A Nano-composite Modified Carbon Paste Europium(III) Sensor

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Based on our previous study which indicates a strong interaction between bis(thiophen)buyane 2,3-dihydrazone (SNSB) and Eu(III) ions, SNSB was used as a sensing element in a nano-composite modified carbon paste electrode. The nano-composite electrodes were made based on multi-walled carbon nanotube (MWCNT), nanosilica (NS), graphite, and room temperature ionic liquid (RTIL), 1-n-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF_4. The best results were obtained for the nano-composite sensor with electrode composition of 2%NS, 5% MWCNT, 15% SNSB, 15% RTIL, and 63% graphite powder. The proposed sensor shows a Nernstian response (19.9±0.2 mV decade^{-1}) in the range of 1.0×10^{-6}-1.0×10^{-2} M with a detection limit of 4.0×10^{-7} M. The response of the sensor is independent of pH in the range of 3.5-9.0. The nano-composite based Eu(III) sensor displayed good selectivity, response time, and lifetime.

1. INTRODUCTION

Lanthanides are used in production of glass and ceramic industry, metallurgy, electronics, and agriculture and natural sciences. Lanthanide ions are becoming very important in different industries and biology [1]. Europium (Eu), one of the lanthanide members, is found to have many applications as a fluorescent agent in anodic rays of television and monitor screens. The available methods for low-level determination of Eu(III) ions in solution include spectroscopy, mass spectrometry (MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS), isotope dilution mass spectrometry, neutron activation analysis, and X-

ray fluorescence spectrometry [2-8]. These methods are either time-consuming, involving multiple sample manipulations, or too expensive for most analytical laboratories. On the contrary, neutral carrier-based ion-selective electrodes (ISEs) can offer an inexpensive and convenient analysis method of rare-earth ions in solution, provided that the acceptable sensitivity and selectivity are achieved.

Potentiometric sensors have shown to be very effective tools for analysis of a wide variety of metal ions [9-11]. They are very simple, fast, inexpensive, and capable of reliable response in wide concentration ranges. PVC membrane electrodes and microelectrodes, coated wires, and carbon paste electrodes are different types of potentiometric sensors. Among them, carbon paste electrodes (CPEs) have attracted interest as a result of their improved renewability, stable response, and low ohmic resistance compared to membrane electrodes [12-14]. In general, CPE-based potentiometric sensors reported are based on incorporation of a selective agent into the carbon paste. The typical carbon paste consists of graphite powder dispersed in a non-conductive mineral oil. Incorporation of mineral oil gives CPEs some disadvantages. Mineral oil is not component-fixed since it is derived from refining of petroleum and processing of crude oil. Thus, contaminants or matrix components may unpredictably influence detection. The mechanical stability of CPEs places between membrane electrodes and all solid state electrodes. In recent decade a number of potentiometric sensors for Eu(III) and other lanthanide ions have been reported using different sensing materials [15-43].

Recently, room temperature ionic liquids (RTIL) with a number of favorite properties such as good solvating properties, high conductivity, non-volatility, low toxicity, good electrochemical and chemical stability, low vapor pressure, low toxicity, low melting temperature, high ionic conductivity were used as binder in CPEs [44–51].

Addition of multiwall carbon nanotubes (MWCNTs) with special physicochemical properties such as ultra-light weights, high mechanical strengths, high electrical conductivities, high thermal conductivities, metallic or semi-metallic behaviors and high surface areas to CPEs, causes improvement of response of this type of sensor [48-52]. In this work a highly selective nano-composite Eu(III) modified carbon paste sensor base on SNSB as sensing material for monitoring of micromolar europium ion is introduced.

2. EXPERIMENTAL SECTION

2.1. Apparatus

The cell used for the potential measurements of the nano-composite based Eu(III) sensor as the indicator electrode and an Ag/AgCl electrode (Azar electrode, Iran) as a reference electrode both of which were connected to a mili-voltmeter.

The cell assembly constructed for the conduction of the electromotive force (Emf) measurements is as follows; Nano-composite based sensor | sample solution | Ag/AgCl–KCl (satd.)

