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Cetylpyridinium-tetraiodomercurate PVC Membrane Sensor for Determination of Iodide in Water Samples and Pharmaceutical Preparation

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A new PVC membrane sensor for iodide has been investigated. The PVC sensor is composed of cetylpyridinium (CP) -tetraiodomercurate (HgI_4^{-2}) as counter ion in a plasticizer solvent. The PVC membrane showed a near Nernstian response in the range 1×10^{-2}M - 5×10^{-6}M iodide at 25°C with an anionic Nernstian slope of 55 ± 0.5 mV per 10 fold. The response time and limit lower of detection are 20sec and 3×10^{-6}M respectively. Effect of different ions on the selectivity of iodide was studied. There are negligible effects were caused by the most of the examined ions. The proposed method shows good recovery and precision values. The obtained data by the proposed method for the assay of iodide in its dosage form (gallamine triiodide) are agreed with the reported spectrofluorometric method. The suggested membrane sensor has been used as indicator sensor for determination of mercury and silver ion using potentiometric titrations.

Keywords: iodide, cetylpyridinium, teteraiodomercurate, sensor, applications

1. INTRODUCTION

Iodine is an essential micronutrient important to vital processes for the production of the thyroid hormones thyroxin and triiodothyronine by the gland. Decrease of iodine leads to a malfunction of the thyroid gland, and an increase of iodine in the human result in inflation in the thyroid [1]. Iodide is present in many of the food, pharmaceuticals and in drinking water. Iodide is added to salt as a source of iodine, to prevent disorders caused by iodine deficiency, iodide in most cases is a complementary to iodine. Iodine present into in two forms, water-soluble iodine (I^-) and soluble organic iodine (IO_3^-). Thus, the estimate of iodine in foods, environmental samples, biological and clinical is required.

Spectrophotometry [2, 3], chemiluminescence [4,5], atomic absorption spectrometry[6], ion-chromatography[7, 8], high performance liquid chromatography [9], and gas chromatography-Mass detection [10], have been informed for assay of iodide.

Ion selective electrodes using PVC membrane sensor being simple, rapid, sensitive, economical, portability applicable over a wide dynamic range and useable in various areas such as environment, food and pharmaceutical analysis[11-13].

Mn(II) porphyrinato derivative [14], Co(II) derivative of salophen (II) [15], Co(II) and Ni(II) cyclam derivatives [16], *N*,*N*-bis (salicylaldehyde-*n*-octyl)diimine cobalt(II) [17] [20], Bis-(o-phenylenediamine)Cu(II)[18], copper(II) complex of *N*,*N*-bis(salicylidene)- 1,2-bis(*p*-aminophenoxy)ethane tetradentate [19], Cd(II) Schiff base complexes [20], molybdenum-salen [21], urea derivative [22] iodide-miconazole ion pair[23] and silver wire [24] as electroactive materials have been published. However most of these methods have not been very productive. Which have a limit calibration range [23,22,16] and suffering from some inferring anion such as thiocyanate, cyanide, perchlorate and salicylate.

The present study aim to develop of a new electroactive material as PVC sensor based on a new ion-pair complex (cetylpyridinium-tetraiodomercurate) for determination of iodide. The sensing material used in the suggested method is easy and affordable and can be prepared in any laboratory compared with the published methods [14-22], as they take much time to prepare and also need to be cleaned and analysis to prove its chemical composition of the electroactive materials [14-22]. Table 1 summarized the published iodide-sensor using different sensing materials. The proposed PVC membrane sensor has a wide dynamic range, highly selective in addition to the prepared ion-pair complex is very simple and no need for further cleaning. Iodide content in water samples and in flaxedil (gallamine triethiodide) (Fig. 1) has been tested using the proposed sensor.

