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ORIGINAL ARTICLE

New PVC-membrane electrode based on charge-transfer inclusion complex between I_2 and 1,4,8,11-tetraazacyclotetracdecane for selective determination of I_3^- ions

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Abstract A new triiodide ion-selective electrode based on charge-transfer complex of iodine with 1,4,8,11-tetraazacyclotetracdecane as membrane carrier was prepared. The best performance of electrode observed with the membrane having the ligand–PVC–NPOE–NaTPB composition 3.0:33:66:0.5 mg which worked well over a wide concentration range 2.8×10^{-6}–1.4×10^{-1} M with a Nernstian slope of 59.6 ± 0.3 mV per decade and a detection limit of 1.2×10^{-6} M. This electrode showed a response time of 25 s and was used over a period of 2 months. The electrode exhibits an anti-Hofmeister selectivity sequence with a performance for triiodide at pH 1.5–10.2. The response mechanism of the electrode was investigated by UV–Vis spectroscopic technique. The electrode was successfully applied as an indicator electrode in the potentiometric titration of ascorbic acid and hydroquinone in drugs.

Keywords I_3^--selective electrode · Charge transfer complex · Tetraaz-14-crown-4

Introduction

Macrocyclic compounds have the ability to form selective and stable complexes with metal ions of compatible dimensions [1]. Cyclic polyethers, such as crown ethers, have widely been used as suitable neutral carriers for constructing highly selective cation sensors [2–4]. In addition to the cation-selective properties of crown ethers, recently electrodes using plasticized poly (vinyl chloride) (PVC) membranes incorporating charge transfer complexes of crown ethers demonstrated potentiometric triiodide selectivity sequence which deviated from the Hofmeister pattern [5, 6]. These deviations result from the strong tendency of the crown ethers for triiodide ions in the form of the (crown ether·I^+) I_3^- [7, 8] adduct.

Determination of triiodide ion is important in clinical and chemical analysis [9, 10], because it is a sufficiently good oxidizing agent to react quantitatively with a number of reductants [10]. It's used for determination of ascorbic acid and hydroquinone in drugs as well as chlorine and dissolved O_2 in water [6, 11]. Therefore, a sensitive method is required for its reliable measurement.

In this paper, we report the results of an investigation of the response characteristics of a 1,4,8,11-tetraazacyclotetracdecane (TACTD) based electrode towards triiodide and the response mechanism in view of the charge transfer interaction. The electrode has been applied to determination ascorbic acid and hydroquinone in drugs.

Experimental

Materials

Reagent grade 2-nitrophenyl octyl ether (NPOE), high relative molecular weight PVC, tridodecyl methyl ammonium chloride (TDMAC) and sodium tetraphenyl borate (NaTPB) all from Fluka, dibutyl phthalate (DBP), molecular iodine, sodium inorganic salts, tetrahydrofurane (THF) all of Merck and used without any further purification. Charge transfer complex between TACTD and I_2, formulated as (TACTD.I^+)I_3, was prepared as described elsewhere [6, 10] (Scheme 1). The resulting (TACTD·I^+)I_3^- solid complex was purified from reagent grade chloroform, vacuum dried

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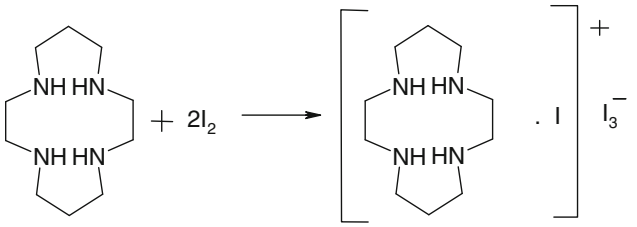


Scheme 1

for 48 h and characterized by elemental analysis and UV–Vis spectroscopy. This complex was used as ionophore in the preparation of PVC membrane ISEs.

A stock KI_3 solution was prepared by dissolving an appropriate amount of I_2 in 4% KI.

Electrode preparation

The general procedure to prepare the PVC membranes was to mix thoroughly 33 mg of powder PVC, 66 mg of plasticizer NPOE in 5 mL of THF as described previously [4–6, 10]. To this solution 3.0 mg of ionophore and 0.5 mg NaTPB were added and mixed well. The resulting mixtures were transferred into a glass dish of 2 cm diameter. The solvents were evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3–5 mm in diameter at the top) was dipped into the mixture for about 5 s so that a non transparent membrane was formed. The tube was then pulled out from the mixture and kept at room temperature for about 4 h. The tube was filled with internal filling solution 1.0×10^{-2} M KI_3. The electrode was finally conditioned by soaking in 1.0×10^{-3} M triiodide solution for about 48 h. A silver/silver chloride wire used as an internal reference electrode.

