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Real-Time Potentiometric Monitoring of Tetrachloroaurate(III) with an Ion-Selective Electrode and Its Applications to $HAuCl_4$ Iodide-Catalyzed Reduction by Hydroxylamine

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Abstract: Ion-selective electrodes for tetrachloroaurate(III) have been developed for potentiometric monitoring of the reduction reaction of tetrachloroaurate(III). Three different plasticized polyvinyl chloride membranes containing tridodecymethylammonium chloride as an anion exchanger were investigated. These membranes differ in the plasticizer used, either 2-nitrophenyl octyl ether (NPOE) or tricresyl phosphate (TCP) or bis-(2-ethylhexyl) sebacate (DOS). The potentiometric response of the electrodes to the tetrachloroaurate(III) concentration was studied by two methods. In the first method, commonly used in the calibration of ion-selective electrodes, successive tetrachloroaurate(III) concentration increments were used and the potential was allowed to stabilize after each concentration step. The second method was developed to mimic the tetrachloroaurate(III) reduction reaction in which there is a continuous decrease in the concentration of tetrachloroaurate(III). This was achieved by continuously diluting an initial concentration of tetrachloroaurate(III) by pumping a diluent solution while keeping the sample volume constant. This method gave an excellent linear response to the tetrachloroaurate(III) concentration. The calibrated electrodes were used for the potentiometric monitoring of the kinetics of a newly observed reaction: the reduction of tetrachloroaurate(III) by hydroxylamine catalyzed by iodide. A mechanism for this reaction is proposed on the basis of the experimental results obtained.

Keywords: tetrachloroaurate(III); ion-selective electrodes; potentiometric monitoring; tetrachloroaurate(III) reduction

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1. Introduction

Ion-selective electrodes (ISEs) are one of the most important classes of chemical sensors. They have several advantages such as a wide linearity range, low detection limit, high selectivity, fast response, low economic cost and viable measurements in turbid solutions, among others. They have been used in a variety of analytical fields, such as clinical analyses, environmental and food industry, in the agricultural industry and in industrial manufacturing [1].

Due to their excellent capabilities, ISEs have been used for the kinetic potentiometric monitoring of various chemical reactions. Despite the advantages and diversity of this class of chemical sensors, references on the use of ISEs for the kinetic monitoring of chemical reactions are not as common and diverse as one might expect. ISEs can be divided into three main classes according to the type of membrane used: glass membrane ISEs, crystalline membrane ISEs and liquid membrane ISEs or their current version, the plasticized polymeric membrane ISEs. A significant selection of published work on the kinetic monitoring of various types of chemical reactions using ion-selective electrodes of the three classes mentioned above is discussed below.

The pH electrode is the best-known glass electrode and has been used in the kinetic study of enzymatic reactions by pH-stat titration, such as the enzyme-catalyzed hydrolysis of urea by urease [2] and, more recently, in assays of the enzymatic degradability of bio-based polymers [3]. The fluoride selective electrode, which is a monocrystalline membrane ISE, has been used in the determination of EDTA by the displacement of fluoride from aluminium complexes by EDTA [4] and in potentiometric assays for acid and alkaline phosphatase based on the enzymatically catalyzed hydrolysis of monofluorophosphate [5]. The liquid membrane picrate selective electrode has been used for the determination of creatinine by kinetic monitoring of the reaction between creatinine and picrate (Jaffé reaction) [6]. The other important type of ISE is the polymeric membrane electrode, currently the most numerous classes of ISEs, to which the ISE developed in this work belongs. Examples of this type of electrode are the hexachloroantimonate(V) selective electrode, used for the kinetic potentiometric determination of iodide and copper based on the redox reaction between hexachloroantimonate(V) and hydroxylamine catalyzed by iodide [7], and the acetylcholine-selective electrode developed to monitor the enzymatic hydrolysis of acetylcholine catalyzed by acetylcholinesterase [8].

Another interesting application of ISEs is their ability to probe the growth dynamics of silver nanoparticles in real time using an ionophore-based silver-selective electrode [9]. On the other hand, a nitrate-selective electrode, one of the most studied polymeric membrane ISE, has been used in the synthesis of copper and silver nanoparticles using polyol [10]. In this case, the authors found that the reaction reduced nitrate from the copper nitrate precursor to nitrite. By monitoring the NO_x^- ($x = 2$ and 3) concentration in propylene glycol, the synthesis process of copper and silver nanoparticles could be followed.

Tetrachloroaurate(III) ion has recently become important for several reasons. Due to its reduction by various reducing agents, tetrachloroauric acid is the common precursor in the synthesis of gold nanoparticles [11]. Reactions of tetrachloroaurate(III) with various nucleophiles in aqueous solution have been reported [12]. In the search for environmentally friendly strategies for gold mining, the use of bacteriophages for the biosorption and bioreduction of tetrachloroaurate(III) has been demonstrated [13]. In the field of modern medicine, the structural effects of tetrachloroauric acid on cell membranes and molecular models have been reviewed [14] due to the evaluation of a number of Au(III) compounds as potential anticancer agents.

