Nano-level monitoring of Er(III) by fabrication of coated graphite electrode based on newly synthesized Schiff base as neutral carrier

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Koteswara Rao Bandi, Anjali Upadhyay, Ashok K. Singh *, A.K. Jain

Department of Chemistry, Indian Institute of Technology-Roorkee, Roorkee 247667, India

ARTICLE INFO

ABSTRACT

Plasticized membranes using N-(-3-((thiazol-2-ylimino)methyl)benzylidene)thiazol-2-amine (S_1) and 5-((-3-((5-mercapto-1,3,4-thiadiazol-2-ylimino)methyl)benzylidene)amino)-1,3,4-thiadiazole-2-thiol (S_2) have been prepared and explored as Er (III) selective electrodes. Effect of various plasticizers viz. dibutylphthalate, tri-n-butylphosphate, dioctylphthalate, acetophenone, 1-chloronapthalene, o-nitrophenyloctylether, and anion excluders viz. sodium tetraphenylborate and potassium tetrakis-p-(chlorophenyl)borate was studied in detail and improved performance was observed. Optimum performance was observed for the membrane electrode having a composition of S_2: PVC: o-NPOE: KTpClPB in the ratio of 4: 38: 55: 3 (w/w, mg). The performance of the PME based on S_2 was compared with CGE. The electrodes exhibit Nernstian slope for Er (III) ion with detection limit 5.4×10^{-8} mol L^{-1} for PME and 6.1×10^{-9} mol L^{-1} for CGE. The response time for PME and CGE was found to be 12 s and 9 s respectively. The practical utility of the CGE has been demonstrated by its usage as an indicator electrode in potentiometric titration of EDTA with Er (III) solution and determination of fluoride ions in mouthwash solution. The proposed electrode was also applied to the determination of added Er^{3+} ion in water and binary mixtures. It is found that the electrode could be able to recover the Er^{3+} ion in 96.2–99.5%.

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1. Introduction

The rare earth elements (REEs) are mainly of two series Lanthanides and Actinides. Despite of their name REEs are not so rare in environment, they widely distributed in throughout the earth's crust in low concentration [1]. The REEs have significant industrial application as competitive to transition elements and wide application have been found in bioinorganic, inorganic chemistry. Erbium is mainly used as laser beams to resurfacing skin, transdermal drug delivery, transdermal peptide delivery, skin vaccination and enhances the RNA delivery [2–5]. It is estimated that the erbium concentration of the earth's crust reaches 24 ppm. The commercial sources of erbium are monazite and bastnasite. Even though the

conclusion of the investigators, the rare earth elements are considered as low acute toxicity rating, these causes several problems to living species [6,7]. Due to their enhanced discharge, toxic properties and other adverse effects, determination of erbium is essential in a variety of environmental samples.
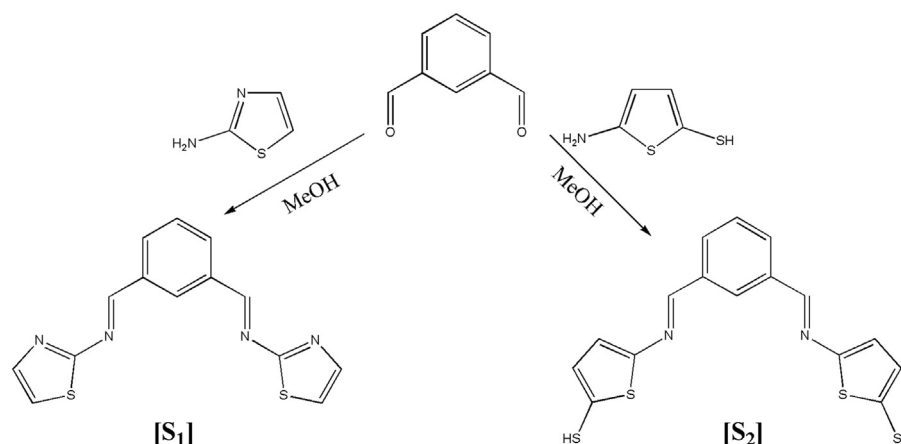
A number of instrumental techniques such as second order derivative spectrophotometry [8], third-derivative spectrophotometry [9], X-ray fluorescence [10], graphite furnace atomic spectrometry techniques [11], inductively coupled plasma mass spectrometry [12], Rutherford backscattering spectrometry [13], and spectrophotometric determination [14] are available for its estimation. These methods provide accurate determination of erbium content but involve large infrastructure backup and support of expertise. These requirements make complicated for such a technique to be used in regular manner for the analysis of large number of samples. For such a purpose analytical technique which is portable, fast and low cost is the evident option. Such requirements are usually met by ion selective electrodes.

