

Poly(vinyl chloride) membrane containing zirconium(IV)selenomolybdate inorganic ion exchanger as dysprosium(III)-ion selective electrode

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Received 25 February 2002; revised 3 February 2003

Poly(vinyl chloride) supported tetracycline sorbed zirconium(IV) selenomolybdate chelating inorganic exchange membrane has been employed for the determination of dysprosium(III) ion. The membrane electrode shows a Nernstian response for Dy(III) over a wide concentration range ($1.0 \times 10^{-1} M - 5 \times 10^{-5} M$) with a slope of 18.3 mV per decade of concentration. The detection limit is $3.8 \times 10^{-5} M$. The electrode is found to possess adequate stability and specific selectivity for Dy(III) over the other closely trivalent lanthanide metal ions with a response time of ~ 15 s. The sensor can also be used in partially non-aqueous medium, e.g., acetone/alcohol having 5-10% (v/v) contents. Its working pH range is 2-9. It is successfully applied for the direct determination of Dy³⁺ in metaborate rock and as an indicator electrode in potentiometric titrations of dysprosium ion with 2-4 % experimental error.

During the past years, the increased demand of high purity rare earths has necessitated the development of separation technology for the removal of lanthanides from rare earth metal sources. The separation and determination of lanthanides from different kind of samples is found in the literature. The classical separation techniques like liquid-liquid extraction, chromatography, ion exchange, etc. are replaced by solid phase extraction and ion selective electrode membranes.

Comparatively less work is reported on the determination of rare earths using ion selective electrodes. Recently, neural ionophores¹⁻⁴, crown ether^{5,6}, liquid ion exchange membranes^{7,8} and solid-state electrodes^{9,10} have been used as an electroactive material for the determination of rare earth metal ions. A limited number of membrane sensors using inorganic ion exchangers have been developed¹¹⁻¹⁵ and most of these suffer from poor selectivity¹⁶. The stability and better performance of chelating resins have prompted the fabrication of chelating ion exchanger based elec-

trodes for the lanthanide elements. The present work reports the potentiometric studies on chelating based heterogeneous membrane electrode *i.e.*, tetracycline sorbed zirconium(IV) selenomolybdate ion exchanger using poly(vinyl chloride) as a binder. Various potentiometric characteristics of the membrane sensor, including response time, potentiometric selectivity as well as the effects of pH and non-aqueous solutions on the potentiometric responses have been investigated.

Experimental

Lanthanide chlorides (La, Ce, Nd, Pr, Eu, Gd, Tb and Dy) were prepared from their respective oxides, which are of analytical grade purity and were purchased from Rare Earth Products Ltd. (India). Solutions of 0.1 M each of lanthanide chlorides were prepared and standardized using xylenol orange as an indicator as described earlier^{17,18}. Ion free doubly distilled water was used throughout the experiments.

Synthesis of zirconium(IV) selenomolybdate (ZSM) ion exchanger

The exchanger, zirconium(IV) selenomolybdate (ZSM) was synthesized as reported earlier¹⁹ by mixing solution of 0.1 M zirconium(IV) oxychloride, 0.1 M selenous acid and 0.1 M ammonium molybdate in the ratio of 2:2:1 at pH 2. Conc. HCl was added to the precipitate to bring the desired pH value and then it was heated to just boil. The precipitate was allowed to stand for 24 h in the mother liquid, decanted, washed with distilled water, filtered by suction and dried at $50 \pm 2^\circ\text{C}$. The dried product, which was broken into small granules when immersed in water, was converted into H⁺ form by placing it in 3 M HNO₃ for 2 days. Finally, the exchanger was washed with deionized water (DIW) to remove the excess of acid and then dried at $50 \pm 2^\circ\text{C}$.

Sorption of tetracycline hydrochloride on zirconium(IV) selenomolybdate (ZSM) ion exchanger

Sorption of tetracycline hydrochloride on ZSM was done according to the procedure previously described²⁰ as follows: ZSM in H⁺ form was heated with 200 cm³ of boiling deionized water for 1 h to remove impurities. It was decanted and shaken with 100 cm³

of 0.1% (v/v) tetracycline hydrochloride for 4 h and left overnight. The solution was then decanted and the obtained light yellow tetracycline sorbed zirconium(IV) selenomolybdate (TC-ZSM) was washed 2-3 times with deionized water in order to remove the excess tetracycline hydrochloride. Finally the product was dried at $40\pm 2^\circ\text{C}$.

