Journal of Advanced Electrochemistry 2(3) (2016) 103–106

ISSN: 2455-0205

Contents List available at JACS Directory

Journal of Advanced Electrochemistry

journal homepage: http://www.jacsdirectory.com/jaec

Synthesis and Uses of Ni(II) Complex with Schiff Base [Benzene-1,2-Diyldimethylylidene]Dicarbamic Acid

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ARTICLE DETAILS

Article history:
Received 17 July 2016
Accepted 05 August 2016
Available online 28 August 2016

Keywords:
Nickel Complex
Ionophore
Monohydrogen Phosphate
Ion-Selective Electrode

ABSTRACT

A nickel complex of Schiff base ligand [benzene-1,2-diyldimethylylidene]dicarbamic acid was synthesized and used for the construction of monohydrogen phosphate selective electrode. The structure of the free ligand and the complex was evaluated by ^{1}H-NMR, ^{13}C-NMR, IR and UV absorption spectroscopy. The stability of the complex of the ligand with various metal ion was calculated in terms of formation constant (K_f). The complex has been successfully used as an electroactive material for the development of monohydrogen phosphate selective electrode. The selectivity coefficient of ionophore was calculated by MPM method indicates the high selectivity of the electrode towards monohydrogen phosphate over other tested anions.

1. Introduction

Complex compounds of metal ions with Schiff base ligands play an important role in environmental, medicinal, pharmaceutical and industrial chemistry. They show remarkable binding ability with various bioactive ions. The affinity of the Schiff base chelated ligand utilized in preparation of various transition metal ion complexes which are either insoluble or less soluble in water. The Schiff base complex of transition metal ion was found to be a good electroactive material for the selective determination of various anionic species in the solution [1-5].

Phosphorus is one of the second most abundant elements in human body. In human body it is found in bones, cells, soft tissues and extracellular fluids. In soft tissues and cell membrane the phosphorus mainly exists in the form of phosphate ester. Plasma phosphate and intracellular phosphate in the formation of hydroxyapatite, the also play a vital role in the metabolism of carbohydrates, lipids and proteins [6, 7]. Due to its importance in our body the selective determination of phosphate ion is a concern of research. The leaching of small amount of phosphate ion from agricultural land can contribute to eutrophication [8]. In the present study a Schiff base complex of Ni(II) has been prepared and used as electroactive material for the selective determination of monohydrogen phosphate ion.

2. Experimental Methods

2.1 Reagents and Instruments Used

The chemicals oxamic acid, benzene-1,2-dicarbaldehyde, Dimethyl phthalate (DMP) (8.5), Diisobutyl phthalate (DBP), Dioctyl phthalate (DOP), Tris(ethyhexyl) phosphate (TEP), bis-(2-ethylhexylsebacate BEHS, sodium tetraphenybal borate (NaTPB) were purchased from Sigma-Aldrich. The high molecular weight Polyvinyl chloride (PVC), acetone, absolute ethanol, and other chemicals were bought from Fluka. All reagents were used as received and no further purification was done.

The UV spectra of the ligand and complex were recorded on Labtronics UV spectrometer in the range of 360 – 160 nm. The ^{1}HNMR and ^{13}CNMR spectra were recorded in $CDCl_3$ on a Bruker Avance 300 MHz spectrometer. The pH and potential measurements were recorded with a digital pH meter and potentiometer (Equiptronics EQ-602).

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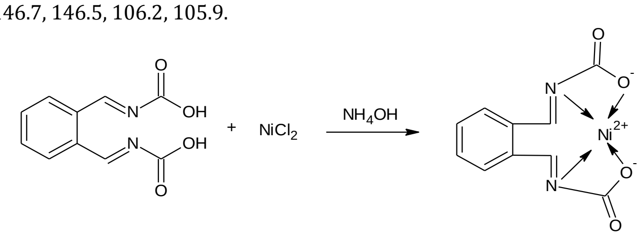
2.2 Synthesis of [benzene-1,2-diyldimethylylidene]dicarbamic acid (L)

The Schiff base ligand, [benzene-1,2-diyldimethylylidene]dicarbamic acid was synthesized by stirring benzene 1,2-dicarbaldehyde (1 mmol in 8 mL DMSO) and carbamic acid (1 mmol in 5 mL DMSO ethanol) in reflux for 100 minutes under nitrogen atmosphere, resulting in a red precipitate [3]. The precipitate was flattered and dissolved in absolute ethanol at room temperature. The ethanol allowed to evaporate in vacuum till the micro crystals of the ligand was obtained (Scheme 1). The analytical and physical data of the ligand are given below.

