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Poly (vinyl chloride) Based Ion Selective Electrode for Determination of Zr (IV) Ions Based on 2, 6-Dibenzylidenecyclohexanone

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Abstract: A selective poly (vinyl chloride)-based membrane sensor using 2,6-Dibenzylidenecyclohexanone as an ionophore have been prepared and explored as Zr (IV) selective electrode. The sensitivity, working range and response time shows a significant dependence on the concentration of ionophore. The electrode prepared with 100 mg of PVC, 10 mg of ionophore and 5 ml of dibutylthylate shows the best performance. The electrode works well in the concentration range of 1×10^{-1}-5×10^{-5} with a nerstian slope 55±2 eV and response time of 18 seconds. The sensor works well over the pH range 3-6. The sensor can be used for the period of over 1 month with out deviation in response characteristics. The selectivity of the electrode was studied and it was found that the electrode exhibited good selectivity for zirconium (IV) over some alkaline earth metal ions. The electrode was also used as indicator electrode for potentiometeric titration of Zr (IV) ions against EDTA solution. *Copyright © 2008 IFSA.*

Keywords: Ion selective electrode, Zirconium (IV), Poly (vinyl chloride)

1. Introduction

Detection of the metal ions has been the always of interest in analytical chemistry and different methods have been employed for detection such as atomic absorption, spectrophotometry, ICPMS and others but, the use of ion selective electrode has attracted much attention for the detection of the particular metal ion in presence of other metal ions. It is considered as versatile analytical tool and recommended widely for quick, easy to use, non-destructive and allow accurate determination of chemical species at relatively low level. The rapid growth in use of ion selective electrode has led to a

search for suitable materials that can be used for preparation of sensitive and selective ion-sensors, chemical sensors or more commonly ion-selective electrodes (ISEs). There is continuous research work going for the synthesis of ions selective membrane electrodes for determination of heavy metal ions such as Cu(II), Pb(II), Th(IV), Hg(II), Cd(II) and Ni(II) [1-6]. Significant number of ionophores including crown ethers, cryptands, aza-crowns and thiocompounds and ion exchangers have been exploited for fabrication of poly(vinyl chloride) (PVC) membrane electrodes for series of alkali, alkaline earth, transition and heavy metal ions [7-12].

The present work reports the synthesis of poly (vinyl chloride) based ion selective electrode using 2, 6-Dibenzylidenecyclohexanone as an electro-active material for determination of Zr(IV) ions. Zirconium is used in alloys such as zircaloy, which is used in nuclear applications and in catalytic converters, percussion caps and furnace bricks. Though zirconium is not noted for toxicity yet it is important to monitor the concentration of Zr (IV) ions. The zirconium dust can ignite in air and should be regarded as a major fire and explosion hazard.

2. Experimental

2.1. Reagents and Instruments

Poly(vinyl chloride), dioctylthylate, all other reagents used were of analytical grade. Elico L 610 pH meter was used for pH measurements and digital Potentiometer EI 118 for potential measurements.

2.2. Synthesis of the Ionophore

The compound 2, 6-Dibenzylidenecyclohexanone was synthesized as described elsewhere [13]. In a 125 mL Erlenmeyer flask are placed the ketone (1 mL), the aldehyde (4 mL), 95 % Ethanol (20 mL), and 2 N aqueous sodium hydroxide (15 mL). The flask is stirred at room temperature until no more precipitate is observed. The product was heated on steam bath for 15 min and then allowed to cool at room temperature. The flask is then cooled in ice and the product is collected by suction filtration. The crude product is washed consecutively with 10 mL portions of (1) 95 % ethanol, (2) 4 % acetic acid in 95 % of ethanol and (3) 95 % ethanol. The product is dried and used as such for further studies.

2.3. Preparation of Master Membrane

The ionophore was mixed thoroughly with PVC (1.0g) dissolved in 15 ml of THF and 5 ml of dibutylthylate was also added to it. The mixing ration of the ion-exchanger was varied with the fixed quantity of the PVC. The resulting solutions were carefully poured on the glass plate and left for overnight evaporation. In this way master membrane of different thicknesses were obtained which were then cut into small discs for fabrication of electrode.

