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La^{3+} Carbon Nanotube (CNT) Based Electrode Using a New (1-[({2-[2-(2-hydroxy-1-naphtyl)-3-(2-{[(E)-1-(2-hydroxy-1-naphtyl)methylidene]amino}ethyl)-1-imidazolidinyl]ethyl}imino)methyl]-2-naphthol)

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Based on the conductometric and fluorescence studies of the binding properties of (1-[({2-[2-(2-hydroxy-1-naphtyl)-3-(2-{[(E)-1-(2-hydroxy-1-naphtyl)methylidene] amino}ethy l)- 1 -imidazolidinyl] ethyl} imino) methyl] - 2 - naphthol) (HHN) and a series of main group, transition and lanthanide cations it was expected to have good potentials as a proper ionophore for constructing an ion selective electrode (ISE) for La^{3+} ions. The compound was hence used as an ionophore in a membrane of a new composite carbon paste electrode comprising acetyl grafted multi-walled carbon nano tube (MWCNT-COOH), graphite and a room temperature ionic liquid (RTIL), 1-n-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF_4. The capability of the ionic liquid and paraffin were also compared and it was observed that membranes comprising 60-65% wt of graphite, 15-20% wt of the RTIL The best performance for nano-composite sensor was obtained with electrode composition of 10% HHN, 20% [bmim]BF_4, 60% graphite powder, and 10% MWCNT-COOH. The electrode exhibited a Nernstian response (19.7±0.3 mV $decade^{-1}$) toward La^{3+} ions in the range of 1.0×10^{-9}-1.0×10^{-2} mol L^{-1} with a detection limit of 8.0×10^{-9} mol L^{-1}. The proposed modified La^{3+} sensor was found to be applicable over a pH range from 3.0 to 9.8.

Keywords: Sensor, ion selective electrode, lanthanum, carbon paste, carbon nanotubes, ionic liquid

1. INTRODUCTION

The figures of merit of ion selective electrodes (ISEs), including their rather fast response and easiness to use, their inexpensive application method, and being capable of producing reliable responses in wide concentration ranges are very well known among chemical analysts [1-12]. Different variations of these devices including PVC membrane electrodes and microelectrodes, coated wires, and carbon paste electrodes are known among those expert in the art, among which carbon paste electrodes (CPEs) have attracted more interest partly due to their improved renewability, stable response, low ohmic resistance as compared to membrane electrodes and their intermediate life time in comparison to membrane electrodes and all-solid state electrodes [13-23].

In general, most reported carbon paste (CP) potentiometric sensors, comprise of an ionophore incorporated into a carbon paste, typically consisting of graphite powder dispersed in a non-conductive mineral oil, which is used to give CPEs some disadvantages. Mineral oils, on the other hand, do not have fixed components due to the fact that they are derived during the process of refining crude oil or petroleum. The presence of contaminants or matrix components used in the construction of sensors may unpredictably influence detection.

Ionic liquids, on the other hand, are ionic salts with relatively low melting points (below 100 °C). Such salts that are liquids at room temperature are called room temperature ionic liquids (RTILs). These compounds have advantages of good solvating properties, high conductivity, non-volatility, low toxicity and good electrochemical stability and conductivity [24,25] and can be used as binders in carbon paste electrodes (CPEs) due to the same [26-28].

Furthermore, carbon nanotubes (CNTs) have recently been used in composition of carbon paste electrodes [29-40]. CNTs have very interesting physicochemical properties, such as an ordered structure with a high aspect ratio, ultra-light weight, high mechanical strength, high electrical conductivity, high thermal conductivity, metallic or semi-metallic behavior and high surface area [41]. The combination of these characteristics makes CNTs unique materials with the potential for diverse applications.

Functionalized carbon nanotubes have also been reported to possess much better solubility properties due to the fact that functionalization breaks the nanotube bundles leading to the better solubility [42]. The nature of the functional group (e.g. –COOH) can also affect the conducting properties of the CNT species especially when in a solution.

