Full Paper

Selective Determination of Acetate Ion Using Nickel Complex of *N*,*N*'-biphenyl-2,2'-diylbis[1-(1*H*-pyrrol-2-yl) ethanimine] as an Ionophore

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Abstract- A new acetate selective poly (vinyl chloride) membrane sensor based on newly synthesized nickel complex of Schiff base, *N*,*N*'-benzene-1,2-diylbis[1-(1*H*-pyrrol-2-yl)ethanimine**]** as an ionophore was prepared. The electrode show Nernstian slope of 31.4 ± 1 mV/decade with improved linear range of 1.6×10^{-7} to 1.0×10^{-2} M, with a lower detection limit of 1.0×10^{-7} M between pH range of 3.0-9.5, giving a relatively fast response within (5s) and can be used for at least 2 months without any divergence in potential. The selectivity coefficient was calculated using matched potential method. The proposed electrode was successfully applied as an indicator electrode for the titration of arsenate ion with sodium thiocynide. It was also be used for the determination of arsenate ion in different water samples.

Keywords- Ion-selective electrode, Selectivity, Nickel, Schiff base, Acetate

1. INTRODUCTION

Ion-selective electrode is the analytical devise, based on the measurement of an electrode potential that is generated at the membrane solution interface [1]. The membrane electrodes based on neutral ionophores are the best analytical tools used for the selective determination of species in various biological and environmental samples, since they measure activity of ion

instead of concentration [2,3]. It is believed that the uses of metal complex as the ionophore in the potentiometric determination of anion based on the selective axial interaction of anion with the metal ion center in the complexes [4–10].

Acetate ion is a common ion involved in various biological reactions. It is manly utilized as acetyl coenzyme [11]. In clinical biochemistry, the determination of the acetate ion is important, especially in the areas of research involving kidney dialysis. Thus the selective determination of acetate ion is a subject of great importance. Various methods such, as spectrophotometry [12], chromatography [13] and enzymatic methods [14] etc., have been used for the determination of acetate ion, but these methods are, relatively expensive and time consuming. The ion-selective electrodes based on ionophore are particularly useful for such determinations because of simple preparation, fast response time, low cost and high selectivity [15-17]

In the present work a nickel complex of Schiff base *N,N'*-benzene-1,2-diylbis[1-(1*H*-pyrrol-2-yl)ethanimine] (Fig. 1) was synthesized and used as a potential carrier for the selective determination of acetate ion.

2. EXPERIMANTAL

2.1. Reagents

2-Acetylpyrrol and 1,2-diamino benzene were purchased from Aldrich Sigma and used as without further purification. High molecular weight poly (vinyl chloride) *i.e.* PVC-powder, dibutyl-butylphosphonate (DBBP), dibutylphthalate (DBP), *o*-nitrophenyl octyl ether (*o*-NPOE)), Oleic acid (OA), 1-chloronaphthalene (CN), sodium tetraphenylborate (NaTPB), tetrahydrofuran (THF), ethanol, chloroform, acetone were purchased from Fluka (Ronkonkoma, NY). All metal nitrates were also brought from Fisher Scientific (India), and the stock solution of metal nitrates was obtained by dissolving fixed amounts of corresponding salt in double distilled water. Double distilled water was used throughout the investigation

2.2. Synthesis of Ionophore

A solution of 1,2-diaminobenzene (0.20 mol, dried over $MgSO_4$) is dissolved in absolute ethanol (30 mL) was slowly added to a solution of 2-acetylpyrro in absolute ethanol (30 mL). After starring the reaction mixture for two hours at 40–50 °C, the ligand solid ligand was filtered off and the residue was extracted thoroughly 2-3 times (50 mL each) with absolute ethanol to remove the unreacted starting materials.
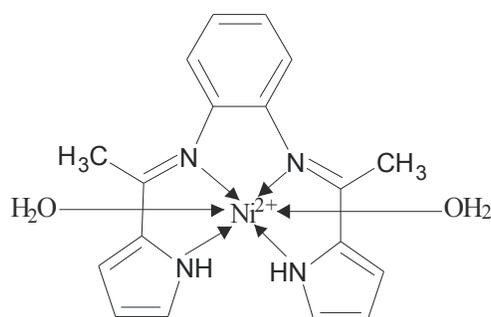
Fig. 1. Nickel complex of *N,N'*-benzene-1,2-diylbis[1-(1*H*-pyrrol-2-yl)ethanimine] (L)

