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A Novel Nano-Composite Tb^{3+} Carbon Paste Electrode

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Based on the results acquired by our previous studies which indicate a strong interaction between N'-(2-naphthoyl)-8-(dimethylamino)naphthalene-2-sulfonohydrazide (L) with Tb^{3+} ions, L was used as the ionophore in a new composite carbon paste electrode. The electrodes were made based on a new nano-composite including multi-walled carbon nanotube (MWCNT), graphite, and room temperature ionic liquid (RTIL), 1-n-butyl-3-methylimidazolium tetrafluoroborate $[bmim]BF_4$. The nano-composite electrode showed improved sensitivity, selectivity, response time, response stability and lifetime in comparison with typical Tb^{3+} carbon paste sensor based L. The best results were observed for nano-composite sensors with electrode composition of 15% L, 15% $[bmim]BF_4$, 60% graphite powder, 10% MWCNT. The new electrode exhibited a Nernstian response (19.9± 0.2 mV $decade^{-1}$) in the range of 7.5×10^{-8}-1.0×10^{-2} M with a detection limit of 6.0×10^{-8} M and in the pH range from 3.0 to 8.0.

Keywords: sensor; ion selective electrode; potentiometry; carbon paste; multi walled carbon nanotubes; nanosilica; ionic liquid

1. INTRODUCTION

Terbium and other Lanthanides, considered only lightly toxic according to the Hodge–Sterner classification, are used for gasoline-cracking catalysts, carbon arcs, and in movie projectors [1]. Spectrophotometry, spectrofluorimetry, inductively coupled plasma mass spectroscopy (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) are the main methods for the low-level monitoring of terbium ions in solutions. Isotope dilution mass spectrometry, neutron activation analysis, X-ray fluorescence spectrometry [2–5], etc. are also used in some laboratories. Being very simple, fast, inexpensive, and capable of reliable response in wide concentration ranges potentiometric sensors have shown to be very effective tools for analysis of a wide variety of metal ions [6-15]. These devices can be found in a variety of forms including PVC membrane electrodes, microelectrodes, coated wire electrodes, and carbon paste electrodes among which, carbon paste electrodes (CPEs) have attracted interest.

This may be due to the improved renewability, stable response, and low ohmic resistance of CPEs in comparison to membrane electrodes [16-18]. Typical potentiometric CPEs are based on the incorporation of a selective agent into a mixture of graphite powder dispersed in a non-conductive mineral oil, which is called carbon paste.

The mineral oil component present in the carbon paste causes disadvantages of the resulting CPEs, the major one is caused by the preparation process of the oils. Mineral oils have unpredictable components due to the fact that these compounds are prepared during refining of petroleum and processing of crude oil, which can influence the detection characteristcs of the resulting CPEs. On one hand, ionic liquids (IL) are salts with relatively low melting points that encompass a subcategory namely room temperature ionic liquids (RTILs) that are such compound being liquid in room temperature. 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 are properties of ILs [19-22] that make them good candidates for being used as binders in CPEs. Carbon nanotubes (CNTs), on the other hand, enjoy interesting physicochemical properties, including ordered structures with a high aspect ratios, ultra-light weights, high mechanical strengths, high electrical conductivities, high thermal conductivities, metallic or semi-metallic behaviors and high surface areas [23-30], the combination of which makes them unique materials that can find a variety of applications.

An example of these applications is the increasing number of reports on the application of CNTs' in CPE compositions [23-29].

Our previous study [31] showed a strong and reversible interactions of N'-(2-naphthoyl)-8-(dimethylamino) naphthalene-2-sulfonohydrazide (L) containing N, O and S donating atom with terbium ion which lead to a good sensing properties. The present work is aimed at constructing a high performance potentiometric carbon paste electrode with improved mechanical resistant and renewable surface for determination of Tb^{3+} ions in real samples using L as a sensing material in new proposed carbon paste composition based on an RTIL, and multi-walled carbon nanotubes (MWCNTs).

2. EXPERIMENTAL PARTS

2.1. Apparatus

The cell used for the measurements included the Tb^{3+} carbon paste electrode as the working 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;

Carbon paste electrode | 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 preparation 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). The used nanosilica is Wacker HDK® H20 with BET surface of the hydrophilic silica of 170-230 m2/g. Distilled deionized water was used throughout all experiments.