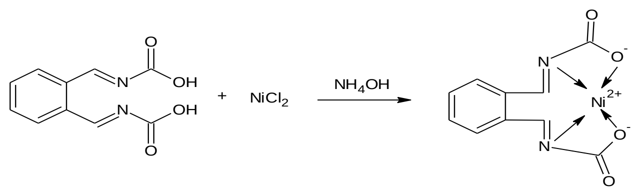
Empirical formula: $C_{10}H_8N_2O_4$, yield: 76 %.

^{1}H NMR (ppm): 8.26 (s, 2H, aromatic), 7.62 (d, 2H, aromatic), 7.32 (s, 4H, iminic), 7.21 (s, 2H, carboxylic acid).

^{13}C NMR (ppm): (6C aromatic); 182.4, 181.4, 180.6, 179.2, 178.3, 176.8, 146.7, 146.5, 106.2, 105.9.



Scheme 1 Synthesis of Schiff base ligand



Scheme 2 Synthesis of Ni(II) complex of the ligand

2.3 Synthesis of Complex

The Nickel (II) complex of Schiff base ligand (L) was synthesized by the method available in the literature (Scheme 2). A solution of $NiCl_2$ (3 mmol in DMSO) was added drop wise into the flask containing solution of Schiff base ligand (3 mmol in 10 mL DMSO) in presence of NH_4OH solution. The mixture was stirred and refluxed at 80 °C under atmosphere of nitrogen

Cite this Article as: Manish Uppal, Gyanendra Singh, Synthesis and uses of Ni(II) complex with Schiff base [benzene-1,2-diyldimethylylidene]dicarbamic acid, J. Adv. Electrochem. 2(3) (2016) 103–106.

till the red coloured solid was obtained. The solid product was then separated by vacuum filtration, washed with cold acetone solution and dried in vacuum desiccator at room temperature.

The bonding between free ligand and metal ion significantly affects the stretching frequencies, therefore the complexation of ligand with Ni(II) ion was investigated by analyzing the IR spectra of free ligand and complex compound (Fig. 1). The IR spectra shown in the figure 1 indicates that the C=N stretching frequency change from 1620 – 1640 cm^{-1} in the free ligands to lower values of 1600 - 1605 cm^{-1} in the Ni(II) complexes, which indicates that azomethine nitrogen is coordinated with the metal ion in the complex. The COO^- stretching frequency also decreases from 1557 – 1565 cm^{-1} to 1550 – 1560 cm^{-1} due to the coordination of oxygen with metal ion. The IR spectral analysis of free ligand and Ni(II) complex is summarized in Table 1.

Table 1 IR spectral data of free lined and Ni(II) complex of ligand

Bond	Free ligand	Ni(II) complex
C-H	3150 - 3155	3150 - 3153
C=N	1620 - 1640	1600 - 1605
C=O	1720 - 1725	1557 - 1565
COO^-	1557 - 1565	1550 - 1560
C=C	1685 - 1700	1685 - 1695
C-N	1760 -1765	1758 - 1763

