

ORIGINAL RESEARCH ARTICLE

Study On Poly (Vinyl Chloride) Based Sensor For Anion Recognition Using 1, 12- diaaza-5,8-dioxo-3[4],9[10]-dibenzoylcyclotetradeca-2,11-diene L₁[DADODBCT]Schiff Based Macrocylic Receptor**Amit Nagar, Sushil Kumar Sindhu , Rahul Kumar Panwar***Department of Chemistry, SSV Post Graduate College Hapur, Ghaziabad (U.P), India*

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ABSTRACT

The chemical diversity of macrocyclic/complexes is immense and provides an invaluable source of inspiration for innovative drug design or analytical extraction reagent. Macrocyclic compounds/complexes generally exhibit semi-rigid backbone conformations, which place appended substituents in well-defined positions in space. Certain ring sizes are preferred. Potentiometric ion selective electrodes or membrane electrodes are available in the field of chemical analysis because lots of specific ions are able to be measured easily and monitored, However, there are relatively few references to anion-selective electrodes compared with the large number of studies dealing with anion-selective electrodes. The use of salens and their metal-complexes as carrier in ion-selective has been little known. The coordination chemistry of transition metal ions reveals that the ion has a remarkable preference for the formation of square planar amine complex.

Key words: Ion Selective Electrodes, analytical extraction reagent.**INTRODUCTION**

The determination of the concentrations of ionic species in aqueous samples is important in many areas of applied analytical chemistry. For sensing of charged species potentiometric sensors offer several advantages. The sensors have generally a large dynamic range because the signal is proportional to the logarithm of the ion activity. Short response time in the order of seconds make the devices very suitable for process control and allow a high sample through-put in, for example flow injection analysis. Moreover, the potentiometric sensor can have very small dimensions, and consequently only small sample volumes are required^[1]. Anion complexation and the design of anion receptors is far less developed than the field of cation receptors^[2]. This is reflected in the large arrears in the development of potentiometric anion sensing. The first publication on cation and anion receptors appeared almost at the same time: in 1967 Pedersen^[3], reported the complexation of alkali metal cations by crown ether, and in 1968 the first synthetic receptor for inorganic anions was reported by Park and Simmons^[4]. However, the field of cation recognition developed much more rapidly and there are now many neutral host molecules for

cations^[5]. The slow development of anion recognition can be related to some inherent differences between anions and cations^[6].

MATERIALS AND METHODS

Ethylenediamine, diethylenetriamine, 1, 2-dibromoethane, 2,6-diaminopyridine, salicylaldehyde, ethylamine, urea succinic acid and benzidine were obtained from Sigma- Aldrich and were of AR grade. Metal salts (E. Merck), other different chemicals (Fluka and Thomas Baker), and solvents (S.D Fine) were commercial products and were used as received. All the other chemicals and plasticizers used in the present investigation were of AR grade purchased from Sigma Chemical Co, USA. Elemental analysis (CHN) of these complexes was carried out on a Carlo-Erba 1106 Elemental Analyzer. Molar conductance was measured on an ELICO conductivity bridge (type CM82T). Magnetic susceptibility measurements were performed on a Gouy Balance at room temperature using CuSO₄ · 5H₂O as calibrant. Infrared spectra were recorded on a Perkin Elmer 137 instrument as KBr pellets. Electronic spectra were recorded in DMSO solution on a Shimadzu UV mini- 1240 spectrophotometer. EPR spectra of

the Metal complexes were recorded as powder samples at room temperature on an E-4 EPR spectrometer using DPPH as the g-marker.

Synthesis of 1, 12- diaaza-5,8-dioxo-3[4],9[10]-dibenzoylcyclotetradeca-2,11-diene L₁[DADODBCT]

The macrocyclic compound 1, 12,-diaaza-5,8-dioxo-3[4],9[10]-dibenzoyl cyclotetradeca- 2,11-diene is prepared in two steps. A 250 ml three-necked round bottom flask was taken; the one neck of flask fitted with water condenser another with a mechanical stirrer. Add 20 mL ethanolic funnel through the third neck of the flask. The solution was heated upto 60⁰c followed by addition of 20mL ethanolic solution of 1,2-dibromoethane 2.15mL [0.5M]. After closing the stopper of the dropping funnel the reaction allowed to cool upto approx. 40⁰c and then a 20mL ethanolic of ethylenediamine 2.7ml [0.5M] was added with continuous stirring. Further the stirring. Then the reaction mixture was kept overnight for slow cooling. A yellow coloured compound was separated out which was filtered and washed with water. Finally very bright lemon yellow coloured compound was obtained [synthesis of macrocyclic compound L₁in (Fig 1)] Yield; 75%, melting point 75⁰c.

