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MWCNT-NH_2/Nanosilica/RTIL/Ionophore Nanocomposite Carbon Paste Electrode For Nd(III)

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Given the results of our previous studies indicating a relatively strong interaction between 2-{[(6-aminopyridin-2-yl) imino] methyl}-phenol (APIMP) and Nd(III) ions, the ligand was incorporated, as the sensing material, into a nano-composite carbon paste electrodes which were prepared using functionalized multi-walled carbon nanotube (MWCNT-NH_2), nanosilica (NS), graphite, and an room temperature ionic liquid namely 1-n-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF_4 (RTIL). The electrodes composed of 2%NS, 5% MWCNT-NH_2, 20% APIMP, 20% RTIL, and 53% graphite powder were found to show the optimum behavior. The sensor shows a Nernstian response of (19.8±0.12 mV decade^{-1}) in the concentration window of 1.0×10^{-6}-1.0×10^{-2} M with a detection limit of 8.0×10^{-7} M. The response of the sensor was found to be stable in the pH of 4.0-8.0 and the nano-composite based Nd(III) sensors displayed good selectivity with respect to a number of lanthanide and transition metal ions as well as a rather long lifetime.

Keywords: Neodymium, sensor, ion selective electrode, potentiometry, carbon paste, functionalized multi walled carbon nanotubes, ionic liquid, nanosilica

1. INTRODUCTION

Lanthanide elements have a vast applications ranging from the production of glass and ceramic industry, to metallurgy electronics, and agriculture. Neodymium is one of the several metals in alloys commonly used in lighter flints. Neodymium is generally used for coloring glass in the manufacture of the green color removal caused by iron contaminants from glass. Regarding the neodymium salts, they are used as colorants for enamels and in powerful permanent magnets such as $Nd_2Fe_{14}B$. These magnets are cheaper, lighter and stronger than samarium–cobalt magnets. Neodymium magnets appear in high-quality products such as microphones, professional loudspeakers, in-ear headphones and computer hard disks, where low weight and reduced size or powerful magnets are required [1,2].

The conventional methods for the determination of low-levels of Nd(III) ions in solutions include 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 [3-8] being either time-consuming, involving multiple sample manipulations, or too cost-intensive for most analytical laboratories.

On the other hand application of carrier-based ion-selective electrodes (ISEs) can offer inexpensive and convenient analyses methods for different anions and cations [9-11] including rare-earth ions, if the used sensors enjoy levels acceptable sensitivity and selectivity.

These devices in comparison with other advance electrochemical techniques [12] also have the benefits of being simple to use, fast, inexpensive, and capable of producing reliable responses in wide ranges of concentration. A very rough classification of the conventional ISEs divides them into the groups of PVC membrane electrodes, microelectrodes, coated wire electrodes, and carbon paste electrodes, among which carbon paste electrodes (CPEs) have currently attracted a great deal of interest due to their improved renewability, stable response, and low ohmic resistance as compared to the other members of the family [13-15].

CPE-based potentiometric sensors reported are generally based on the incorporation of the ion carrier into a carbon paste matrix, which consists of graphite powder dispersed in a non-conductive mineral oil. Due to the fact that mineral oils do not have a fixed composition, the classic CPE electrodes suffer some disadvantages caused by the contaminants or matrix components. CPEs can be placed between membrane electrodes and all solid state electrodes, in terms of mechanical stability.

Regarding the increasing number of potentiometric sensors for Nd(III) and other ions as using different sensing materials [16-39], and in case the aforementioned problems are dealt with effectively, it would be an important breakthrough in the field to develop such sensors in the form of CPEs.

Room temperature ionic liquids (RTIL), which have a number of interesting properties including their 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 have recently been used as binders in the construction of CPEs which seems to have solved the problems of using mineral oils [40-44].

Addition of functionalized multiwall carbon nanotubes (F-MWCNT) with special physicochemical properties of ultra-low weight, high mechanical strength, high electrical conductivities, high thermal conductivity, metallic or semi-metallic behaviors and high surface areas to CPEs, has also been found to cause improvement in the response of such sensors [45-48].

In this work a highly selective modified nano-composite carbon paste sensor based on APIMP as the sensing material has been developed and tested for the monitoring of Nd(III).

