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# An in-situ electropolymerization based sensor for measuring salt content in crude oil



Rashed M. Aleisa, Naim Akmal\*

Saudi Aramco Research and Development Center (R&amp;DC), Dhahran 31311, Saudi Arabia

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## ABSTRACT

Determining salt content is a vital procedure in the petroleum industry during the process of crude oil transportation, refining and production. Monitoring the salinity value using a fast and direct technique can substantially lower the cost of crude oil in its processing and its production stages. In the present work, a novel analytical method was developed to detect the amount of salt present in crude oil in a quick and reliable manner. The measurement is based on the rate of in-situ electropolymerization of a monomer such as aniline in association with the salt content in the crude oil. The salt dispersed in the hydrocarbon matrix is used as an electrolyte in the electrolytic system to induce an electropolymerization reaction upon the induction of voltages, in which the salt content is measured corresponding to the polymeric film formation on the working electrode surface. Acetonitrile and N-methylpyrrolidone (NMP) were used in the electrochemical cell as solvents, and cyclic voltammetry tests were performed for Arabian crude oil solutions in the presence of aniline. The method has shown an excellent detection response for very low concentrations of salt. Four Arabian crude oils with salt concentrations of 34.2, 28.5, 14.3 and 5.71 mg L<sup>-1</sup> have produced current intensity of 180.1, 172.6, 148.1 and 134.2 μA at an applied current potential of 1.75 V (vs. Ag/AgCl), respectively. A Calibration curve was obtained in the range of 5–35 mg L<sup>-1</sup>, giving limits of detection and quantitation at 1.98 and 5.95 mg L<sup>-1</sup>, respectively. The in-situ electropolymerization based sensor has significant advantages over the existing techniques of salt monitoring in crude oil such as fast response, temperature independency, electrode stability, and minimum sample preparation.

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## 1. Introduction

In the oil and gas industry, the concentration of salt in crude oil produced depends mainly on the production source such as a drilling well and a reservoir [1]. Interaction of hydrochloric acid and dolomitic limestone with the contents of the well during its treatment causes the formation of sodium, magnesium, and calcium chlorides in the crude oil [2]. Additionally, the injection of seawater into the wellhead for enhancing oil recovery leads to crude oil contamination mostly by sodium chloride [1,3]. Salinity in crude oil creates problem for the petroleum industry. Large quantities of salt in crude oil may cause severe corrosion in pipelines, storage tanks, preheat exchangers, and condensers [1–5]. Additionally, deactivation and fouling of catalysts may take place during the refining process due to the high salinity of the hydrocarbons [4]. The salt content also negatively impacts the market price of crude oil per barrel which ultimately lowers

net return on investment [5]. The total amount of salt present in crude oil can vary dramatically, wherein it can be as high as 200,000 mg L<sup>-1</sup> or as low as 10 mg L<sup>-1</sup> [3]. Refining plants are equipped with a desalting process that is capable of reducing the amount of salts to a predefined level. Hence, the crude oil is analyzed before and after the desalting process to monitor the salt value and determine the efficiency of the desalting process.

Measurement of salt in crude oil is generally based on indirect techniques i.e., by measuring the electrical property of the hydrocarbon mixture [3]. This technique measures the difference in the electrical potential between conducting electrodes in a mixture of crude oil and solvents, wherein the salinity of the solution mixture is tied to the conductivity values reported [3]. Various analyzers utilizing such sensing techniques have been developed and are commercially available [1]. However, this sensing technique poses significant limitations such as reliability, long life-span, and accuracy during real-time analysis. Furthermore, electrode surface in these sensors is prone to corrosion, which changes its surface characteristics leading to erroneous readings. The physical deterioration of the electrode surface produces a larger error, especially during the measurement of low salt concentrations.

\* Corresponding author. Tel.: +966 13 876 8334; fax: +966 13 876 8565.

E-mail address: [naim.akmal@aramco.com](mailto:naim.akmal@aramco.com) (N. Akmal).

In addition, the laboratory method based on the ASTM method (D-3230) for measuring salt content in crude oil requires prior extraction of salt and extensive use of solvents [3].

We present in this paper, the development of an indirect and novel method based on electro-initiated polymerization via the controlled potential method to monitor the amount of salt present in crude oil [6]. The electropolymerization reaction is based on a free radical mechanism as the monomer polymerizes through applied potentials (i.e., voltages) in the presence of electrolytes. The mechanism and kinetics of many electropolymerizable monomers have received great attention in the past [7–10]. Various monomers can be used in electropolymerization methods including aromatic benzoid compounds such as aniline and phenylenediamine. The reaction of these monomers is usually an oxidative coupling polymerization with a small possibility of reductive polymerization [6]. The analytical solution described below utilizes this technique which involves the basic elements of an electrolytic chemical cell. In essence, the salt present in the crude oil can be utilized as a conductive solution for an electropolymerizable monomer, which on contact with electrical applied voltages, will start the polymerization process. The relationship between solution conductivity and the produced amount of polymeric material has been previously studied [11]. It is expected that an increase in electrolyte concentration will increase the rate of electropolymerization reaction [11]. Hence, the salt concentration in an electrolytic system can be measured by calculating the rate of electropolymerization (i.e., amount of the produced polymer on the working electrode). This hypothesis is intended to be used to measure the salt concentration in crude oil with a similar electrolysis method. This technique is expected to provide a direct read-out of the salt value in a real-time analysis of crude oil without extensive sample preparation, leading to an enhanced capability of salt monitoring during crude oil transportation and processing.

