International Journal of Advance Research in Science and Engineering
Volume No.07, Special Issue No.03, March 2018
www.ijarse.com
IJARSE
ISSN: 2319-8354

Synthesis of Heterocyclic Based Potential Ionophores

Shankar Suman[1], **Ram Singh***[2]

[1,2*]*Department of Applied Chemistry, Delhi Technological University, Delhi, (India)*

ABSTRACT

Ionophore plays a key role in the sensitivity of an ion-selective electrode (ISE). The creation of cavities and cleft in the ionophore that are complementary to the size and charge of a particular ion can lead to very selective interactions. One of the most important figures of merit for ISEs is the selectivity towards a specific analyte, which is generally limited by the interaction of ionophore within the membrane with other ions in solution. Ionophores have been synthesized using Schiff's bases.

Schiff bases have been playing an important part in the development of coordination chemistry. Schiff base metal complexes have been studied extensively because of their attractive chemical and physical properties and their wide range of applications in numerous scientific areas. These types of complexes have been vigorously explored in recent years and such studies have been the subject of many papers and reviews.

The present work emphasizes the synthesis and characterization of ionospheres based on Schiff's base complexes of semicarbazide and thiosemicarbazide.

I.INTRODUCTION

Ionophore plays a key role in the sensitivity of an ion-selective electrode (ISE) [1]. The ion-selective electrodes (ISEs) have their applications in clinical, industrial and environmental analysis [2,3]. The ISEs are very simple, cheap and low maintenance chemical sensors. These parameters make it advantageous over other analytical techniques. The measurements with ISEs are done in potentiometric mode and hence the chemical composition of the sample remains intact can be utilized for further analysis [2,3]. The ISEs are suitable for the monitoring of heavy metal pollutants in natural water systems where high selectivity and low detection limit are required [4-7]. The ionophore based chemical sensors utilize host-guest chemistry to get high selectivity to specific ions of interest. The creation of cavities and cleft in the ionophore that are complementary to the size and charge of a particular ion can lead to very selective interactions.

Ionophores have been synthesized using Schiff's bases [8]. The Schiff's bases are imine compounds having general structure >C=N-. This was first time reported by Hugo Schiff in 1864 [9]. This base is prepared by condensing carbonyl compounds and amines in different conditions and in different solvents with the elimination of water molecules. Hence, this is also sometimes called nitrogen analogue of an aldehyde or ketone. The presence of a dehydrating agent normally favours the formation of the product. Schiff-bases are generally regarded as good ligands. These bases play an important part in the development of coordination chemistry. In Schiff's base, the nitrogen atom of the azomethine group contains a lone pair of electrons in a sp^2

hybridized orbital which facilitates its chelating ability. Schiff base metal complexes have been widely studied due to their attractive chemical and physical properties and wide range of applications in numerous scientific areas [10-16]. These types of complexes have been vigorously explored in recent years and such studies have been the subject of many papers and reviews. The metal complexes of the Schiff bases are prepared by reacting metal salts with Schiff base ligands under suitable reaction conditions. Few applications of Schiff base metal complexes are:

(i) ***As electroluminescent materials*****:** Organic electroluminescent (EL) devices are useful in flat-panel displays [17]. The principle was based on employing a multilayer device structure containing an emitting layer and a carrier transport layer of suitable organic materials. The three major categories of materials applied in the fabrication of organic EL devices are organic dyes, chelate metal complexes and polymers. Out of the three, chelate metal complexes having high-luminance blue emitting nature find use as materials for red, green, and blue (RGB) emission [17].

(ii) ***In non-linear optical devices*****:** Nonlinear optics (NLO) deals with the interactions of applied electromagnetic fields with various materials. This interaction generates new electromagnetic fields with change in frequency, phase, or other physical properties. This types of materials are able to manipulate photonic signals efficiently are useful in optical communication, optical computing, and dynamic image processing [18-22].

(iii) ***In electrochemical sensors*****:** Schiff bases have been used as carriers in the preparation of potentiometric sensors for determining cations and anions [23-31]. The metal-Schiff base complex has been used in the fabrication of chloride PVC-based membrane sensor [32].

(iv) ***In medicinal chemistry*****:** Many Schiff bases are known to be medicinally important and used to design medicinal compounds [33-36]. However, the metal-Schiff base complexes showed either increase or decrease in their efficiency towards biological evaluations [37-39].