2.4. Preparation of Ion-selective Electrode

A 12 mm disc was cut from the master membrane (M-1) and glued to one end of the Pyrex glass tube. The glass tube was filled with 0.1 M $ZroCl_2$ solution used as internal solution. The membrane was equilibrated for 3 days in a 0.1 M $ZroCl_2$ solution and for one hour at least before use for the potential measurements. Test solutions were prepared by gradual dilution of the stock solution. Potential measurements were performed at 25±2 ^oC using the digital potentiometer (EI) 118. The electrochemical representation of the cell is given as

Ag, AgCl|KCl (satd): Sample solution|ISE membrane|0.1 M KCl|Ag, AgCl

The detection limit, slope response curve, response time and working pH range of the electrode were evaluated to study the characteristics of the electrode.

3. Characteristics of the Membrane

3.1. Water Content

The conditioned membrane was put in the dimineralized water to elute out the diffusible salts dried with whattman paper remove excess of the moisture on the surface of membrane. The membrane was then dried in the oven at 50±2 ^{o}C for 24 hours. The water content was calculated as

$$\% \text{ Total wet weight} = \frac{W_w - W_d}{W_w} 100 \quad ,$$

where W_w – weight of the wet membrane, W_d – weight of dry membrane.

3.2. Response Time

The response time of the electrode was measured by recording the potential at different intervals of time (after every 4 seconds) till the potential attains the constant value. Initial potential was measured at zero seconds, just immediately after dipping the electrode in the solution of 10- fold higher concentration.

3.3. Thickness of the Membrane

Thickness of the membrane was measured as average thickness of the membrane measured with screw gauge.

3.4. Effect of pH

The value of electrode potential was measured at different pH (1-8) for the constant ion concentration of 1×10^{-2} M $ZroCl_2$.

3.5. Selectivity Coefficients

One of the most important characteristics of the ion-selective electrode is its response to foreign ions discussed in terms of selectivity coefficient K_{ij}. Different methods are employed but for the present sensor we used the Matched Potential Method for determination of selectivity coefficient. The method is independent of the *Nicolsky-Eisemann* equation hence the limitations suffer in terms of values for unequal charges are prevented. In this method we measure the potential of primary ion on addition of it to reference solution and the in separate experiment we measure the potential of interfering ion on successively addition of it to reference solution until the potential matched the one obtained before, by adding of primary ion.

$$K_{ij} = \frac{\text{Activity of primary ion}}{\text{Activity of interfering ion}}$$

3. Results and Discussion

Ion selective electrodes had attracted much attention during the recent times and have been employed for the determination of trace amount of elements. Here in this paper we report the zirconium selective electrode. The compound 2, 6-dibenzylidenecyclohexanone used as ionophore was synthesized as described earlier the scheme for the synthesis is given in Fig. 1. Three different membranes were prepared by varying the amount of ionophore in ionophore-PVC mixture. It was observed that increasing the amount of ionophore a slight increase in the thickness of the membrane accompanied with increase in response time (Table 1). The concentration range over which the electrode shows linear range is also effected by the concentration of ionophore in mixture. On the basis of quick response time and linear concentration range membrane M-1 was selected for further studies**.** The potential response of the electrodes was measured over the concentration range of 1×10^{-1}-1×10^{-8} M of Pb^{2+} ion. The Fig. 2 reveals that the concentration range as well as detection limit varies with change in composition of the membrane. The best result was obtained for the membrane M-1. Fig. 3 gives the calibration graph for the membrane 1.The limit of detection determined by intersection of two extrapolated segments of calibration graph was 5.0×10^{-5} M. The electrode shows quick response time of 18 seconds on changing the concentration from 10^{-1}-10^{-2} M after which the potential becomes constant (Fig. 4). The sensor was tested over the period of 1 month to investigate its stability, during which calibration graph was plotted from time to time. No change was observed in working concentration range, slope and response time. However it is necessary to keep the membrane dipped in 0.1 M $ZroCl_2$ when not in use. The effect of pH on electrode response was studied in the range of 1-8 using 1×10^{-2} M $ZroCl_2$ solutions, adjustment of pH were done with dilute hydrochloric acid or ammonia. The response of the sensor was significantly affected by pH as sharp changes in electrode potential below pH 3 as well as above pH 6 were observed (Fig. 5). The reason for this behavior may be due to formation of hydroxides at high pH, which decreases the response, and at low pH the electrode responded to H^+ ions results in higher potential. Hence the most suitable pH range for the sensor is between pH 3 and pH 6. The thickness of the membrane was measured with micrometer and all the three membranes were approximately of same thickness. The thickness of the membrane (M-1) was found to be 0.28 mm and the % water content of the wet membrane (M-1) was found 0.032.