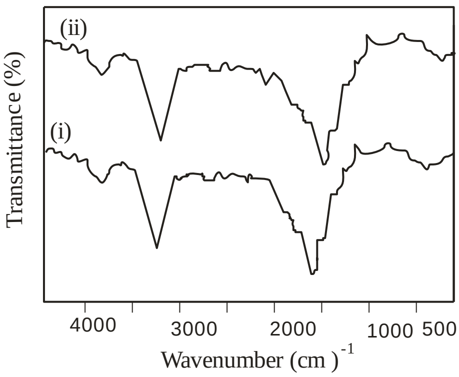


Fig. 1 IR spectra (i) Free ligand (ii) Ni-complex of ligand

Furthermore, in order to obtain more information about the complexation between ligand and metal ion, the electronic absorption spectra of the Schiff base ligand (5.0×10^{-5} M concentration) in the presence of increasing concentration of Ni(II) ion in acetonitrile solution at room temperature was recorded (Fig. 2). The Fig. 2 indicates that a strong absorption band of ligand at 220 nm decreases with increasing the concentration of Ni(II) ion and a new broad band appears at >250 nm. The resulting absorption at 220 nm and its complex with Ni(II) ion at 280 nm indicates the complexation equilibrium of ligand with metal ion in solution.

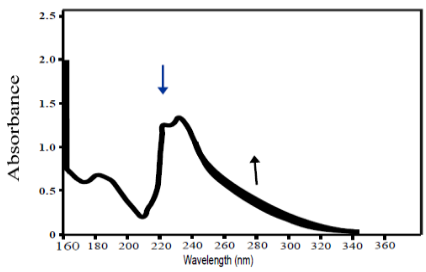


Fig. 2 UV absorption spectra of complexation reaction of ligand and Ni(II) ion

2.4 Calculation of Formation Constant

The stability of the complex compound of newly synthesized Schiff base ligand with different metal ions was investigated in terms of formation constant (K_f). The K_f values were calculated by molar conductance ratio using Eq. (1) and (2). All the measurements were performed at constant ionic strength of solution [9].

$$K_f = \frac{[ML^+]}{[M^+][L]} \times \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \quad (1)$$

$$[L] = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{ML})} \quad (2)$$

Here, Λ_M, Λ_{ML}, and Λ_{obs} are the molar conductance of the cation before addition of ligand; complex and solution during titration, C_L and C_M are the analytical concentration of the ionophore added, and the analytical concentration of the cation respectively. The solutions of various metal ions were prepared by dilution the standard solution. The complex formation constants, K_f, and the molar conductance of complex, Λ_{obs}, were obtained by using a nonlinear least squares program KINFIT [10, 11], and the results are summarized in Table 2. The data presented in Table 2 indicates that the formation constant of Schiff base ligand [benzene-1,2-diyldimethylylidene]dicarbamic acid (L) with Ni(II) ion is highest. Thus the ligand forms most stable complex with Ni(II) ions as compared to other tested metal ions.

Table 2 Formation complex values of complexation reaction of ligand and metal ions

Metal ions	Formation constants ($\log K_f$)	Metal ions	Formation constants ($\log K_f$)
Ni(II)	4.36 ± 0.10	Cd(II)	2.87 ± 0.10
Mn(II)	3.21 ± 0.12	Ag(I)	2.63 ± 0.11
Pd(II)	3.12 ± 0.10	Au(I)	2.60 ± 0.14
Co(II)	3.10 ± 0.11	Ca(II)	2.42 ± 0.15
Zn(II)	3.24 ± 0.13	Na(I)	2.18± 0.15
Pt(II)	3.11 ± 0.13	Li(I)	2.36 ± 0.13

3. Results and Discussion

The newly synthesized Ni(II) complex of Schiff base lignad [benzene-1,2-diyldimethylylidene]dicarbamic acid has sufficient lipophilic groups which may bind the other ionic species in the solution. The Ni(II) complex of the ligand is insoluble in water and thus can be used as electroactive material for the selective determination of ionic species in various samples. Due to these characteristics the complex was used as electroactive material for the selective determination of hydrogen phosphate (HSO_4^{2-}) ion in various samples.

To prepare membrane electrode the membrane components i.e. high molecular weight PVC, plasticizer (DMP, DBP, DOP, TEP and BEHS), anionic additive and Ionophore (Schiff base complex) were dissolved in 20 mL THF and shaken to remove the air. The solution so obtained was transfer into a glass ring of ~20 mm diameter. The THF was allowed to evaporate for about 24 hrs. The membrane of about ~0.3 mm of thickness and 5 mm of diameter were removed from glass plate and fixed at one end of a glass tube [12]. A saturated silver electrode than inserted in the tube to make electrical contact, another standard silver electrode was used as external reference electrode. The potential measurements were calculated by following cell assembly.

