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A Dynamic Electrode for the Selective Determination of Aluminum in Solution

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Abstract- 1,1'-[benzene-1,4-diyldimethylylidene]bis(3-phenylurea)) was synthesized and tested for the fabrication of aluminum selective membrane electrode. The membrane electrode with dimethyl phthalate (DMP) as plasticizer works satisfactorily in the linear concentration range of 1.3×10^{-6} to 1.0×10^{-1} M with best optimized composition of DMP: PVC: ionophore: NaTPB of 60:35:3:2 (%, w/w). The membrane electrode has a fast response time (5 s) and wide pH range (2.5–8.5). The selectivity coefficients were calculated with fixed interference method. The membrane sensor was also used as an indicator electrode for the titration of Al(III) with EDTA and Na_3PO_4.

Keywords- Aluminum, Ion-selective electrode, Ionophore, Selectivity

1. INTRODUCTION

Aluminum is the most abundant metal the earth's crust. It is mainly found in combine states in different minerals. It is widely used in the manufacturing of automobiles, electrical equipment's, water purification, and building materials [1]. It does not have any biological role and considered as nonessential element for our biological process [2]. The water soluble form of aluminum can cause some harmful effect. The uptake of aluminum can take place through food, through breathing and by skin contact [3]. The toxicity can be traced to deposition in bone and central nerves system, which is particularly increased in patients with reduced renal function. The high concentration of aluminum can lead to serious health problems i.e. damage to the central nerves system, dementia, loss of memory, severe trembling. Finely divided aluminum and aluminum oxide powder has been reported as a cause of pulmonary fibrosis and lung damage (Shaver's Disease) [4,5]. Due to high commercial value and health effect the determination of aluminum is solution is an important area of research.

The development of ion selective electrode based on neutral carrier becomes a major research area in the field of analytical chemistry and supramolecular chemistry as reflected by the reports published during past years [6–15]. Due to less binding ability as compared to transition elements and interference caused by some ions like Cu(II), Cd(II), Pb(II), Cr(III) and Hg(II), the determination of aluminum by ion-selective electrode is always a challenging work. The main aim this work is the synthesis of Al(III) selective ionophore and fabrication of membrane electrode for the selective determination of Al(III) in solution.

2. EXPERIMENTAL

The phenyl urea and benzene-1,4-dicarbaldehyde was brought from Sigma Aldrich (Bangalore, India). High molecular weight Poly(Vinyl Chloride) (PVC), Dimethyl phthalate (DMP), Dioctyl phthalate (DOP), Tris(ethyhexyl) phosphate (TEP), bis-(2-ethylhexylsebacate BEHS, sodium tetraphenyl borate (NaTPB) and tetrahydrofuran (THF) were purchased from Merck. All metal nitrates were also purchased from Merck. Doubled-distilled water was used to prepare the metal nitrate solutions. Saturated silver electrodes (SSE) were used as reference electrodes the potential measurements were carried out using Corning ion analyser 250 pH/mV meter (USA) at room temperature .

The ionophore 1,1'-[benzene-1,4-diyldimethylylidene]bis(3-phenylurea) was prepared by starring a solution of phenylurea (1.20 mmol in 10 mL THF) and benzene-1,4-dicarbaldehyde (1.25 mmol in 10 mL THF) at room temperature for 8 hrs. The ionophore was obtained as white crystals, which was separated and washed with ethanol and water. The physical analysis of compound is as follows:

Molecular formula: $C_20H_{18}N_4O_2$

Molecular mass: 370.40

Yield: 79%

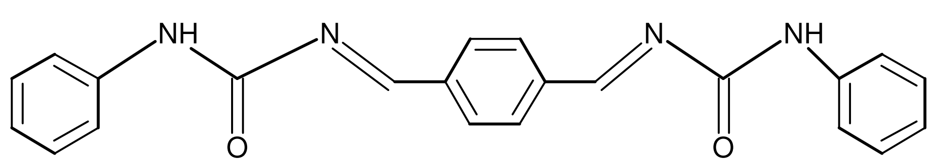

Fig. 1. 1,1'-[benzene-1,4-diyldimethylylidene]bis(3-phenylurea)

^{1}H-NMR ($CDCl_3$, ppm): 7.83 (t, 2H, aromatic), 7.72 (t, 2H aromatic), 7.60 (t, 2H, aromatic), 7.53 (d, 2H, aromatic), 7.45 (d, 2H, aromatic), 6.72 (d, 2H, aromatic), 6.70 (d, 2H, aromatic), 6.62 (s, H, NH), 6.58 (s, H, NH), 3.24 (S, H, CH), 3.20 (s, H, CH).

