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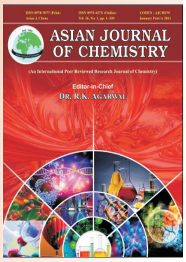

Novel Potentiometric Sensors of Ion Imprinted Polymers for Specific Binding of Yttrium(III)

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A novel potentiometric sensor of yttrium(III) ion was designed by embedding the yttrium(III) ion-imprinted polymer (Y^{3+}IIP) particles in poly(vinyl alcohol) matrix. The (Y^{3+}IIP) was prepared by using a single pot method. The sensor shows a Nernstian response for yttrium(III) over a wide concentration range (5×10^{-7} to 5×10^{-2} M) with a slope of 29.8 mV per decade. The detection limit can reach as low as 3×10^{-7} M. The proposed sensor has a fast response time (less than 10 s) and offers a high selectivity with respect to several alkali, alkaline earth and transition metal ions and can be used in a pH range of 6.5-8.5. This sensor was applied as an indicator electrode in the potentiometric titration and has been successfully used for the determination yttrium(III) in the yttrium-aluminium alloy sample with direct potentiometry.

Keywords: Potentiometric sensor, Ion imprinted polymer, Polymerparticles, Yttrium(III).

INTRODUCTION

Because of their special photogenic, magnetic, mechanical and nuclear properties, rare earth metals are very important in industry. They are widely used in production of glass and ceramic industry, metallurgy, electronics and agriculture and natural sciences. Therefore, developing methods for sensitive accurate and rapid determination of yttrium(III) are of great of importance. Some lanthanide have been determined by ion selective electrods[1-4], but less work for the determination of Y^{3+} has been reported.

Most of methods have been developed to determine trace amounts of inorganic ions by numerous ion selective electrods based on poly(vinyl chloride) matrix. The poly(vinyl alcohol) was mainly used in the biosensors[5-7]. However, the ion selective electrode based on poly(vinyl alcohol) matrix has not been reported.

Ion-selective electrode has advantages of fast, accurate, reproducible and selective determination of various specious. It is used to measure directly ions in complex samples. It has been shown to be very useful tools for chemical, clinical and environmental analysis[8-11]. In the past many years, a variety of mainly cation-selective carriers have been synthesized[11]. Since published articles on ionophore based ion selective electrods[12], there are increasingly use of ion sensor in the fields of environment, agriculture and medicine. In recent years, attention has been paid to molecularly imprinted technology (MIT) for their chemical sensors applications[4,13-14].

In this work, a novel potentiometric sensor of yttrium(III) ion was designed by embedding the yttrium(III) ion imprinted polymer (Y^{3+}IIP) particles in poly(vinyl alcohol) matrix and (Y^{3+} IIP) as a neutral carrier and *o*-nitrophenyloctyl ether (*o*-NPOE) as a plasticizer. The reason for chosing (Y^{3+}IIP) as neutral carrier was that (Y^{3+}IIP) had a good adsorption and selectivity for the yttrium(III). Therefore, (Y^{3+}IIP) and Y^{3+} could firmly combine with each other. This electrode showed a good Nernstian response and had a wider working concentration range, faster response time and bigger hardness of membrane than the poly(vinyl chloride) membrane.

EXPERIMENTAL

Yttrium(III) chloride, acetylacetone (Hacac), 4-vinylpyridine (4-VP), ethylene glycol dimethacrylate (EGDMA), 2,2-azobisisobutyronitrile (AIBN), *o*-nitrophenyloctylether (*o*-NPOE), sodium tetraphenyl borate (NaTPB) and high relative molecular weight poly(vinyl chloride) and poly(vinyl alcohol) (PVA)were obtained from Aldrich (Milwauke, USA).

Preparation of yttrium(III) ion imprinted polymer: As described earlier[15], the preformed binary complex of yttrium(III) with acetylacetone and 4-vinylpyridine (monomer) acting also as functional monomer was dissolved in 15 mL of methanol (porogen), the cross-linking monomer (EGDMA) and the initiator (AIBN) were added subsequently. The polymerization mixture was sonicated and degassed with nitrogen for 15 min, after that, cured at 60 °C for 24 h. Non-imprinted polymers were prepared similarly but the template was excluded from the procedure. The polymers were ground and sieved to particle sizes ranging from 50 to 150 μm. Extraction of the template molecule was carried out with 0.1M EDTA, acetic acid + methanol (1:1) followed by deionized water. This procedure was repeated several times to remove the unreacted ingredients and the template molecule. The polymers were let dry at ambient temperature, before their use as a potentiometric sensor.

