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Amperometric and potentiometric determination of iodide using carbon electrodes modified with salophen complex

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ABSTRACT

A statistical treatment was carried out on electrochemical methods intended for iodide determination as a tracer in seawater reservoirs. Comparison was made for amperometric and potentiometric detection, including the use of a modified carbon electrode. The potentiometric method showed a good linear correlation coefficient ($r = 0.9926$) with a Nernstian behavior in a concentration range of 10^{-5} to 1 mol L^{-1} (1.3 mg L^{-1} to 127 g L^{-1}) and a limit of detection of 1.3 mg L^{-1} (10 μmol L^{-1}). The amperometric method showed a good linear correlation coefficient ($r = 0.9988$) with a linear response over a concentration range of 1 to 4 mg L^{-1} (8 to 31.5 μmol L^{-1}) and a limit of detection of 0.5 mg L^{-1} (4 μmol L^{-1}). The statistic treatment has shown that the potentiometric method is promising to measure the iodide concentration in samples with high iodide content and the amperometric method is appropriate to measure the iodide concentration in samples with low iodide content, for example, in the case of produced water from petroleum reservoirs. Moreover, the salophen modified electrode can be readily used for routine analysis in laboratory.

1. Introduction

Oil reservoir tracers are chemical substances that are mixed to the injection fluid, usually water, allowing following its movement, and consequently the oil and water movements by sampling the produced water from the oil wells [1]. Since the beginning of the last century tracers have been employed in underground porous media of oil reservoir to extract information of reservoir properties, such as porosity, dispersion coefficient, fracture width, block size, etc. [2].

When considering a tracer species to be used in oil reservoirs, the most important tracer's properties are their stability, negligible reactivity with the porous reservoir rocks and its capability to be measured in a very low concentration level (around 0.1 mg L^{-1}) [3]. In addition, it cannot be expensive and must be water soluble, environmentally friendly, safe and easy to handle [4]. Iodide is such a good example of a chemical tracer that presents all of these properties.

The predominant dissolved iodine species in aquatic systems are the ions iodide and iodate and the organo-iodine compounds. Different iodine species may exhibit dramatically different mobility, bioavailability and chemical behaviors in the environment [5]. Iodine distribution in seawater depends on the depth and geographic position. Inorganic iodine is found in the range of 50 to 60 μg L^{-1}, while iodide concentration is about 30 μg L^{-1} close to the shore and at the ocean surface, and about 1 μg L^{-1} at deep levels. In the sea, iodide is produced from iodate by biological and other reduction processes. The redox cycle at work in surface water, involving iodate and iodide, has a significant effect on the ocean iodine concentrations [4,6].

It is a big challenge to develop a sensible and selective method to measure iodide concentration in produced water from off shore oil wells because the interference of seawater which also contains low concentration of iodate and iodide and a high chloride concentration. In addition, seawater contains significant concentration of carbonate and sulfate and has high ionic strength [3]. These conditions require preliminary steps of separation and concentration when using the traditional methods.

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Several analytical methods have been used for determination of iodine, iodate and iodide, such as chemiluminescence [7,8], inductively coupled plasma–mass spectrometry (ICP–MS) [9], inductively coupled plasma–atomic emission spectrometry (ICP–AES) [10], neutron activation analysis [11], diffuse reflectance spectroscopy [12], flow-injection analysis [13,14], ion chromatography [15], gas chromatography with mass spectrometry detection [16,17] and spectrophotometric detection [18]. However, most of them are expensive, involve several steps and they are time consuming. Some electrochemical techniques have been employed recently due to their high sensitivity, low cost, ease operation and good portability. Coupled with specially designed sensing interfaces, electrochemical techniques could offer a wide range of possibilities in analytical science [19–22]. Based on the iodide's electroactivity, electrochemical methods are commonly used to detect and measure iodide concentration without prior separation [18,23–30].

Tian and Nicolas [31] have studied iodine speciation in seawater by square wave voltammetry with cathodic stripping and a polarographic analyser with static mercury drop electrode. The total iodine was measured after an oxidation step using sodium hypochlorite and the formed iodine was measured by differential pulse voltammetry at the same electrode. As the total iodine in seawater is in two oxidation states, I(-I) (iodide) and I(V) (iodate), the iodate was determined by difference. Although polarographic methods have many advantages, such as low detection limits and high sensibility, the mercury static drop electrode presents high toxicity and cannot be apply for a high number of samples. Because of this, other kinds of electrodes were developed to iodide measurements. Some of them are the chemically modified electrodes (CME).

A chemically modified electrode was used for the first time by Murray et al. [32] in 1975 to control the physical-chemistry nature of the electrode/solution interface in such a way to improve the electrode reactivity and selectivity. Modified electrodes have also been used to quantify iodide. A potentiometric procedure based on the anodic stripping using carbon paste electrode containing a liquid paste of tricresyl phosphate was proposed by Švancara et al. [33]. A synergic accumulation effect, involving ion pairing and iodide extraction, and an electrolytic pre-treatment with a liquid paste are responsible for the selectivity of the method and allowed the iodide determination in table salt with a 20 mg L^{-1} detection limit. Zare et al. [34] studied also a chemically modified selective electrode to measure iodide in table salt. In this case, the electrode was made by a PVC membrane containing the $[Co^{III}(salophen)(pip)_2]^+$ complex. This potentiometric sensor has presented a linear response to iodide in the range of 64 μg L^{-1} to 12.7 g L^{-1}, Nernstian slope of -58.9 mV $decade^{-1}$ and a 38 μg L^{-1} detection limit. The proposed electrode was successfully applied for the direct determination of iodide in edible salt and as an indicator electrode in potentiometric titration of I^- against Ag^+.