Ion selective electrodes can analyze large number of samples virtually in small time, in the presence of different interferents and can even be adapted to online monitoring. In view of vital advantages of ion selective electrodes (ISE's) for exploration, a number of good ISE systems have become commercially accessible for an assortment of chemical species. A number of ISE's for estimation of erbium concentration have also been recently reported [15–25]. Although these sensors

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Scheme 1. Structure of ligands N-(-3-((thiazol-2-ylimino)methyl)benzylidene)thiazol-2 amine (S₁) and 5-((-3-((5-mercapto-1,3,4-thiadiazol-2-ylimino)methyl)-benzylidene)amino)-1,3,4-thiadiazole-2-thiol (S₂).

are useful in the determination Er^{3+}, there are some shortcomings in the characteristic properties such as narrow working concentration range, non Nernstian potential response, narrow pH range, high detection limit and high response time. Thus there is a need to prepare the sensor with high sensitivity and selectivity. Ionophore plays main role in the sensitivity and selectivity of ion-selective electrode. A good ionophore shows strong affinity for a particular ionic species and poor for others. Different group of compounds such as heterocycles [26], porphyrins [27], macrocycles [28], calixarenes [29], solid electrodes [30], nanoparticles [31] have been used as ionophore. The difficulty in the development of ISE is that good ionophores are not available. Thus we aimed to synthesize novel Schiff bases having multiple binding sites and with the advancement of chemical research, novel multidentate Schiff bases (N-(-3-((thiazol-2-ylimino)methyl)benzylidene)thiazol-2-amine (S₁) and 5-((-3-((5-mercapto-1,3,4-thiadiazol-2-ylimino)methyl)benzylidene)amino)-1,3,4-thiadiazole-2-thiol (S₂)) were synthesized (Scheme 1).

Preliminary complexation study of these Schiff bases has shown that they form stable complexes with only erbium and weak complexes with other metals, which indicating the strong affinity for erbium and poor for other metals. Thus the polymeric membrane electrode and coated graphite electrodes were prepared using the Schiff bases (S₁ and S₂) and the performance characteristics were compared. From the electoanalytical studies, it was found that the PME based on S₂ is showing good results, which might be due to the presence of extra thiol group. The extra thiol group is expected to facilitate the more binding capacity towards Er^{3+} ion.

2. Experimental

2.1. Reagent

Reagent grade sodium tetraphenylborate (NaTPB), potassium tetrakis p-(chloro phenyl)borate (KTpClPB), dibutylphthalate (DBP), dioctyl-phthalate (DOP), acetophenone (AP), 1-chloronapthalene (1-CN), o-nitrophenyloctyl ether (o-NPOE), tri-n-butylphthalate (TBP), tetrahydrofuran (THF) and high molecular weight poly(vinylchloride) were procured from E. Merck (Germany) and used without any further purification. 1,3-Benzenedicarboxaldehyde, 5-amino-1,3,4-thiadiazole-2-thiol and thiazol-2-amine were obtained from Sigma Aldrich, Delhi, India. The nitrate and chloride salts of all the cations used were of analytical grade and used without any further purification. The solutions of metal salts were prepared in doubly distilled water and standardized whenever necessary.

2.2. Synthesis

2.2.1. Synthesis of Schiff base N-(-3-((thiazol-2-ylimino)methyl) benzylidene)thiazol-2-amine (S₁) and 5-((-3-((5-mercapto-1,3,4-thiadiazol-2-ylimino)methyl)benzylidene)amino)-1,3,4-thiadiazole-2-thiol (S₂)

0.1341 g (1 mmol) of 1,3-Benzenedicarboxaldehyde was dissolved in 15 mL of methanol. To this 15 mL of methanolic solution of amine (thiazol-2-amine (0.2002 g, 2 mmol) for the synthesis of S₁ and 5-amino-1,3,4-thiadiazole-2-thiol (0.2663 g, 2 mmol) for the synthesis of S₂) was added drop wise with continuous stirring and the stirring was continued for 1 h. The resulting mixture was refluxed for 2–3 h at 60 °C, the volume of the solution was reduced to half and kept for crystallization. The product was filtered and further purified by column chromatography (ethyl acetate/hexane).

S₁; Yield: 67%. Anal. Calc. for $C_{14}H_{10}N_4S_2$: C, 56.35; H, 3.38; N, 18.78; S, 21.49. Found: C, 56.09; H, 3.45; N, 18.54; S, 21.92. IR (KBr, cm⁻¹) 1583 ($-C = N$), ¹H NMR (CDCl₃, 500 M Hz): δ 7.43 (m, 3H), 7.86 (d, 2H), 7.99 (d, 2H), 8.62 (s, 1H), 8.94 (s, 2H).

S₂; Yield: 71%. Anal. Calc. for $C_{12}H_8N_6S_4$: C, 39.59; H, 2.21; N, 23.06; S, 35.19 Found: C, 39.24; H, 2.37; N, 22.88; S, 35.51. IR (KBr, cm⁻¹) 1613 ($-C = N$). ¹H NMR (CDCl₃, 500 M Hz): δ 7.36 (m, 1H), 7.91 (d, 2H), 8.42 (s, 1H), 8.68 (s, 2H), 8.72 (s, 2H).

2.3. Electrode preparation

It is well known that the performance of an ion selective electrode depends to a great extent on the composition of its membranes. Therefore the membranes were optimized by varying the composition of membrane ingredients such as ionophore, plasticizer, additive and PVC. The ionophore (S₁ and S₂), PVC, cation excluder (NaTPB/KTpClPB) and different plasticizers (o-NPOE, DBP, 1-CN, TBP, DOP and AP) were dissolved in 2 mL of THF in different relative amounts. The volume of the solution was reduced to half by continuous stirring with a glass rod. A homogeneous viscous solution was obtained, it was poured into an acrylic ring placed on a clean and smooth glass plate. The solution was allowed to stand overnight which resulted in the slow evaporation of THF. The evaporation of THF resulted in the form of a transparent membrane of 0.1 mm thickness and 1 cm diameter. The membrane was removed carefully and attached to end of a pyrex tube with araldite. In this way, different membranes were prepared by varying the composition of membrane ingredients and its electrochemical behavior was studied. The membranes were equilibrated with 0.01 M ErCl₃ solutions for 2 days.