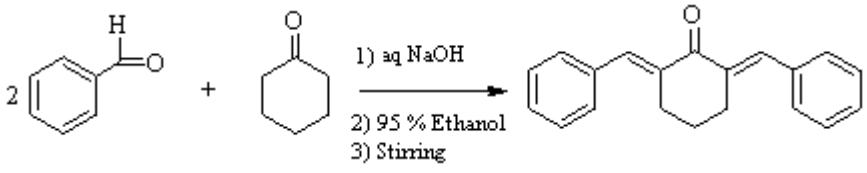

Fig. 1. Synthesis of 2, 6-Dibenzylidenecyclohexanone.

Table 1. Synthesis and properties of 2,6-Dibenzylidenecyclohexanone based membrane.

Membrane sample	Composition of membrane Ionophore (mg)	PVC(mg)	Thickness (mm)	Concentration range	Response time (sec)	Slope (mV)
M-1	10	100	0.28	1×10^{-1} - 5×10^{-5}	18	55
M-2	20	100	0.30	1×10^{-1} - 1×10^{-4}	25	50
M-3	30	100	0.33	1×10^{-1} - 1×10^{-4}	25	45

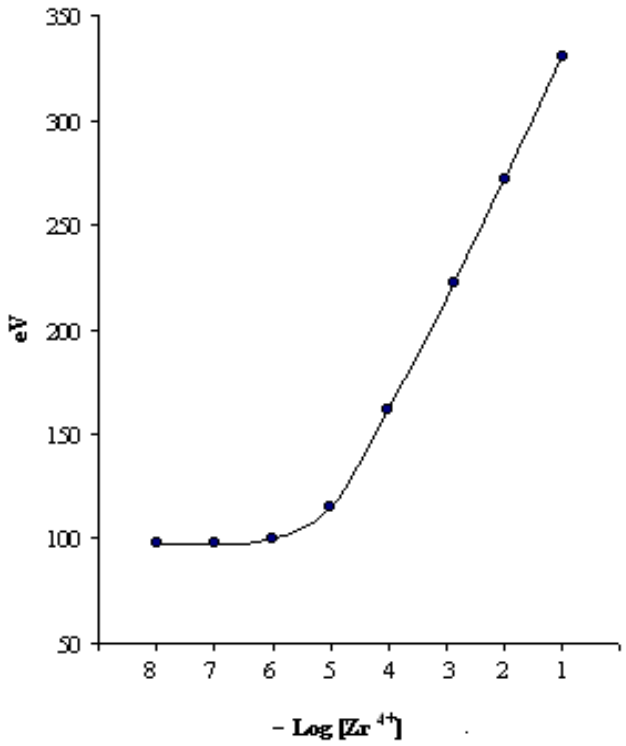

Fig. 2. Calibration curve for the membrane electrode.

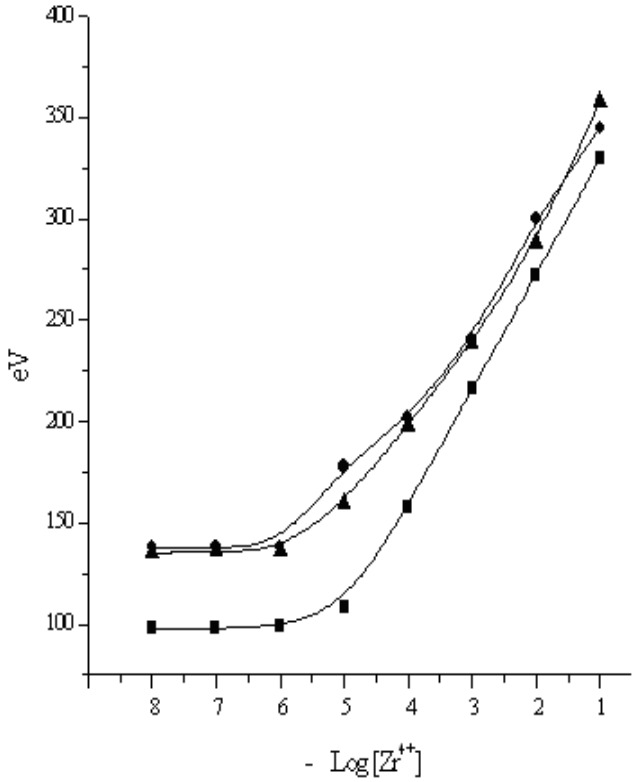

Fig. 3. Variation of membrane potentials with different amount of ionophore.