The selectivity of ISE is an important parameter and describes the ability of the electrode to differentiate between different types of ions. The selectivity coefficients are usually determined by two methods: separate solution method (SSM) and fixed interference method (FIM) [15]. Both are based on the Nikolsky–Eisenman equation and require close to Nernstain slopes for primary and interfering ions [40-42].

II.EXPERIMENTAL SECTION

All the chemicals used in the synthesis were purchased from reputed companies and used as received. Thin-layer chromatography was used to monitor reaction progress. Compounds were purified by crystallization. Melting points were determined on a melting point apparatus and are uncorrected. IR (KBr) spectra were recorded using Perkin-Elmer FTIR spectrophotometer and the values are expressed in cm^{-1}. The ^1H NMR spectra were recorded on Bruker Spectrospin spectrometer at 300 MHz using TMS as an internal standard. The chemical shift values are recorded on δ scale and the coupling constants (J) are in Hz.

Synthesis of Schiff Base (3): The carbonyl compound (1 mmol) was dissolved in minimum amount of ethanol. The equimolar amount of semicarbazide (1 mmol) was dissolved in water. Both the solution was mixed and sodium acetate (1 mmol) was added in it. The reaction mixture was initially cooled in ice cooled water. A yellow brown precipitate was formed. The solution was further heated at 40^o C for 2 hr. The reaction mixture was cooled to room temperature. A yellow brown solid precipitated out. The solution was filtered and solid was washed with ethanol and dried over P_2O_5. The ligands were re-crystallized from benzene.

Copper complex of 3a: A hot ethanolic solution of **3a** (1 mmol) was mixed with an ethanolic solution of copper nitrate in the molar ratio of 2:1. The solution was made slightly basic with a drop of ammonium hydroxide. Instantly a greenish precipitate was formed. The mixture was refluxed for 2 hours at 40^o C. On cooling the contents the brown coloured compound separated out. The same was filtered, washed with 50% ethanol, recrystallized in ethanol and dried in vacuum.

$$CuNO_3 + 2\ 3a \rightarrow [\ Cu(3a)_2]$$

FT-IR (KBr) cm^{-1}: (NH_2)3329; (CH) 2942; (C=N) 1589; (C=O) 1725; (C-S-C) 657

$$CuNO_3 + 2\ 3b \rightarrow [\ Cu(3b)_2]$$

FT-IR (KBr) cm^{-1}: (NH_2) 3705; (NH) 3422; (C=N) 1534; (C=S) 824; (C-S-C) 710

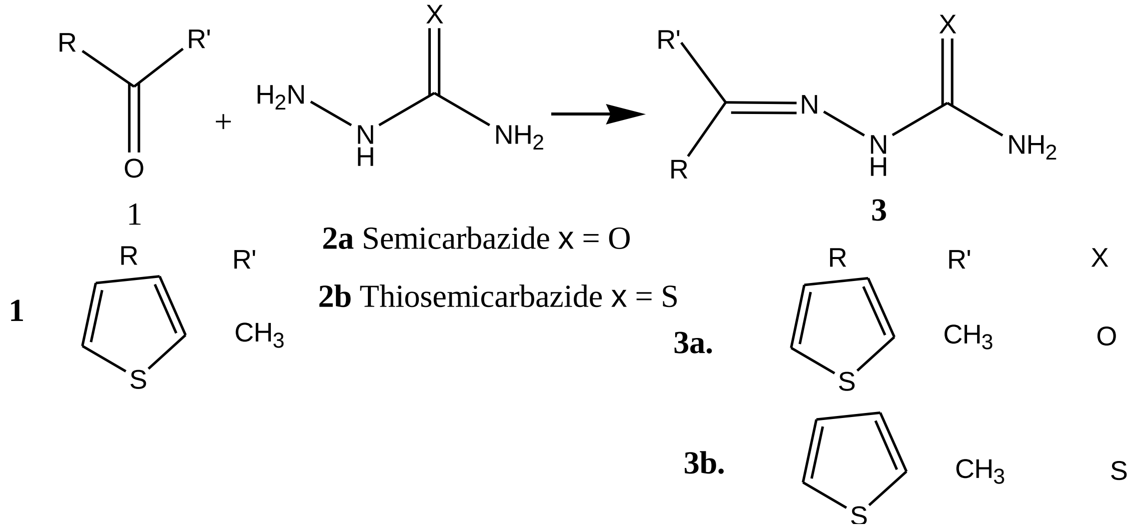
Preparation of Electrodes. A mixture of Cu-L ionophore (2 mg), powdered PVC (35 mg), and plasticizer (50 mg) was taken in 3 mL of THF. The resulting clear mixture was evaporated slowly to obtain an oily concentrated mixture. A Pyrex tube (5-mm O.D.) was then dipped into the mixture for ∼20 s to get a nontransparent membrane on it. The tube was then pulled out from the mixture and kept at room temperature for ∼2 h. The tube was then filled with an internal solution of sodium sulphate (Na_2SO_4) (1.0×10^{-3} M). The electrode was finally conditioned for 48 h by soaking in a sodium sulfate solution (1.0×10^{-2} M). A silver/silver chloride electrode was used as the internal reference electrode.

