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Application of carbon nanotubes-ionic liquid hybrid in a sensitive atorvastatin ion-selective electrode

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ABSTRACT

Atorvastatin (ATR) was determined by a potentiometric method. The ion-pair of ATR and cetyltrimethylammonium bromide (CTAB) was used as a suitable ionophore. A graphite paste electrode was modified with ATR-CTAB ion-pair, multiwalled carbon nanotubes (MWCNTs), and an ionic liquid, 1-butyl-3-mtehyl-imidazolium hexafluorophosphate ($BMIMPF_6$). The amounts of electrode ingredients were optimized (graphite powder: paraffin oil: ATR-CTAB: MWCNTs: $BMIMPF_6$ (58:26:5:8:3 *w*/*w*%). Surface characterization was done by using scanning electron microscopy. The potential measurements were recorded at optimized pH by using acetate buffer solution (0.1 mol L^{-1}, pH 5.5). At the above experimental conditions, calibration curve (E vs. log [ATR]) was linear ($R^2 = 0.9977$) in the concentration range of 1.0×10^{-9}–1.0×10^{-3} mol L^{-1} (0.0012–1209 mg L^{-1}) of ATR with a Nernstian slope of 58.14 ± 0.2 mV decade^{-1}, and detection limit of 1.0×10^{-9} mol L^{-1} (0.0013 mg L^{-1}). After each injection of ATR to the buffer solution, the potential was stabilized in a very short time (average response time ~ 6 s) at 25 °C. The modified graphite paste electrode had a long lifetime (>4 months). Recovery of the spiked drug to blood serum samples (95.3–98.2%) revealed the reliability of electrode response to ATR. Blood serum samples from consumers were analyzed by the proposed method; the results were comparable with those from HPLC standard method. The potentiometric analysis of ATR tablets by the proposed electrode resulted in a relative error of 0.8% and 1.5% for 20 and 40 mg per tablets, respectively. Finally, the electrode was used in potentiometric titration of ATR (1.0×10^{-3} mol L^{-1}) by CTAB (1.0×10^{-3} mol L^{-1}). Excellent accuracy (≈100%) was obtained from the volume of the titrant at the endpoint.

1. Introduction

One of the interesting research fields in electroanalytical chemistry is developing new sensors for analysis of biological, pharmaceutical, toxicants and other compounds. An ideal sensor responds to the compound of interest selectively, even in highly complex matrices. Other desirable characteristics of a sensor are short response time, wide dynamic concentration range, low detection limit, repeatability and reproducibility, long lifetime, low cost, simple operation, etc.

In order to approach an ideal electrochemical sensor, modification of the electrodes surfaces seems to be inevitable. Among uncountable substances used for chemical modification of electrodes, nanomaterials have a unique place, due to their good conductivity, large surface area/volume ratio, excellent electrocatalytic activity and high mechanical strength. Therefore, they have been used in the construction of sensors, extensively [1–4]. Although various nanomaterials can be used, carbon nanomaterials have been widely applied to electrode modification, because carbon is a good current conductor, electrochemically inactive, inexpensive and robust (therefore, carbon electrodes have been used in different forms such as, glassy carbon, graphite, pyrolytic carbon, graphite paste, etc.). Different shapes and sizes of carbon nanomaterials can be obtained according to the selected experimental conditions, e.g., carbon nanotubes (CNTs), carbon nanodots and graphene [5–7]. CNTs (single-walled and multi-walled) have been used extensively for electrode modification [8].

In some cases, synergistic effects have been observed when different materials were used for electrode modifications [9–11]. For example, one of the problems in using CNTs is their tendency to agglomerate. The hybrid of CNTs with ionic liquids (IL) shows a good synergy, i.e. the latter will disperse CNTs more effectively. The superiority of using IL-CNTs instead of CNTs alone, have been confirmed by using in several modified electrodes [12–14].

In this work, we were exploring for a sensitive potentiometric sensor to determine atorvastatin (ATR, Fig. 1) in biological and pharmaceutical

Abbreviations: ISE, ion-selective electrode; ATR, atorvastatin; CTAB, cetyltrimethylammonium bromide; $BMIMPF_6$, 1-butyl-3-mtehyl-imidazolium hexafluorophosphate; MWCNTs, multiwalled carbon nanotubes.

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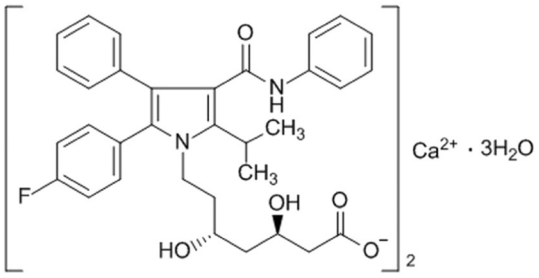

Fig. 1. structural formula of ATR.

samples. ATR is widely used as an effective cholesterol-lowering drug. Like other pharmaceutical compounds, it has a therapeutic concentration range in biological fluids. Below this concentration, ATR is not effective in lowering cholesterol level, while excessive concentrations of ATR will produce side effects such as, myopathy and rhabdomyolysis. In order to determine ATR residuals in biological fluids (blood serum or plasma, and urine), chromatographic method is the first choice [15,16]. In addition to its high cost, chromatographic experiment is time-consuming, needs skilled operator, pretreatment of the samples (e.g. preconcentration) for low levels of the drug, etc. Alternative analytical methods have been proposed by researchers, such as, spectrometry [17,18], voltammetry [19,20] and potentiometry [22,23]. The last is one of the simplest analytical methods, although it can be highly efficient. The method is based on the measurement of potential difference (ΔE) between reference and indicator electrodes. Ion selective electrode (ISE) is an indicator electrode which selectively responds to the ion of interest. In order to be so, the presence of ionophore in the ISE composition is usually necessary. Moreover, the use of nanomaterials in ISEs has improved their analytical characteristics, effectively [24–26]. Well-prepared ISEs show high selectivity and sensitivity to the ion of interest, fast response and long lifetime. They are inexpensive and their operation is very simple. Many ISEs have been constructed for various inorganic [27,28] and organic species [29,30].