Electrode preparation and potentiometric measurements

Poly(vinyl chloride) (0.6 g) in 6 mL of tetrahydrofuran was mixed with chelating inorganic exchanger (0.2 g) and the resulting solution was carefully cast on a glass slide plate and left for slow evaporation to obtain a thin membrane²¹. Then, an appropriate size of membrane was cut from the master membrane and was mounted at the lower end of the membrane holder. A 0.1 mol dm^{-3} metal solution was used as an internal reference while the saturated calomel electrodes were used as reference electrodes. The membrane potential measurement was carried out using a cell set-up of the following type:

External saturated calomel electrode (SCE)	Test solution	Membrane	Internal solution	Internal saturated calomel electrode (SCE)
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Membrane potentials were measured with an Equiptronic-India Digital potentiometer [EQ 602] at $27\pm 1^\circ\text{C}$. Before each set of measurements, the electrodes were conditioned overnight in an appropriate buffer solution containing 0.01 M DyCl_3 solution.

Determination of Dy^{3+} in metabasic rocks

Accurately weighed 0.25 g finely rock powder was mixed with lithium metaborate in the ratio 1:5 and transferred to a crucible. The fusion was carried at about $500\text{--}600^\circ\text{C}$. The fused mass was directly poured to a beaker containing 50 mL of 10% nitric acid. The contents were stirred for 30-50 min until all the solids were dissolved and evaporated the solution until the volume becomes less than half. The solution was brought to the mark with distilled water, filtered and its potential was measured.

Results and discussion

Characterizations of the sensor membranes are essential to correlate the movement of ions in the membrane with the potential generating across it. The

physical characteristics of the heterogeneous chelating ion exchanger membrane (TC-ZWP) analyzed to correlate with the movement of the ions in the membrane phase, potential generated across it and the selectivity of ions of interest. The properties of the membrane *viz.*, thickness (0.45 mm), water content (21.85%), porosity (0.0022), electrolytic absorption ($31\text{ }\mu\text{g}$) and swelling (0.12%) were determined as described earlier²²⁻²⁴. The values suggested that the membrane is of least porosity and swelling. The electrolyte absorption reveals that the diffusion will take place through the exchange sites present in the membrane phase. So this membrane is expected to be selective in their response to a particular ion, hence leading to high selectivity of the membrane electrode.

The concentration of the internal solution DyCl_3 in the electrode was varied from 1.0×10^{-2} to $1\times 10^{-5}\text{ M}$ and the potential response of the Dy^{3+} ion selective electrode was measured. It was found that the variation of the concentration of the internal solution does not cause any significant difference in the potential response, except for an expected change in the intercept of the resulting Nernstian slopes. About $1.0\times 10^{-2}\text{ M}$ concentration of the reference DyCl_3 solution is quite appropriate for the smooth functioning of electrode system.

The optimum equilibration time for the membrane electrode in the presence of $1.0\times 10^{-2}\text{ M DyCl}_3$ was 4-5 days after which it would generate stable potentials in contact with dysprosium solutions. The electrode shows a linear response to the activity of Dy^{3+} ion in the range of 5.0×10^{-5} to $1.0\times 10^{-1}\text{ M}$ (Fig. 1). The slope of the calibration graph was found to be $\pm 18.3\text{ mV}$ per decade of concentration. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was $3.8\times 10^{-5}\text{ M}$.

The static response time of the membrane sensor was found to be $\sim 15\text{ s}$ for Dy^{3+} at the concentration $1.0\times 10^{-3}\text{ M}$. This is actually the average time required for the electrode to reach a potential within $\pm 1\text{ mV}$ of the final equilibrium value after successive immersion of a series of Dy^{3+} ions, each having a 10-fold difference in concentration. The results thus obtained are indicative of a rapid diffusion in the achievement of equilibrium between the aqueous layer and the membrane sensor, and rapid complex formation and exchange of ions in the membrane²⁵. The membrane electrodes can be used for at least 2 months without any measurable divergence.

The effect of *pH* on the response of TC-ZSM-PVC membrane electrode to $1.0 \times 10^{-2} M$ Dy^{3+} solution over a *pH* range of 1.0-13.0 was studied. It was found that the membrane electrode can be suitably used in the *pH* range 2-9. However, the observed sharp change in potential response below *pH* 2.0 indicates that the membrane sensor responds to hydrogen ions while at above *pH* 9.0 may be attributed to the interference of OH^- ions.

The performance of the electrode was also investigated in partially non-aqueous medium using acetone-water and ethanol-water mixture. Potential versus concentration plots of 5 and 10% (v/v) acetic and ethanolic solutions revealed that the electrode assembly works satisfactorily up to 10% (v/v) acetic and ethanolic solution. The matrix swelled continuously in higher proportions of acetone and ethanol after few hours. In these mixtures, the working concentration range and slope remains unchanged. The response time of the membrane electrode was found to be steady for few hours and then the potential deviates drastically (Table 1).