Given that our conductometric and fluorescence studies had shown strong interactions between HHN (Figure 1) and La^{3+} ions, while the same interactions were found to be low for other common interfering ions, we decided to construct a high performance potentiometric electrode with improved mechanical resistant and renewable surface for determination of La^{3+} ions in real samples using HHN as a sensing material in new proposed carbon paste composition based on RTIL , and multi-walled COOH-grafted carbon nanotubes (MWCNT-COOH).

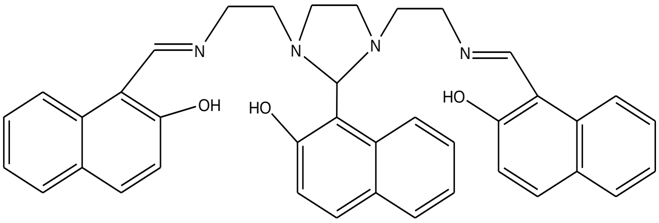

Figure 1. Chemical structure of HHN

2. EXPERIMENTAL PART

2.1. Apparatus

The glass cell in which La^{3+} carbon paste electrode was contained an Ag/AgCl electrode (Azar electrode, Iran) as a reference electrode. The La^{3+} CPE was used as the working electrode. Both electrodes were connected to a mili-voltmeter.

The following cell was assembled for the conduction of the EMF (electromotive force) measurements;

Carbon paste electrode | sample solution | Ag/AgCl–KCl (satd.)

Conductivity measurements were carried out with a Metrohm 644 Conductometer. A dip-type conductivity cell, made of platinum black, with a cell constant of 0.69 cm^{-1} was used. In all measurements, the cell was thermostatic at the desired temprature ±0.05ºC using an ATBIN immersion thermostat.

All fluorescence measurements were carried out on a Perkin-Elmer LS50 luminescence spectrometer.

2.2. Reagents and materials

Graphite powder with 1–2 μm particle size distribution (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.

The MWCNT sample used, had a 10-40 nm diameter, 1-25 μm length, SBET: 40-600 m^2/g and with 95% purity was purchased from Research Institute of the Petroleum Industry (Iran) and were functionalized according to the method below.

In order to graft the –COOH functional groups on the MWCNTs, they were initially purified by boiling in 14 mol/L HNO_3 for 5 h, washing with deionized water, filtering, and further washing with excess deionized water and ethanol. The purified MWCNTs were next dried at 100 °C in an oven. The functionalization of pMCNTs was carried out in a H_2SO_4/H_2O_2 solution (4:1 V/V) for 0.5 h. The functionalized MCNTs then washed with deionized water and filtered, and again washed with excess deionized water and ethanol. Finally the MCNT-COOH sample was dried at about 100 °C for future use. Distilled deionized water was used throughout all experiments.

2.3. Electrode Preparation

The general procedure to prepare the carbon paste electrode was as follows:

Different amounts of HHN along with an appropriate amount of graphite powder, MWCNT-COOH and ionic liquid were thoroughly mixed. The resulting mixture was then transferred into a glass tube with 5 mm i.d. and a height of 3 cm. After homogenization of the mixture, the paste was carefully packed into the tube tip to avoid possible air gaps, which can increase the electrical resistance of the electrode.

A copper wire was inserted into the opposite end of the La^{3+}-CPE to establish an electrical contact. The external surface of the carbon paste was then smoothed with soft abrasive paper. A new surface was yielded by scraping out the old surface and replacing new carbon paste. The electrode was finally conditioned for 48 h by soaking it in a 1.0×10^{-3} mol L^{-1} $La(NO_3)_3$ solution [43].