2.4. Electrode Preparation

The CPEs were prepared through a general procedure as follows: The desired amounts of the ionophore HDEBH along with an appropriate amount of graphite powder, ionic liquid, nanosilica 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 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 48 h by soaking it in a 1.0×10^{-3} M $Tb(NO_3)_3$ solution [27-29].

3. RESULTS AND DISCUSSION

3.1. Optimization of the CPEs

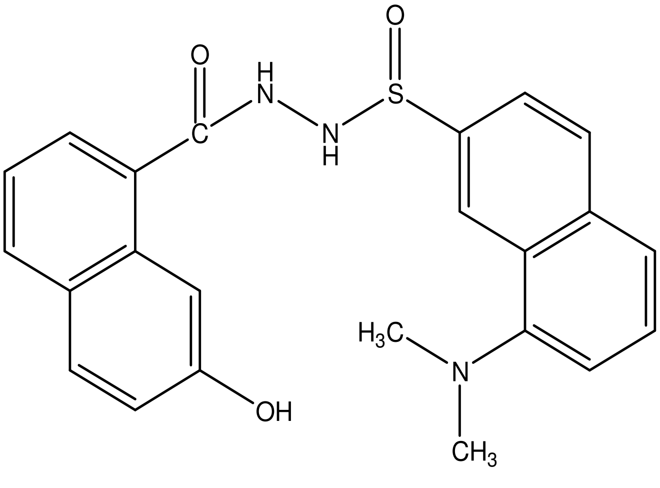

Figure 1. Chemical structure of L

The ionophore used as the main ingredient of any ion-selective sensors is known to strongly influence the selectivity of such devices [32-36]. L (Fig. 1) was used in constructing a set of CPEs with a variety of compositions some of which were modified using the ionic liquid, MWCNT, and nanosilica having the results of solutions studies in hand. The CP electrodes were then tested as sensing devices for Tb^{3+} ion selective sensors and the results are illustrated in Table 1. The results show that the absence of the ionophore L (compositions 1-3) in the composition of the carbon paste electrode leads to rather constant responses that are probably caused by the inherent (and probably un-selective extraction of the cation into the sensing CPE surface). It was also observed that changing the amounts of the graphite powder as the filler and the RTIL from 90-80 and 10-20 respectively, does not change the potential response of the sensor.

It is noteworthy that graphite powder being a hydrophobic, high surface area compound improves the extraction of the ions into the surface of the CPE and also the mechanical resistant of the electrode.

Table 1. The optimization of the carbon paste ingredients

No.	Composition (%)					Slope (mV decade^{-1})	Linear range (M)	R^2
	L	Graphite	Paraffin	RTIL	MWCNT			
1	--	90	--	10	--	4.3 ± 0.2	1.0×10^{-2} - 1.0×10^{-4}	0.895
2	--	85	--	15	--	4.7 ± 0.3	1.0×10^{-2} - 1.0×10^{-4}	0.873
3	--	80	--	20	--	4.7 ± 0.2	1.0×10^{-2} - 1.0×10^{-4}	0.888
4	7	78	--	15	--	13.5 ± 0.4	1.0×10^{-2} - 1.0×10^{-6}	0.908
5	10	75	--	15	--	15.8 ± 0.3	1.0×10^{-2} - 1.0×10^{-6}	0.987
6	15	70	--	15	--	16.3 ± 0.1	1.0×10^{-2} - 4.0×10^{-7}	0.993
7	20	65	--	15	--	16.3 ± 0.2	1.0×10^{-2} - 4.0×10^{-7}	0.993
8	15	65	--	15	5	18.7 ± 0.4	1.0×10^{-2} - 2.0×10^{-7}	0.976
9	15	62	--	15	8	19.7 ± 0.3	1.0×10^{-2} - 1.0×10^{-7}	0.988
10	15	60	--	15	10	19.9 ± 0.2	1.0×10^{-2} - 7.5×10^{-8}	0.997
11	15	60	15	--	10	17.7 ± 0.1	1.0×10^{-2} - 5.0×10^{-6}	0.954