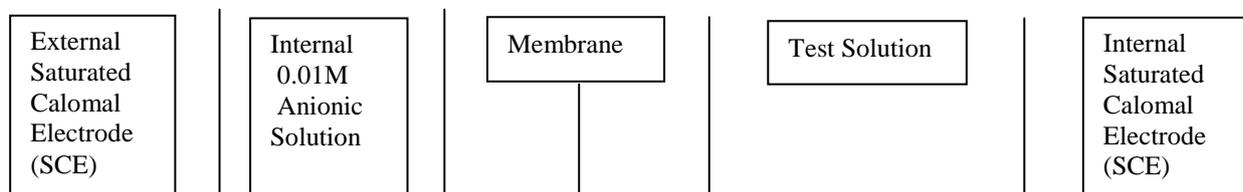
Electrode preparation (General) [7]:

The solution for PVC membrane was prepared by through mixing of the 33% PVC, 66% dibutylphthalate, 1% L₁ (ionophore) were mixed and dissolved in THF. 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 0.2-0.4 mm was obtained. The discs of 6 mm diameter were cut and pasted onto a glass-tube, which consisted of an Ag-AgCl wire immersed in an internal solution of 0.01 M anionic solution by immersion in the 0.01 M its respective anionic metal solution at least 2-3 days prior to use.

To obtain the better response and the sensitivity of the anionic electrodes, different plasticizers, additives, cationic excluders and amount of the PVC and ionophores, are used in the different proportions. The details of the compositions for various preparations of the anionic-selective electrodes are given in Results and Discussion section.

EMF measurements

Electrode potential measurements were performed at constant temperature (25 ± 0.5°C). The representative electrochemical cell for the EMF measurement is as follows:

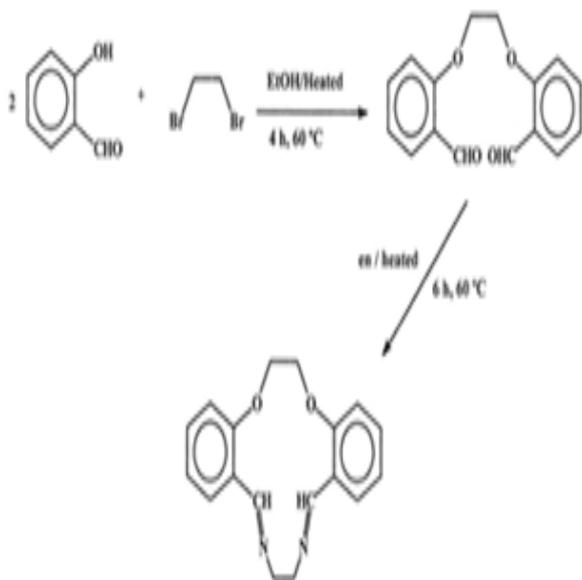


The potential readings of the electrodes were measured in stirred solution via a digital pH-meter (Elico LI-10, India). As reference electrode the saturated calomel was used. The performance of the electrodes was examined by measuring EMFs of the primary ion solutions in the concentration range from 10⁻⁸ to 10⁻¹ M. The activities of metal ions in solution were calculated according to the Debye-Huckel approximation [8-10].

RESULTS AND DISCUSSION

In this system, 1,12-diaaza-5,8-dioxo-3(4),9(10)-dibenzoylcyclotetradeca-2, 11-diene (L₁, DADODBCT) was used in the construction of a PVC-based membrane electrode. This sensor shows very good selectivity for salicylate ion over a wide variety of common inorganic and organic anions shown in (Figure 1), It exhibits Nernstian behavior with a slop of -59.1+ 0.5 mV per decade.

The working concentration ranges of the sensor are 1.0 x 10⁻¹ – 5.0 x 10⁻⁶ m with a detection limit of 3.0 x 10⁻⁶ M. The response time of the sensor is very fast (<8s), and can be used for at least twelve weeks in the pH rang of 4.0-9.2. (Table 1) shows the best performance was obtained with a membrane composition of 30% PVC, 65% dibutylphthalate, 3% L₁ (ionophore) and 2% hexadecyltrimethyl-ammonium bromide shown (Figure 2). Thus, the influences of the membrane composition, nature of solvent mediator and additive on the response characteristics for all the membrane sensors were investigated. The proposed sensor was successfully applied as an indicator electrode for titration of salicylate with calcium ion.