External Saturated Silver Electrode	Internal Solution (0.01 M)	Selective membrane	Test solution	Internal Saturated Silver Electrode

The membrane components were optimized my investigating the potential response of membranes of varying composition towards hydrogen phosphate ion. It was observed that the membrane with the composition of PVC: plasticizer (OA, CN, and DBP): additive: ionophore in the ratio of 32 %: 65 %: 1 %: 2 % (w/w) was found to be best in terms of response mechanism towards target anion (Table 3).

The use of plasticizers as membrane components significantly influenced response mechanism of the PVC based ion selective electrode because they provides the suitable medium for the complexation kinetics of ligand and ion. So different plasticizers were tested (with varying composition) to obtain the best possible response characters of the electrode assembly. The data presented in Table 3 indicates that the electrode based on BEHS as plasticizer has a wide concentration range of 1.2×10^{-6} – 1.0×10^{-2} M, with a lower detection limit of 1.0×10^{-6} M and has a slope of -30.0 ± 1.0 mV/decay of activity. The lower detection limit of all electrodes (no. 1-5) is in good agreement with the dielectric constants of the plasticizers. The best results were obtained with BEHS as plasticizer probably due to the low polarity of BEHS which provides the best environment of the complexation of low charge density anion (hydrogen phosphate ion) and ionophore. The lower detection limit decreases with decreasing the dielectric constant of the plasticizer. The potential response of the electrode with different plasticizers is shown in Fig. 3.

Table 3 Optimization of membrane components

Electrode No.	Membrane Composition (%)				Linear working Range (M)[a]	Slope (mV/dec. of activity)[a]	Response Time (sec)
	PVC	Additive	Plasticizer	Iono-phore			
1	32	1, NaTPB	65, BEHS	2	1.2×10^{-6}- 1×10^{-2}	-30.00 ± 1	5
2	32	1, NaTPB	65, TEP	2	4.6×10^{-6}- 1×10^{-2}	-28.20 ± 1	5
3	32	1, NaTPB	65, DOP	2	2.5×10^{-5}- 1×10^{-2}	-28.60 ± 1	8
4	32	1, NaTPB	65, DBP	2	2.5×10^{-5}- 1×10^{-2}	-25.40 ± 1	12
5	32	1, NaTPB	65, DMP	2	1.8×10^{-5}- 1×10^{-2}	-23.30 ± 1	14

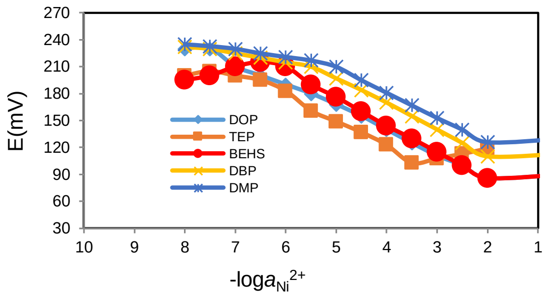


Fig. 3 Calibration curve of fluoride selective electrode with different plasticizers

The pH of the test solution may affect the potential response of the membrane electrode due to competition kinetics of H^+ with ionophore during the complexation reaction. Thus the effect of pH on potential response was calculated in the range of 1.0 – 8.0. It was observed that the potential of the electrode remains almost constant within the pH range of 3.0 – 6.0. However a significant change in potential was observed beyond this pH which may be due to the interference caused by H^+ and OH^- ion. Thus the electrode can be used for the determination of hydrogen phosphate ion with in a pH range of 3.0 – 6.0.

The average time in which the electrode reached the equilibrium value potential is called response time of the electrode assembly. In the present study the response time was calculated by changing the concentration of the test solution from lower concentration (10^{-6} M) to higher concentration (10^{-2} M). The average response time for whole concentration range was about 8 seconds. To evaluate the reversibility of the electrode the response time was also calculated by changing the concentration for higher (10^{-2} M) to lower concentration (10^{-6}) again the response time remains almost same. However the response time for higher concentration is slightly more than that of lower concentration.