The membranes of various compositions and plasticizers were fabricated by the methodavailable in the literature[16]. The PVC-based membranes have been fabricated by dissolving a mixture of PVC, plasticizer (DOP, TEP, BEHS, and DOS), NaTPB and ionophore in THF (15 mL). The components were added in terms of weight percentage. The resulting solution was stirred well and poured in a glass casting ring on a smooth tile. The solvent was allowed to evaporate at room temperature for 24 h in order to obtain the uniform membrane. A membrane sheet about 0.3 mm of thickness and 5 mm diameter was cut away from inner edge and glued it to one end of a glass tube with the help of araldite to avoid leakage.

The Emf measurements were carried out with the cell assembly given below:

Internal reference Silver electrode, KCl (saturated)	Internal reference solution (0.01 M Al^{3+})	Al^{3+} ion Selective Membrane	Test solution of Al^{3+} ion	External reference Silver electrode, KCl (saturated)

3. RESULTS AND DISCUSSION

The researches based on membrane carrier have grown exponentially in last decay, because an ISE measure the activity of ion in solution [17]. These properties of ISEs make them good candidature to be used for elemental analysis particularly in medicinal, food, and pharmaceutical industries. The present study include the use of 1,3-[Bis(3-phenylthioureidomethyl)]benzene as ionophore for the constriction of Al(III) selective membrane sensor.

The composition of membrane ingredients of ion selective electrode significantly influenced the response characters of electrode. In present study the membranes of various compositions were prepared by using various plasticizers (i.e. DMP, DOP, TEP and BEHS), anionic additive (NaTPB), ionohpore (1,3-[Bis(3-phenylthioureidomethyl)]benzene) and PVC as binder material. After several experiments it was found that the membrane with DMP as plasticizer has best possible characters. To find out the best possible composition the membrane of various amount of DMP was prepared and their response characters were investigated (Table 1). The data presented in table 1 clearly indicates that the membrane with composition of PVC: DMP: NaTPB: ionophore of 35: 60: 2: 3 (%,w/w) respectively has wide linear concentration range 1.3×10^{-6}–1.0×10^{-1} M, detection limit (1.0×10^{-6} M), and fast response time (5 s). It was observed that the amount of ionophore more than 3% (electrode no. 5, 6 and 7) does not improved the response characters of the electrode assembly. Thus 3% ionophore as membrane ingredient is sufficient of the selective determination of Al(III) in solution .

Plasticizers have a significant effect on the potential response of membrane electrodes. In the present study the effect of various plasticizers i.e. DMP, DOP, TEP and BEHS on the potential response of the membrane electrode was investigated. The data presented in Table 1 clearly indicates that the DMP (electrode no. 1) gives the best results. This could be due to the high polarity of DMP as compared to other plasticizers. The detection limit of electrode assembly was obtained from the intersection of two straight lines portions of calibration curve (Fig. 2). The change in EMF beyond 1.0×10^{-6} M is due to the release of Al(III) from inner electrolyte and transported across the membrane. The variation of potential at lower concentration may also be due to the interference of anions due to failure of Donnan exclusion phenomena. It was also observed that the detection limit of membrane sensors using different plasticizers decreases as the dielectric constant of plasticizers decrease.

Table 1. Optimization of membrane composition of erbium sensors

Electrode No.	**Membrane Composition (%, w/w)**				**Linear working range (M)[a]**	**Slope (mV/dec. of activity)[a]**	**Response Time (s)**
	PVC	**Additive**	**Plasticizer**	**Ionophore**			
1	35	2, NaTPB	60, DMP	3	1.3×10^{-6}-1×10^{-1}	20.0±0.3	10
2	34	2, NaTPB	61, DOP	3	3×10^{-5}- 1×10^{-1}	18.8±0.3	16
3	34	2, NaTPB	61, TEP	3	5×10^{-5}- 1×10^{-1}	17.4±0.3	20
4	34	2, NaTPB	61, BEHS	3	5×10^{-6}- 1×10^{-1}	17.2±0.3	16
5	34	2, NaTPB	60, DMP	4	1.3×10^{-6}- 1×10^{-1}	20.0±0.3	10
6	33	2, NaTPB	60, DMP	5	1.2×10^{-6}- 1×10^{-1}	20.1±0.3	10
7	32	2, NaTPB	60, DMP	6	1.3×10^{-6}-1×10^{-1}	20.0±0.3	10
8	34	3, NaTPB	60, DMP	3	1.4×10^{-5}- 1×10^{-1}	19.4±0.3	11

[a] Mean value±standard deviation (three measurements)

The use of anionic additive NaTPB in membrane electrode reduces the interference of anions and to decrease the electrical resistance of membrane electrode. The NaTPB itself an ion exchange, which compete with the ionophore in complexation reaction. Therefore the membranes of various amount of NaTPB were fabricated and their responses were investigated. It was observed that 2% NaTPB as membrane component is sufficient to give the best potential responses.