The present work describes the preparation of a graphite paste electrode (GPE) as ISE for ATR analysis in human blood serum and urine samples, and pharmaceutical preparations. The ionophore (ion-pair) was prepared by precipitation of ATR by cetyltrimethylammonium bromide (CTAB). Moreover, it was shown that the addition of multiwalled carbon nanotubes (MWCNTs) and an IL (1-butyl-3-mtehyl-imidazolium hexafluorophosphate, $BMIMPF_6$) to the GPE greatly improved the potential response to ATR.

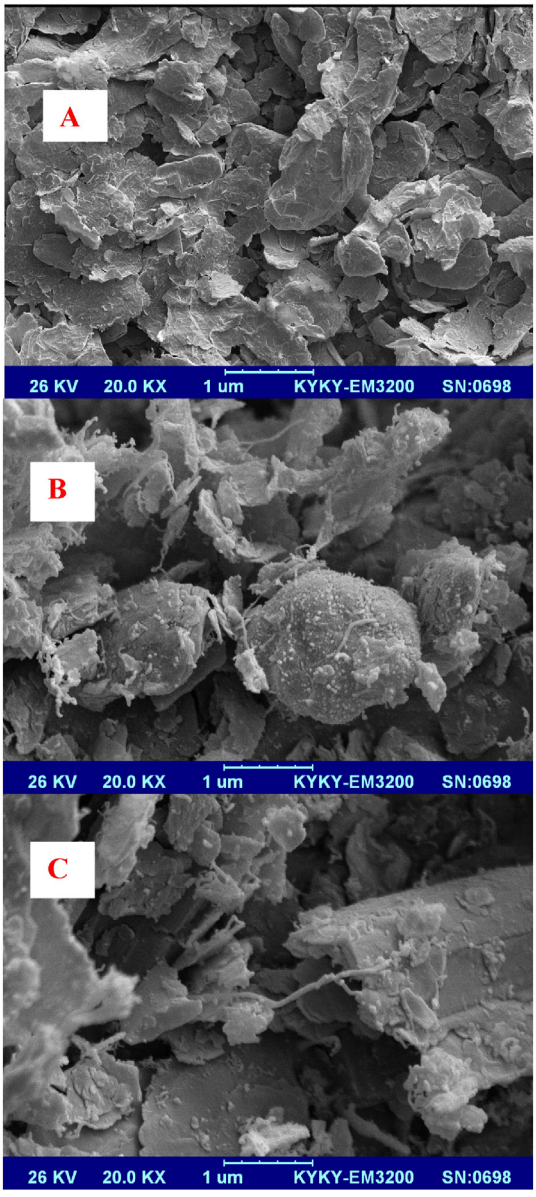

Fig. 2. SEM images of (A) GPE; (B) MWCNTs-GPE; (C) IL-MWCNTs-GPE.

Table 1
Optimization of ingredients of ATR – ISE.

No.	Graphite powder (%)	Paraffin oil (%)	Ion pair (%)	MWCNTs (%)	$BMIMPF_6$ (%)	Slope (mV/decade)	Linear concentration range (mol L^{-1})
1	70	30	–	–	–	26.9	2.0×10^{-6}–2.0×10^{-4}
2	69	30	1	–	–	54.69	1.0×10^{-6}–5.0×10^{-4}
3	67	30	3	–	–	56.95	5.0×10^{-7}–7.0×10^{-4}
4	67	28	5	–	–	57.47	2.0×10^{-7}–1.0×10^{-3}
5	65	27	8	–	–	56.88	2.0×10^{-7}–7.0×10^{-4}
6	63	27	10	–	–	55.65	2.0×10^{-7}–5.0×10^{-4}
7	65	27	5	3	–	56.72	2.0×10^{-8}–5.0×10^{-4}
8	65	25	5	5	–	57.35	2.0×10^{-8}–1.0×10^{-3}
9	60	27	5	8	–	59.68	1.0×10^{-8}–1.0×10^{-3}
10	59	26	5	10	–	59.93	2.0×10^{-8}–1.0×10^{-3}
11	58	25	5	12	–	60.20	2.0×10^{-8}–1.0×10^{-3}
12	65	27	–	8	–	52.99	2.0×10^{-6}–7.0×10^{-4}
13	67	27	5	–	1	58.72	5.0×10^{-8}–5.0×10^{-4}
14	65	27	5	–	3	59.58	1.0×10^{-8}–7.0×10^{-4}
15	64	26	5	–	5	60.94	2.0×10^{-8}–5.0×10^{-4}
16	67	30	–	–	3	41.92	1.0×10^{-8}–5.0×10^{-4}
17	58	26	5	8	3	59.57	1.0×10^{-9}–1.0×10^{-3}