The sensitivity of the electrode is dependent on composition of membrane components. A significant change in the detection limit, working concentration range and slope was observed after 2 months of the electrode because the components get leached out from the membrane with time. Thus the membrane can be used for a period of 2 months without significant change in potential response (Table 4).

Table 4 Life time of electrode no. 1

Time (weeks)	Detection limit (M)	Slope (mV/decay)
1	1.0×10^{-6}	-30.0 ± 1
3	1.0×10^{-6}	-30.0 ± 1
5	1.3×10^{-6}	-29.40 ± 1
7	1.5×10^{-6}	-29.00 ± 1
8	2.0×10^{-6}	-28.30 ± 1
9	4.6×10^{-5}	-23.50 ± 1
10	2.3×10^{-4}	-20.30 ± 1

The selectivity of the electrode no. 1 based on newly synthesized Schiff base complex of Ni(II) towards target ion in presence of other interfering ions was investigated in terms of selectivity coefficient, which was calculated as per IUPAC recommendations by match potential method (MPM). According to match potential method the potential of the electrode was measured with a fixed activity of primary ion (target ion A). In another experiment, an interfering ion (B) is successively added to an identical reference solution (containing primary ion), until the measured potential matches the one obtained with the primary ions. The selectivity coefficient, K^{MPM}, is then calculated by the resulting primary ion activity to the interfering ion activity ratio, $K^{MPM} = a_A/a_B$. The selectivity coefficients for various anions are summarized in Table 5 [13].

Table 5 Selectivity coefficients of various interfering ions (A^-)

Interfering ion B	Selectivity coefficient ($K^{MPM}_{Ho,B}$)
F-	1.8×10^{-4}
Cl-	2.3×10^{-4}
Br-	2.5×10^{-4}
I^-	3.2×10^{-4}
CN^-	1.6×10^{-4}
$C_2O_4^{2-}$	2.4×10^{-4}
S^{2-}	1.2×10^{-4}
CO_3^{2-}	1.4×10^{-4}
SCN^-	1.6×10^{-4}
CH_3COO^-	3.4×10^{-4}
$H_2PO_4^-$	5.6×10^{-4}

3.1 Analytical Application

The proposed Schiff based PVC membrane monohydrogen phosphate electrode was successfully applied for monitoring of monohydrogen phosphate ion concentration in waste water samples. 5 mL of waste water sample was dissolved in the double distilled water in a 100 mL flask. 2 mL of this solution 0.5 mL 0.01 M EDTA solution was added and diluted with water up to 100 mL. The concentration of target ion was measured by the monohydrogen phosphate electrode no. 1, using the calibration method. The obtained values were compared with those obtained by spectrophotometry method and the date summarized in Table 6.

Table 6 Monohydrogen Phosphate Concentration in Water Samples

Water samples	Mean concentration (mg/L)	Spectrophotometry (mg/L)
Tap water	0.05 ± 0.05	0.05 ± 0.10
River water	0.15 ± 0.10	0.16 ± 0.12
Industrial waste water	0.68 ± 0.12	0.70 ± 0.05

The electrode was also used as an indicator electrode for the titration of monohydrogen phosphate with standard Ba^{2+} ion. A 50 mL solution of 0.1 M Na_2HPO_4 was titrated with 0.1 M $Ba(NO_3)_2$ solution. The resultant curve has sharp inflation point which indicates the end point of the reaction (Fig. 4).