All these facts led us to search for the potentiometric monitoring of tetrachloroaurate(III) ion using a new ion-selective electrode. The detection of tetrachloroaurate(III) would provide an approach to monitor its chemical reactions and processes and to gain insight into their mechanisms. The standard ion transfer potential of tetrachloroaurate(III) $\Delta_m^w \phi^\circ$ between water and a polyvinyl chloride membrane plasticized with 2-nitrophenyl octyl ether (NPOE) was previously determined [15]. This parameter is directly related to the Gibbs standard energy corresponding to the ion transfer process between water and the membrane (organic phase) and to the partition coefficient of the corresponding ion between the two phases [16]. The standard ion transfer potential value found for tetrachloroaurate(III), 51 mV, is much higher than that reported for chloride from water to NPOE [17], −521 mV, which means that the potentiometric selectivity of a tetrachloroaurate(III)-selective membrane electrode based on a dissolved conventional anion exchanger towards chloride must be extremely high. This should make it possible to monitor the decrease in the concentration of the tetrachloroaurate(III) anion, even at low concentrations, in the presence of the high concentration of chloride coming from the hydrochloric acid medium.

The selective electrodes developed in this work have been used for the potentiometric monitoring of a newly observed reaction, the reduction of tetrachloroauronate(III) by hydroxylamine catalyzed by iodide.

2. Materials and Methods

2.1. Reagents and Solutions

Poly(vinyl chloride) (PVC) of high molecular weight, 2-nitrophenyl octyl ether (NPOE), tricresyl phosphate (TCP), bis-(2-etylhexyl) sebacate (DOS), tridodecylmethylammonium chloride (TDMACl, anion exchanger) and tetrahydrofuran (THF) were Selectophore grade from Sigma-Aldrich (Darmstadt, Germany). Tetrachloroauric(III) acid trihydrate 99% was obtained from Sigma-Aldrich. All other reagents used were of analytical reagent grade. A 0.1 M hydrochloric acid solution, 0.01 M tetrachloroaurate acid solution was prepared by taking 39.8 mg of tetrachloroauric(III) acid trihydrate and diluting to 10 mL with HCl 0.1 M solution. A 0.1 M potassium iodide solution and 5 M hydroxylamine hydrochloride solution were used. Milli-Q water was used throughout.

2.2. Apparatus and Electrodes

For potentiometric measurements, the following instruments and devices were used: an Thermo 900200 (Thermo Fisher Scientific Inc., Beverly, MA, USA) double-junction Ag/AgCl reference electrode with 1×10^{-2} M KCl solution in the outer compartment, and a home-made 6-channel potentiometer. During the acquisition of the potentiometric responses, the working solution was constantly stirred by magnetic stirring.

A Malvern Zetasizer Nano ZS (Malvern Instruments Ltd., Malvern, UK) was used for dynamic light scattering (DLS). Each measurement was set to 15 runs of 15 s each, so that the resulting distribution was obtained by averaging those of each run.

Absorption spectra were recorded using a T92 + UV–Visible spectrophotometer (PG Instruments, Lutterworth, UK).

2.3. Membrane Preparation

Three membranes with different compositions were prepared using different plasticisers (NPOE, TCP or DOS), PVC and TDMACl as an anion exchanger. The membranes were prepared by dissolving approximately 200 mg of the corresponding plasticiser, 100 mg of PVC and 1.5 mg of the anion exchanger in 3 mL of THF. This solution was poured into a glass ring (Fluka, inner diameter 28 mm, height 30 mm), placed on a glass plate (Fluka) and allowed to settle overnight until the THF had completely evaporated, resulting in a thin plastic membrane. The exact compositions of the membranes are given in Table 1.

Table 1. Composition of the membranes tested.

Membrane	PVC (wt.%)	NPOE (wt.%)	DOS (wt.%)	TCP (wt.%)	TDMACl (wt.%)
1	33.01	66.53			0.65
2	33.06		66.34		0.46
3	33.00			66.48	0.50

The electrodes prepared were conditioned in a 5.0×10^{-5} M tetrachloroauric acid solution in 0.1 M HCl. The duration of the initial conditioning was approximately 24 h. The storage of the electrode and a short conditioning between experiments were also carried out in this solution.