2.2. Reagents and materials

Graphite powder with a 1–2 μm particle size (Merck) and high-purity paraffin oil (Aldrich) were used for construction of the carbon pastes. The ionic liquid (1-n-butyl-3-methylimidazolium

tetrafluoroborate ([bmim]BF$_4$) and chloride and nitrate salts of the cations were purchased from Merck and used as received. The multi-walled carbon nanotubes (MWCNTs) with 10-40 nm diameters, 1-25 µm length, SBET: 40-600 m^2/g and with 95% purity were purchased from Research Institute of the Petroleum Industry (Tehran, Iran). Ionophore SNSB was synthesized as described elsewhere [36]. The nanosilica used is Wacker HDK$^®$ H20 with BET surface of the hydrophilic silica of 170-230 m^2/g. Distilled deionized water was used throughout all experiments.

2.4. Electrode Fabrication

The modified CPEs were prepared through a general procedure as follows: The desired amounts of the ionophore SNSB along with an appropriate amount of graphite powder, nano silica, ionic liquid or paraffin oil and MWCNTs were thoroughly mixed. The resulting mixture was transferred into a glass tube of 5 mm i.d. and a height of 3 cm. The mixture was then homogenized before being packed into the tube tip to avoid possible air gaps which can increase the electric resistance of the electrodes. A copper wire was then inserted into the opposite end of the modified CPE to establish electrical contact. The external surface of the carbon paste was smoothed with soft paper. A new surface was produced by scraping out the old surface and replacing the new carbon paste. The electrode was finally conditioned for 72 h by soaking it in a 1.0×10^{-3} M EuCl$_3$ solution [49-51].

3. RESULTS AND DISCUSSION

3.1. Optimization of the CPEs

The sensing material or ion carrier used as the main ingredient of any ion-selective sensors is known to strongly influence the selectivity of such devices [15-25].
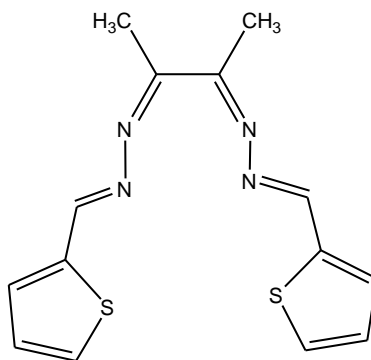

Figure 1. Chemical structure of SNSB

SNSB (Fig. 1) was used in fabrication a series of nano-composite CPEs with a variety of compositions some of which were modified using the ionic liquid, NS and MWCNT. The

compositions of these sensors are given in Table 1. As can be seen from Table 1, in the absence of the ionophore SNSB (compositions 1-3) in the composition of the carbon paste electrode, the responses of the sensors are very weak. It was also observed that changing the amounts of the graphite powder as the filler and RTIL as binder, does not significantly change the potential response of the sensor.

The addition of ionophore 5-20% to the composition of carbon paste electrodes increases the potential responses of the CP electrodes (composition 4-7). As can be seen from Table 1, addition of 15% SNSB to CP electrode shows the best response. In this case an increasing in the slope of CP electrode from 2.7 ± 0.2 to 17.7 ± 0.2 mV decade^{-1} was shown. However, the slope of the sensor is sub-Nernstian. This improvement in slope of the sensor is due to the selective tendency of SNSB towards Eu(III) ions. As seen from Table 1, further addition of the ionophore to 20% wt. (no. 7), however, did not lead to any changes in the response of the electrode.

As can be seen from Table 1 unmodified CPEs having the optimized composition (electrode no. 6) shows a sub-Nernstian slope of ~17.7 mV decade^{-1} of Eu(III) activity. The electrode compositions were modified by adding %3, %5 and %7 wt. of MWCNT to the composition (Nos. 8-10) which led to improvements in the sensitivity of the sensor from the sub-Nerstian value of 17.7 ± 0.3 mV decade^{-1} to 19.8 ± 0.2 mV decade^{-1}. This is most probably due to improving the conductivity of the composition, which in turn changes the chemical signal to an electrical one. As seen from Table 1, additional of MWCNT (no.10) in CPE composition has not any effect on sensitivity of the Eu(III) sensor.