Shim et al. [35] developed an iodide sensor to be used with square wave voltammetry to measure iodide in commercial sanitizers. The sensor was a carbon paste made with graphite powder and mineral oil and contained the $[Cu(quinine)(NO_3)_2]$ complex. Dipping the electrode in 1 mM iodide solution produced the $[Cu(quinine)I_2]$ complex by ligand exchange, which is selective to iodide. This voltammetric sensor has a linear response to iodide concentration in the range of 1.3 μg L^{-1} to 126 μg L^{-1} and a detection limit of 1.3 μg L^{-1}.

In our previous work amperometric and spectrophotometric methods were developed for measuring iodide tracer concentration in water produced from offshore oil reservoirs. The amperometric method using platinum ultramicroelectrode (Pt UME) exhibited a linear response from 1 to 10 mg L^{-1} with limit detection of 1 mg L^{-1}. Both methods showed to be accurate, linear, homoscedastic and their recoveries were 101 ± 2 and 100 ± 3%, respectively. High amounts of sulfate, however, interfere in the spectrophotometric method [18].

We report in this article a low cost, sensible and fast analytical method to determine iodide in produced water from oil reservoir using a chemically modified electrode. This study was performed in sodium chloride solution to simulate seawater conditions. The samples containing iodide and some interfering species (e.g. chloride, sulfate, bromide, and fluoride) were analyzed by means of chronoamperometry and chronopotentiometry. Furthermore, statistical analyses were employed to validate data obtained using CME (salophen complex) with glassy carbon and carbon paste for electrochemical analysis of iodide.

2. Experimental section

2.1. Materials and instrumentation

Sodium chloride (NaCl), potassium iodide (KI), cobalt(II) acetate and lithium perchlorate ($LiClO_4$) were purchased from Sigma–Aldrich (Saint Louis, MO). Methanol, ethanol and dimethylsulfoxide (DMSO) were purchased from Merck. All the reagents were of analytical grade and used without further purification, and all solutions were prepared in water purified by the Milli-Q Millipore system (resistivity ≥18 MΩ cm).

Electrochemical measurements were controlled with a potentiostat/galvanostat (Autolab, PGSTAT 100 model, Eco Chemie).

2.2. Synthesis and electrochemical characterization of the $[Co^{II}(salophen)]$ complex

The H_2Salophen ligand (*N,N′*-disalicylidene-1,2-phenylendiamine dianion) was prepared, as described by Amirnasr et al. Briefly, the condensation of 1,2-phenylendiamin with salicilaldehyde was made using a 1:2 stoichiometric ratio, in methanol, and the product was purified by recrystallization using ethyl acetate [36].

$[Co^{II}(salophen)]$ complex was made mixing the ligand solution in methanol with a water solution of cobalt(II) acetate. The mixture was kept at 60–70 °C under mixing, until a dark Orange precipitate was formed (typically after 1 to 2 h). The precipitate was recrystallized from ethanol. Scheme 1 shows a route to obtain the complex $[Co^{II}(salophen)]$.

The electrochemical characterization of the $[Co^{II}(salophen)]$ complex was carried out using a conventional single-compartment three-electrode glass cell by cyclic voltammetry applying the following conditions: scan rate to 0.1 V s^{-1}; potential range from -1.8 to 0.8 V vs Ag/AgCl/$LiClO_4$. $[Co^{II}(salophen)]$ (0.01 mol L^{-1}) was dissolved into DMSO and a solution 0.1 mol L^{-1} DMSO with 0.1 mol L^{-1} $LiClO_4$ was used as the support electrolyte. The working electrode was a Pt UME (diameter 25 μm) embedded in glass which was mechanically polished with emery paper (grade 600, 1200 and 2000; gradually) and cleaned with distillated water before use. In this experiment, a platinum wire was used as the counter electrode while an Ag/AgCl/$LiClO_4$ saturated in ethanol was the reference electrode.

2.3. Glassy carbon and carbon paste electrodes. Further modifications

Two kinds of electrodes were prepared. The complex $[Co^{III}(salophen)]^+$ was electrodeposited on glassy carbon electrode using a conventional single-compartment three-electrode glass cell. $[Co^{II}(salophen)]$ was dissolved into DMSO containing 0.1 mol L^{-1} of $LiClO_4$ (support electrolyte solution) to obtain a complex concentration equal to 0.01 mol L^{-1}. The electrodeposition of the complex was carried out by means of cronoamperometry at 0.6 V vs Ag/AgCl/$LiClO_4$ during 60 s. The working electrode in this experiment was a glassy carbon electrode (diameter 3.0 mm) embedded in polytetrafluoroethylene shrouds, which was mechanically polished with emery paper (grade 2000) and cleaned in distillated water before use. In this experiment, a high surface area platinum wire was used as a counter electrode while an Ag/AgCl/$LiClO_4$ saturated in ethanol was the reference electrode.