Theory of the Ion Selective Electrodes

The potential difference across an ion-sensitive membrane is:

$$E = K - (2.303RT/nF) \log(a)$$

where K is a constant to account for all other potentials, R is the gas constant, T is Temperature, n is the number of electrons transferred, F is Faraday's constant, and a is the activity of the analyte ion. A plot of measured potential versus $\log(a)$ will therefore give a straight line.

ISE are susceptible to several interference. Samples and standards are therefore dilute 1:1 with total ionic strength adjuster and buffer. The buffer consists of 1 M NaCl to adjust the ionic strength, acetic acid/acetate buffer to control pH, and a metal complexing agent. ISEs consist of the ion-selective membrane, an internal reference electrode, an external reference electrode, and a voltmeter. A typical meter is shown in the document on the pH meter.

Table 1: Optimization of Membrane Ingredients

Number of Membrane	Composition wt %				Slope ^a
	PVC	Plastisizer	TAA	HTAB	
1	30	DBP, 68	-	2	-3.5±0.6
2	30	DBP, 67	3	-	-37.7±0.2
3	30	DBP, 65	5	-	-35.2±0.5
4	30	DBP, 66	2	2	-52.3±0.3
5	30	DBP, 65	3	2	-59.1±0.3
6	30	DBP, 66	4	2	-56.4±0.4
7	30	DBP, 64	3	3	-59.0±0.5
8	30	NPOE, 64	3	3	-42.0±0.6
9	30	NPOE, 62	5	3	-41.5±0.4
10	30	BA, 65	3	2	-38.3±0.2

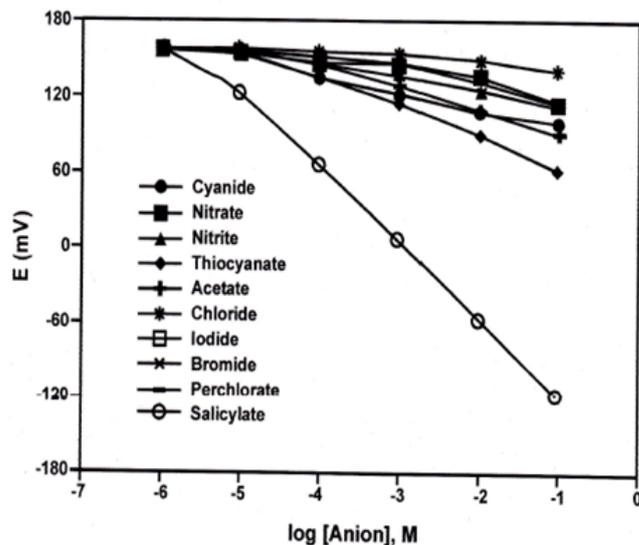


Figure 1: Potential responses of different ions, on ion selective electrodes based on L1 (L1=1,12-diaaza-5,8-dioxo-3(4),9(10)-dibenzoylcyclotetradeca 2,11- diene(DADODBCT))

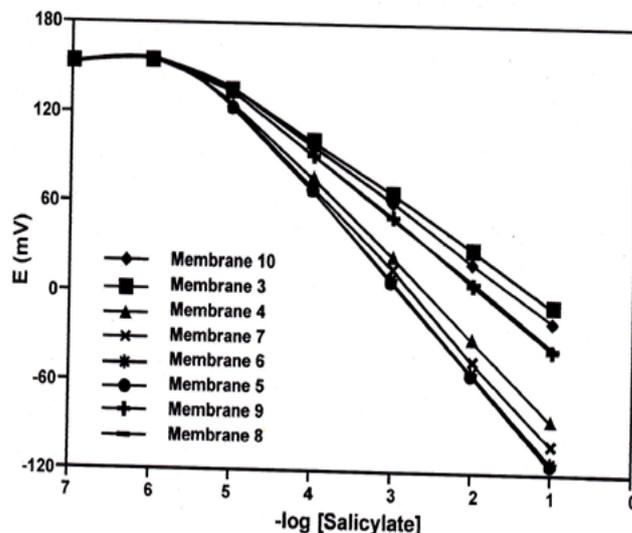


Figure 2: Potential response of Salicylate sensors with different composition at pH 7.

CONCLUSION

The conclusion drawn from the present studies that the Schiff based macrocyclic complexes provide a suitable matrix for the fabrication of membrane sensors for anions. These membrane electrodes are selective to specific anions and can be successfully used as indicator electrodes in the direct analysis of synthetic as well as real samples. These electrochemical sensors also have enough lifetime for estimation of samples.

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