The nickel complex of the ligand was synthesized by starring a solution of ligand (in 30 mL ethanol) with $NiSO_4.6H_2O$ (0.001 mol) at 80–84 °C for 6 hours. The ionophore was separated as a brown colored complex, which was filtered, washed with cold ethanol and dried over $MgSO_4$ (Fig. 1). The IR spectrum of free ligand shows the bands in the region 1610–1640 cm^{-1} indicates the presence of azomethine (C=N) group in ligand. On complex formation the position of these bands shifted towards lower side, which indicates that the coordination takes please through the nitrogen of azomethine (C=N) group. The band due to N-H stretching of pyrrole ring undergoes a shift on complexation suggesting the involvement of ring nitrogen in bonding. There is a broad band in the range 3400–3300 cm^{-1} which is due to (OH) indicating the presence of water of hydration or coordinated water. Thus it has been concluded that the ligand acts as tetradentate chelating agent.

2.3. Fabrication of electrode

The membranes of various compositions were prepared by dissolving membrane components, i.e., ionophore, plasticizers (o-NPOE, DBP, DBBP, OA and CN), anionic additive (NaTBP), and PVC in THF [18]. The resulting solution was poured into a glass mould and THF was allowed to evaporate off at room temperature over 24 h. A flexible membrane with a thickness of 0.4 mm was obtained. The discs of 6 mm diameter were cut and pasted onto a glass-tube.

All membrane electrode potential measurements were performed at constant temperature (25±1 °C). The representative electrochemical cell for the EMF measurements is as follows:

External Saturated Silver Electrode	Internal 0.01 M anionic solution	Acetate selective membrane	Test solution	Internal Saturated Silver Electrode

3. RESULTS AND DISCUSSION

The response mechanism of membrane electrode is highly dependents on nature and composition of membrane components. Therefore membranes of various compositions and plasticizers were prepared and their potential response was investigated (Table 1). The data presented in table indicates the membrane no. 1 with the composition of PVC: o-NPOE: ionophore: NaTBP of 32: 65: 2: 1 (w/w, %) has a detection limit of 1.0×10^{-7} M in a linear concentration range of $1.6 \times 10^{-7} - 1.0 \times 10^{-2}$ M.

The plasticizer as membrane components provides the high mobility of membrane components and provides the best possible environment for complexation reaction. Thus the properties of plasticizers may also affect the response mechanism of ion selective electrodes. Due to this reason the membrane of various plasticizers were prepared and their potential responses were investigated (Fig. 2). The membrane (no. 9) without plasticizer works in linear concentration range of $2.0 \times 10^{-5}-1.0 \times 10^{-2}$ M and has a detection limit of 1.0×10^{-5} M with slope of calibration curve 23.70 ± 1 mV/decay.

Table 1. 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	Ionophore			
1	32	1, NaTPB	65, o-NPOE	2	$1.6 \times 10^{-7}. 1 \times 10^{-2}$	-31.40 ± 1	5
2	32	1, NaTPB	65, DBP	2	$2.4 \times 10^{-6}. 1 \times 10^{-2}$	-26.80 ± 1	12
3	32	1, NaTPB	65, DBBP	2	$1.8 \times 10^{-6}. 1 \times 10^{-2}$	-25.40 ± 1	16
4	32	1, NaTPB	65, OA	2	$4.2 \times 10^{-6}. 1 \times 10^{-2}$	-24.60 ± 1	20
5	32	1, NaTPB	65, CN	2	$5.0 \times 10^{-6}. 1 \times 10^{-2}$	-24.70 ± 1	21
6	30	1, NaTPB	66, o-NPOE	3	$1.7 \times 10^{-7}. 1 \times 10^{-2}$	-31.35 ± 1	5
7	30	1, NaTPB	65, o-NPOE	4	$2.4 \times 10^{-7}. 1 \times 10^{-2}$	-31.30 ± 1	5
8	35	1, NaTPB	60, o-NPOE	2	$8.4 \times 10^{-7}. 1 \times 10^{-2}$	-26.40 ± 1	8
9	60	10, NaTPB	0.00	30	$2.0 \times 10^{-5}. 1 \times 10^{-2}$	-23.70 ± 1	32