2.4. Calibration of the Tetrachloroaurate(III) Selective Electrodes

2.4.1. Calibration Procedure of Electrodes by Consecutive Tetrachloroaurate(III) Increments

The three $[AuCl_4]^-$ selective electrodes, together with the reference electrode, were immersed in 50 mL of 0.1 M HCl. Once the potential values had stabilized, successive additions of appropriate volumes of tetrachloroaurate solution were made to cover the concentration range from 1.0×10^{-7} to 1.0×10^{-5} M. After each addition, the potential values were allowed to stabilize. The potentials obtained after each addition were plotted versus the logarithm of the molar concentration of tetrachloroaurate(III) to obtain the corresponding calibration graph of the electrodes.

2.4.2. Calibration Procedure by Continuous Dilution

The three $[AuCl_4]^-$ selective electrodes and the reference electrode were immersed in 50 mL of 0.1 M HCl and allowed to stabilize. Then, 250 µL of 1.0×10^{-2} M tetrachloroaurate acid solution was added and the potential was allowed to stabilize. A dilution procedure was used in which 0.1 M HCl solution was pumped into the sample solution at a constant flow rate of 10 mL/min using a peristaltic pump, while at the same time the resulting solution was continuously removed at the same flow rate using another channel of the peristaltic pump in the reverse direction. In this way, the total volume of the sample was kept at a constant level. The reaction vessel was magnetically stirred at high speed to ensure rapid mixing. The dilution process was maintained for 1000 s.

The *E-t* plot of each electrode from the time the pump was switched on was used to obtain the corresponding calibration plot *E*-log *C*. To do this, the *C-t* plot corresponding to the continuous dilution was calculated from the equation [18]

$$C(t) = C_0 e^{\left(\frac{-Wt}{V}\right)} \tag{1}$$

where C_0 is the initial tetrachloroaurate(III) concentration, 5.0×10^{-5} M, W is the flow rate, 10 mL/min, t is the time and V is the initial volume, 50 mL. Finally, the corresponding plots *E*-log *C* were obtained by plotting *E(t)* versus log *C(t)*.

2.4.3. Procedure for the Kinetic Potentiometric Monitoring of the Tetrachloroaurate(III) Reduction by Hydroxylamine Catalyzed by Iodide

The ISEs and the reference electrode were immersed in 50 mL of 0.1 M HCl solution with constant stirring for about 50 s. Then, 250 µL of $[AuCl_4]^-$ 1.0×10^{-2} M was added. When the potential had stabilized, 400 µL of 5 M hydroxylamine hydrochloride solution was added, followed by 5 µL KI 0.1 M. The reaction was allowed to run for approx. 12 min. The potential was recorded throughout the procedure. Before measuring a new sample, the electrodes were washed with water and gently dried.

3. Results

Gold(III) in an aqueous medium containing chloride is present in the form of several chlorohydroxy complexes of the general formula $[AuCl_{4-i}(OH)_i]^-$, where i = 0–4. The relative proportions of the different complex species depend on the chloride concentration in the medium and the pH. The hydrolysis reactions of $[AuCl_4]^-$ to give the different complexes and the corresponding equilibrium constants have been reported [19].

In the present work, the vast majority of the gold(III) is initially in the form of the tetrachloroaurate(III) anion, for which a 0.1 M HCl medium is used. According to the first hydrolysis equilibrium,

$$AuCl_4^- + OH^- \leftrightarrows AuCl_3OH^- + Cl^- \quad \mathrm{K} = 10^{7.87}$$

the calculated value for the $[AuCl_4^-]/[AuCl_3OH^-]$ ratio is $10^{4.13}$.

3.1. Potentiometric Response of the Electrodes towards Tetrachloroaurate(III)

Firstly, the calibration of the constructed electrodes was tested using $[AuCl_4]^-$ successive increments. A wide range of concentrations was used, from 1.0×10^{-7} M to 1.2×10^{-4} M. The dynamic response of the electrodes obtained as described in Section 2.4.1 is shown in Figure 1a. The electrodes show a fast response to the $[AuCl_4]^-$ concentration steps from about 1.0×10^{-5} M, while they are slower at lower concentrations. The calibration curves obtained by plotting the potential obtained after each injection against the logarithm of the tetrachloroaurate(III) concentration obtained are shown in Figure 1b. The slope values of the calibration plots are not entirely constant over the whole concentration range tested, being higher in an intermediate concentration zone.