Apparatus

All EMF measurements were carried out with the following assembly:

$$\mathrm{Ag|AgCl,\ KCl\ (3\ M)|internal\ solution\ (1.0\times10^{-2}\ M\ KI_3)|}$$
$$\mathrm{PVC\ membrane|test\ solution|KCl\ (Sat'd.)|Hg_2Cl_2|Hg}$$

A Metrohm ion analyzer model 632 pH/mV meter was used for potential and pH measurements at 25 °C. Recording UV–Vis spectrophotometer (model Cary) with 10 mm quartz cell was used for absorbance measurements.

Results and discussion

Charge-transfer complexes formed in the reactions of polynitro compounds with many organic electron-donors such as aromatic hydrocarbons, aromatic amines, aliphatic amines, olefins and crown ethers have attracted considerable interested and growing importance in recent years [12–18]. Crown ethers are known to form stable charge-transfer complexes with iodine [18]. It is well known that substitution of some oxygen atoms of crown ether rings by nitrogens causes a large increase in the stability of their iodine charge-transfer complexes. Thus, if the membrane contains such charge-transfer complex that is able to bind to I_3^- anion, the membrane becomes selective toward this anion. Due to such interesting features, we examined 1,4,8,11-tetraazacyclotetracdecane as a potential sensing material in construction of new PVC-base I_3^--selective electrodes.

It is well known that sensitivity, linearity and selectivity obtained for a given ionophore depend significantly on the membrane composition and nature and amount of additive used [19–24]. Thus, the influence of membrane potential response of the I_3^- sensor was investigated, and the results are summarized in Table 1. It is seen that, NPOE (electrodes 3–5, 8–11) is more effective solvent mediator than other plasticizer in preparing the I_3^- ion selective electrode. As can be seen, the addition of NPOE as a suitable plasticizer leads to a significant improvement in the linear

Table 1 Optimization of the membrane ingredients

No.	Ionophore (mg)	PVC (mg)	DBP (mg)	NPOE (mg)	TDMAC (mg)	NaTPB (mg)	Slope (mV/decade)	Linear range [M]
1	1.5	33	66	–	–	–	50.0	8.2×10^{-5}–0.0×10^{-2}
2	3.0	33	66	–	–	–	98.0	7.0×10^{-4}–2.0×10^{-2}
3	1.0	33	–	66	–	–	40.0	1.6×10^{-5}–1.0×10^{-2}
4	2.0	33	–	66	–	–	72.0	1.6×10^{-5}–1.0×10^{-2}
5	3.0	33	–	66	–		80.0	9.6×10^{-5}–1.8×10^{-1}
6	1.5	33	66	–	–	1.0	101.0	1.6×10^{-5}–1.4×10^{-1}
7	1.5	33	66	–	1.0	–	85.0	1.6×10^{-5}–2.2×10^{-1}
8	4.0	33	–	66	–	0.5	89.0	1.2×10^{-5}–1.0×10^{-2}
9	5.0	33	–	66	–	0.5	96.0	7.9×10^{-6}–1.0×10^{-2}
10	3.0	33	–	66	0.5	–	110.0	1.2×10^{-5}–1.0×10^{-1}
11	3.0	33	–	66	–	0.5	59.6	2.8×10^{-6}–1.4×10^{-1}

concentration ranges and slopes. It should be noted that nature of plasticizer influences both the dielectric constant of the membrane and the mobility of the ionophore and its complex. Moreover, the optimum amount of ionophore was determined to be 3.0 mg (electrode No. 11). Concentrations above 3.0 mg ionophore in membranes (electrodes No. 8 and 9) showed super-Nernstian response toward triiodide ion. The concentration of uncomplexed analyte anion (I_3^-) in the membrane phase might be responsible for the super-Nernstian response obtained toward I_3^- ions [5].