3. RESULTS AND DISCUSSION

3.1. Carbon paste electrode composition

The fact that selectivity of ion-selective electrodes is highly dependent on the ionophore used is very well known [44-53]. Based on the conductometric, as well as fluorescence studies (Table 1), HHN was used to fabricate both modified and unmodified CPEs with a variety of compositions. Results achieved by these CPEs are given in Table 2. As it is seen, an electrode containing all other ingredients (70% graphite, 20% RITL and 10% MWCNT-COOH) except for the ionophore (no. 1) showed a very low potential-concentration slope of 3.9±0.2 mV/ decade of concentration, indicating the inertness of the balnk membrane composition towards La^{3+}. CPEs were also constructed using 80% wt of graphite, 15% wt of paraffin and 5% wt of HHN showing a better, yet not acceptable slope of 10.1±0.2 (no.2) in a much wider concentration range of 1.0×10^{-2}-1.0×10^{-7} as compared to the very narrow one of no. 1 (1.0×10^{-2}-1.0×10^{-3}). Decreasing the amount of graphite from 80% in no. 2 to 75% wt and 70% wt in Nos. 3 and 4 while increasing the amount of HHN from 5% to 10% and 15% increased the potential slope about 2.7 units to 12.8±0.2 mV/ decade of concentration and kept it almost there. Further additions of 5%, 7% and 10% of MWCNT-COOH while keeping the amount of HHN at the optimum value of 10% wt (Nos. 5-7) further improved the potential response to a maximum of 16.7±0.1 mV/ decade of concentration where it remained constant, while improving the lower linearity range from 1.0×10^{-7} M to 0.5×10^{-8} M. It was however observed that replacing the paraffin with the RITL improved the potential response from 16.7±0.1 in no. 7 to 19.5±0.2 in no. 8 also improving the lower linearity range to 1.0×10^{-8} M , which was further improved to the Nernstian value of 19.7±0.3, although the lower linearity range was a bit deteriorated. This composition was considered as being the optimum one.

3.2. Measuring range and detection limit

The response of the optimal modified La^{3+} carbon paste sensor (no. 9) was tested across La^{3+} ion concentration range of 1.0×10^{-10}-1.0×10^{-1} M. The linearity range of an ion selective electrode is defined as the activity range between the upper and lower detection limits. The applicable range of the proposed sensor extends from 8.0×10^{-9} to 1.0×10^{-2} M (Figure 2). By extrapolating based on the linear portion of the electrode's calibration curve, the detection limit of the CPE was calculated to be 4.0×10^{-9} M.

Table 1. Flourecence and conductomeric studies of the interaction between HHN and some cations

Cation	**Log $K_{f,(conductometric)}$**	**Log $K_{f,(Fluorescence)}$**	**Cation**	**Log $K_{f,(conductometric)}$**	**Log $K_{f,(conductometric)}$**
La^{3+}	6.79 ± 0.09	6.96 ± 0.17	Nd^{3+}	2.21 ± 0.07	<2.0
Na^{+}	<2.0	<2.0	Sm^{3+}	2.79 ± 0.09	2.85 ± 0.11
Li^{+}	<2.0	<2.0	Eu^{3+}	2.67 ± 0.07	2.86 ± 0.17
K^{+}	<2.0	<2.0	Gd^{3+}	3.27 ± 0.05	3.85± 0.17
Mg^{2+}	<2.0	<2.0	Tb^{3+}	2.17 ± 0.09	<2.0
Ca^{2+}	<2.0	<2.0	Dy^{3+}	2.59 ± 0.06	2.68 ± 0.17
Cu^{2+}	2.31 ± 0.07	2.43 ± 0.05	Ho^{3+}	2.37 ± 0.03	2.88 ± 0.17
Zn^{2+}	<2.0	<2.0	Er^{3+}	2.18 ± 0.04	<2.0
Co^{2+}	2.12 ± 0.03	<2.0	Tm^{3+}	2.29 ± 0.04	<2.0
Cd^{2+}	2.75 ± 0.07	2.63 ± 0.13	Yb^{3+}	2.47 ± 0.09	2.65 ± 0.15
Ni^{2+}	2.07 ± 0.02	<2.0	Lu^{3+}	2.12 ± 0.05	<2.0
Fe^{3+}	2.88 ± 0.06	2.34± 0.08	Ce^{3+}	2.67 ± 0.02	2.35 ± 0.11
Pb^{2+}	2.95 ± 0.07	3.05 ± 0.11	Pr^{3+}	2.73 ± 0.09	<2.0
Hg^{2+}	2.81 ± 0.05	2.52 ± 0.05			