In order to investigate the selectivity of the membrane electrode toward Dy^{3+} with respect to various

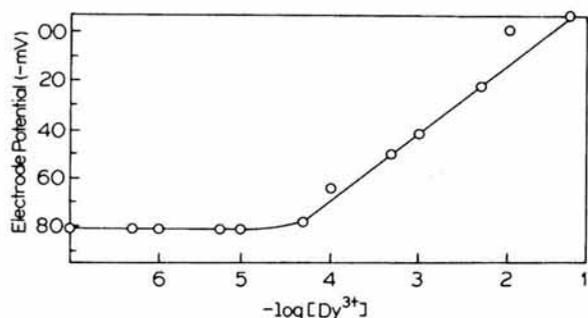


Fig. 1—Calibration curve of Dy^{3+} -selective (TC-ZSM)-PVC based membrane electrode

interfering ions, the potentiometric selectivity coefficients (K_{Dy}^{pot}) were evaluated by the mixed solution method^{26,27} using solution containing a fixed amount of Dy^{3+} ion ($1.0 \times 10^{-5} M$) and varying amount of the interfering ion (M^{n+}), according to:

$$K_{Dy}^{pot} a^{3/n} M = a_{Dy} \left\{ \exp \left(\frac{(E_2 - E_1)F}{RT} \right) \right\}^{-1} a_{Dy} \quad \dots (1)$$

where, E_1 and E_2 are the electrode potentials for the solution of Dy^{3+} ions alone and for the solution containing interfering ions and dysprosium ions respectively. According to Eq. 1, K_{Dy}^{pot} values for ions can be evaluated from the slope of the graph of $a_{Dy} \{ \exp [(E_2 - E_1)F] \}^{-1} a_{Dy}$ versus $a^{3/n}$. The resulting K_{Dy}^{pot} values for various lanthanides metal ions are in range from 22.22×10^{-3} to 196.07×10^{-3} . As seen, for all ions used, the selectivity coefficients are in the order of 10^{-3} indicating that they would not significantly disturb the functioning of the Dy^{3+} selective membrane.

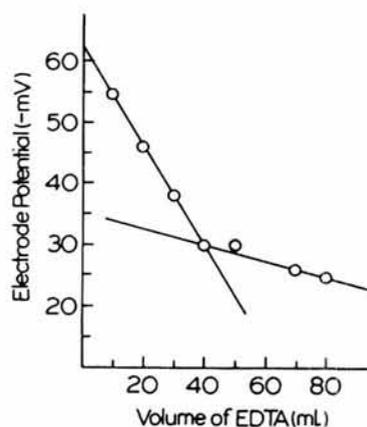


Fig. 2—EDTA titration curve for (TC-ZSM)-PVC based membrane electrode

Table 1—Response time for non-aqueous solvents (Dy^{3+} -selective membrane electrode)

S. No.	Time (h)	Potential (-mV) 10% ethanol	Potential (-mV) 5% ethanol	Potential (-mV) 10% acetone	Potential (-mV) 5% acetone
1	5	17	14	11	09
2	10	17	14	11	09
3	15	17	14	11	09
4	20	17	14	11	09
5	25	17	14	11	09
6	30	17	14	11	09
7	35	28	22	11	15
8	40	33	37	30	35
9	45	45	51	47	48

The practical utility of the proposed membrane sensor as an indicator electrode was tested in the titration of 25.0 mL of 1.0×10^{-2} M Dy^{3+} ions with 1×10^{-2} M EDTA solution. The results in Fig. 2 show a sharp inflection point with perfect stoichiometry.

The electrode was successfully applied to the direct determination of dysprosium in metabasic rock samples. With the use of the membrane sensor's calibration curve, the dysprosium content (9.02 ppm) in the metabasic rock obtained from triplicate measurements with electrode was found to be in satisfactory agreement with that determined by atomic absorption spectrometry (9.35 ppm). The errors are found to be within 2-4%.

Chelating inorganic ion exchange PVC matrix supported membrane as a sensor for Dy(III) ion offers the advantages of thermal stability, simplicity, sensitivity, reliability, low cost, fast response and long life. Incorporation of tetracycline sorbed zirconium(IV) selenomolybdate (TC-ZSM) in poly(vinyl chloride) matrix provides a good detector for the determination of Dy(III) in analytical samples without significant interference from other trivalent lanthanide metal ions.

Acknowledgements

One of the authors, Mr. Himanshu Agarwal, Senior Research Fellow (SRF), is thankful to Council of Scientific and Industrial Research, New Delhi, India for providing financial help. Thanks are due to Prof. S.K. Srivastava, Ex-Head, Department of Chemistry, Roorkee University, Roorkee, India for his constant help throughout the work.

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