The introduction of L however leads to a meaningful increase in the potential response of the CP electrode which is, based on the previous observations, due to the enhanced and as was later observed, selective extraction of Tb^{3+} ion into the sensing surface of the electrode. This was a further support to the initial assumptions made about the selective tendency of L towards Tb^{3+} ions. This trend further continued by increasing the amount of L in the composition of CPE to 10 (no. 5) and 15 (no. 6) percents increasing the potential response to 15.8±0.3 mV decade^{-1} and 16.3±0.1 respectively. Further increase in the amount of the amount of the ionophore to 20% wt. (no. 7), however, did not lead to any considerable changes in the response of the electrode. It was hence decided that 15% wt. is the optimum amount of the ionophore in the CPE. The electrode compositions were further modified by adding %5, %8 and %10 wt. of MWCNT to the composition (Nos. 8-10) which led to improvements in the potential response of the sensor from the sub Nernstian value of 18.7±0.4 mV decade^{-1} to the Nernstian values of 19.7±0.3 mV decade^{-1} and 19.9±0.2 mV decade^{-1} due to improving the conductivity of the composition, which in turn changes the chemical signal to an electrical one.

On the other hand unmodified CPEs having the optimized composition (electrode no. 11) shows a sub-Nernstian slope of ~17.7 mV decade^{-1} of Tb^{3+} concentration showing the better extraction capabilities of the used RTIL as a medium used in a CPE sensor. As it is evident from the data in Table 1, merely replacing the paraffin oil (no. 11) with RTILs (no. 10) in the CPE increases the potential response slope about 2.2 mV decade^{-1} of concentration due to increasing the extraction of high charge-density Tb^{3+} cations therein, probably due to the much higher dielectric constant of the latter.

The unique dimensions and unusual current conduction of CNTs are among the properties that make them ideal candidates as components in electrical circuits. The increase in the conductivity of the sensing compositions can lead to improvements in the dynamic working range (compare the results of electrodes 1-7 with those of 7-10) and response time of the sensor. As implied by the results, if the transduction property of the sensor increases, the potential response of the sensor improves to Nernstian values. So, as it can be seen a composition of 15% L, 15% [bmim]BF_4, 60% graphite powder, 10% MWCNT 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

Taking a quick look at Table 1, it is evident that in the absence of L as the ionophore the sub-Nernstian response is found to be linear in the range of 1.0×10^{-2} - 1.0×10^{-4}, which is due to the inherent extracting properties of the electrode in the absence of the ionophore.

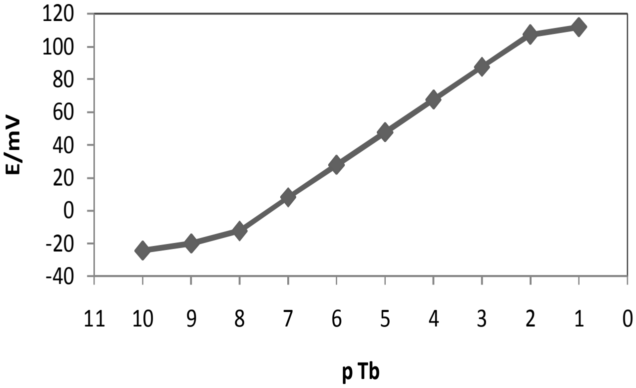

Figure 2. The calibration curve of the Tb^{3+} nano-composite CPE based on L (Electrode no. 10)

Introduction of L into the composition and increasing its amount upto 20% wt. is found to decrease the lower linearity range of the calibration curves from 1.0×10^{-4} M to 1.0×10^{-6} M and 1.0×10^{-7} M respectively due to improvements in the extracting capability of the CPE which is also evident from the changes in the potentiometric response values. In the case of the best composition (no. 10), as it is seen, the lower linearity range of the calibration curve is even lower and equals to 6.0×10^{-8} M most probably due to the modifications in the electric properties of the electrode due to the presence of the optimum amount of the MWCNT i.e. 10% wt.

The response of this modified Tb^{3+} CPE (no. 10) was further tested in Tb^{3+} ion concentration range of 1.0×10^{-1}-1.0×10^{-10} M and the results are shown in Fig. 2. 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. 10 ranges from 1.0×10^{-2}-7.5×10^{-8} 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 6.0×10^{-8} M.