The data presented in Table 1 and Fig. 2 indicates that the membrane with o-NPOE as plasticizers gives the best possible responses, linear concentration range ($1.8 \times 10^{-7}-10^{-2}$ M), detection limit (1.0×10^{-7}), slope of calibration curve (-31.40 ± 1 mV/decay) and fast response time of about 5s. It was observed that the decreasing the concentration of o-NPOE (below 65–66%) for constant concentration of ionophore and NaTPB significantly effects the response mechanism of electrode assembly. It was also observed that more than 2%

concentration of ionophore (electrode no. 6 and 7) does not have much effect of linear concentration range, detection limit, slope and response time. The anionic additive as membrane component may interfeare in the complexation kinetic of ionophore and target ion, thus the concentration of NaTPB should be carefully controlled. In the present study it was observed that 1% of NaTPB relative to other components is sufficient for best possible response.
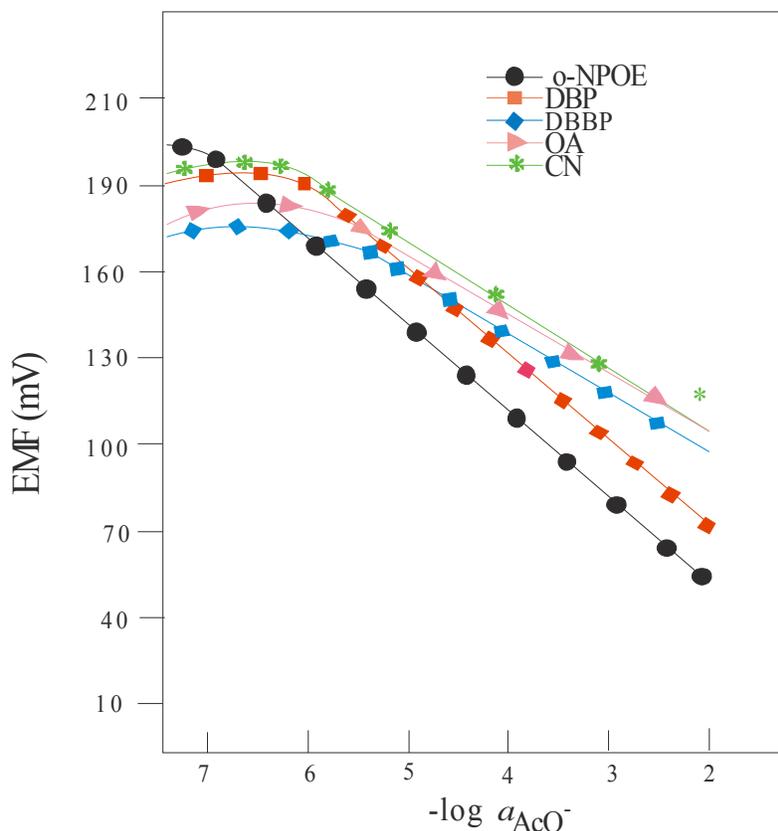
Fig. 2. Effect of plasticizer on potential for electrode no. 1