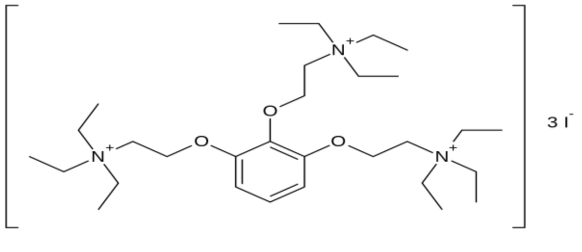

Figure 1. Chemical structure of gallamine triethiodide

2. EXPERIMENTAL

2.1. Instrument

HANA pH/mV meter (211, Microprocessor pH meter) was used for all potentiometric measurements. Calomel reference electrode (Catalogue No. 476350) was used. Measurement of pH was carried out using Ross glass pH electrode.

Table 1. Different electroactive materials used as membrane sensors for iodide.

Electroactive material	Linear range (M)	Slope	pH	Response time(s)	Ref.
Mn(II)porphyrinato	1×10^{-2} -7.5×10^{-6}	-59.4	2-8	≤8	14
Co(II) complex of Salophen	5.0×10^{-7} - 1.0×10^{-1}	-58.9	3.1- 9.8	15	15
Cyclam derivatives of Co(II) and Ni(II)	1×10^{-1} - 4×10^{-5} 5.0×10^{-3} -7.6×10^{-6}	-58.6 -53.0	- -	3 3	16
Schiff base complexes of Co(II)	2.3×10^{-2}-8.4×10^{-7}	-55.7	4-8	40	17
Bis-(o-phenylenediamine) Cu(II) complex	1.0×10^{-2} -1.0×10^{-6}	-60.3	3 - 6	-	18
N,N-bis(salicylidene)-1,2-bis(*p*-aminophenoxy) ethane tetradentate copper (II) complex	1.0×10^{-1} - 8.2×10^{-7}	-58.8	2- 5	18	19
Cd(II) Schiff base	1.0×10^{-2} - 8.1×10^{-6}	-59.3	2.5- 9	11	20
Molybdenum-salen as a neutral carrier	1.0×10^{-1} - $9.1\times10^{-}6$	-60.3	2.0 - 8.5	10	21
Urea derivative	1.0×10^{-2}-1.0×10^{-5}	-57.7	0.8 - 7	10	22
Miconazole iodide	1×10^{-2} -1×10^{-5}	-59.8	2.5 - 8.5	20	23
Silver wire treated with Hg^{2+}	1×10^{-2}- 1×10^{-6}	-60	--	15-120	24
Cetylpyridinium-tetraiodomercurate	1×10^{-2}- 5×10^{-6}	-55	3- 8	20	The present work

2.2. Reagents

A high molecular weight Polyvinyl chloride powder (PVC), o-nitrophenyl octyl ether, dioctylphathalte, dibutylsebacate, and tetrahydrofuran of purity of more than 99 % were purchased from Aldrich Chemical Company. Cetylpyridinium chloride (CPC) was acquired from sigma. Potassium iodide, silver nitrate and mercuric acetate were acquired from sigma. Gallamine triethiodide (flaxedil®) (ampoule, 2 ml) contain 40 mg of gallamine triethiodide was acquired from Alexandria Pharmaceutical Company, Egypt. Acetate buffer of pH 4.0 was produced by mixing an appropriate amount of sodium acetate and acetic acid.

2.3. Preparation of the cetylpyridinium- tetraiodomercurate ion-pair

Two hundred mg of potassium iodide in water is added to solution of 10 mg of $HgNO_3$ in water then the product solution (tetraiodomercurate) was added to a solution of 20mg of cetylpyridinium chloride. A white precipitate of CP-tetraiodomercurate ion-associate is produced [25]. The precipitate is dried at room temperature, till the dried powder was obtained. Into three separate

Petri dishes, 10 mg portion of ion-pair (CP-tetraiodomercurate), 190 mg PVC, 350 mg of plasticizer, respectively was added. All constituent being will mix, and then about 5 ml THF was added to each Petri dish. The sensing membranes have been formed after evaporate all solvent (after 24h). The PVC membrane was attached to the electrode body using tetrahydrofuran and the filling solution with internal reference electrode were carried out according the reported method [26, 27].