2. EXPERIMENTAL SECTION

2.1. Apparatus

The electrochemical cell used for the determination of EMF the included the Nd(III) sensor as the indicator electrode and an Ag/AgCl electrode (Azar electrode, Iran) as the reference electrode and had a format as below:

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 the 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 Co. and were used without further treatment. The NH_2- functionalized multi-walled carbon nanotube (MWCNT-NH_2) sample used was synthesized as described elsewhere [49]. APIMP was prepared as described elsewhere [50]. The nanosilica used was purchased from Wacker HDK®H20 and BET of the hydrophilic silica was 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: Desired amounts of APIMP, graphite powder, nano silica, ionic liquid or the paraffin oil and MWCNT-NH_2s were thoroughly mixed and then transferred into a glass tube (5 mm i.d. and 3 cm in length). To avoid the formation of air gaps in the structure of the CPE, the mixture was then homogenized before being packed into the tube tip. This can help avoid unwanted increases in the electric resistance of the electrodes. Next copper wire was inserted into the opposite end act as an electrical contact and the external surface of the CPE was cleaned with soft abrasive paper, which was repeated prior to any measurement. The electrode was finally rested for 48 h by being soaked in a 1.0×10^{-3} M $NdCl_3$ solution [45-47, 51].

3. RESULTS AND DISCUSSION

3.1. Optimization of the CPEs

The ionophore (here APIMP) is the main ingredient of any ISE which determines the selectivity of such devices [52-56]. To test the selectivity of APIMP (Fig. 1) as well as the role of the composite concentration on its behavior, the ionophore was used to fabricate a series of nano-composite CPEs having a variety of compositions, some of which were modified using the ionic liquid, NS and MWCNT-NH_2 according to Table 1.

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

No.	**Composition (%)**					**Slope (mV decade^{-1})**	**Linear range (M)**
	Graphite	RTIL	APIMP	MWCNT-NH$_2$	NS		
1	90	10	-	-	-	1.9 ± 0.2	1.0×10^{-2} - 4.0×10^{-4}
2	85	15	-	-	-	2.4 ± 0.1	1.0×10^{-2} - 4.0×10^{-4}
3	80	20	-	-	-	2.6 ± 0.3	1.0×10^{-2} - 4.0×10^{-4}
4	75	25	-	-	-	2.6 ± 0.2	1.0×10^{-2} - 2.0×10^{-4}
5	75	20	5	-	-	15.1 ± 0.2	4.0×10^{-2} - 1.0×10^{-5}
6	70	20	10	-	-	17.3 ± 0.1	3.0×10^{-2} - 5.0×10^{-6}
7	65	20	15	-	-	18.0± 0.3	1.0×10^{-2} - 5.0×10^{-6}
8	60	20	20	-	-	18.6 ± 0.2	1.0×10^{-2} - 3.0×10^{-6}
9	55	20	25	-	-	18.6 ± 0.1	1.0×10^{-2} - 1.0×10^{-6}
10	58	20	20	2	-	19.3 ± 0.2	1.0×10^{-2} - 1.0×10^{-6}
11	56	20	20	4	-	19.6 ± 0.1	1.0×10^{-2} - 1.0×10^{-6}
12	55	20	20	5	-	19.7 ± 0.2	1.0×10^{-2} - 1.0×10^{-6}
13	54	20	20	5	2	19.8 ± 0.2	1.0×10^{-2} - 1.0×10^{-6}
14	53	20	20	5	3	19.8 ± 0.2	1.0×10^{-2} - 1.0×10^{-6}

As can be seen from the data, the CPEs lacking APIMP (compositions 1-4), did not show any considerable responses of the concentration changes of the target ion (from 1.9±0.2 to2.6±0.2 mV decade^{-1}. Even changing the amount of the graphite powder as the filler and RTIL as the binder did not significantly affect the potential response.

