻³)	-log[Cl ⁻]	E (mV)	-log[Cl ⁻]	[Cl ⁻]	Error (%)	S.D.	C.V. (%)
1.5×10 ⁻¹	0.823	54	0.822	1.50×10 ⁻¹	0.33		
1.5×10 ⁻²	1.823	116	1.831	1.47×10 ⁻²	1.6		
1.5×10 ⁻³	2.823	1.72	2.819	1.51×10 ⁻³	1.0	0.002	0.24
1.5×10 ⁻⁴	3.823	232	3.818	1.52×10 ⁻⁴	1.3		
1.5×10 ⁻⁵	4.823	293	4.825	1.49×10 ⁻⁵	0.33		

determined for five different concentrations of chloride ion and the percentage error and precision parameters were calculated (Table 1). The results presented in Table 1 reveal that the method is accurate and precise.

Effect of pH

The pH dependence of the electrode potential was also studied (Fig. 2). The potential remains constant in the pH range of 3.8-6.8. This may be taken as the working range of pH of the electrode. The concentration of chloride ion taken was 0.5×10^{-2} mol dm⁻³ for these studies.

Interference studies

The influence of interfering ions on the response behaviour of ion-selective electrode is usually described in terms of selectivity coefficient. The potential response of the chloride ion sensor to different ions have been investigated by determining the selectivity coefficient of the electrode (K_{ij}^{Pot}) using a transformation of the Nikolski-Eizenman (N-E) equation²⁹. Its value is determined by the ability of the disturbing ion to affect the electrode potential relative to that of the main ion. The resulting K_{ij}^{Pot} values are summarized in Table 2. The results show that presence of Na⁺, Ca²⁺, Mn²⁺, Co²⁺, Fe²⁺, Ni²⁺, Cu²⁺, Zn²⁺, CH₃COO⁻, NO₃⁻, SO₄²⁻, Br⁻ and NO₂⁻ do not affect the selectivity of the chloride ion electrode significantly over the concentration range studied.

Application studies

The presently developed sensor was used for the determination of chloride ion present in treated industrial effluent from a fertilizer industry and also in a drinking water sample. The results have been compared with the standard argentometric method³⁰ and the results are presented in Table 3. The results show that the method is reliable, precise and accurate. The sensor may be recommended for the routine analysis of Cl⁻ in industrial effluents.

Table 2 — Selectivity coefficients of various foreign ions

Foreign ion	K_{ij}^{Pot}
Zn ²⁺	5.0×10^{-3}
Fe ³⁺	3.3×10^{-3}
Cu ²⁺	8.9×10^{-3}
Mn ²⁺	1.8×10^{-2}
Co ²⁺	5.6×10^{-3}
Na ⁺	9.7×10^{-3}
K ⁺	9.7×10^{-3}
Ca ²⁺	4.3×10^{-3}
SO ₄ ²⁻	4.4×10^{-3}
NO ₃ ⁻	2.0×10^{-2}
Br ⁻	6.1×10^{-3}
CH ₃ COO ⁻	2.0×10^{-2}
NO ₂ ⁻	9.7×10^{-3}

Table 3 — Determination of Cl⁻ in industrial effluent and natural water

Sample	Present method		Argentometric method ³⁰	
	Chloride found* ppm	S.D*	Chloride found* ppm	S.D*
Industrial effluent	240	0.04	238	0.05
Drinking water	48	0.03	50	0.02

*Average of 6 replicates

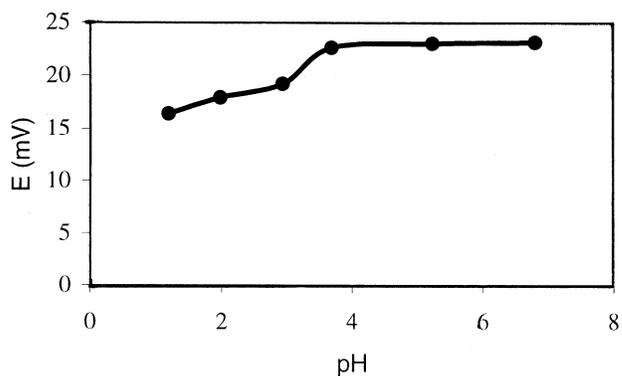


Fig. 2— Potentiometric responses of the membrane towards chloride ion solution of concentration 0.5×10^{-3} mol dm⁻³ at different pH values.