The schematic representation of the preparation of yttrium(III) ion imprinted polymer and the imprinting and removal of yttrium(III) ion from the imprinted polymer is shown in Fig. 1.

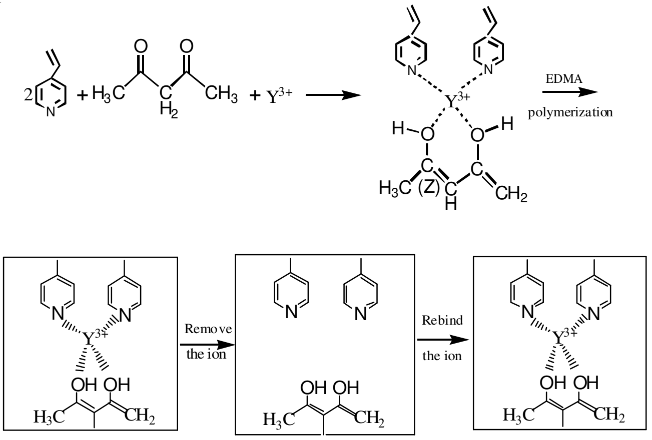

Fig. 1. Schematic representation of the yttrium(III) ion imprinted polymer synthesis

Preparation of membrane: The poly(vinyl alcohol) membrane electrode with (Y^{3+}IIP) particles were fabricated by following the general procedure. 45 mg poly(vinyl alcohol) was dissolved in 3 mL of water at 90 °C, when it cool to room temperature, 45 mg (Y^{3+}IIP) particles (45-100 um size) were added. Homogenized by a glass stick and then poured into the solution, which was prepared by dissolving 0.2 mL of *o*-nitrophenyloctylether and 25 mg of sodium tetraphenyl borate in 2.5 mL of tetrahydrofuran (THF) in a teflon mould of 21mm i.d. The tetrahydrofuran solvent was allowed to evaporate at room temperature, so as to obtain homogenous ion-imprinted polymer based membrane having a thickness of 0.58 mm. A blank membrane was also prepared in a similar manner, maintaining the same composition, without (Y^{3+}IIP) particles. The membrane was glued to one end of a pyrex glass tube with araldite. The tube was then filled with an internal filling solution (mixture of 1mM KCl and 1mM yttrium(III) solution).

Simultaneously, a poly(vinyl chloride) membrane electrode of yttrium(III) was designed, so as to compare with the poly(vinyl alcohol) membrane electrode.

Conditioning of membranes and electromotive force measurements: The (Y^{3+}IIP) based ion selective electrode was conditioned for 2 days in a 1.0 × 10^{-3} M yttrium(III) solution and then stirred in hexamine buffer for 1 h to remove bound yttrium(III) ions. The test solution whose pH was maintained at 7.0 ± 0.3 after the addition of *tris*-HCl buffer was taken and the potentials were measured by varying the concentration in the range of 1 × 10^{-7} to 1 × 10^{-1} M. A pHs-3C model ion analyzer (Shanghai, China) was used for potential measurements at 25.0 ± 0.1 °C. The measurements were carried out with saturated calomel electrode (SCE) as reference electrode with the following cell assembly.

Ag wire |1 mM KCl + 1mM Y^{3+}(internal solution)|Y^{3+}IIP membrane||test solution| Hg-Hg_2Cl_2, KCl (satd.).

RESULTS AND DISCUSSION

The yttrium(III) ion imprinted polymer particles having specific recognition sites has been successfully used for the solid phase extractive preconcentration of yttrium(III) ion. In this paper, the suitability of the ion-imprinted polymer material dispersed in *o*-nitrophenyloctylether and embedded in poly(vinyl alcohol) to selectively recognize yttrium ion has been examined.

The potential response obtained with the electrodes prepared with (Y^{3+}IIP) membrane and blank membrane are shown in Fig. 2. As seen from Fig. 2, the plot obtained for the sensor with (Y^{3+}IIP) particles showed a greater slope of 29.8 mV per decade over a wider concentration range of 5 × 10^{-7} to 5 × 10^{-2} M of yttrium(III), which is the expected Nernstian slope for the trivalent cations. The limit of detection was 3 × 10^{-7} M yttrium(III) calculated based on the IUPAC definition. The poly(vinyl chloride) membrane electrode exhibited a slope of 19.7 mV per decade over a wide concentration range of 5 × 10^{-7} to 1 × 10^{-2} M.