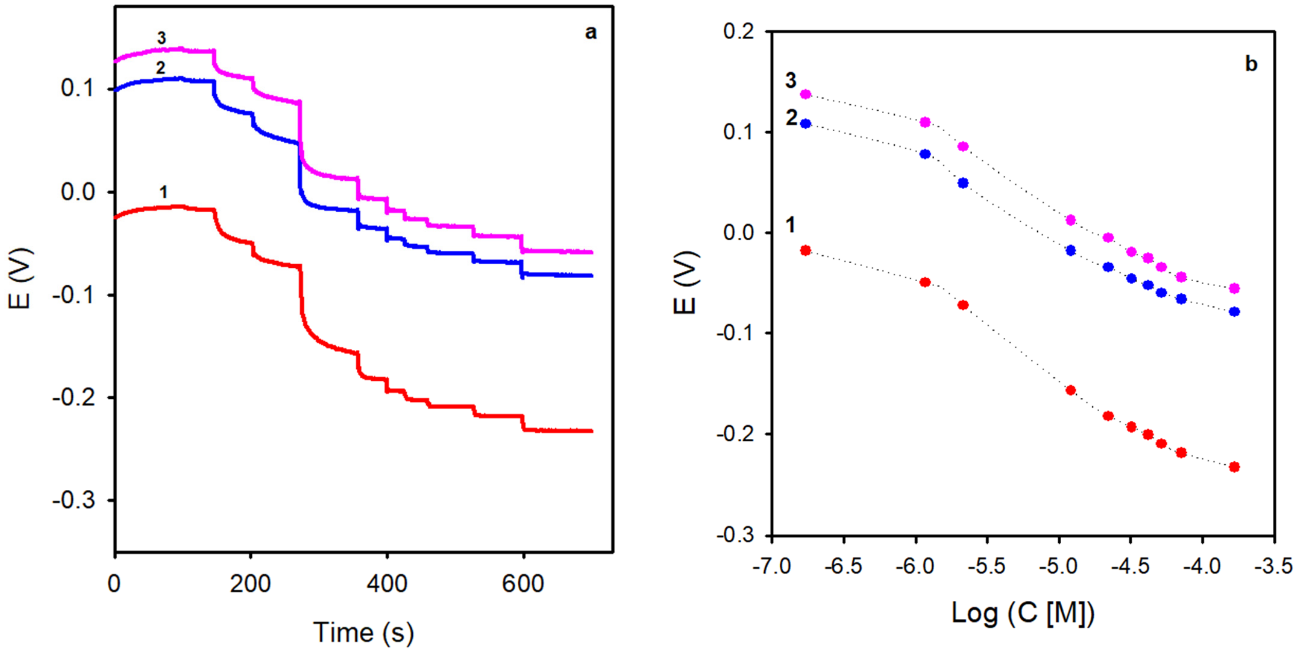


Figure 1. (**a**) Dynamic potential response of the electrodes towards tetrachloroaurate(III), 1 (red), 2 (blue) and 3 (pink). (**b**) Calibration graph *E*(V) vs. log (C[M]). Electrodes: 1 (red), 2 (blue) and 3 (pink).

In the present work, we have also tested another calibration procedure, based on a continuous dilution of a tetrachloroaurate(III) solution, which is close to the concentration variation that takes place in the gold(III) reduction reactions. The profile *C*-*t* obtained as described in Section 2.4.2 is shown in Figure 2.

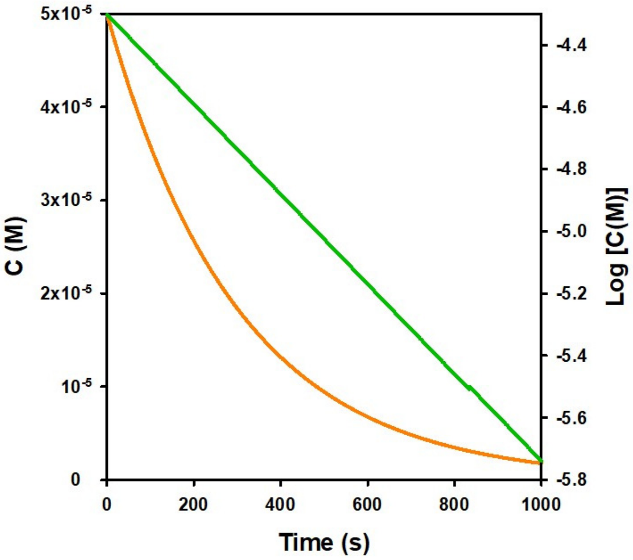


Figure 2. Tetrachloroaurate(III) concentration profile obtained by the continuous dilution process, *C* vs. *t* (left, orange) and log *C* vs. *t* (right, green).

Figure 3 shows the experimental *E*-*t* recordings obtained with the three electrodes by following the whole procedure described in Section 2.4.2. The initial potential values of the electrodes correspond to their response to the 0.1 M HCl solution. When 250 µL of

1×10^{-2} M tetrachloroaurate(III) was injected to achieve a final concentration of 5×10^{-5} M (see arrow A), a sudden and large potential decrease was observed, which indicates that all of the electrodes respond to tetrachloroaurate(III). Once the potential values of the electrode become stabilized, the dilution process was started (see arrow B). As can be seen, the potential of the electrodes starts to increase corresponding to a decrease in the tetrachloroaurate(III) concentration. To construct the corresponding calibration graphs, Figure 4, the potential during this dilution step was plotted versus the calculated log *C*. A linear relationship *E* vs. log *C* was obtained for the three electrodes in the whole concentration range assayed. The slopes obtained from the calibration plots were as follows: −49.8, −46.0 and −53.2 mV/decade for Electrodes 1, 2 and 3, respectively.