Table 1. The optimization of the nano-composite based Eu(III) carbon paste ingredients

No.	Composition (%)					Slope (mV decade^{-1})	Linear range (M)
	Graphite	RTIL	SNSB	MWCNT	NS		
1	90	10	-	-	-	2.5 ± 0.2	$1.0 \times 10^{-2} - 4.0 \times 10^{-4}$
2	85	15	-	-	-	2.7 ± 0.3	$1.0 \times 10^{-2} - 4.0 \times 10^{-4}$
3	80	20	-	-	-	2.7 ± 0.2	$1.0 \times 10^{-2} - 4.0 \times 10^{-4}$
4	80	15	5	-	-	14.1 ± 0.1	$1.0 \times 10^{-2} - 2.0 \times 10^{-5}$
5	75	15	10	-	-	16.3 ± 0.2	$1.0 \times 10^{-2} - 1.0 \times 10^{-5}$
6	70	15	15	-	-	17.7 ± 0.2	$1.0 \times 10^{-2} - 5.0 \times 10^{-6}$
7	65	15	20	-	-	17.7 ± 0.3	$1.0 \times 10^{-2} - 5.0 \times 10^{-6}$
8	67	15	15	3	-	18.9 ± 0.3	$1.0 \times 10^{-2} - 3.0 \times 10^{-6}$
9	65	15	15	5	-	19.8 ± 0.2	$1.0 \times 10^{-2} - 1.0 \times 10^{-6}$
10	63	15	15	7	-	19.8 ± 0.3	$1.0 \times 10^{-2} - 1.0 \times 10^{-6}$
11	63	15	15	5	2	19.9 ± 0.2	$1.0 \times 10^{-2} - 1.0 \times 10^{-6}$
12	62	15	15	5	3	19.9 ± 0.3	$1.0 \times 10^{-2} - 1.0 \times 10^{-6}$

As can be seen from Table 1, addition of nanosilica to the modified CPE (nos. 11,12) causes an increasing in the slope from 19.8 to 19.9 mV decade^{-1}.

However, as can be seen from Table 1 a composition of 15% SNSB, 15% [bmim]BF$_4$, 63% graphite powder, 5% MWCNT and 2% nanosilica was chosen as the optimum composition showing a Nernstian slope of 19.9±0.2 mV decade^{-1}.

3.2. Measuring range and detection limit

The potential response of the nano-composite based Eu(III) CPE (no. 11) was further tested in Eu(III) ion concentration range of 1.0×10^{-1}-1.0×10^{-8} M and the results are illustrated in Fig. 2.
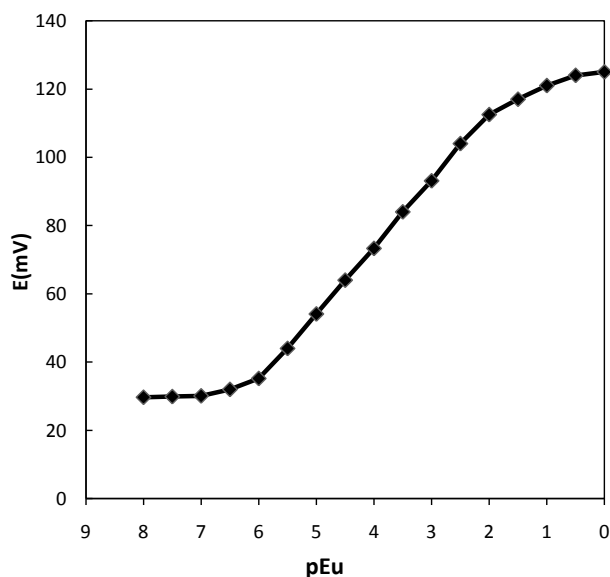

Figure 2. The calibration curve of the Eu(III) nano-composite modified CPE based on SNSB (Electrode no. 11)

As it is well known in the literature the measuring range of the CPE is defined as the activity range between its upper and lower detection limits. The applicable range of the CPE with a composition according to no. 11 ranges from 1.0×10^{-2}-1.0×10^{-6} M (Fig. 2).