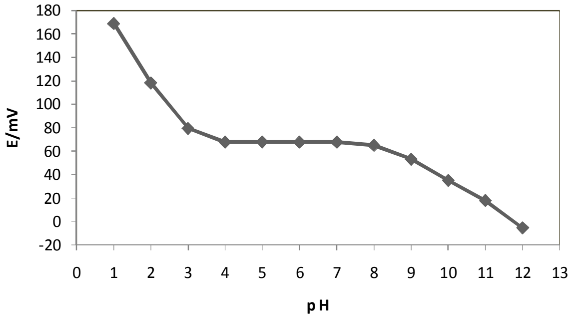

Figure 3. Effect of pH on the potential response of the Tb^{3+} nano-composite CPE based on (Electrode no. 10) in the test solution of Tb^{3+} ion (10^{-5} M)

3.3. Effect of pH

The effect of pH on the response of the optimal CPE (no. 10), was studied by monitoring the potential shown by the electrode in a fixed concentration of Tb^{3+} ion solution (1.0×10^{-5} M) while varying the pH values. pH of the solution was varied from (1-12) by adding concentrated HNO_3 or NaOH solutions thereto. The potential changes as a function of pH is shown in Fig. 3.

The response of the sensor is observed to be independent from pH in the range from 3.5-8.0. Potential fluctuations at pH values greater than 8.0 might be due to the formation of soluble or insoluble Tb^{3+} hydroxy complexes, such as soluble $Tb(OH)^{2+}$and $Tb(OH)_2^+$, or insoluble $Tb(OH)_3$. This phenomenon at pH values of 3.5 and less can be attributed to partial protonation of the donor atoms of L in the sensor [37-40].

3.4. Response time

Response time of the electrochemical sensors 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. Experimental parameters including stirring or the flow rate, the concentration and composition of each test solution, any previous application or preconditioning of the electrode, and the testing temperature can all affect the experimental response time of a sensor [41-47]. The response time of the proposed modified CPE was found to be less than 16 s.

3.5. Selectivity

Being the most important characteristic of any sensor, selectivity describes an ion selective electrode's relative specificity toward the target ion in the presence of interfering ions. The MPM potentiometric selectivity coefficients [48-52] of the proposed Tb^{3+} nano-composite carbon paste electrode were evaluated and the results are depicted in Table 2. As it can be seen, the selectivity coefficients of our sensor are 1.4×10^{-3} or lower for all tested cations. These results seem to indicate that interference effects upon the performance of the electrode assembly are negligible. The results of selectivity coefficients are in correspondance with the complex formation constant of L with common cations based on fluorescence study which has been listed in Table 3 [31].

Table 2. The selectivity coefficients of various interfering cations for electrode no. 10; concentration of the reference solution of Tb^{3+} ion was 1.0×10^{-5} M and the concentration of interfering ions was between 1×10^{-4} to 1.0×10^{-1} M

Cation	Selectivity Coefficient	Cation	Selectivity Coefficient
Ca^{2+}	1.6×10^{-4}	Gd^{3+}	9.3×10^{-3}
Mg^{2+}	1.4×10^{-4}	Pb^{2+}	5.7×10^{-3}
K^{+}	1.5×10^{-4}	La^{3+}	4.7×10^{-3}
Na^{+}	1.3×10^{-4}	Cr^{3+}	9.3×10^{-3}
Li^{+}	1.2×10^{-4}	Sm^{3+}	4.6×10^{-3}
Cu^{2+}	7.5×10^{-3}	Eu^{3+}	7.3×10^{-3}
Ho^{3+}	8.4×10^{-3}	Pr^{3+}	8.8×10^{-3}
Co^{2+}	5.1×10^{-3}	Lu^{3+}	7.4×10^{-3}
Zn^{2+}	3.4×10^{-3}	Cd^{2+}	4.6×10^{-3}
Tm^{3+}	8.1×10^{-3}	Dy^{3+}	1.4×10^{-3}
Er^{3+}	8.3×10^{-3}	Ce^{3+}	4.9×10^{-3}
Ni^{2+}	5.0×10^{-3}	Yb^{3+}	7.4×10^{-3}
		Nd^{3+}	7.5×10^{-3}