2.4. Procedure

The iodide PVC membrane sensor was calibrated by inserting the electrode in combined with the reference electrode into 100ml measuring cell containing 9.0 ml of acetate buffer. Then the potential of the developed sensor was recorded against different iodide concentration ranging from 1×10^{-2}M to 1×10^{-6}M. A calibration curve was carried out by plotting the measured potentials related - log [iodide]. The unknown iodide concentration was estimated from the already calibration curve. Standard addition techniques was also used to calculate the unknown concentration by measuring the E, mV of unknown concentration and after the addition of standard known concentration [28].

2.5. Determination of iodide in flaxedil

Ten ampoules were mixed together. An appropriate concentration of iodide was prepared in separate volumetric flasks. The pH of each solution was controlled to pH 4 using acetate buffer. The E, mV of each solution was recorded as recommended form the previous procedure. The unknown iodide was estimated from the previously standard curve. In addition, the standard addition technique [28] was applied to calculate the unknown iodide.

3. RESULTS AND DISCUSSION

3.1. Sensor Developments

CP-tetraiodomercurate ion associate as sensing materials in different plasticizer namely: DOP, DBS and o-NPOE were examined. The general possession of the developed sensor in different plasticizer was evaluated. The PVC membranes containing CP-tetraiodomercurate as electroactive material and plasticized with three various plasticizers (DOP, DBS and o-NPOE) have been tested. Results are presented in Table 2. Ortho nitrophenyl octyl ether has appeared to be a Nernstian behavior.

Table 2. Analytical guidelines of CP- tetraiodomercurate PVC sensor.

Parameter	Iodide- PVC Sensor
Calibration curve	1×10^{-2} to 5×10^{-6}M

Slope	-55.0 ± 0.5
Intercept	- 414.0
Correlation coefficient, (r)	0.998
Lower limit of quantification, M	5×10^{-6}
Lower limit of detection, M	3×10^{-6}
Sensor response time, s	20
Working pH range	3 - 8

According to IUPAC guideline [29], the potentiometric response of CP-tetraiodomercurate as sensing material in o-NPOE has been evaluated. Table 2 shows the obtained results. The PVC membrane sensor show a calibration graph with rectilinear range of 1×10^{-2} - 5×10^{-6}M of iodide with anionic slope of 55 ± 0.6 mV/concentration decade with lower limit of detection of 3×10^{-6}M. The identical least squares equation extracted from the calibration curve is

$$E \text{ (mV)} = (-55.0 \pm 0.6) \log [\text{iodide}] - (414 \pm 0.5) \qquad (1)$$

3.2. Study of the plasticizer type

The general behavior of iodide sensor was tested in the presence of various plasticizer. Dioctylphathalate, DBS or o-NPOE have been examined as plasticizer in iodide PVC sensor. The calibration slope of the PVC sensor using either DOP or DBS was ~ 50 mV/decade. PVC-sensor plasticized with o-NPOE appears a good characteristics achievement. The calibration curve offer a wide dynamic range of slope of 55 ± 0.5 mV/ decade and lower limit of detection of 3×10^{-6}M. Due to its high dielectric constant (ε=24) of o-NPOE compared with low dielectric constant of DOP (ε=7) and DBS (ε=4), o-NPOE increase the membrane selectivity affects great dissolution of ion-pair within the membrane. Ortho-NPOE was used for all forthcoming study.