It is well known that addition of lipophilic salt additives to ion-selective electrodes has been an effective means of improving the response characteristics of them [24, 25]. These reports demonstrate that by incorporation a certain amount of fixed anionic sites into membranes containing positively charged carriers, the observed slope were closer to those expected by theory. In this study, sodium tetraphenyl borate as anionic additive and tridodecyl methyl ammonium chloride (TDMAC) as cationic additive were added to the membrane and the results are shown in Table 1. As can be seen use of NaTPB as an anionic additive improves the emf response of the electrode remarkably. Take into account that a charge carrier mechanism is responsible for electrode response. It is well known that in ISEs based on electrically charged carriers, use of ionic sites with the same charge sign as the primary ions can significantly improve the response properties and selectivity of the sensor [25–27]. Thus, due to Nernstian behavior and wide linear range a membrane with a composition of ionophore (3.0 mg), NPOE (66.0 mg), PVC (33.0 mg) and NaTPB (0.5 mg) (electrode No. 11) was chosen for further studies.

The EMF response of proposed I_3^- electrode indicated a rectinlinear range from 1.4×10^{-1} to 2.8×10^{-6} M for 1,4,8,11-tetraazacyclotetracdecane ionophore (Fig. 1). The slope of calibration curve was 59.6 ± 0.3 mV decade^{-1} for mentioned electrode with detection limit of 1.26×10^{-6} M.

Optimum equilibrium time for the membrane sensor in a 1.0×10^{-3} M I_3^- solution was 24 h. Later on it was found to generate stable potentials in contact with triiodide solutions. The dynamic response time $t_{95\%}$ for the triiodide

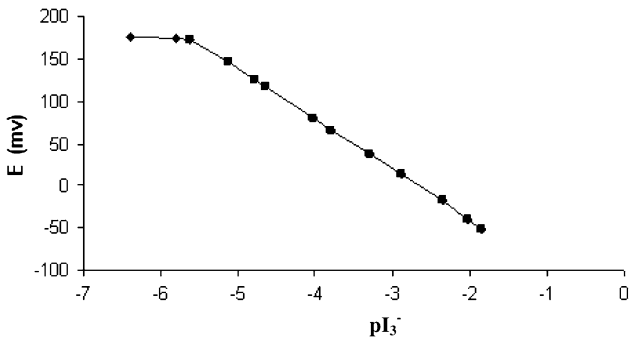


Fig. 1 Calibration graph for the I_3^- ion-selective electrode

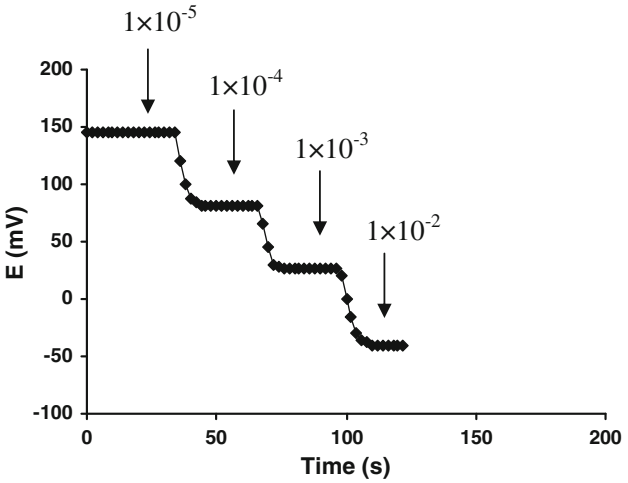


Fig. 2 Dynamic response of I_3^- ion-selective electrode towards different concentrations of triiodide ion

Table 2 Stability and repeatability of triiodide membrane electrode

Days	Slope (mV decade^{-1})	Linear range (M)
1	59.60 ± 0.3	2.8×10^{-6}–1.4×10^{-1}
10	59.60 ± 0.3	2.8×10^{-6}–1.4×10^{-1}
20	59.60 ± 0.3	2.8×10^{-6}–1.4×10^{-1}
30	59.50 ± 0.3	2.8×10^{-6}–1.4×10^{-1}
40	59.15 ± 0.5	2.8×10^{-6}–1.4×10^{-1}
50	58.95 ± 0.7	2.8×10^{-6}–1.4×10^{-1}
60	58.61 ± 1.1	5.0×10^{-6}–1.4×10^{-1}
67	53.50 ± 1.3	1.2×10^{-5}–1.4×10^{-1}

selective electrode after successive immersion of a series of I_3^- ion solutions, each having a 10 fold difference in concentration was measured. A potential–time plot for the electrode response is given in Fig. 2. The response time of