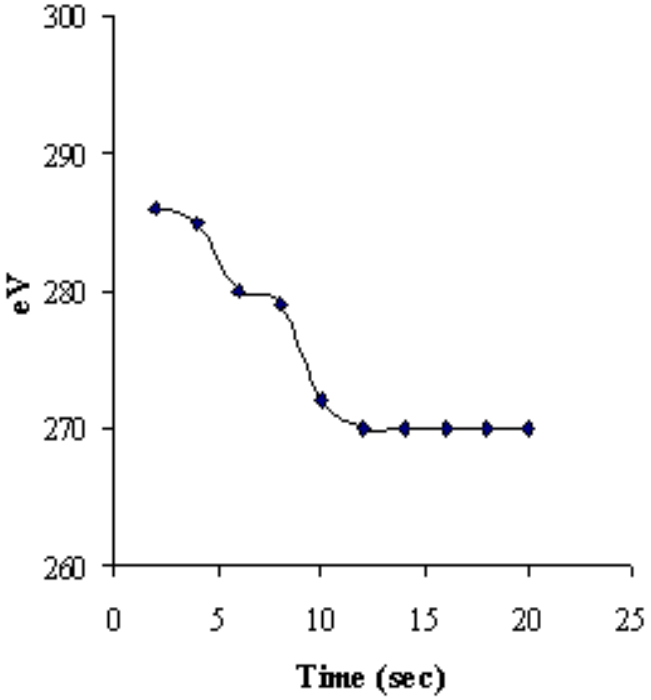

Fig. 4. Response of the electrode at different time intervals.

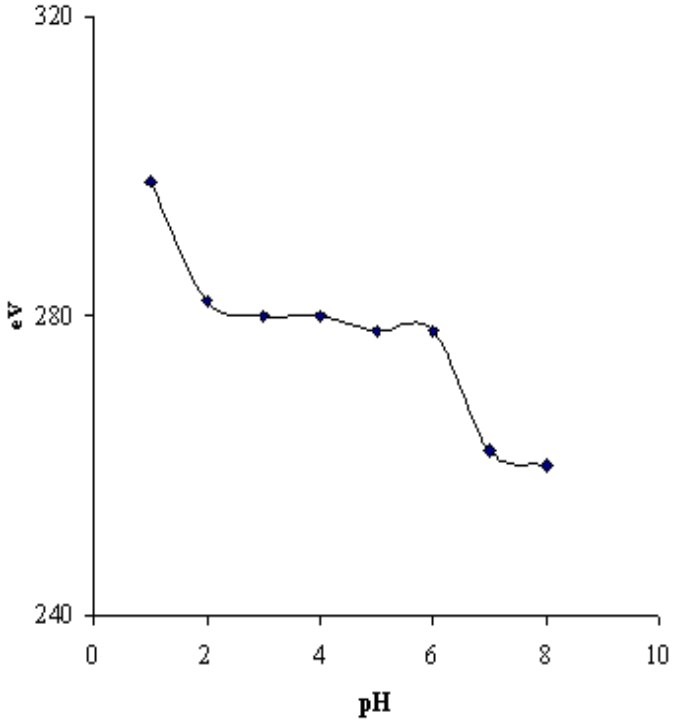

Fig. 5. Effect of pH on electrode response.

The most important feature of the sensor is its selectivity towards primary ion against the foreign ions. The selectivity coefficients for different divalent metal ions towards the Zr^{4+} sensor were determined. It is apparent from the Table 2 that the values determined in range of 10^{-3}, less than unity hence the sensor prepared is selective towards Zr^{4+} ions in presence of other interfering ions listed in Table 2. Response of the electrode towards various divalent metal ions shows (Fig. 6) that the electrode is selective towards zirconium (IV) ions as compared to other divalent ions. The practical utility was

explored by carrying the potentiometric titrations of the 0.01M $ZrOCl_2$ against 0.01 M EDTA solution as titrant using the sensor as indicator electrode. The potential was recorded after addition of every 0.5 mL of EDTA solution to 5 mL of 0.01M $ZrOCl_2$ diluted to 20 mL with demineralized water. The addition of EDTA decreases the potential as a result of decrease in free Zr^{4+} ions due to formation of complex with EDTA. The amount of Zr^{4+} ions can be accurately determined by titration curve (Fig. 7) providing sharp endpoint.

Table 2. Selectivity coefficients for Zr^{4+} selective electrode for various interfering ions.