3.3. Influence of the measuring media and response time

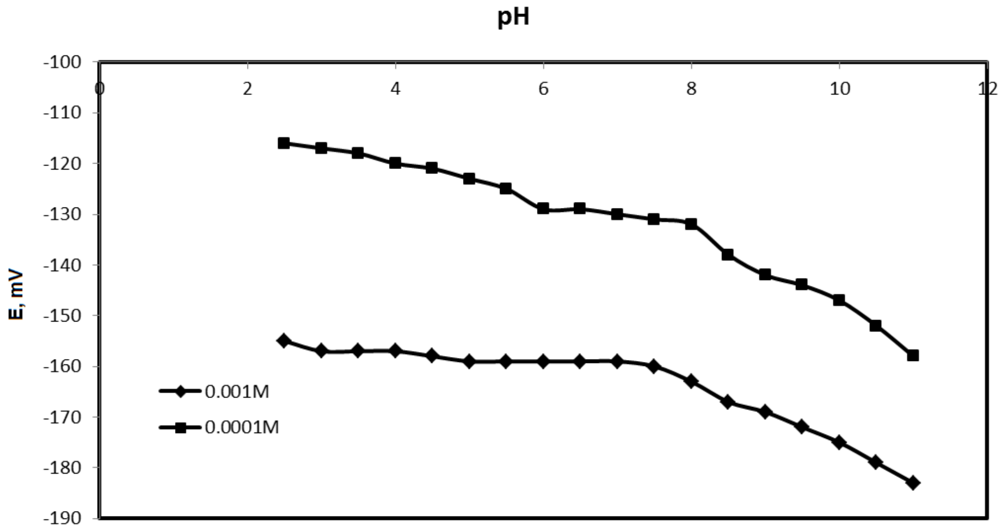

Figure 2. pH study of iodide-PVC sensor.

The electrode response for different iodide concentrations was examined at several pH values. Two solution of iodide was examined using different pH range. The pH was controlled using dilute solution of acidic solution or basic solution.

As shown in Fig. 2, the electrode response was approximately constant for each concentration in the pH range of 3 - 8. The electrode appears anionic slope of about 55 mV over the pH range of 3.0 - 8.0. Acetate buffer of pH 4.0 proved to be the best buffer, which the potential response almost stable to be less than ±1 mV changes with anionic slope of 55 mV per tenfold change.

The average response time[29] was observed to be 20 s for concentration of $\geq 1\times10^{-3}$M and $\leq$ 25 s for concentration 1×10^{-4} M. For about one month, the membrane sensor was proved accurate results, during that time the potential slope is constant within approximately ±1 mV per decade change.

3.4. Effect of Interference.

The effect of the tested ions on the response of iodide-PVC sensor was examined. The selectivity coefficients ($K_{A,B}^{pot}$) of the sensor was assayed utilizing the separate solutions method [30]. The next equation was used to estimate the selectivity coefficient using the separate solution method:

$$-\log K_{A,B}^{pot} = E_B\text{-}E_A/S$$

Where E_A and E_B are the potential reading observed after 1 min of the sensor response related to iodide and interfering species (same concentration, each). *S* is slope of the electrode (mV/ concentration). There is no interference from the investigated ions; results are shown in Table 3.

Table 3. Interference study of the proposed iodide sensor.

Interferent, J	$K_{I,B}^{Pot}$	Interferent, J	$K_{I,B}^{Pot}$
Na^+	3.9×10^{-3}	NO_3^-	3.8×10^{-3}
K^+	4.1×10^{-3}	$CH_3\,COO^-$	3.8×10^{-3}
Ca^{2+}	4.1×10^{-4}	Citrate	1.1×10^{-4}
Zn^{2+}	4.2×10^{-4}	SO_4^{2-}	4.1×10^{-4}
Mg^{2+}	4.1×10^{-4}	$Cr_2O_7^{2-}$	5.3×10^{-4}
Pb^{2+}	4.3×10^{-4}	F^-	5.5×10^{-3}
NH_4^+	3.9×10^{-3}	Borate	1.8×10^{-4}
Cl^-	5.8×10^{-3}	PO_4^{3-}	2.3×10^{-4}

3.5. Validity of the proposed method

3.5.1. Limit of quantification and limit of detection

The sensor showed a linear response over the concentration range of 1×10^{-2} - 5×10^{-6} M iodide with a Nernstian anionic slope of 55 ± 0.5 mV/concentration decade. The potential and concentration show a logarithmic relation: $X = S \log [AC] + Y$, where *X* is the potential, *S* is the slope, and *Y* is the intercept (- 414.0 mV) and correlation coefficient (r) equal 0.998 (Fig.3). According IUPAC guidelines, both lower limit of detection (LOD) and limits of quantification (LOQ) were assayed [29]. The lower limit of quantification was 5×10^{-6}, while LOD was 3×10^{-6} M.