The response time was measured by recording the potential response of electrode as a function of time, when it is immersed in the solution of target ion. The electrode gets the stable potential in a very short time of about 5s. Thus this time was taken as the optimum response time of membrane electrode.

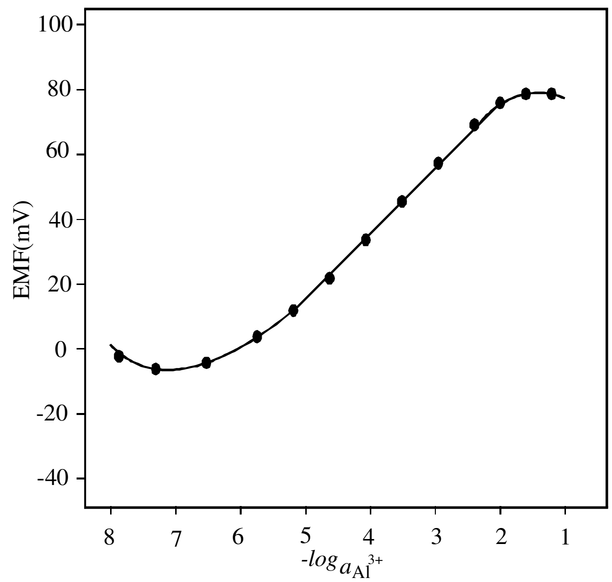

Fig. 2. Calibration curve of Al(III)-selective membrane electrode no. 1

Since the response mechanism of an ion-selective electrode involves the complexation and decomplexation kinetics between ions and ionophore, therefore no ion selective electrode could be design exclusively to a particular ion, although the ionophore could be more responsive a particular ion over other ions. Thus the selectivity of membrane electrode no. 1 towards Al(III) in presence of other ions was investigated in terms of selectivity coefficient $\left(K^{Pot}_{Al^{3+},M^{n+}}\right)$ and the data are presented in Table 2. The selectivity coefficient was calculated by Fixed interference method (FIM) as recommended by IUPAC at 1.0×10^{-3} M concentration of primary ion [18, 19].

$$K^{POT}_{Al^{3+},M^{n+}} = \frac{a_{Al^{3+}}}{a_{M^{n+}}^{z_{Al^{3+}}/z_{M^{n+}}}}$$

Where $a_{Al^{3+}}$ is the activity of the primary ion and $a_{M^{n+}}$ is the activity of interfering ion $z_{Al^{3+}}$ and $z_{M^{n+}}$ are their respective charges

Table 2. Calculation of selectivity coefficient by Fixed Interference Method

Interfering Ion	Selectivity Coefficient ($logK^{POT}_{Al^{3+}, M^{n+}}$)
	Fixed Interference Method
Fe^{3+}	2.3×10^{-4}
Cr^{3+}	3.8×10^{-4}
Tl^{+}	2.9×10^{-4}
Mn^{2+}	2.7×10^{-4}
Co^{2+}	2.6×10^{-4}
Zn^{2+}	3.6×10^{-4}
Ca^{2+}	4.0×10^{-4}
Cs^{+}	3.6×10^{-4}
Cu^{2+}	3.9×10^{-4}
K^{+}	2.9×10^{-4}
NH_4^{+}	3.2×10^{-4}
Li^{+}	4.0×10^{-4}
Na^{2+}	3.3×10^{-4}
Mg^{2+}	3.7×10^{-4}
Pb^{2+}	3.2×10^{-4}
Ce^{3+}	3.1×10^{-4}
Eu^{3+}	3.3×10^{-4}

The influence of concentration of internal solution on the potential response of Al(III)-selective membrane electrode was studded by changing the concentration of internal solution from 1.0×10^{-4} to 1.0×10^{-1} M. Experiments shows that 1.0×10^{-2} M concentration of internal solution is quite suitable for the smooth functioning of electrode assembly.