To calculate the detection limits of the CPE extrapolation of the linear portion of the electrode's calibration curve was used and this parameter found to be 4.0×10^{-7} M.

3.3. Effect of pH

The influence of pH of the solution on the potential response of the best nano-composite CPE (no. 11), was evaluated by recording of the potentials which shown by the proposed sensor in a 1.0×10^{-3} M Eu(III) ion solution while varying the pH values. For having different pH of the solution (2.0-12.0) concentrated HNO$_3$ or NaOH was used.
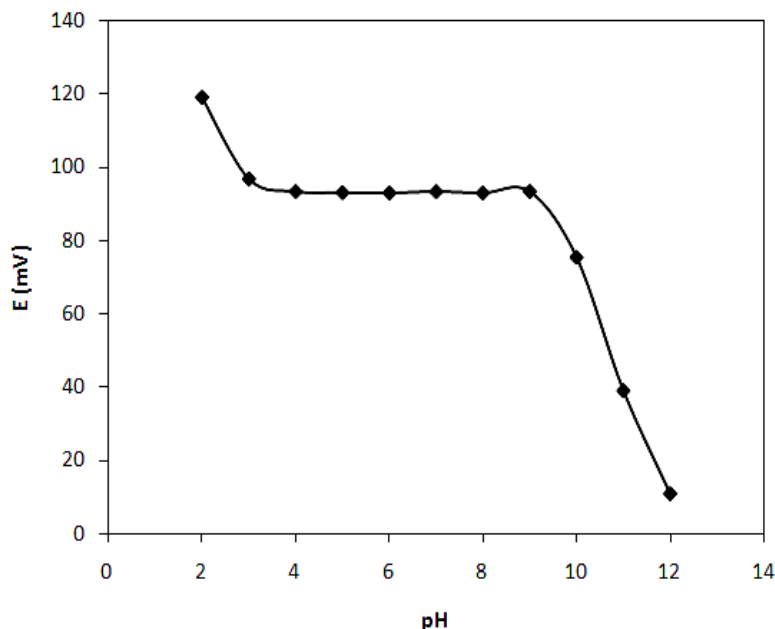
Figure 3. Effect of pH on the potential response of the Eu(III) nano-composite CPE based on (Electrode no. 11) in the test solution of Eu(III) ion (10^{-3} M)

The recorded potentials as a function of pH are shown in Fig. 3. As seen from Fig. 3, the potential responses of the nano composite modified Eu(III) carbon paste electrode is constant in the pH range of 3.5-9.0. Potential drifts at higher pH values than 9.0 are due to the formation of some soluble or insoluble lanthanum hydroxy complexes. At lower pH values than 3.5 potential drifts is due to partial protonation of the donor atoms of SNSB in the modified CPE [36].

3.4. Response time

In analytical application, response time of an electrochemical sensor is very important. It is evaluated through measuring the average time required to achieve potential values within ±0.1 mV of the steady-state potential of the electrode after its immersion in a series of solutions of the target ions, each having a ten-fold difference in concentration [27-30]. A numbers of experimental parameters such as temperature of testing solution, type and speed of stirring, the concentration and composition of each test solution, and preconditioning of the electrode can affect the response time of any sensor [9-11]. The response time of the proposed nano-composite CPE was less than 10 s for whole concentrations of Eu(III) ions.

3.5. Selectivity of the sensor

Selectivity coefficients for any sensor, specially in the case of concentration determination of the target ion in the presence of a number of other ions with higher concentration than target ion is very important.

Table 2. The selectivity coefficients of various interfering cations for electrode no. 11; concentration of the reference solution of Eu(III) ion was 5.0×10^{-6} M and the concentration of interfering ions was between 1×10^{-4} to 1.0×10^{-1} M