3.5.2. Precision and Accuracy

To estimate the precision and accuracy of the suggested method, iodide ion was analyzed within the day and within three different days. As reported by Miller et al [31] accuracy and precision was estimated. The results are shown in Table 4. RSD% was recorded of less than 0.6% and accuracy was more than 98.5%.

Table 4. Accuracy and precision of the suggested iodide-PVC sensor.

Parameter	Iodide -PVC (126.9µg/ml) Within-day	Iodide -PVC (126.9µg/ml)* Within-days
R, %*	99.4	98.5
RSD, %**	0.4	0.6
Slope	55.0 ± 0.5	55.0 ± 0.8
Correlation coefficient	0.999	0.998

* n= 5 measurements
*Recovery % and ** relative standard deviation%

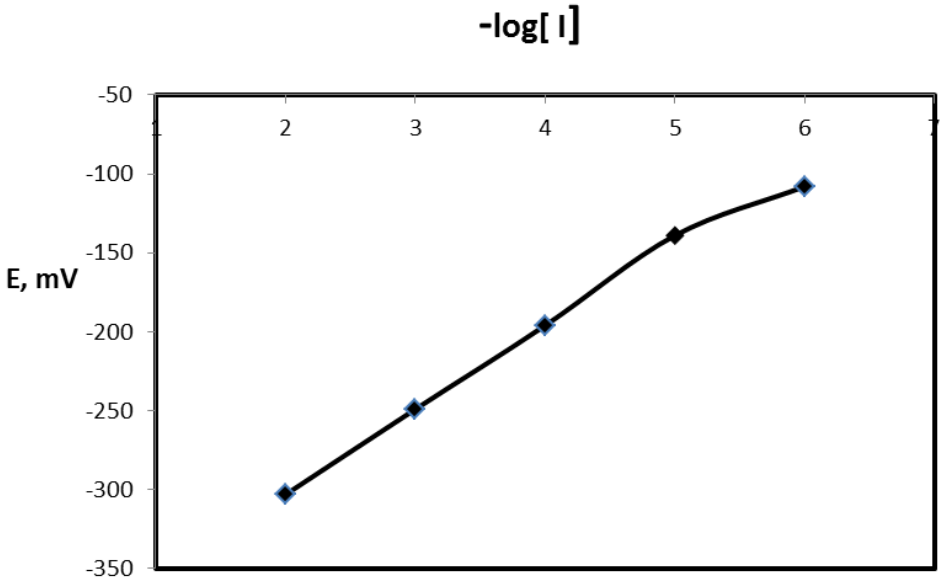

Figure 3. Calibration curve of iodide using iodide sensor.

3.5.3. Ruggedness

To estimate the ruggedness of the investigated method, the analysis of iodide was carried out two different machines and two different operators within the day, and different days. As reported by Miller et. [31] both accuracy and precision was assayed. The RSD% of less than 2.1% was obtained for repetitive measurements using different machines and operators. Also the accuracy of the suggested method was more than 98.0%. The results prove that the method is good ruggedness.

3.5.4. Robustness

The robustness of suggested method is evaluated by studding the optimum condition of the different parameters which simulating the electrode potential. The hydrogen ion concentration, response time, effect of different composition of the membrane, and effect of plasticizer was examined and optimized. Under the optimum condition, the obtained results indicate that the method is completely robust. The pH factor should be controlled. The optimum pH range should be in the range of 3.0- 8.0 and the maximum pH value was noticed at pH 4.0.