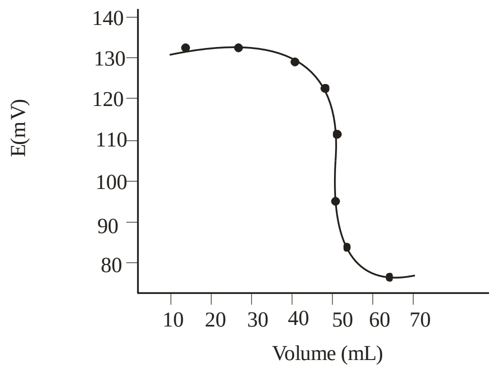


Fig. 4 Titration curve of Na_2HPO_4 with Ba^{2+} ion

4. Conclusion

A Nickel (II) complex of Schiff base ligand [benzene-1,2-diyldimethylylidene]dicarbamic acid was synthesized and used for the selective determination of monohydrogen phosphate in various water samples. The structure of the complex and free electrode was evaluated by IR and UV absorption spectroscopy. The selectivity coefficient was calculated by MPM method. The electrode with the composition of PVC: BEHS: NaTPB: ionophore in the ratio of 32%: 65%: 1%: 2% (w/w) has a wide concentration range of 1.2×10^{-6} – 1.0×10^{-2} M with lower detection limit of 1.0×10^{-6} M. The electrode no. 1 could be uses in a pH range of 3.0 – 6.0 for a period of 2 months without any change in response characters.

References

[1] S.M. Wilkinson, T.M. Sheedy, E.J. New, Synthesis and characterization of metal complexes with schiff base ligands, J. Chem. Educ. 93 (2016) 351-354.

[2] F. Shabani, L.A. Sagatforoush, S. Ghammamy, Synthesis characterization and anti-tumor activity of iron(III) Schiff base complexes with unsymmetrical tetradentate ligands, Bull. Chem. Soc. Ethiop. 24 (2010) 193-199.

[3] L. Sacconi, P. Nannelli, U. Campigli, Complexes of nickel(ii) with schiff bases formed from salicylaldehydes and n-substituted ethylenediamines, Inorg. Chem. 4 (1965) 818-822.

[4] G.M. Mockler, G.W. Chaffey, E. Sinn, H. Wong, Nickel(II) complexes of some quadridentate schiff base ligands, Inorg. Chem. 11 (1972) 1308-1314.

[5] P. Devi, R.K. Hemakumar Singh, Complex of Nickel(II) with schiff bases derived from condensation of salicylialdehyde and bis-ni(amuh)$_2$Cl$_2$, Rasayan J. Chem. 3 (2010) 2 266-270.

[6] P. Norouzi, M.R. Ganjali, F. Faridbod, S.J. Shahtaheri, H.A. Zamani, Electrochemical anion sensor for monohydrogen phosphate based on nano-composite carbon paste, Int. J. Electrochem. Sci. 7 (2012) 2633-2642.

[7] D.P. Zollinger, E. Bulten, A. Christenhusz, M. Bos, W.E.V. Derlinden, Computerized conductometric determination of stability constants of complexes of crown ethers with alkali metal salts and with neutral molecules in polar solvents, Anal. Chim. Acta. 198 (1987) 207-222.

[8] K. Mittal, A. Kumar, N. Gupta, S. Kaur, S. Kumar, Anal. Chim. 8-Hydroxyquinoline based neutral tripodal ionophore as a copper (II) selective electrode and the effect of remote substitutents on electrode properties, Anal. Chim. Acta 585 (2007) 161-170.

[9] P. Debye, E. Huckel, Theory of electrolytes, Phys. Z. 24 (1923) 185-206.

[10] E. Bakker, E. Pretsch, P. Buhlmann, Selectivity of potentiometric ion sensors, Anal. Chem. 72 (2000) 1127-1133.

[11] S. Singh, G. Rani, A Dynamic electrode for the estimation of praseodymium(III) using 1,5-bis-(o-aminophenol)- 3-thiapentane as an ionophore, Acta. Chim. Slov. 59 (2012) 169-176.

[12] Craggs, G.J. Moody, J.D.R. Thomas, PVC matrix membrane ion-selective electrodes, Construction and laboratory experiments, J. Chem. Educ. 51 (1974) 541-544.

[13] F.J. Saezde Viteri, D. Diamond, Determination and application of ion-selective electrode model parameters using flow injuction and sample optimization, Anal. 119 (1994) 749-758.

Cite this Article as: Manish Uppal, Gyanendra Singh, Synthesis and uses of Ni(II) complex with Schiff base [benzene-1,2-diyldimethylylidene]dicarbamic acid, J. Adv. Electrochem. 2(3) (2016) 103–106.