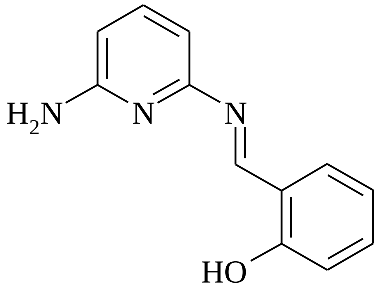

Figure 1. Chemical structure of APIMP

Upon the addition of the ionophore, in amounts of 5-25%, to the composition of carbon paste electrodes considerable increases in the potential response of the CP electrodes (composition 5-9) was observed and presence of 20% of APIMP to CP electrode was found to lead to a very good response behavior, increasing the potential response from 2.6±0.2 to 18.6±0.1 mV decade^{-1}. The response was still sub-Nernstian which was not improved by the further increase in the amount of the ionophore up to 25% wt. (no. 9). But the addition of 2-5% wt of MWCNT-NH$_2$ (Nos. 10-12) was found to improve the potential response to 19.3 ±0.2 and 19.7± 0.2 mV decade^{-1} of Nd(III) activity respectively. There is no need to mention that this was equivalent to reducing the amount of the graphite powder in the composition. This is most probably due to the improvements in the conductivity of the CPEs.

Further addition of 2% and 3% wt of nanosilica (NS) to the CPEs (nos. 13,14) was found to cause increases in the slope from 19.7 to 19.8 mV decade^{-1}.

Eventually, as can be concluded from the data in Table 1 a composition of 20% APIMP, 20% [bmim]BF_4, 53% graphite powder, 5% MWCNT-NH_2 and 2% nanosilica (no. 13) leading to CPEs with a Nernstian slope of 19.8±0.2 mV decade^{-1}, was chosen concluded to be optimum.

3.2. Measuring range and limit of detection

The response of the CPE with the optimum composition (no. 13) was examined in a range of 1.0×10^{-1}-1.0×10^{-8} M and the results are depicted in Fig. 2.

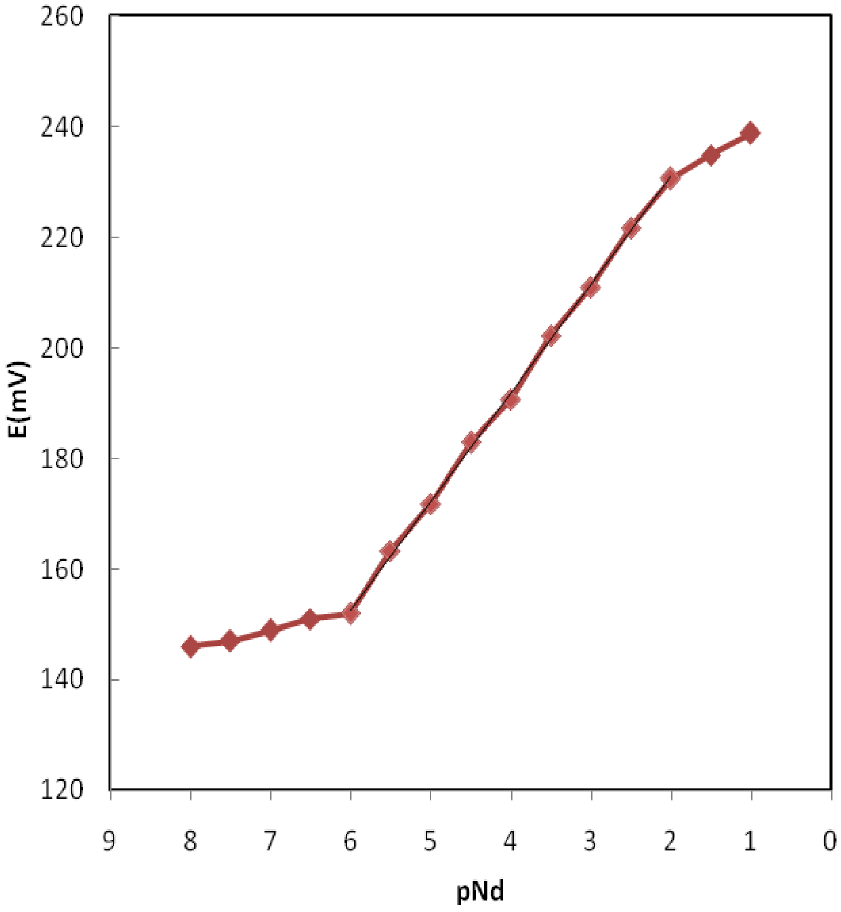

Figure 2. The calibration curve of the Nd(III) nano-composite modified CPE based on APIMP (Electrode no. 13)

The results show that the CPEs have a linear response behavior in the concentration range of 1.0×10^{-2}-1.0×10^{-6} M (Fig. 2). Further, the detection limit of the CPE was evaluated by extrapolating the linear portions of the electrode's calibration curve and was found to be 8.0×10^{-7} M.