## 2. Experimental

### 2.1. Materials and apparatus

Acetonitrile, thiophene, aniline, NMP, methanol, butanols, dibenzothiophene (DBT), sodium chloride (powder), dichloromethane, and hexane were purchased from Sigma-Aldrich, and methyl-tetra-butyl-ether (MTBE) was purchased from Burdick and Jackson (Honeywell). Arabian crude oil samples were obtained from the Abqaiq oil field in Saudi Arabia. Deionized water (DI) with  $18 \text{ M}\Omega \text{ cm}^{-1}$  was obtained by the Milli-Q system in our laboratory. The silver/silver chloride reference electrode (Ag/AgCl), platinum disk electrodes, and polishing kit were purchased from (BASi) Bioanalytical Services. Cyclic voltammetry experiments were performed on the EG&G potentiostat (Model 263A). The reference electrode (Ag/AgCl) was fitted with a flexible connector. All chemicals were used as received without any further purification.

### 2.2. Electropolymerization of aniline, DBT, and thiophene

The electropolymerization reaction was conducted using a similar procedure described in the literature [6–9]. Initially, 0.25 g of sodium chloride was dissolved in 1.0 mL of DI water to be used as the electrolyte solution. The mixture was then added to a 0.5 mL solution of aniline in the presence of 2.0 mL of acetonitrile. The prepared mixture was stirred using a magnetic stirrer for 15 min at an ambient temperature. Counter, reference and working electrodes were placed inside the mixture, and cyclic voltammetry was performed on the solution using an EG&G potentiostat. The potentiostat was scanned in the range of  $-3.0$  to  $4.0 \text{ V}$  (vs. Ag/AgCl) electrode at a sweeping rate of  $10 \text{ mV/s}$ . The solution stirring

rate during the cyclic voltammetry was kept low because a high stirring rate can hinder the rate of electropolymerization [10]. The experiment was repeated for other monomers as well (i.e., DBT and thiophene) under the same experimental conditions.

### 2.3. Electropolymerization of aniline in the presence of crude oil

The electropolymerization of aniline in the presence of crude oil was carried out using the same procedure as described before. However, NMP was added to the solution to enhance the electroconductivity of the mixture. 1.0 mL of aniline was initially dissolved in 5 mL of acetonitrile using a magnetic stirrer under an ambient temperature. In a separate container,  $3.0 \mu\text{L}$  of crude oil was dissolved in 5 mL of NMP under the same conditions. Both solutions were then mixed together and stirred for 15 min with a magnetic stirrer. A standard amount of aqueous sodium chloride solution with a concentration of  $3.4 \times 10^{-6} \text{ mol L}^{-1}$  was added to the mixture while stirring to ensure a standard concentration of salt present in the mixture. The final solution was placed inside a small glass vessel fitted with three electrodes. Once the electrodes were connected to the potentiostat, a sweeping potential was applied across the counter and working electrodes in the reaction cell using the same cyclic voltammetry parameters. These steps were repeated for four different Arabian crude oil samples, with four different quantities of salt ranging from 4 to  $35 \text{ mg L}^{-1}$ . The actual amount of salt present in the crude oil was determined by the ASTM Standard Method (D-3230).

## 3. Results and discussion

### 3.1. Electrolysis of monomers using cyclic voltammetry

A platinum disk electrode, with a small surface area ( $1 \text{ cm}^2$ ), was used as the working electrode so that very small quantities of analyte (i.e., crude oil) in micro liters are sufficient for the in-situ electropolymerization, while a platinum electrode with a larger surface area ( $1.5 \text{ cm}^2$ ) was employed as a counter electrode. Electrodes and solution were placed in a specially designed vessel, in which the electrode surface and the reference electrode junction area were completely immersed in the mixture to sustain electrical interference without noise or abnormalities. The sweeping of electrical voltages, at the monomer specific electropolymerization potential, induces the formation of a thin layer of polymeric film on the working electrode surface. The final output of the electrical scanning potentials represents the voltammogram of current vs. voltage; where the peak current (intensity) reflects the amount of the produced polymer on the working electrode. The intensity of the peak can be then correlated to the amount of salt present in the hydrocarbon matrix.

The first stage of the analytical method development consists of selecting an appropriate monomer for the in-situ electropolymerization reaction. DBT, thiophene, and aniline were therefore tested as potential monomers. The reaction was conducted without the crude oil mixture using only a  $1.2 \times 10^{-5} \text{ mol L}^{-1}$  of aqueous sodium chloride solution. The resulting voltammograms of each monomer are shown in Figs. 1–3 for DBT, thiophene, and aniline, respectively. An electropolymerization reaction was not observed in the DBT solution as seen from the absence of a current peak in Fig. 1. This could be due to the steric hindrance effect present in the DBT structure that impedes the initiation of free radicals in a low salt content. Electrolysis of thiophene has produced a polymeric film as apparent from the current peak in Fig. 2. The thiophene monomer was electropolymerized at a current potential of  $1.6 \text{ V}$  (vs. Ag/AgCl), which produced a current intensity of  $135 \mu\text{A}$ . However, a further repetition of the

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