Table 2. The optimization of the carbon paste ingredients

No	**Composition (%)**					**Slope mV/ decade of concentration**	**Linear range/M**	**R^2**
	Graphite	Binder		MWCNT -COOH	HHN			
		Paraffin	RTIL					
1	70	-	20	10	-	3.9 ± 0.2	1.0×10^{-2}-1.0×10^{-3}	0.9851
2	80	15	-	-	5	10.1 ± 0.2	1.0×10^{-2}-1.0×10^{-7}	0.9984
3	75	15	-	-	10	12.8 ± 0.2	1.0×10^{-2}-1.0×10^{-7}	0.9991
4	70	15	-	-	15	12.9 ± 0.1	1.0×10^{-2}-1.0×10^{-7}	0.9992
5	70	15	-	5	10	15.2 ± 0.3	1.0×10^{-2}-1.0×10^{-7}	0.9985
6	68	15	-	7	10	16.1 ± 0.4	1.0×10^{-2}-1.0×10^{-7}	0.9981
7	65	15	-	10	10	16.7 ± 0.1	1.0×10^{-2}-5.0×10^{-8}	0.9980
8	65	-	15	10	10	19.5 ± 0.2	1.0×10^{-2}-1.0×10^{-8}	0.9984
9	60	-	20	10	10	19.7 ± 0.3	1.0×10^{-2}-8.0×10^{-9}	0.9991

3.3. pH effect on the electrode response

In order to study the effect of pH on the response of the optimal modified La^{3+} sensor (no. 9), the potential was measured for a fixed concentration of La^{3+} ion solution (1.0×10^{-5} mol L^{-1}) at different pH values. The pH was varied from (1-13) by addition of concentrated HNO_3 or NaOH. The change in potential as a function of pH is shown in Figure 3, which indicates the response of the sensor is independent of pH in the range from 2.5-9.5, in which range there is no visible interference from H^{+} or OH^{-} ions. Fluctuations at pH greater than 9.5 might be due to the formation of soluble or insoluble La^{3} hydroxy complexes, such as soluble $La(OH)^{2+}$and $La(OH)_2^{+}$, or insoluble $La(OH)_{3,aq}$. The fluctuations at a pH values below 2.5 were attributed to partial protonation of HHN the sensor [51-53].

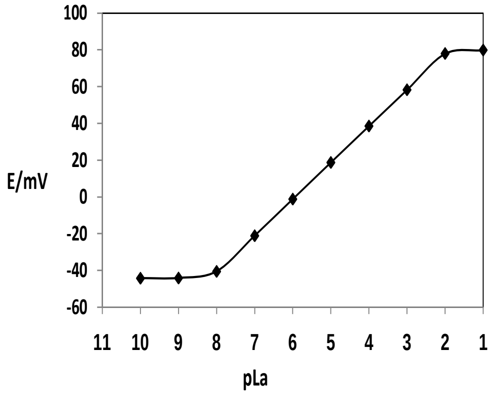

Figure 2. The calibration curve of the La^{3+} nano-composite carbon paste electrode based on HHN (composition no. 9)