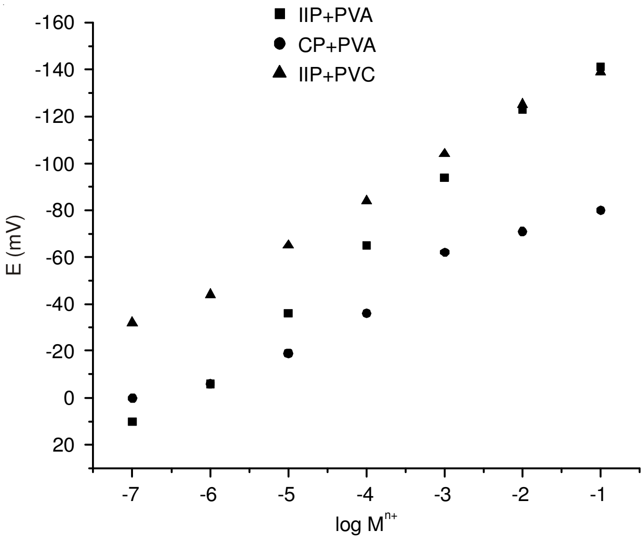

Fig. 2. Potential responses of ion selective electrods with (Y^{3+}IIP) and blank membrane

Effect of membrane composition: The sensitivity and selectivity of the ion selective electrodes depend not only on various ionphores of the membrane but also on the composition[16-18]. Thus, different composition of membrane using (Y^{3+}IIP) particles were prepared to optimize the ion selective electrods. For this purpose, we prepare yttrium(III) sensitive ion selective electrode based on (Y^{3+}IIP) particles dispersed in 2-nitrophenyloctyl ether (NPOE) and embedded in poly(vinyl chloride) (PVC) or poly(vinyl alcohol) (PVA) matrix. The effect of different compositions on (Y^{3+}IIP) based ion selective electrode was investigated. Fig. 2 shows the potential response obtained for electrodes prepared with different membrane. It is interesting to note that the response gradient of Y^{3+}-poly-(vinyl alcohol) membrane electrode to pY is 29.8 mV, which indicates that the electron number transported across the electrode membrane is 2 rather than 3. It is suggested that a possible explanation for this is that there is hydroxyl ion in the poly(vinyl alcohol) membrane, oxygen atoms have single electron and Y^{3+} has an empty orbit, so Y^{3+} could accept single electrons from oxygen atoms of poly(vinyl alcohol) and interact with each other. Therefore, poly(vinyl alcohol) and Y^{3+} could firmly combine with poly(vinyl alcohol). Then this electrode showed a good Nernstian response slope (29.8 mv) and had a wide working concentration range and fast response.

The ratio of poly(vinyl alcohol) to (Y^{3+}IIP) particles was found to play a key role in the efficiency of the ion selective electrode since the amount of the (Y^{3+}IIP) particles determines the number of binding sites available for the complexation of yttrium(III) ion. The results in Table-1 show that the membrane with the weight of poly(vinyl alcohol) and (Y^{3+}IIP) particles in the ratio 1:1 gives the best performance.

TABLE-1
EFFECT OF SOAKING TIME ON THE RESPONSE CHARACTERISTICS OF (Y^{+3}IIP) BASED ISE [POLY(VINYL ALCOHOL) MEMBRANE ELECTRODE]

Soaking time	Nernstian response range (M)
1 day	1.0×10^{-5} to 1.0×10^{-4}
2 days	5.0×10^{-5} to 5.0×10^{-2}
3 days and subsequent days	5.0×10^{-7} to 5.0×10^{-2}

Response studies carried out with the membranes soaked for different times in 1 mM yttrium(III) solution, showed that a minimum time of 3 days was required, after which the membrane would generate stable potentials (Table-1).

Effect of pH: The influence of pH on the potentiometric response of the proposed sensor was examined over a pH range of 6-9 for Y^{3+} standard solutions of 5×10^{-5} M. The pH of the solution was adjusted with either nitric acid or sodium hydroxide solutions. The influence of the pH response on the ion selective electrode is shown in Fig. 3.