EMF Measurements. The EMF measurement with the polymeric membrane electrodes will be carried out with the following cell assemblies:

Ag-AgCl | KCl (3 M) | internal solution, 1.0×10^{-3} M Na_2SO_4 | PVC membrane | test solution | $Hg\text{-}Hg_2Cl_2$, KCl (satd)

III.RESULTS AND DISCUSSION

Schiff's base ligands are potential ionophore for heavy metal ions in the PVC membrane electrodes. This is due to its excellent metal-binding capacity. The Schiff's base is easily prepared from carbonyl compound and amine or aniline derivatives. In present case, carbonyl compounds **1** was dissolved in minimum amount of ethanol and equimolar amount of semicarbazide was dissolved in water and was mixed. Further, sodium acetate was added in it. The reaction mixture was initially cooled in ice cooled water. A yellow brown precipitate of the product was formed which was re-crystallized from benzene (Scheme 1).



Scheme 1: Synthesis of Schiff's base Ligand

The copper complexes of the synthesized ligand were prepared by mixing a hot ethanolic solution of **3a** with an ethanolic solution of copper nitrate in the molar ratio of 2:1. The solution was made slightly basic with a drop of ammonium hydroxide. Instantly a greenish precipitate was formed. The mixture was refluxed for 2 hours at 40^{o} C. On cooling the contents the brown coloured compound separated out. The analytical data of the complexes and ligands were consistent with the structure. The complexes have been stable at the room temperature. The prepared complexes were further used for the preparation of electrodes having PVC membrane. The other spectroscopic data and potentiometric measurements are under progress.

IV.CONCLUSION

We have synthesized Schiff's base using methyl-2-thienyl ketone and methyl-2-furyl ketone and semicarbazide and thiosemicarbazide. The prepared ligands were complexed with copper nitrate and used for the preparation of electrode. In the preliminary experiments, we found that the plasticized PVC based membranes containing Cu-L as a ionophore, generated stable potentials in solutions containing the sulfate ion. The membranes revealed remarkable selectivity for SO_4^{2-}. The detail studies are in progress.

REFERENCES

[1.] A. Homafar, F. Maleki, Z. Abbasi, Energy and Environmental Engineering, 1 (2013) 99-104.
[2.] E. Bakker, P. Buhlmann, E. Pretsch, Chem. Rev. 97 (1997) 3083–3132.
[3.] P. Buhlmann, E. Pretsch, E. Bakker, Chem. Rev. 98 (1998) 1593–1687.
[4.] D.R. Lynam, L. Piantanida, J.F. Cole, Environmental Lead, Academic Press, New York, 1981.
[5.] T. Sokalski, A. Ceresa, T. Zwickl, E. Pretsch, J. Am. Chem. Soc. 119 (1997) 11347–11348.
[6.] T. Sokalski, A. Ceresa, M. Fibbioli, T. Zwickl, E. Bakker, E. Pretsch, Anal. Chem. 71 (1999) 1210–1214.

[7.] T. Sokalski, T. Zwickl, E. Bakker, E. Pretsch, Anal. Chem. 71 (1999) 1204–1209.

[8.] A.K. Singh, V.K. Gupta, B. Gupta, Analytica Chimica Acta, 585 (2007) 171–178.

[9.] H. Schiff, Annalen, 131 (1864) 118.

[10.] P.A. Vigato, S. Tamburini, Coordination Chemistry Reviews, 248 (2004) 1717–2128.

[11.] N.E. Borisova, M.D. Reshetova, Y.A. Ustynyuk. Chemical Reviews, 107 (2007) 46-79.

[12.] P.G Cozzi, Chemical Society Reviews, 33 (2004) 410-421.

[13.] M. Kojima, H. Taguchi, M. Tsuchimoto, K. Nakajima, Coordination Chemistry Reviews 237 (2003) 183-196.