3.6. Application of the proposed sensor

The application of the iodide PVC sensor for assay of iodide was tested by measuring the accurate amount of iodide in pure solution. Iodide was determined using the proposed PVC membrane sensor. The iodide concentration over the concentration range 2.0 - 1269.0 μg/ml was examined using the proposed method. The mean recovery was 98.0% with a mean relative standard deviation of 1.9%.

The determination of iodide in flaxedil was examined by the investigated method. Results were appearing in Table 5, the results indicated that the method is appearing a good recovery values (98.5%) and RSD value (1.7%).

Table 5. Determinations of iodide in flaxedil® using the suggest method.

Added (μg/ml)	Found (μg/ml)	Recovery % ± RSD
42.75	42.37	99.1 ± 2.1
85.5	83.96	98.2 ± 1.7
128.25	125.94	98.2 ± 1.5
171.0	169.11	98.9 ± 1.5

The determination of iodide in flaxedil was investigated using the proposed PVC membrane sensor is compared with those of reported using the reported spectrofluorometric method [32] are given in Table 6. Proposed method show an average recovery of 98.52% with RSD value of 1.5% compared with reported method of a recovery value of 98.9% and RSD value of 1.6% [31]. The results indicate that tested method could be used in quality control laboratory for determine of iodide.

Moreover, the developed method has been also applied for assay of iodide in spiked different water sample. Results of determination were cited in Table 7, show the recovery of iodide ion spiked with different water: tape, river, waste and 5% saline water. The results show recovery value of 99.5, 99.2, 99.6 and 98.8% for tape, river, waste and saline water, respectively.

Table 6. Assay of iodide in flaxedil® using iodide PVC sensor compared with reported method.

Preparation	Proposed method* Recovery, % ± (RSD, %)	Reported method [32] Recovery,% ± (RSD, %)
Flaxedil (40 mg/2ml)	98.52 ± (1.5)	98.9 ± (1.6)

Table 7. Determination of iodide in spiked water sample

Sample	Iodide added(μg/ml)	Iodide found (μg / ml)	Recovery %
Tape Water	127.0	126.5	99.6
River water	127.0	126.0	99.2
Waste water	127.0	126.6	99.7
Saline water 5%	127.0	125.5	98.8

3.7. Uses of iodide -PVC sensor as indicator sensor

The developed sensor has been investigated as indicator sensor for potentiometric titrations of some metal ions, using precipitation titration reaction. Titration of mercury and silver ions with potassium iodide using iodide PVC sensor has been carried out (Figures 4 and 5). From the results, mercury and silver ion reacts with iodide in ratio of 2:1 or 1:1 for mercury and silver, respectively. The titration curves were symmetrical with a potential jump of about 250mV, in case of mercury or silver ion, respectively using the proposed sensor. Indicating that the high sensitivity of the developed sensor.