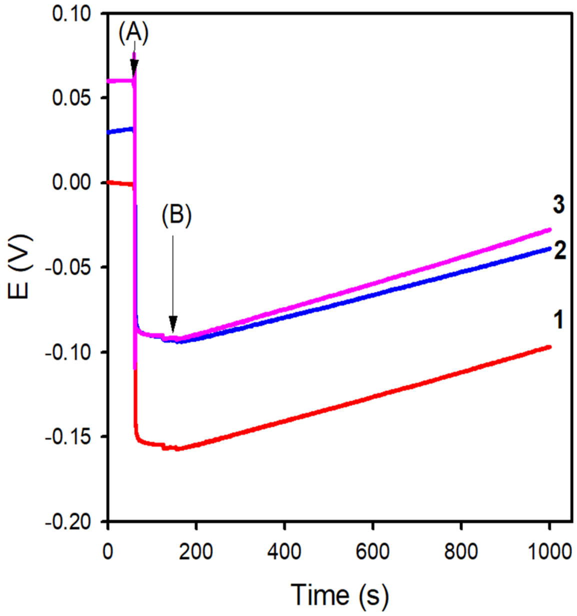


Figure 3. Potential vs. time recording during the whole calibration procedure by continuous dilution for Electrode 1 (red), 2 (blue) and 3 (pink). Initial solution, HCl 0.1 M. (**A**) Injection of 250 µL of 1.0×10^{-2} M tetrachloroaurate(III) solution. (**B**) Pump switching on.

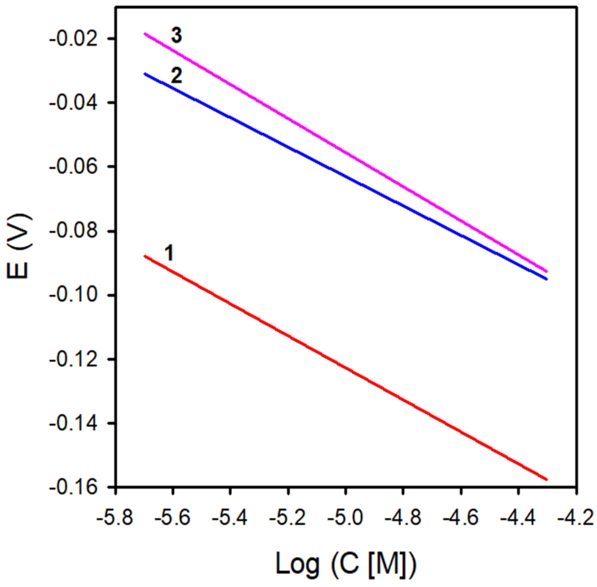


Figure 4. Calibrations graphs obtained for Electrodes 1 (red), 2 (blue) and 3 (pink) by the continuous dilution procedure.

Since the linear response extends down to the lowest tested concentration of tetrachloroaurate(III), 2×10^{-6} M, in the presence of a very high chloride concentration, 0.1 M, the selectivity of the electrodes towards $[AuCl_4]^-$ against chloride is very high.

3.2. Potentiometric Monitoring of Tetrachloroaurate Reduction by Hydroxylamine Catalysed by Iodide

A potential versus time recording corresponding to a typical $[AuCl_4]^-$ reduction experiment was carried out as described in Section 2.4.3 is shown in Figure 5. After injecting $[AuCl_4]^-$ into a 0.1 M HCl solution to reach 5.0×10^{-5} M $[AuCl_4]^-$, a rapid and large potential drop of the potential of all of the electrodes was observed, due to their potentiometric response to $[AuCl_4]^-$. Once the potential was stabilized, hydroxylamine solution was injected to reach a concentration of 4.0×10^{-2} M and no potential change was observed in any electrode. This indicates that no reaction between tetrachloroaurate(III) and hydroxylamine takes place during this time. However, when iodide solution was injected further to reach a concentration of 1.0×10^{-5} M, a continuous increase in potential was observed for all electrodes. This was attributed to a decrease in $[AuCl_4]^-$ due to its reduction. Since no potential increase was observed in an analogous experiment without the addition of hydroxylamine, it was concluded that the reducing agent was hydroxylamine and that iodide acted as a catalyst.