[14.] J. Costamagna, J. Vargas, R. Latorre, A. Alvarado, G. Mena, Coordination Chemistry Reviews, 119 (1992) 67-88

[15.] A. Syamal, M.R. Maurya, Coordination Chemistry Reviews, 95 (1989) 183-238

[16.] K. C. Gupta and A. K. Sutar, Coord. Chem. Rev., 2008, 252, 1420.

[17.] C.W. Tang, S.A. VanSlyke, Applied Physics Letters, 51 (1987) 913-915.

[18.] D.R. Kanis, M.A. Ratner, T.J. Marks, Chemical Reviews 94 (1994) 195-242.

[19.] L.R. Dalton, A.W. Harper, R. Ghosn, W.H. Steier, M. Ziari, H. Fetterman, Y. Shi, R.V. Mustacich, A.K.Y. Jen, K.J. Shea, Chemistry of Materials, 7 (1995) 1060-1081.

[20.] R.G. Benning, Journal of Material Chemistry, 5 (1995) 365-378.

[21.] S.R. Marder, D.N. Beratan, L.T. Cheng, Science, 252 (1991) 103-106.

[22.] T. Verbiest, S. Houbrechts, M. Kauranen, K. Clays, A. Persoons, Journal of Material Chemistry, 7 (1997) 2175-2189.

[23.] T. Shamspur, I. Sheikhshoaie, M.H. Mashhadizadeh, Journal of Analytical Atomic Spectrometry, 20 (2005) 476-478.

[24.] S. Sadeghi, M. Eslahi, M.A. Naseri, H. Naeimi, H. Sharghi, A. Shameli, Electroanalysis, 15 (2003) 1327-1333.

[25.] M. H. Mashhadizadeh, I. Sheikhshoaei, S. Saeid-Nia, Sensors and Actuators B chemical, 94, (2003) 241-246.

[26.] R. K. Mahajan, I. Kaur, M. Kumar, Sensors and Actuators B chemical, 91 (2003) 26-31.

[27.] M. H. Mashhadizadeh, I. Sheikhshoaei, Analytical and Bioanalytical Chemistry, 375, (2003) 51.

[28.] L. P. Singh, J. M. Bhatnagar, Talanta, 64 (2004) 313-319.

[29.] A.R. Fakhari, T.A. Raji, H. Naeimi, Sensors and Actuators B chemical, 104 (2005) 317-323.

[30.] T. Jeong, H.K. Lee, D.C. Jeong, S. Jeon, Talanta, 65 (2005) 543-548.

[31.] M.R. Ganjali, T. Poursaberi, M. Hosseini, M. Salavati-Niasari, M. Yousefi, M. Shamsipur, Analytical Sciences, 18 (2002) 289-292.

[32.] M.R. Ganjali, M.R. Pourjavid, M. Rezapour, T. Poursaberi, A. Daftari, M. Salavati-Niasari, Electroanalysis, 16 (2004) 922-927.

[33.] J. Patole, D. Shingnapurkar, S. Padhye, C Ratledge, Bioorganic & Medicinal Chemistry Letters, 16 (2006) 1514-1517.

[34.] V.T Dao, M.K Dowd, M.T Martin, C Gaspard, M Mayer, R.J. Michelot, European Journal of Medicinal Chemistry, 39 (2004) 619-624.

[35.] A. Khan, S. Sarkar, D. Sarkar, International Journal of Antimicrobial Agents, 32 (2008) 40-45.

[36.] M.S. Iqbal, A.H. Khan, B.A. Loothar, I.H. Bukhari, Medicinal Chemistry Research, 18 (2009) 31-42.

[37.] P.G. Kulkarni, G.B. Avaji, Bagihalli, S.A Patil, P.S. Badami, Journal of Coordination Chemistry 62 (2009) 481-492.

[38.] G. Puthilibai, S. Vasudevan, S.K. Rani, G. Rajagopal, Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy, 72 (2009) 796-800

[39.] P.G Avaji, C.H.V Kumar, S.A Patil, K.N. Shivananda, C. Nagaraju, European Journal of Medicinal chemistry, 44 (2009) 3552-3559.

[40.] M. Guzinski, G. Lisak, J. Kupis, A. Jasinski, M. Bochenska, Analytica Chimica Acta 791 (2013) 1– 12.

[41.] A. Hulanicki, T. Sokalski, A. Lewenstam, Mikrochim. Acta 3 (1988) 119–129.

[42.] T. Sokalski, M. Maj-Zurawska, A. Hulanicki, Mikrochim. Acta 1 (1991) 285–291.