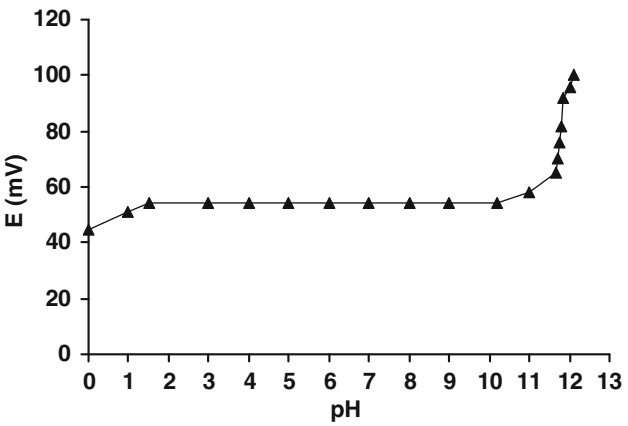


Fig. 3 Effect of pH of test solution on the potential response of the triiodide ion-selective electrode based on (TACTDI$^+$)I_3^-

the PVC membrane thus obtained was 25 s for concentrations $\leq 1.0 \times 10^{-3}$ M. It should be noted that the equilibrium potentials essentially remained constant for about 5 min, after which only a very small divergence within the resolution of the pH meter was recorded. The standard deviation of ten replicate measurements is ±0.3 mV.

The electrode was tested a period of 67 days to investigate the stability. During this period the electrode was stored in distilled water when not in use. Before each measurement the electrode was conditioned for approximately 30 min and response was examined and the results are shown in Table 2. As can be seen, the electrode displayed no significant change in the performance in the terms of slope and linearity for a long period of about 2 months.

The influence of pH on the response of electrode to 1.0×10^{-3} M potassium triiodide solution over a pH range from 1 to 12 was studied, and the result are shown in Fig. 3. As can be seen, the potential readings for the electrode are almost identical and constant over pH range 1.5–10.2. However, the observed change below and above this pH range may be due to protonation of macrocycle as well as disproportionate reaction between I_3^- and OH^- resulting in the formation of hypoiodate and iodide [5, 6, 10], both of which are insensitive to the membrane electrode. This behavior can be described by following reactions (Eqs. 1, 2):

$$I_2 + 2OH^- \rightarrow IO^- + I^- + H_2O \quad (1)$$

$$3IO^- \rightarrow 2I^- + IO_3^- \quad (2)$$

The selectivity is clearly one of the most important characteristics of an electrode, determining whether a reliable measurement in the target sample is possible or not. In this work, the potential response of the proposed I_3^- ion-selective electrode to other anions was investigated by matched potential method (MPM) [26–28]. According to the MPM, the selectivity coefficient, $K_{A,B}$ is determined as expression $K_{A,B} = \Delta A/a_B$ where $\Delta A = a'_A - a_A$, a_A is the initial primary ion activity and a'_A the activity of A in the presence of interfering ion, a_B. It should be noted that concentration of triiodide ion used as a primary ion in this study was 1.0×10^{-3} M. The resulting K values are summarized in Table 3. As can be seen all the diverse anions used cannot significantly disturb the functioning of the I_3^- ion-selective membrane electrode. It is interesting to note that the observed selectivity considerably differ from the so-called Hofmeister selectivity sequence. When the selectivity of the sensor differs from the Hofmeister selectivity sequence, it is generally not governed by simple anion lipophilicity, but by specific chemical interactions between the carrier and anions. Here, in, the highly selectivity of the membrane electrode for triiodide ion over other anions used likely arises from the strong tendency of the TACTD for triiodide ion in the form of the $(TACTD{\cdot}I^+)(I_3^-)$ adduct [5, 6, 10].

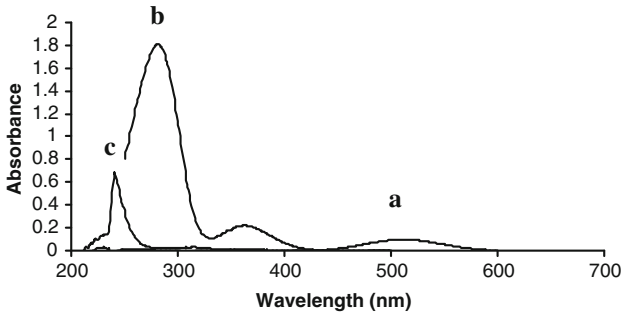


Fig. 4 UV–Visible absorption spectra of an extracted I_3^- ion from water in a chloroform solution without charge transfer complex (*A*), extracted I_3^- ion from water in a chloroform solution of 1×10^{-3} M TACTD (*B*), and a chloroform solution of 1.0×10^{-3} M TACTD (*C*)