Interfering ions	Selectivity coefficients
Mg^{2+}	1.2×10^{-4}
Ca^{2+}	2.1×10^{-3}
Sr^{2+}	1.6×10^{-3}
Ba^{2+}	2.2×10^{-2}
Cu^{2+}	3.2×10^{-3}
Zn^{2+}	1.2×10^{-2}
Cd^{2+}	1.1×10^{-3}
Hg^{2+}	2.5×10^{-3}

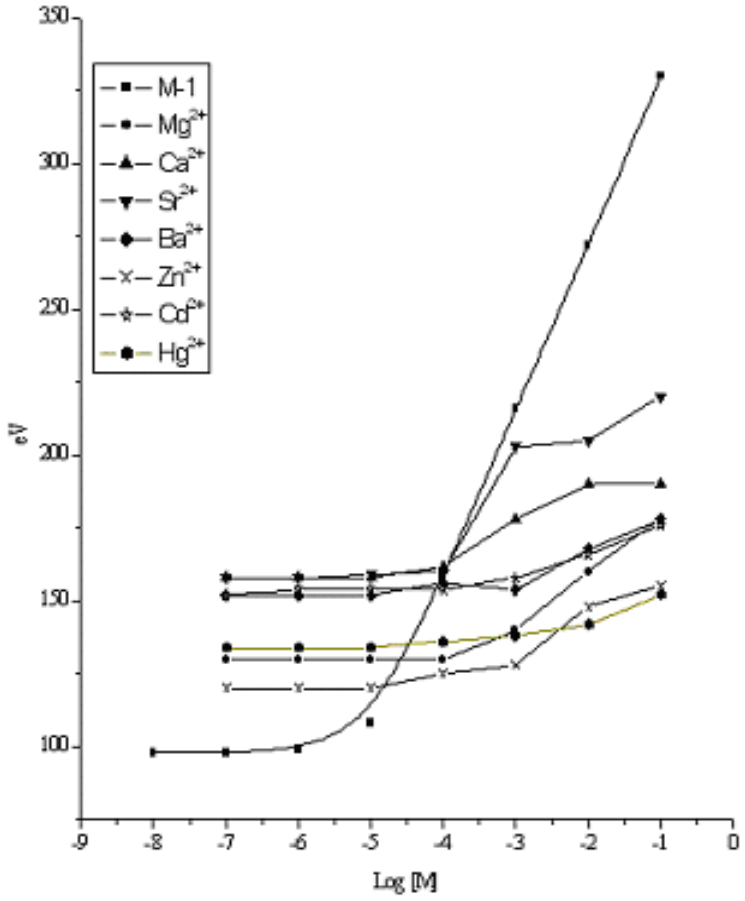

Fig. 6. Potential responses of ion-selective electrode based on 2,6-Dibenzylidenecyclohexanone for various metal ions.

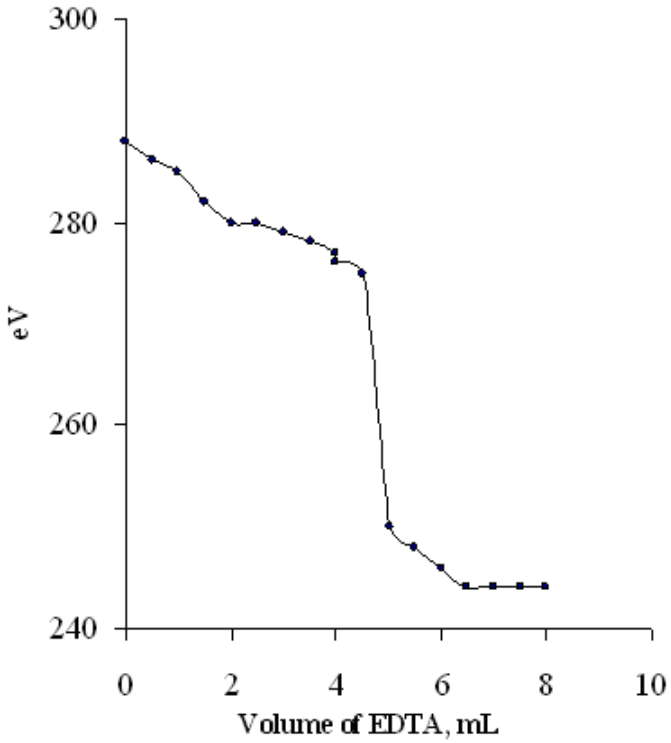

Fig. 7. Precipitation titration of Zr^{4+} against EDTA solution.

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