3.6. Lifetime of the Tb^{3+} CPE

Table 3. Complex formation constant of L with different cations

Cation	log K_f	Cation	log K_f
La^{3+}	2.18±0.04	Tm^{3+}	3.11±0.11
Gd^{3+}	3.18±0.07	Nd^{3+}	2.61±0.04
Pb^{2+}	<2	Tb^{3+}	6.77±0.17
Cr^{3+}	3.51±0.05	Er^{3+}	2.37±0.08
Sm^{3+}	2.27±0.03	Lu^{3+}	2.59±0.04
Cu^{2+}	<2	Co^{2+}	<2
Cd^{2+}	<2	Ni^{2+}	<2
Pr^{3+}	3.19±0.05	Zn^{2+}	<2
Eu^{3+}	2.33±0.11	Ca^{2+}	<2
Ce^{3+}	2.22±0.05	Mg^{2+}	<2
Dy^{3+}	3.19±0.06	K^+	<2
Yb^{3+}	2.18±0.04	Na^+	<2
Ho^{3+}	2.40±0.06	Li^+	<2

Most ion selective sensors have lifetimes ranging from 4–10 weeks after which the slope of the sensor response decreases leading to subsequent increases in the detection limits.

The lifetime of the proposed nano-composite Tb^{3+} CPE was evaluated for a period of 11 weeks, during which the sensor was used for two hours per day. The obtained results showed that the proposed sensors can be used for at least 10 weeks during which the slope of the potential response calibration curve shows negligable changes.

After this time, a slight gradual decrease in the slope from 19.9±0.2 to 17.2±0.3 mV decade^{-1} is observed, as is an increase in the detection limit from 6.0×10^{-8} M to 5.1×10^{-7} M (Table 4). This phenomenon can be attributed to the loss of RTIL and ion carrier from the composition of the sensing materials.

3.7. Real sample analysis

To evluate the applicability of the Tb^{3+} nano-composite CPE for real samples the electrode was used for determining the concentration of the Tb^{3+} ions in tab water samples. The 10.0 mL of each water sample (tab and river water samples, Tehran, Iran) was taken and diluted with distilled water in a 25.0 mL volumetric flask. The potential of this solution was measured by the proposed sensors. The results obtained with the sensor are summarized in Table 5. As it is observed in Table 5, the obtained results are comparable with those acquired through the ICP-OES analysis of the same samples, which is a good indication of the the applicability of the Tb^{3+} nano-composite CPE for real sample analysis.

Table 4. Lifetime of Tb^{3+} nano-composite CPE

Week	Slope (mV $decade^{-1}$)	DL (M)
1	19.9 ± 0.2	6.0×10^{-8}
2	19.8 ± 0.3	6.3×10^{-8}
3	19.9 ± 0.4	6.9×10^{-8}
4	19.6 ± 0.1	7.0×10^{-8}
5	19.5 ± 0.3	8.2×10^{-8}
6	19.6 ± 0.2	8.9×10^{-8}
7	19.6 ± 0.3	9.1×10^{-8}
8	19.7 ±0.2	9.6×10^{-8}
9	19.4 ± 0.4	9.8×10^{-8}
10	19.1 ± 0.2	1.0×10^{-7}
11	17.2 ± 0.3	5.1×10^{-7}

Table 5. Results of the determination of terbium ion in tab water samples using the Tb^{3+} nano-composite CPE of the present invention as compared to the results obtained through ICP-OES

Samples	Proposed electrode (ppm)	ICP (ppm)
1	67.2^{a}± 0.3	66.5± 0.2
2	78.4± 0.2	74.3± 0.3
3	63.5± 0.3	66.2± 0.3

a. Results are based on three measurements

4. CONCLUSIONS

The performance of the Tb^{3+} nano-composite carbon paste electrode, which is based on L, MWCNT and ionic liquid is introduced is improved by using RTIL instead of mineral oil (paraffin), and also by using MWCNTs as enhanced signal transducers. The modified CPEs show better potentiometric response than typical CPEs in terms of sensitivity, Nernstian slope, linear range, and response stability. The proposed sensor exhibits a long lifetime (about three months).

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