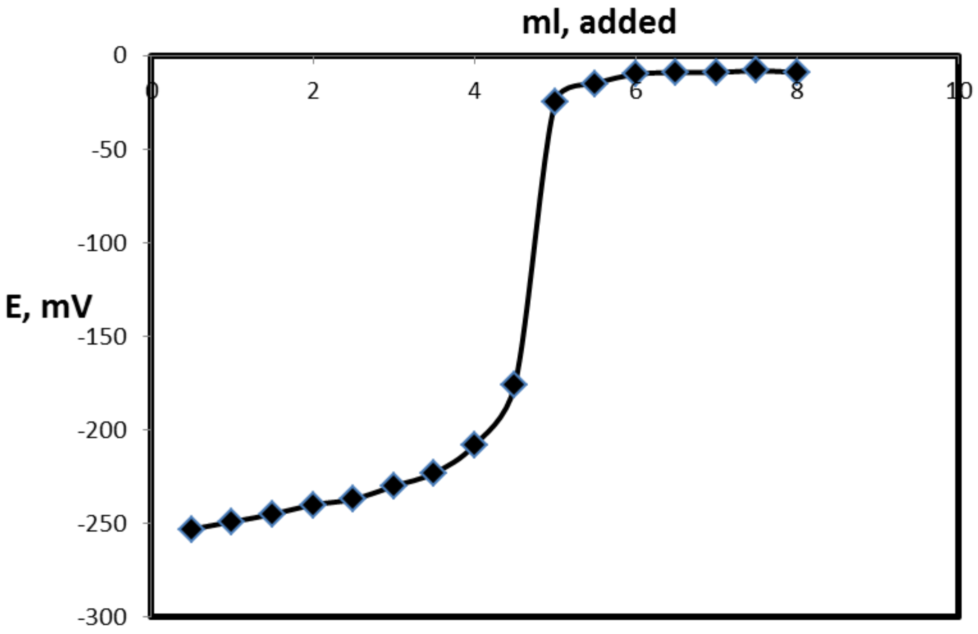

Figure 4. Titration of 0.01M of silver with 0.01M of potassium iodide

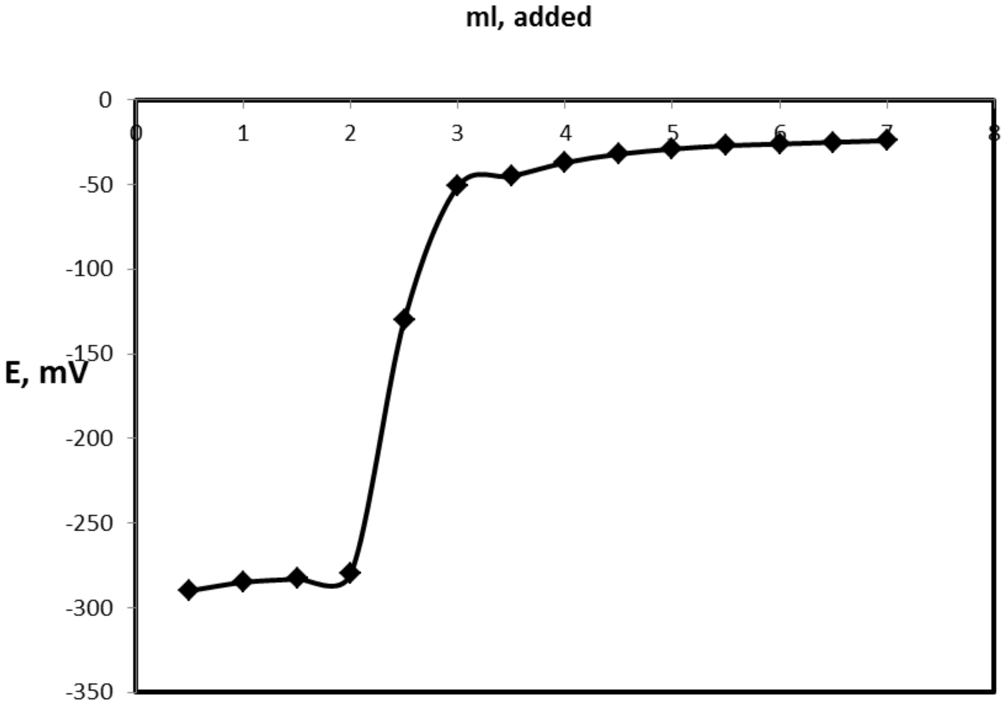

Figure 5. Titration of 0.01M of mercury with 0.01M of potassium iodide.

4. CONCLUSION

Tetraiodomercurate-cetylpyridinium ion-pair complex as sensing material has been used to develop a new sensor for determination iodide. The developed iodide sensor shows good analytical characteristics in the pH range of 3-8, which exhibit a wide dynamic range, and good selectivity. The suggested procedure has been applied to determination of iodide in flaxedil as well as in different water samples which has good accuracy and precision in comparable with the reported procedure. Moreover, the proposed sensor has been applied for determination of some metal ions using potentiometric titration.

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