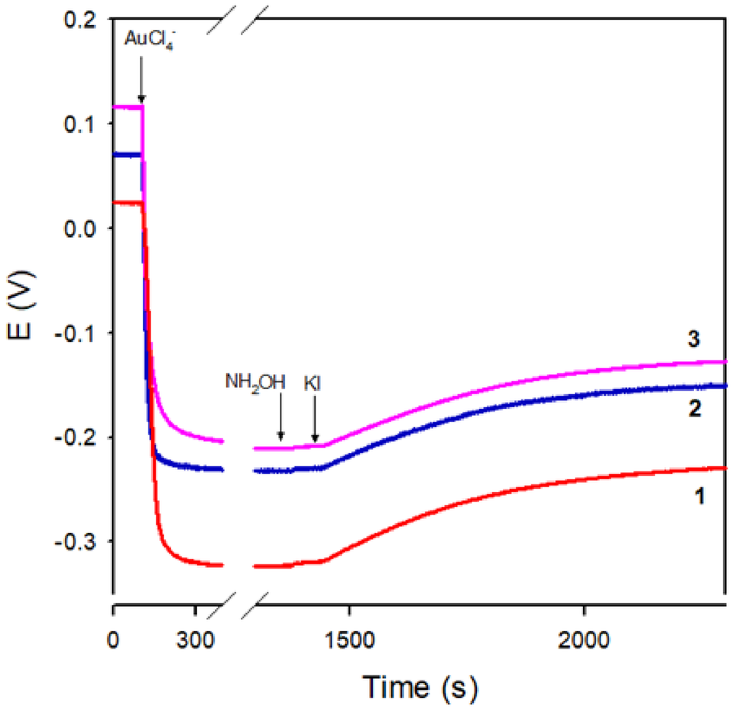


Figure 5. Potential versus time recording. Conditions: 50 mL HCl 0.1 M; 250 μL $[AuCl_4]^-$ 1.0×10^{-2} M; 400 μL NH_2OH 5.0 M; 5 μL KI 0.1 M; Electrodes: 1 (red), 2 (blue) and 3 (pink).

Also, as can be seen in Figure 5, the potential does not eventually return to the initial value. This may be due to the fact that the reduction product of $[AuCl_4]^-$ is $[AuCl_2]^-$ and that the electrode also responds potentiometrically to the latter anion. In fact, $[AuCl_2]^-$ is also the reduction product proposed by other authors under different experimental conditions [20,21].

In the case where the electrode response is due to $[AuCl_4]^-$ and $[AuCl_2]^-$, the equation for the potential response would be of Nikolsky–Eissenman type [22].

$$E = E^0 + S\log\left(\left[AuCl_4^-\right] + K_{ij}\ \left[AuCl_2^-\right]\right) \tag{2}$$

where K_{ij} is the selectivity coefficient of the $[AuCl_4]^-(i)$ electrode against $[AuCl_2]^-(j)$.

If the reaction kinetics are considered to be of pseudo first order with respect to $[AuCl_4]^-$, the potential vs. time Equation (3) is obtained, where C_0 is the initial tetrachloroaurate(III) concentration and k is the rate constant. By regrouping terms, Equation (4) is obtained. To test the validity of these hypotheses, the experimental E versus t values obtained after the addition of iodide were fitted to Equation (4) for the three electrodes. The results of the fitting were excellent, as shown in Figure 6. Table 2 shows the values obtained for the parameters: slope (S), selectivity coefficient (K_{ij}), kinetic constant (k) and the correlation coefficient.

$$E(t) = E^0 + S\log\left(C_0e^{-kt} + K_{ij}\,C_0\left(1 - e^{-kt}\right)\right) \tag{3}$$

$$E(t) = E^0 + S\log\left[C_0\left(e^{-kt} + K_{ij}\,\left(1 - e^{-kt}\right)\right)\right] \tag{4}$$