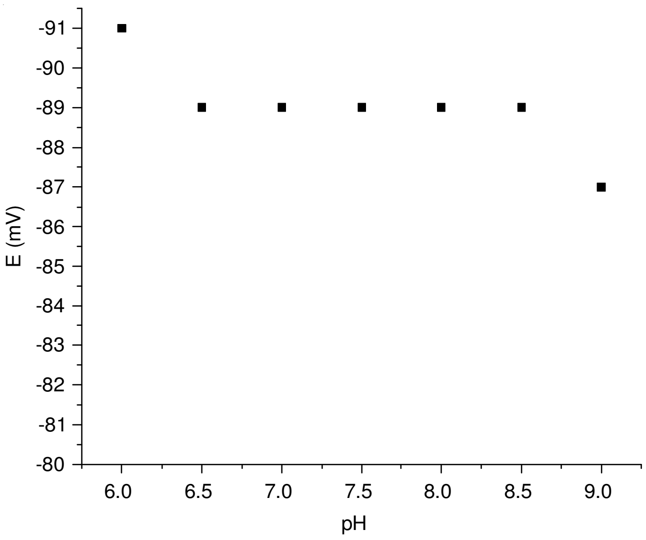

Fig. 3. Effect of pH of the test solution [5×10^{-5} M of yttrium(III)] on the potential response of the (Y^{3+}IIP) based ion selective electrode [poly(vinyl alcohol) membrane electrode]

The pH plot shows that the variation of solution pH over the range of 6.5-8.5 has no significant effect on the potentiometric response for the sensors. When pH < 6.5, the sensor responses were severely influenced. It is the reason that the N of the 4-VP that bond the H_3O^+. The sensor responses were also influenced when pH > 8.5, but the reason is that the Y^{3+} was reduced by OH^-.

Dynamic response time: The dynamic response time of the sensors were examined by recording the potential readings at time intervals of 10s over 2 min. Fig. 4 indicates that the time required to reach 95 % of equilibrium was less than 10 s. The response time was recorded by changing the yttrium(III) concentration in solution over a concentration range from 1×10^{-5} to 1×10^{-2} M. These results indicate that the sensors could be encouraged their use in automated systems.

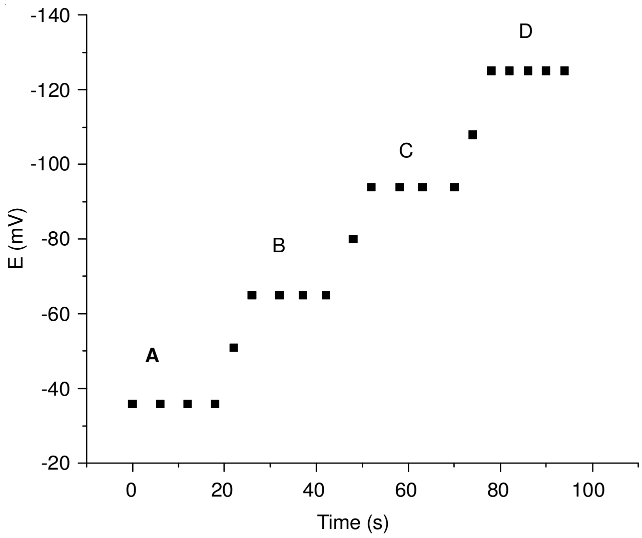

Fig. 4. Dynamic response of the (Y^{3+}IIP) based ion selective electrode (poly(vinyl alcohol) membrane electrode) for stepwise concentration change of yttrium(III) (a) 1.0×10^{-5} M; (b) 1×10^{-5} M; (c) 1×10^{-5} M; (d) 1×10^{-5} M

Sensor selectivity: The influence of interfering ions on the response behavior of the ion-selective membrane electrode is usually described in terms of the selectivity coefficients. The potentionmetric selectivity coefficients of the yttrium(III) membrane sensor were evaluated by the separated potential method (SPM) according to the following equation[19]:

$$K^{pot}_{A,B} = \frac{\alpha_A}{\alpha_B^{Z_A/Z_B}}$$

where α_A is primary ion, α_B is interfering ion and Z is the charge of ion.

The resulting selectivity coefficient values are given in Table-2. From the data given in Table-2, it is immediately obvious that the proposed Y(III) sensor is highly selective with respect to most of cations. As can be seen from Table-2, the selectivity coefficients for other metal ions tested are equal or smaller than 1.3×10^{-2}, indicating that they would not significantly disturb the functioning of the proposed Y(III) membrane sensor. The high selectivity of the membrane electrode for Y^{3+} ions over other cations used, most probably arises from the strong tendency of the carrier molecules for Y^{3+} ions.