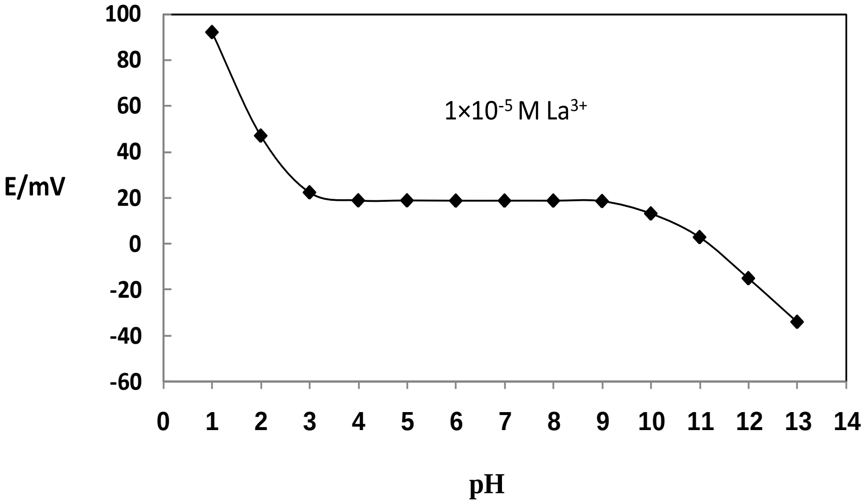

Figure 3. Effect of pH on the potential response of the La^{3+} nano-composite carbon paste electrode based on HHN (composition no. 9) in the test solution of La^{3+} ion (10^{-5} mol L^{-1})

3.4. Response time

Response time is a key feature of any sensor [54-62]. For electrochemical sensors, this parameter is evaluated by measuring the average time required to achieve a potential within ±0.1 mV of the final steady-state potential upon successive immersion of a series of interested ions, each having a ten-fold difference in concentration. Experimental conditions such as stirring or the flow rate, the ionic concentration and composition of the test solution, the concentration and composition of the solution to which the electrode was exposed before performing the experiment measurement, any previous usage or preconditioning of the electrode, and the testing temperature can all affect the experimental response time of a sensor. For the proposed modified La^{3+} sensor, the response time over the whole concentration range was less than 25 s (Figure 4).

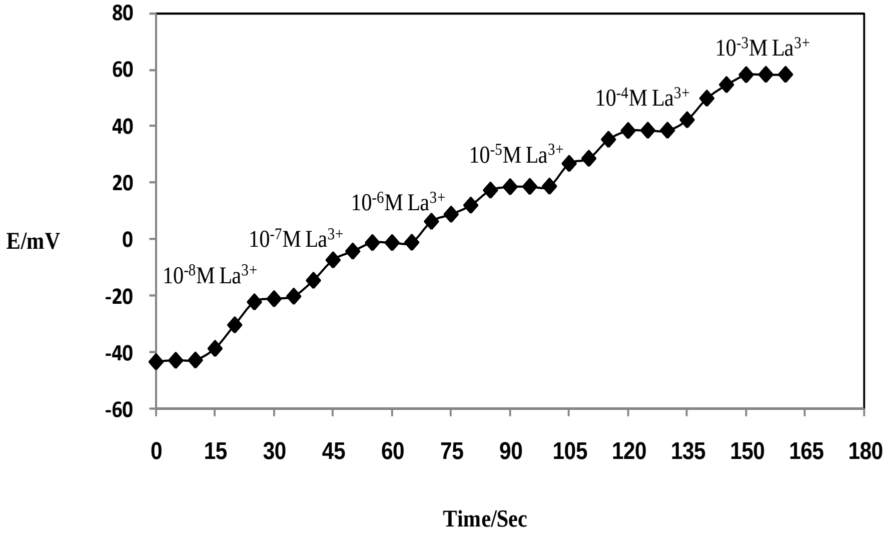

Figure 4. Dynamic response characteristics of the La^{3+} electrode for from 1×10^{-8}- 1×10^{-3} M of La^{3+}

3.5. Selectivity

Selectivity is the most important characteristic of any sensor, and describes an ion selective electrode's specificity toward the target ion in the presence of interfering ions, The potentiometric selectivity coefficients of the proposed La^{3+} carbon paste electrode were evaluated by matched potential method (MPM) [63-69], and the results are depicted in Table 3. As it can be seen from Table 4, the selectivity coefficients of the CPE for the representative and transitione mtal ions tested was in the range of 4.5×10^{-4} or less, while for the lanthanide ions this value was 8.5×10^{-4}or lower. These results seem to indicate that interference effects upon the performance of the electrode assembly are negligible.