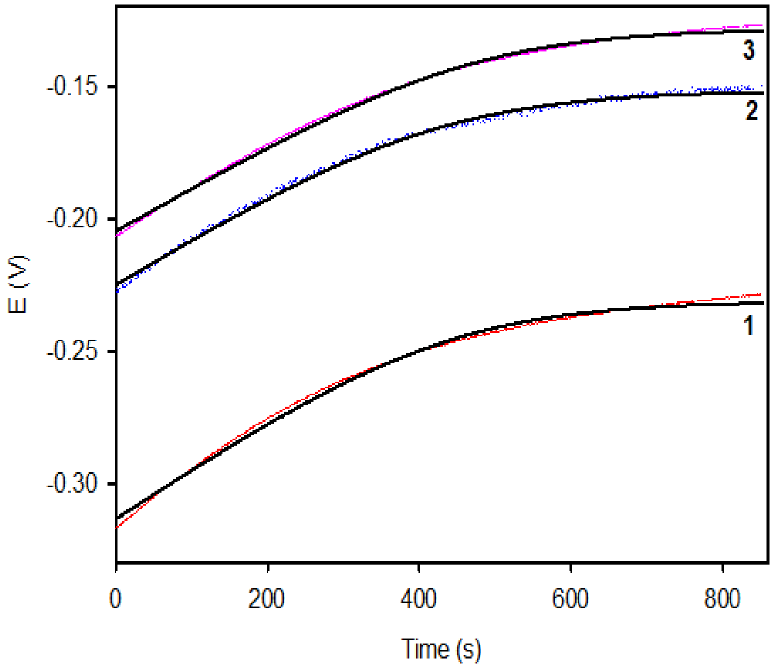


Figure 6. Experimental *E-t* recording obtained with electrodes, 1 (red), 2 (blue) and 3 (pink) and the corresponding plots fitted to equation (black).

Table 2. Parameters values found in the fitting of experimental data to equation.

Membrane	E^0 (V)	S (V/dec)	K_{ij}	k (s^{-1})	r^2
1	−0.546	−0.0541	0.0302 ± 0.0003	(8.20 ± 0.03) × 10^{-3}	0.996
2	−0.441	−0.0502	0.0349 ± 0.0003	(8.10 ± 0.03) × 10^{-3}	0.997
3	−0.404	−0.0464	0.0226 ± 0.0001	(8.20 ± 0.03) × 10^{-3}	0.998

Table 2 shows the values obtained for the parameters: slope (S), selectivity constant (Kij) and kinetic constant (k). The values obtained for the kinetic constant from the three electrodes were very similar. The selectivity coefficients for the three electrodes were relatively similar. These values of the selectivity coefficient indicate that Electrodes 1, 2 and 3 are approximately 33, 29 and 43, ($1/Kij$), times, respectively, more selective towards $[AuCl_4]^-$ than $[AuCl_2]^-$, which is due to the smaller size of the latter.

3.3. Spectophotometric and DLS Measurements

The reduction reaction of tetrachloroaurate(III) in the presence of hydroxylamine hydrochloride and iodide was also studied by UV spectrophotometry and DLS using the same concentrations as those used in the potentiometric study at different times from the mixing of the reagents. The UV spectra from 200 to 400 nm obtained at 0, 5, 10 and 15 min are shown in Figure 7. At time zero, when all the gold(III) is in the form of tetrachloroaurate(III), two peaks with maxima at 213 and 325 nm were obtained. These values are in line with those obtained by Mironov et al. [19] (note that in this work the spectra are shown with wave numbers). The height of both peaks decreases with time and after 15 min they are close to zero. No other peak appears during the reaction. The DLS recording shows no nanoparticle formation during the time studied (15 min).

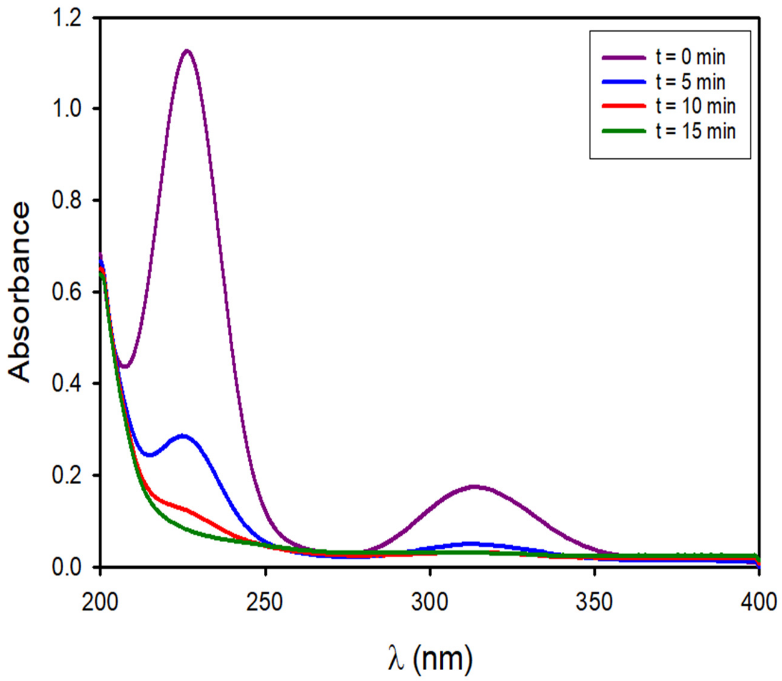
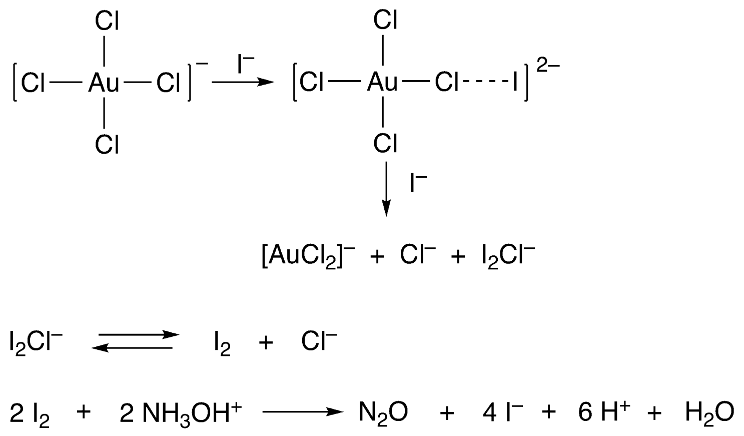