TABLE-2
COMPARISON OF SELECTIVITY COEFFICIENTS OF YTTRIUM(III) WITH RESPECT TO VARIOUS INORGANIC IONS USING (Y^{3+}IIP) PARTICLES BASED ISE [(POLY(VINYL ALCOHOL) MEMBRANE ELECTRODE]

M^{n+}	Selectivity coefficient	M^{n+}	Selectivity coefficient
Li^+	5.0×10^{-5}	Cu^{2+}	4.0×10^{-3}
NH_4^+	6.3×10^{-5}	Zn^{2+}	3.2×10^{-3}
Ag^+	5.0×10^{-5}	Pb^{2+}	1.3×10^{-2}
Al^{3+}	7.9×10^{-6}	Cd^{2+}	1.0×10^{-2}
Ba^{2+}	4.0×10^{-3}	Ca^{2+}	1.3×10^{-3}
Mg^{2+}	2.0×10^{-3}	–	–

Stability and reusability: The important criteria required for chemical sensors in addition to selectivity are their stability and reusability. The above developed (Y^{3+}IIP) ion selective electrode was found to be stable (deviation is less than 1 mV for 5×10^{-5} M of yttrium) for 3 months and can be reused for more than 30 times without any loss in sensing ability.

Analytical application: The (Y^{3+}IIP) based ion selective electrode was applied as an indicator electrode in the potentiometric titration of 25.0 mL of 0.05 mM yttrium(III) with 10 m M EDTA solution and the results are shown in Fig. 5. As can be seen from the Fig. 5, trace amount of yttrium can be determined with the (Y^{3+}IIP) based ion selective electrode *via* potentiometric titration comparable to conventional ion selective electrods.

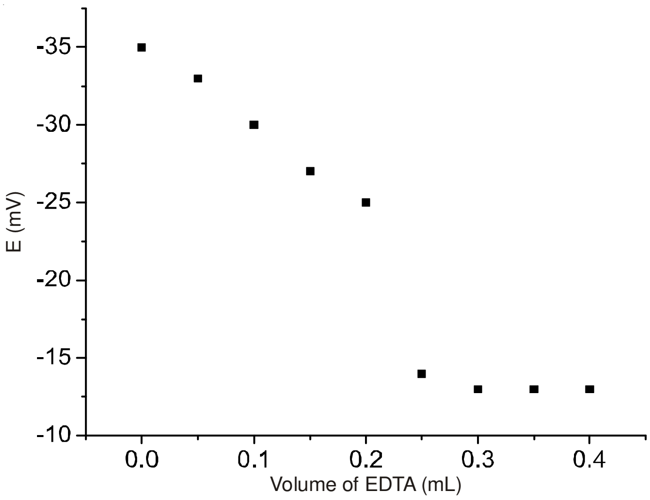

Fig. 5 Potentiometric titration curve of 25 mL of 0.05 mM yttrium(III) with 10 mM EDTA using (Y^{3+}IIP) based ion selective electrode [poly(vinyl alcohol) membrane electrode]

The ion-imprinted polymer based ion selective electrode was successfully used in the indirect potentiometric determination of Y-Al alloy sample. The results summarized in Table-3 show that the determined value of Y(III) is in well agreement with the labeled value. Furthermore, the excellent recovery results indicating the suitability of the developed procedure for routine analysis of Y-Al alloy sample.

TABLE-3
ANALYTICAL RESULTS AND RECOVERY TEST BY USING (Y^{3+}IIP) BASED ISE [(POLY(VINYL ALCOHOL) MEMBRANE ELECTRODE] (N = 6)

Sample	% of Y(III)			Recovery (%)
	Added	Found	Labelled	
Y-Al alloy		1.48 ± 0.02	1.50	
	0.50	1.99 ± 0.03		102
	1.00	2.47 ± 0.03		99

Conclusion

Potentiometric sensors for yttrium(III) ions were developed with the molecularly imprinted polymer technique. Ion selective electrods carrying these membranes are highly selective to yttrium(III) ions and require only few seconds to reach the equilibrium potential. Improved analytical features with regard to sensitivity, detection limits and selectivity are achieved by imprinting the target analyte within the copolymerization of 4-vinylpyridine and EGDMA. Further studies could be performed in order to obtain other MIP polymers of higher binding rates and specific response for yttrium(III) ions. The MIP/poly(vinyl alcohol) sensors are useful to perform the analysis of commercial samples and environmental water, both in steady state and in flow media. The potentiometric devices are simple, low cost and easy to operate. The proposed assay procedure is precise, accurate and inexpensive regarding reagent consumption and equipment involved. The tubular devices are particularly suitable for routine applications.

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