The influence of pH of the test solution on the potential response of electrode assembly was studded at different concentrations (1.0×10^{-2}, 1.0×10^{-3}, 1.0×10^{-4} M) in the pH range of 1.0–10.0. The pH was adjusted by adding 0.1M HNO_3 or hexamine–HCl buffer solution. The data presented in Fig. 3 indicates that the potential is constant within the pH range of 2.5–8.5. Therefore this range was taken as the optimum pH range of membrane electrode. However variation in potential below (pH<2.5) and above (pH>8.5) this range was observed. This is due to the interference of hydrogen ion in the charge transfer process at lower pH and formation of hydroxyl complex of aluminum at higher pH. The performance of proposed electrode was also compared with the reported electrodes (Table 3) [21–23].

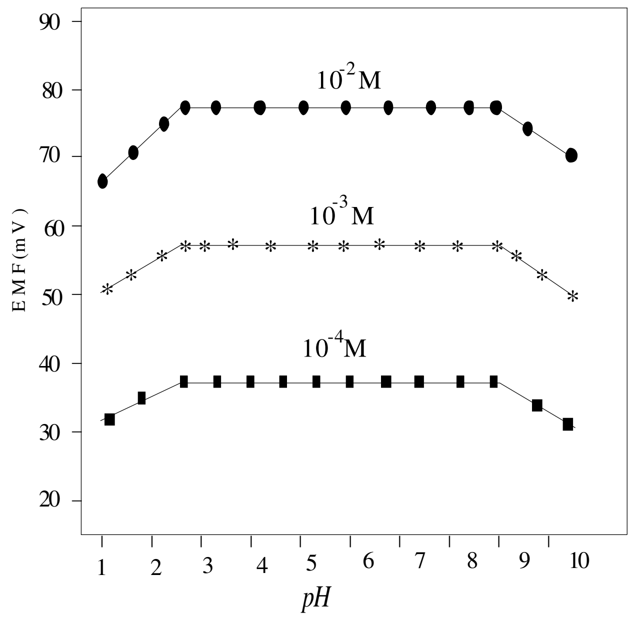

Fig. 3. Effect of pH on potential response of membrane electrode no. 1

Table 3. Performance comparison of proposed electrode with some reported electrodes

Concentration range (M)	**Response time (s)**	**Slope**	**Reference**
1.3×10^{-6} -1.0×10^{-1}	10	20.0±0.3	This work
1.0×10^{-6} -1.0×10^{-1}	10	19.6±0.4	20
5.0×10^{-6} -1.0×10^{-2}	10	19.3±0.8	21
1.8×10^{-5} -1.0×10^{-1}	10	20.1	22
9.0×10^{-6} -1.0×10^{-1}	-	20.0±0.2	23

3.1. Analytical applications

The membrane electrode was successfully used as an indicator electrode for the titration of 30 mL, 1.0×10^{-2} M, Al(III) ion against 1.0×10^{-3} M, EDTA and 1.0×10^{-2} M, $Na_3(PO_4)$ solution. Both the curves have sharp inflection point, which dictate the practical utility of membrane electrode (Fig. 4).

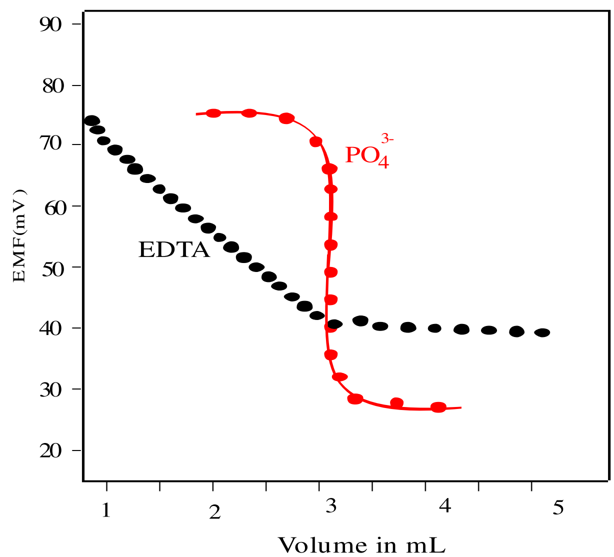

Fig. 4. Titration curve of Al(III) ion with EDTA and Na_3PO_4

4. CONCLUSION

A newly synthesized neutral ionophore 1,1'-[benzene-1,4-diyldimethylylidene]bis(3-phenylurea)) was used as electroactive material for the selective determination of Al(III). The membrane electrode with the composition of DMP: PVC: ionophore: NaTPB of 60:35:3:2 (%, w/w) works satisfactorily in the linear concentration range of 1.3×10^{-6} to 1.0×10^{-1} M. The membrane electrode has a fast response time (5 s) and wide pH range (2.5–8.5). The selectivity coefficients were calculated with fixed interference method. The membrane sensor was also used as an indicator electrode for the titration of Al(III) with EDTA and Na_3PO_4.

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