3.3. pH Influence

The effect of the pH of the test solution on the response behavior of CPEs with the optimum composition was studied by monitoring the potential response of the sensor in 1.0×10^{-4} and 1.0×10^{-5} M Nd(III) solutions while varying the pH values in the range of 1.0-12.0 through adding concentrated HNO_3 or NaOH.

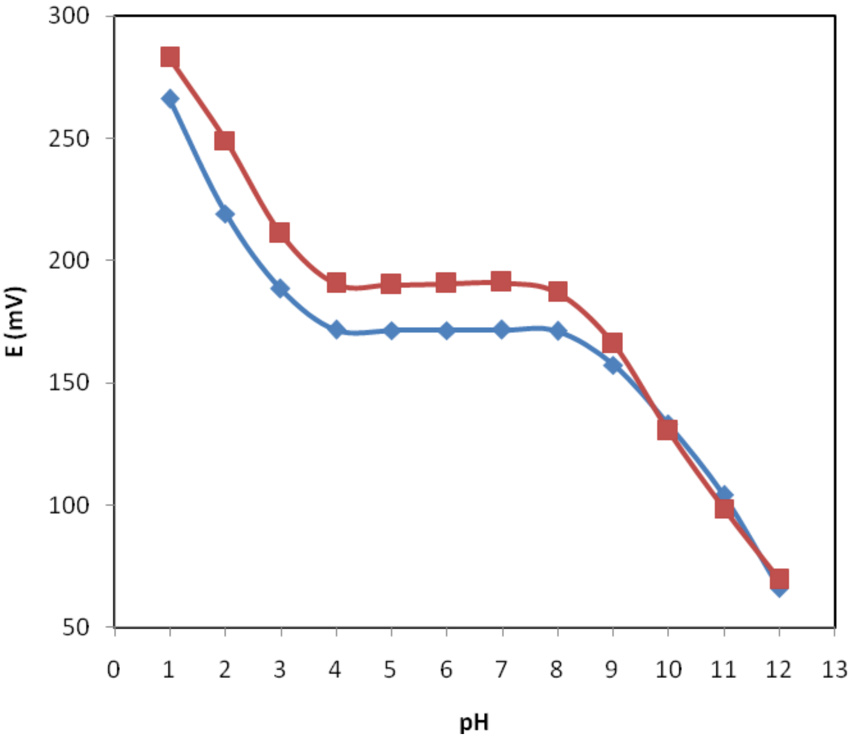

Figure 3. Effect of pH on the potential response of the Nd(III) nano-composite CPE based on (Electrode no. 13) in the test solution of Nd(III) ion (10^{-4} and 10^{-5} M)

The results as depicted in Fig. 3 reveal that the potential response of the Nd(III) CPEs are pH-independent in the range of 4.0-8.0. Potential drifts at higher pH values are attributed to the formation of soluble or insoluble Nd(III) hydroxy complexes and/or precipitates. At pH values less than 4.0 the potential drifts most probably due to partial protonation of the donor atoms in APIMP.

3.4. Response time

The response time of the CPEs was evaluated through studying the average time the CPEs took to produce potential values within ±0.1 mV of their steady-state potentials upon their immersion in a series of solutions of Nd(III), each having a ten-fold difference in concentration. Parameters including the temperature, type and speed of stirring, the concentration and composition of each solution, and preconditioning of the electrode are also known to influence the response time the sensors and they were hence kept at constant values throughout the experiments. The tests revealed the response time of the CPEs to be less than 20s in the whole concentration range.

3.5. Selectivity and lifetime of the CPEs

As can be conluded from the name of the devices, selectivity behavior of ion selectyive sensors, is of determining importace.