Figure 7. Absorption spectra of tetrachloroaurate(III) 5×10^{-5} M, hydroxylamine hydrochloride 0.04 M and iodide 1×10^{-5} M, at different times from their mixing.

3.4. Mechanism of the Studied Reaction

From the potentiometric monitoring of the reaction between tetrachloroaurate(III) and hydroxylamine hydrochloride and iodide in 0.1 M hydrochloric acid, the following mechanism is proposed (Scheme 1).



$$[AuCl_2]^- + Cl^- + I_2Cl^-$$

$$I_2Cl^- \rightleftharpoons I_2 + Cl^-$$

$$2\,I_2 + 2\,NH_3OH^+ \longrightarrow N_2O + 4\,I^- + 6\,H^+ + H_2O$$

Scheme 1. Proposed reactions for the iodide-catalyzed reduction of tetrachloroaurate by hydroxylamine hydrochloride.

First, tetrachloroaurate(III) begins to reacts slowly with iodide, which is in a large deficit with respect to $[AuCl_4]^-$, to form $[AuCl_2]^-$ and iodine, which in the presence of 0.1 M HCl would be mainly in the form of the $[I_2Cl]^-$ complex. This is supported by the results and mechanism proposed by Elding et al. [20] for the reaction between $[AuCl_4]^-$ and iodide under certain conditions. These authors also showed that $[AuCl_2]^-$ does not absorb between 200 and 500 nm. In our spectrophotometric study, shown in Figure 7, we found that no absorbance is observed other than that due to $[AuCl_4]^-$, which is then compatible with $[AuCl_2]^-$ as the reduction product. Moreover, the complete disappearance of $[AuCl_4]^-$ after 15 min agrees with the rate constant obtained here from the potentiometric monitoring. Furthermore, in our case, where hydroxylamine hydrochloride is present at a high concentration, a fast reaction would take place between the iodine resulting from the dissociation of $\left[I_2Cl\right]^-$ and the hydroxylamine cation, returning iodine to iodide (catalyst) and yielding N_2O as the oxidation product of the hydroxylamine cation. This is supported by the results of Liu et al. [23], who studied the reaction between hydroxylamine and iodine. Finally, a direct reaction between $[AuCl_4]^-$ and hydroxylamine has also been reported [21], but under different conditions from ours, which explains why it was not observed. Taking all this into account and the fact described in Section 3.2 that no significant potential change was observed by the addition of hydroxylamine alone on tetrachloroaurate(III), we confirm the hypothesis given in Section 3.2 that iodide acts a catalyst of the reaction between tetrachloroaurate(III) and iodide.

3.5. Further Prospects

There are several possibilities to extend the applications of the selective tetrachloroaurate(III) electrodes constructed in this work to the potentiometric monitoring of other reactions involving $[AuCl_4]^-$. Of particular interest are reactions involved in the formation of gold nanoparticles and in gold recovery processes from tetrachloroaurate(III) solutions. The suitability of the electrodes for these purposes seems very plausible in view of the low concentrations of $[AuCl_4]^-$ that they can detect and the expected high selectivity of the electrodes towards this anion in the presence of other common inorganic anions. This high selectivity is predicted from the standard potentials reported for the water/NPOE system. The corresponding values for bromide, nitrate and iodide are −428, −372 and −277 mV respectively [17]. These values are much lower than the value reported for tetrachloroaurate(III) [15], 51 mV, which indicates a very high selectivity for tetrachloroaurate(III) against these anions. Against sulphate, which is a divalent anion, the selectivity would be even higher.

4. Conclusions

The ion-selective electrodes developed respond potentiometrically to tetrachloroaurate(III). By using a calibration procedure that mimics the continuous concentration decreases that take place in tetrachloroaurate(III) reduction reactions, the electrodes permit the potentiometric monitoring of the reaction of tetrachloroaurate(III) in the presence of hydroxylamine together with iodide traces. A reaction mechanism has been proposed and the corresponding rate constant has been obtained. The developed electrodes could serve for the potentiometric monitoring of other tetrachloroaurate(III) reactions.

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