Cation	Selectivity Coefficient	Cation	Selectivity Coefficient
Li^+	1.2×10^{-5}	Gd^{3+}	1.5×10^{-2}
Na^+	1.6×10^{-5}	Yb^{3+}	7.7×10^{-4}
K^+	1.9×10^{-5}	Tb^{3+}	1.0×10^{-2}
Mg^{2+}	2.2×10^{-5}	La^{3+}	1.1×10^{-2}
Ca^{2+}	3.4×10^{-5}	Sm^{3+}	2.0×10^{-2}
Cu^{2+}	5.5×10^{-4}	Dy^{3+}	7.7×10^{-4}
Pb^{2+}	8.4×10^{-4}	Pr^{3+}	2.4×10^{-4}
Co^{2+}	5.1×10^{-4}	Lu^{3+}	5.5×10^{-4}
Zn^{2+}	3.4×10^{-4}	Ce^{3+}	1.2×10^{-2}
Tm^{3+}	9.1×10^{-4}		
Er^{3+}	8.8×10^{-4}		
Nd^{3+}	9.3×10^{-4}		
Ho^{3+}	8.3×10^{-4}		

For the present work matched potential method (MPM) was used for evaluation of selectivity coefficients [53-57] of the nano-composite modified CPE and the results are depicted in Table 2. As can be seen from Table 2, the selectivity coefficients of the proposed sensor for a number of mono, di and teivalents cations were determined and results showed the obtained selectivity coefficients are smaller than 2.5×10^{-2}. The obtained selectivity coefficien indicate that interference effects upon the performance of the electrode assembly are relatively low.

3.6. Lifetime of the Sensor

Life time is one of the imprtant factor for any sensor. Litherature survey revealed that for most ion selective sensors, lifetimes range are between 4–10 [49-51]. After this time, a significant change will observed in the slope and detection limt of the sensor. The lifetime of the proposed nano-composite base Eu(III) sensor was evaluated for a period of 15 weeks, during which the sensor was used for two hours per day. The changes in the slope and detection limit of the modified CPE were measured and the results are given in Table 3. As can be seen from Table 3, the proposed nano-composite Eu(III) sensor can be used for at least 13 weeks. without significant changes on its slope and detection limits. After 13 weeks, this time, a significant decreasing in the slope from 19.9±0.2 to 17.3±0.1 mV decade^{-1} and a gradual increasing in detection limit from 4.0×10^{-7} to 1.5×10^{-6} was

observed. This phenomenon is most probaly due to the loss of RTIL and SNSB from the composition of the fabricated nano composite modified Eu(III) carbon paste electrode.

Table 3. Lifetime of Eu(III) nano-composite modified CPE

Week	Slope (mV decade^{-1})	DL (M)
1	19.9 ± 0.2	4.0×10^{-7}
2	19.8 ± 0.3	4.3×10^{-7}
3	19.7 ± 0.1	4.2×10^{-7}
4	19.8 ± 0.3	4.5×10^{-7}
5	19.8 ± 0.2	4.5×10^{-7}
6	19.7 ± 0.3	4.9×10^{-7}
7	19.8 ± 0.1	4.8×10^{-7}
8	19.7 ± 0.2	5.1×10^{-7}
9	19.6 ± 0.1	5.0×10^{-7}
10	19.7 ± 0.3	5.5×10^{-7}
11	19.6 ± 0.1	5.8×10^{-7}
12	19.7 ± 0.3	6.2×10^{-7}
13	19.6 ± 0.2	6.4×10^{-7}
14	17.3 ± 0.1	1.5×10^{-6}
15	14.1 ± 0.1	8.5×10^{-6}

4. CONCLUSION

According to our previous study, which indicates a strong interaction between bis(thiophen)buyane 2,3-dihydrazone (SNSB) and Eu(III) ions, SNSB was used as a suitable ionophore in a nano-composite modified carbon paste electrode. The composite paste was made of multi-walled carbon nanotube (MWCNT), graphite, and room temperature ionic liquid (RTIL) as a suitable binder. The best result was obtained in nano-composite electrode composed of 2%NS, 5% MWCNT, 15% SNSB, 15% RTIL, and 63% graphite powder. The proposed sensor shows a Nernstian response (19.9 ± 0.2 mV decade^{-1}) in the range of 1.0×10^{-6}-1.0×10^{-2} M with detection limit of 4.0×10^{-7} M. The response of the sensor is pH independent in the range of 3.5-9.0. The nano-composite based Eu(III) sensor displayed good selectivity, response time (about 10 s), and lifetime (13 weeks).

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