Mechanism of electrode response

In order to investigate interaction between TACTD and I_3^-, UV–Visible spectra were obtained. UV–Visible observation spectra of an extracted I_3^- from water in chloroform solution without TACTD (curve A), extracted

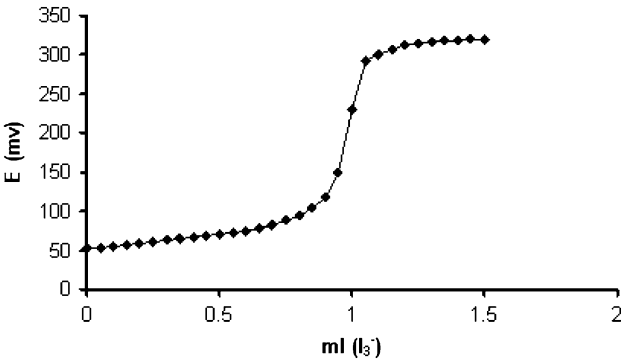


Fig. 5 Potentiometric titration curve for 50 mL of 1.0×10^{-3} M triiodide solution with 1.0×10^{-1} M sodium thisulfate by using the proposed sensor based on $(TACTDI^+)I_3^-$ as an indicator electrode

Table 3 Selectivity coefficients, $-\log K_{pot}^{A,B}$ for the solvent polymeric membrane electrode

Aniones	$-\log K_{pot}^{A,B}$	Aniones	$-\log K_{pot}^{A,B}$
SCN^-	4.9	$H_2PO_4^-$	5.1
Br^-	4.6	N_3^-	4.3
F^-	4.4	IO_3^-	5.0
ClO_4^-	5.1	I^-	3.4
NO_3^-	4.5	CH_3COO^-	4.2

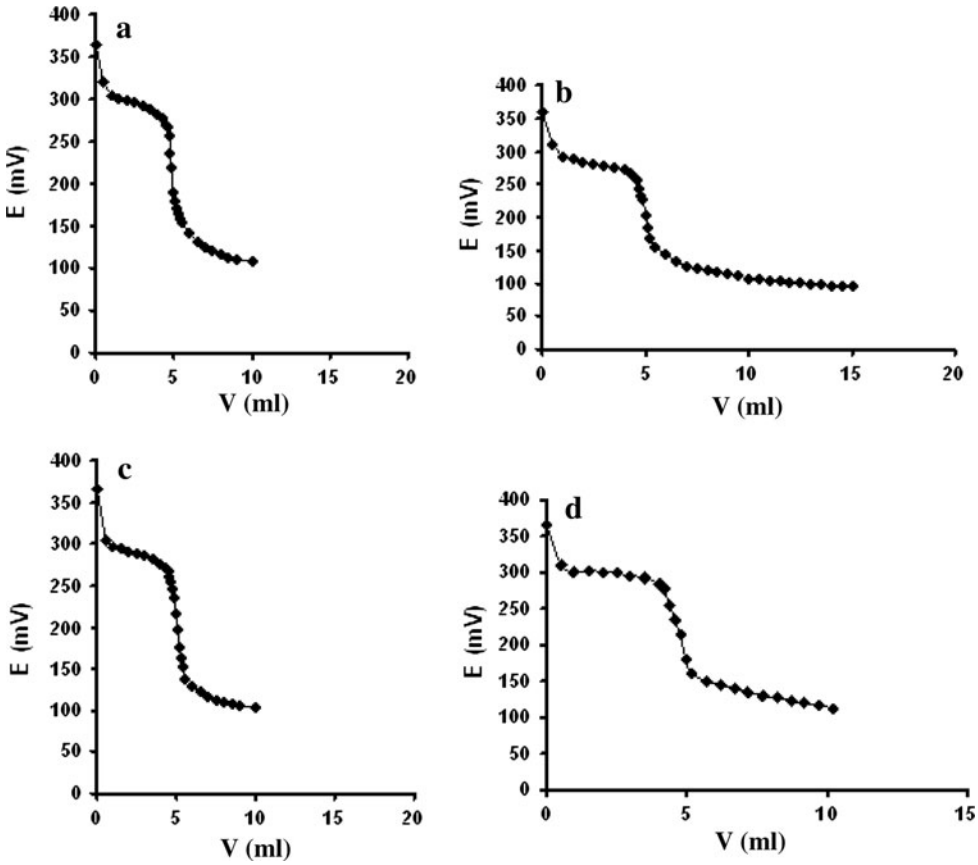


Fig. 6 Potentiometric titration curves ascorbic acid with 1.0×10^{-2} M NaI_3: **a** effervescent powder, **b** effervescent tablet, **c** pure powder of vitamin c, **d** vitamin c ampoule