Table 2. The selectivity coefficients of various interfering cations for electrode no. 13; concentration of the reference solution of Nd(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
Na^+	1.7×10^{-5}	Gd^{3+}	1.6×10^{-2}
K^+	1.9×10^{-5}	Yb^{3+}	2.5×10^{-3}
Nd^{3+}	2.3×10^{-3}	Tb^{3+}	2.4×10^{-3}
Ho^{3+}	1.2×10^{-3}	La^{3+}	2.3×10^{-2}
Ca^{2+}	3.4×10^{-4}	Sm^{3+}	2.7×10^{-2}
Cu^{2+}	1.5×10^{-3}	Dy^{3+}	3.1×10^{-3}
Pb^{2+}	6.6×10^{-3}	Pr^{3+}	2.9×10^{-3}
Co^{2+}	1.1×10^{-3}	Lu^{3+}	2.9×10^{-3}
Zn^{2+}	1.0×10^{-3}	Ce^{3+}	2.1×10^{-2}
Tm^{3+}	3.3×10^{-3}	Er^{3+}	2.4×10^{-3}

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

Week	Slope (mV decade^{-1})	DL (M)
1	19.7 ± 0.2	8.0×10^{-7}
2	19.7 ± 0.3	8.0×10^{-7}
3	19.6 ± 0.1	8.8×10^{-7}
4	19.7 ± 0.3	8.8×10^{-7}
5	19.7 ± 0.2	8.5×10^{-7}
6	19.5 ± 0.3	8.9×10^{-7}
7	19.6 ± 0.1	8.5×10^{-7}
8	19.6 ±0.2	8.5×10^{-7}
9	19.5 ± 0.1	9.0×10^{-7}
10	19.5 ± 0.3	9.0×10^{-7}
11	19.4 ± 0.1	9.4×10^{-7}
12	19.2 ± 0.3	1.0×10^{-6}
13	19.0 ± 0.2	1.0×10^{-6}
14	15.5 ± 0.1	9.2×10^{-6}
15	14.0 ± 0.1	9.6×10^{-6}
16	13.1± 0.1	9.8×10^{-6}

Hence we included matched potential (MPM) studies of the selectivity coefficients [51-55] the results of which are summarized in Table 2 which shows that the selectivity coefficients of CPEs for a number of mono, di and teivalents cations to be in the ranges of 2.7×10^{-2}-1.7×10^{-5}. This indicates that the tested ions do not have considerable interferences with the response of the CPEs.

Lifetime is another very imprtant issue for any sensor. We found that for most ion selective sensors the lifetime values range from 4 to 10 weeks after which the slope and detection limt of the sensor are consinderablly altered.

The lifetime of the proposed Nd(III)-selective CPEs was studied for a period of 16 weeks. In this period, the sensor was used for one hour per day and the changes in its slope and detection limit were recorded (Table 3). As seen in Table 3, the CPEs can be used for at least 13 weeks. without significant changes in their slope and detection limits. After this periood, a significant decrease in the slope from 19.7±0.2 to 15.5±0.1 mV decade^{-1} and a gradual increase in the detection limit from 8.0×10^{-7} to 9.2×10^{-6} were observed. This can be attributed to the loss of the RTIL and APIMP from the CPEs as a result of application over time.

4. CONCLUSION

A potentiometric electrode were constructed for determination of Nd(III). The sensors demonstrated advanced performances with a fast response time, a lower detection limit of 8.0×10^{-7} M and potential responses across the range of 1.0×10^{-6}-1.0×10^{-2} M. 2-{[(6-aminopyridin-2-yl) imino] methyl}-phenol (APIMP) was employed as a sensing element in construction of both electrodes. A nano-composite carbon paste electrode was designed to improve the analytical responses. The carbon paste electrode incorporation of modified multi-walled carbon nano-tube (MWCNT-NH_2) and nano-silica showed a better response especially in term of lifetime and response time. The best nano-composite electrode was composed of 2%NS, 5% MWCNT-NH_2, 20% APIMP, 20% RTIL, and 53% graphite powder. The response of the sensor was found to be stable in the pH of 4.0-8.0.

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