The pH response for the electrode no.1 was also examined using 0.01 M and 0.001 M solution of acetate ion. The pH of the solution was adjusted with 0.1 M HNO_3 and 0.1 M NaOH solutions. The potential response of electrode remains independent in the pH range of 3.0–9.5 (Fig. 3). Beyond this pH range, potential drift were observed on both side which may be interference caused by H^+ and OH^- at lower pH and at higher pH respectively. The electrode response was also investigated in partially non-aqueous medium using methanol-water, ethanol-water and acetone-water mixtures. The membrane electrode (no.1) worked well up to 30% non-aqueous contents without any significance change in potential response (Table 2).
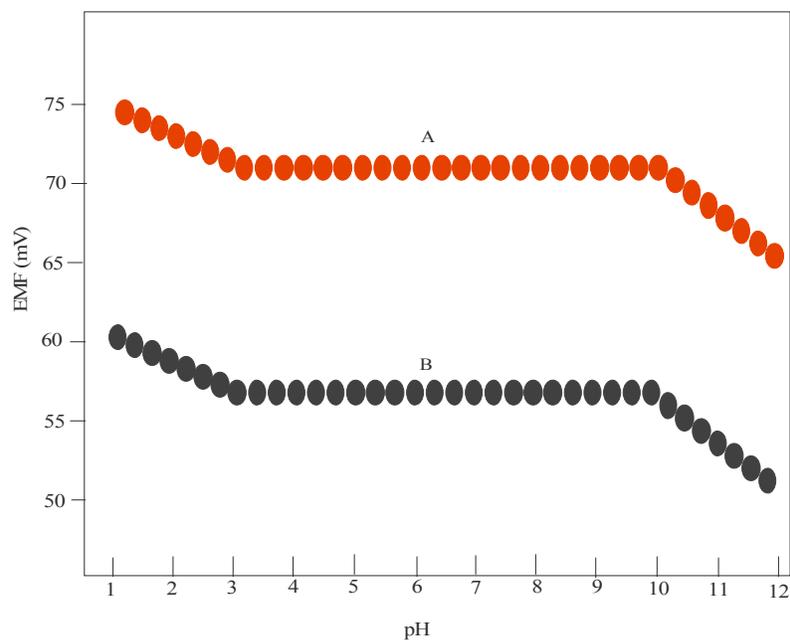
Fig. 3. Effect of pH of on, A 0.01 M solution and B 0.0001 M solution of acetate ion

Table. 2. Effect of partially non-aqueous medium on the working of electrode no. 1

Non-aqueous content (%v/v)	Slope (mV /decade) of activity	Detection limit (M)	Response time (seconds)
0	-31.40±1	1.0×10^{-7}	5
Methanol - Water			
10	-31.40±1	1.0×10^{-7}	5
20	-31.20±1	1.0×10^{-7}	5
30	-31.00±1	1.2×10^{-7}	5
40	-25.90±1	1.0×10^{-6}	8
Ethanol - Water			
10	-31.40±1	1.0×10^{-7}	5
20	-31.30±1	1.0×10^{-7}	5
30	-31.40±1	1.2×10^{-7}	5
40	-25.70±1	1.0×10^{-6}	8
Acetone - Water			
10	-31.40±1	1.0×10^{-7}	5
20	-31.40±1	1.0×10^{-7}	5
30	-31.30±1	1.2×10^{-7}	6
40	-24.80±1	1.0×10^{-6}	7

The average time required for the acetate selective membrane electrode to reach a potential within ±1 mV of final equilibrium value after successive immersion of a series of acetate ion solutions, each having a 10-fold difference in concentration was measured [19]. The average static response time of the PVC-membrane thus obtained was about 5 s over the entire linear concentration range. The proposed electrode no.1 was could be used over a period of at least 2 months without any significant change in its response characteristics.

The selectivity of membrane electrode towards primary ion over other tested cations was investigated by the matched potential method (MPM) [20,21]. According to the MPM, the selectivity coefficient is defined as the activity ratio of the primary ion (A) and the interfering ion (B) that gives the same potential change in a reference solution. The selectivity coefficient, $K_{A,B}^{pot}$, is determined as expression $K_{A,B}^{pot} = \dfrac{\Delta A}{a_B}$ 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, a_B is the activity of interfering ion. The concentration of primary ion was kept constant (0.001 M). The resulting values thus obtained for the proposed electrode are summarized in Table 3.