3.6. Lifetime

The average lifetime for most ion selective sensors ranges from 4–10 weeks. After this time the slope of the sensor decreases, and the detection limit increases. The lifetime of the proposed nano-composite La^{3+} sensor was evaluated for a period of 21 weeks, during which the sensor was used two hours per day. The obtained results, illustrated in Table 4, showed that the proposed sensors can be used for at least 19 weeks and over. After this time, a slight gradual decrease in the slope from 19.7±0.3 to 19.3±0.2 mV per decade is observed, as is an increase in the detection limit from 4.0×10^{-9} M to 8.0×10^{-9} M (Table 4). It is well understood that the loss of plasticizer and ion carrier is the primary reason for limited lifetimes of many electrochemical sensors.

Table 3. The selectivity coefficients of various interfering cations

Cation	Selectivity	Cation	Selectivity
Na^+	2.5×10^{-6}	Nd^{3+}	1.4×10^{-4}
Li^+	1.5×10^{-6}	Sm^{3+}	4.0×10^{-4}
K^+	4.1×10^{-6}	Eu^{3+}	3.8×10^{-4}
Mg^{2+}	5.6×10^{-6}	Gd^{3+}	8.5×10^{-4}
Ca^{2+}	7.7×10^{-6}	Tb^{3+}	2.3×10^{-5}
Cu^{2+}	7.5×10^{-5}	Dy^{3+}	2.1×10^{-4}
Zn^{2+}	4.2×10^{-5}	Ho^{3+}	6.3×10^{-5}
Co^{2+}	4.9×10^{-5}	Er^{3+}	2.4×10^{-5}
Cd^{2+}	2.1×10^{-4}	Tm^{3+}	4.1×10^{-5}
Ni^{2+}	2.4×10^{-5}	Yb^{3+}	1.7×10^{-4}
Fe^{3+}	4.3×10^{-4}	Lu^{3+}	2.3×10^{-4}
Pb^{2+}	4.5×10^{-4}	Ce^{3+}	2.1×10^{-4}
Hg^{2+}	4.4×10^{-4}	Pr^{3+}	2.5×10^{-4}

Table 4. Lifetime of La^{3+} nano-composite carbon paste electrode

Week	Slope (mV/decade of conc.)	Detection Limit (M)	Week	Slope (mV/decade of conc.)	Detection Limit (M)
1	19.7 ± 0.3	4.0×10^{-9}	12	19.4 ± 0.2	6.0×10^{-9}
2	19.6 ± 0.2	4.0×10^{-9}	13	19.4 ± 0.1	7.0×10^{-9}
3	19.8 ± 0.3	4.0×10^{-9}	14	19.4 ± 0.3	7.0×10^{-9}
4	19.7 ± 0.1	4.0×10^{-9}	15	19.4 ± 0.4	7.0×10^{-9}
5	19.7 ± 0.3	5.0×10^{-9}	16	19.4 ± 0.3	7.0×10^{-9}
6	19.6 ± 0.1	5.0×10^{-9}	17	19.3 ± 0.1	7.0×10^{-9}
7	19.6 ± 0.2	5.0×10^{-9}	18	19.3 ± 0.3	8.0×10^{-9}
8	19.5 ± 0.2	6.0×10^{-9}	19	19.3 ± 0.2	8.0×10^{-9}
9	19.5 ± 0.3	6.0×10^{-9}	20	19.1 ± 0.1	8.0×10^{-9}
10	19.6 ± 0.2	6.0×10^{-9}	21	19.1 ± 0.2	8.0×10^{-9}
11	19.6 ± 0.3	6.0×10^{-9}	22	18.9 ± 0.3	1.0×10^{-8}

4. CONCLUSIONS

1. In this work, La^{3+} nano-composite carbon paste electrode based on, (1-[({2-[2-(2-hydroxy-1-naphtyl)-3-(2-{[(E)-1-(2-hydroxy-1-naphtyl)methylidene]amino}ethyl)-1-imidazolidinyl]ethyl}imino)methyl]-2-naphthol), graphite, MWCNT-COOH and ionic liquid was introduced.
2. The performance of La^{3+} nano-composite carbon paste sensor could be greatly improved by using RTIL instead of mineral oil (paraffin), and also by using MWCNT-COOH as enhanced signal transducers.

3. The modified CPEs showed 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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