I_3^- in a chloroform solution of 1.0×10^{-3} M TACTD (curve B) and a chloroform solution of 1.0×10^{-3} M TACTD without I_3^- (curve C) is shown in Fig. 4. As is obvious from Fig. 4, the existence of new bands at 295 and 363 nm are known to be characteristic of the triiodide contact ion pair $(TACTD{\cdot}I^+)(I_3^-)$ [5–8, 10, 15, 18] since neither the crown ether nor I_3^- are absorbed significantly in this spectral region. The observed changes indicate formation of a charge-transfer complex due to interaction of I_3^- with TACTD that is responsible for electrode response.

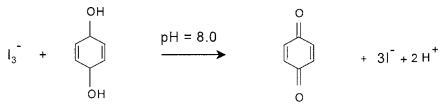
Analytical application of the triiodide ion selective electrode

Direct potentiometric titration of triiodide by thiosulfate

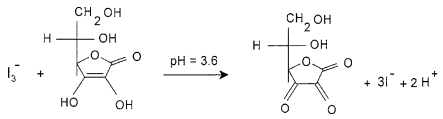
The proposed triiodide membrane electrodes were found to work well under laboratory conditions. It was successfully applied to the titration of 50.0 mL of 1.0×10^{-3} M KI_3 solution with 1.0×10^{-1} M thiosulfate, according to Eq. 3, and the resulting titration curve is shown in Fig. 5. As can be seen, the amount of I_3^- ions in the solution can be accurately determined with the electrode.

$$2S_2O_3^{2-} + I_3^- \rightarrow 3I^- + S_4O_6^{2-} \quad (3)$$

The electrode was also successfully applied to the potentiometric titration of ascorbic acid and hydroquinone with a standard solution of I_3^-. The analysis was based upon the oxidation of ascorbic acid and hydroquinone to dehydroascorbic acid and quinon by I_3^- Eqs. 4 and 5:



(4)



(5)

As can be seen, the amount of ascorbic acid and/or hydroquinone could be accurately determined with the electrode. The assays of ascorbic acid in pure vitamin C (Merck), powder (from Rose Daru Pharmaceutical Company, Tehran, Iran), ampoule, and multivitamin tablet and hydroquinone in tablet were carried out using the proposed electrode. The resulting data are summarized in Table 4.

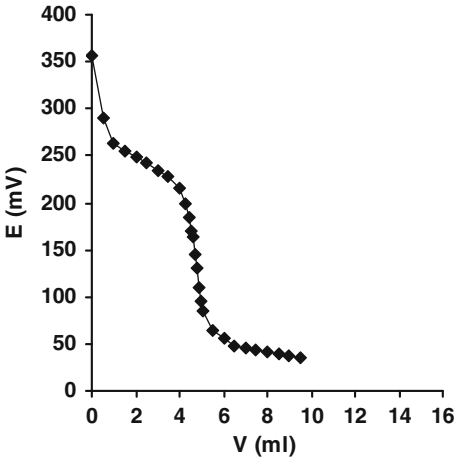


Fig. 7 Potentiometric titration curve 50.0 mL 1.0×10^{-3} M hydroquinone solution with 1.0×10^{-2} M NaI_3

Table 4 Results of the determination of ascorbic acid, hydroquinone in drug

	Labeled	Found proposed method[a]	Classical method[b]
Ascorbic acid			
Tablet	500 (mg/tablet)	495.4 ± 0.6	505 ± 0.5
Eff. tablet	75 (mg/eff. tablet)	74.15 ± 1.0	76.7 ± 1.2
Ampul	500 (mg/unit)	497.7 ± 0.7	495.5 ± 0.8
Pure powder vitamin c	–	8.65 ± 0.9	8.63 ± 1.1 (g/L)
Hydroquinone			
Pure powder	–	5.23 ± 1.3 (mg/L)	5.25 ± 1.5 (mg/L)

[a, b] Average of three replicate measurements $(\bar{X} \pm \mathrm{SD})$.

As can be seen, there are good agreements between the results obtained by the proposed method and labeled on samples (Figs. 6, 7; Table 4).

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