Table 3. Selective coefficient of various interfering anions for the best membrane sensors

Interfering ion	Selectivity coefficient ($K_{A,B}^{pot}$)			
	Membrane number			
	1	6	7	8
CNO^-	9.1×10^{-4}	8.01×10^{-4}	7.37×10^{-4}	6.41×10^{-4}
Br^-	4.45×10^{-4}	5.08×10^{-4}	4.73×10^{-4}	6.42×10^{-4}
$C_2O_4^{2-}$	3.51×10^{-4}	4.00×10^{-4}	3.72×10^{-4}	5.05×10^{-4}
NC^-	2.81×10^{-4}	3.20×10^{-4}	2.98×10^{-4}	4.05×10^{-4}
NO_2^-	2.21×10^{-4}	2.52×10^{-4}	2.34×10^{-4}	3.18×10^{-4}
NO_3^-	1.41×10^{-4}	1.61×10^{-4}	1.49×10^{-4}	2.03×10^{-4}
CN^-	1.12×10^{-4}	1.28×10^{-4}	1.19×10^{-4}	1.61×10^{-4}
Cl^-	3.16×10^{-4}	3.60×10^{-5}	3.35×10^{-5}	4.55×10^{-4}

3.1. Analytical Application

The proposed membrane acetate electrode was successfully applied as an indicator electrode in potentiometric titration of 20 mL of 0.01 M acetate ion solution with 0.01 M Ag^+ ion (Fig. 4). The electrode was also used for the determination of acetate anion concentration in vinegar sample and food preservative samples (Table 3). The values obtained by proposed electrode were quite comparable with labeled concentration of acetate ion in tested samples.

The response characters of the electrode were also compared with the previously reported electrodes (Table 4).
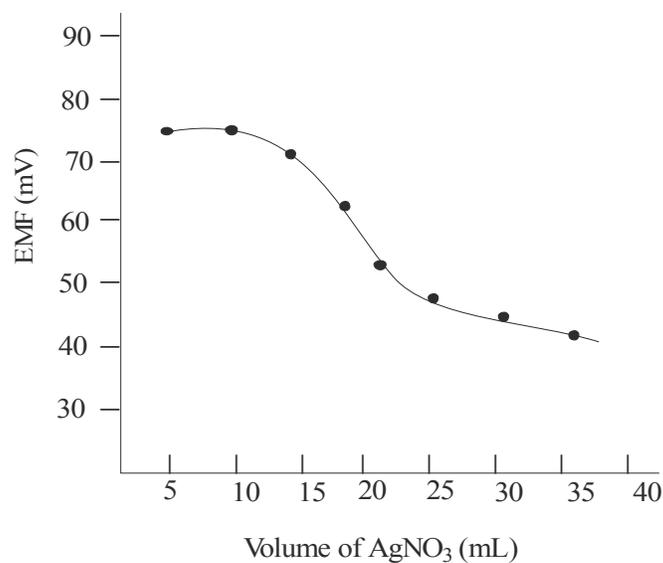
Fig. 4. Potentiometric titration curve of 0.01 M $AgNO_3$ solution with a 0.01 M acetate ion solution, using the proposed sensor as an indicator electrode

Table 3. Determination of acetate ion (g/100 mL) in different samples

Sample	Proposed Sensor	Labeled
Vinegar	5.90	5.00
Food preservative	1.98	2.00

Table 4. Comparison study of proposed electrode

Concentration range (M)	Detection limit (M)	pH range	Response time (s)	Reference
$5.0\times10^{-6} - 1.0\times10^{-1}$	1.2×10^{-6}	6.5 – 7.5	<15	[21]
$6.0\times10^{-5} - 1.0\times10^{-2}$	4.0×10^{-6}		10	[22]
$1.6\times10^{-7} - 1.0\times10^{-2}$	1.0×10^{-7}	3.0 – 9.5	5	This work

4. CONCLUSION

A nickel complex of newly synthesized Schiff base, *N,N*'-benzene-1,2-diylbis[1-(1*H*-pyrrol-2-yl)ethanimine] was synthesized and used as ionophore for the construction of acetate selective poly vinyl chloride membrane electrode. The proposed electrode works satisfactorily in linear concentration range of 1.6×10^{-7}-1×10^{-2} M with detection limit of 1.0×10^{-7} M, static response time (5 s) with a Nernstian slope of -31.4 mV/dec. of activity between pH range 3.0-9.5, and can be used for a period of 2 months without any change in response characteristics. The proposed membrane electrode was successfully applied as an indicator electrode for the titration of acetate ion (0.01 M) with a standard silver nitrate solution (0.01 M).

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