Conclusion

A chloride ion-selective electrode, based on the polymeric schiff base complex of amino methylated polystyrene and salicylaldehyde is developed. The electrode works at a convenient pH range of 3.8-6.8 without interference from other ions. Determinations can be carried out at a concentration range of 2.5×10^{-5} - 0.5×10^{-1} mol dm⁻³. A quick response time of less than 30 s and a comparatively long stable shelf life of 3 months are the striking advantages of the presently developed electrode. Further, the developed electrode is highly convenient, as there is no need of any plasticizer or solvent for its fabrication.

Acknowledgement

The authors wish to express sincere thanks to the Council of Scientific and Industrial Research, Government of India, New Delhi, for financial assistance.

References

- Mousavi M F, Alizadeh N, Shamsipur M & Zohar N, *Sens Actuators B*, 66 (2000) 98.
- Cho Dong Hoe, Chung Koo Chun, Jeong Seong Suk & Park Myon Yong, *Talanta*, 51 (2000) 761.
- Mortensen J, Legin A, Ipatov A, Rudnitskaya A, Vlasov Y & Hjuleer K, *Anal Chim Acta*, 403 (2000) 273.
- Chen L, He X, Zhao B & Liu Y, *Anal Chim Acta*, 417 (2000) 51.
- Lu X, Chen Z, Hall S B & Yang X, *Anal Chim Acta*, 418 (2000) 205.
- Mousavi M F, Barzegar M B & Sahari S, *Sens Actuators B*, 73 (2001) 199.
- Abbaspour A & Izadyar A, *Talanta*, 53 (2001) 1009.
- Perez-Olmos R, Rios A, Fernandez J R, Lapa R A S & Lima J L F C, *Talanta*, 53 (2001) 741.
- Stefan R I, Baiulescu G E & Aboul-Ensein H Y, *Crit Rev Anal Chem*, 53 (1997) 307.
- Mojtaba Shamsipur, Jalali & Fahimeh, *Anal Sci*, 16 (2000) 549.
- Ganjali M R, Daftari A, Mizarni F & Niasari M S, *Bull Korean Chem Soc*, 24 (2003) 23.
- Xu R & Bloor D M, *Langmuir*, 16 (2000) 9555.
- Cho Dong-Hoe, Chung Koo-Chun, Jeong Seong-Suk & Park Myon-Yong, *Talanta*, 51 (2000) 761.
- Monia Fibbioli, Micheal Berger, Schmidtchen Franz P & Erno Pretsch, *Anal Chem*, 72 (2000) 156.
- Oh Hyejin, Mi Choi Eun, Jeong Haesang, Chun Nam Kye & Jeon Seungwon, *Talanta*, 53 (2000) 535.
- Moody G J, Oke R B & Thomas J D R, *Analyst*, 95 (1970) 910.
- Issa Y M, Hassouna M M, Abdel-Gawad F M & Hussien E M, *J Pharm Biomed Anal*, 23 (2000) 493.
- Jain A K, Prashant Singh & Lok Pratap Singh, *Indian J Chem*, 33A (1994) 272.
- Khoroshilov A A, Bulgakova K N & Sychev Yu N, *Khim Tekhnol*, 43 (2000) 124.
- Aslar N, Kenar A, Atakol O & Kilic E, *Anal Sci*, 17 (2001) 1269.
- Hyo Kyoung Lee, Kiju Song, Hyung Ran Seo & Seungwon Jeon, *Talanta*, 62 (2004) 293.
- Mojtaba Shamsipur, Mohammad Yousefi, Morteza Hosseini, Mohammad Reza Ganjali, Hashem Sharghi & Hossein Naeimi, *Anal Chem*, 73 (2001) 2869.
- Lee H K, Song K, Seo H R & Jeon S, *Bull Korean Chem Soc*, 23 (2002) 1409.
- Erich D Steinle, Ulrich Schaller & Mark E Meyerhoff, *Anal Sci*, 14 (1998) 79.
- Bobacka J, *Anal Chem*, 71 (1999) 4932.
- Hulanicki A & Michalska A, *Electroanalysis*, 7 (1995) 692.
- Zielinska R, Mulik E, Michalska A, Achmatowicz S & Majzurawska M, *Anal Chim Acta*, 451 (2002) 243.
- Syamal A & Singh M M, *Indian J Chem*, 33A (1994) 58.
- Ren K, *Talanta*, 52 (2000) 1157.
- Standard Methods for the Examination of Water and Wastewater*, 16th edn (American Public Health Association), 1985, 287.