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Application of electrochemical impedance spectroscopy: A phase behavior study of babassu biodiesel-based microemulsions

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ABSTRACT

Microemulsions are thermodynamically stable systems of two immiscible liquids, one aqueous and the other of organic nature, with a surfactant and/or co-surfactant adsorbed in the interface between the two phases. Biodiesel-based microemulsions, consisting of alkyl esters of fatty acids, open a new means of analysis for the application of electroanalytical techniques, and is advantageous as it eliminates the required pre-treatment of a sample. In this work, the phase behaviours of biodiesel-based microemulsions were investigated through the electrochemical impedance spectroscopy (EIS) technique. We observed thatan increase in the amount of biodiesel in the microemulsion formulation increases the resistance to charge transfer at the interface. Also, the electrical conductivity measurements revealed that a decrease or increase in electrical properties depends on the amount of biodiesel. EIS studies of the biodiesel-based microemulsion samples showed the presence of two capacitive arcs: one high-frequency and the other low-frequency. Thus, the formulation of microemulsions plays an important role in estimating the electrical properties through the electrochemical impedance spectroscopy technique.

1. Introduction

Babassu (*Orbignya phalerata*) plants, belonging to the family of Arecaceae, is a native species of South America and is largely cultivated in different states of Brazil [1–3]. The cusi oil extracted from the seeds of these palms, which basically consists of saturated fatty acids, such as lauric (48%), myristic (16%), palmitic (10%) and other unsaturated acids, is an important source for the production of biodiesel [4]. Biodiesel and other biofuels from biomass or vegetable oils are considered as renewable and biodegradable sources of energy, and offer a reduction in air pollution compared to fossil fuels [5].

Biodiesel, as a fuel, offers advantages over fossil fuel; however it also presents disadvantages: poor cold flow properties, high viscosity, and low chemical and thermal stabilities which cause the formation of wax, when exposed to low temperature [6]. Furthermore, its low conductivity, due to its high resistance, hindered the applications of electroanalytical techniques, which intend to decrease the interests of its measurement. An alternative, more physically realistic approach is to consider the use of a surfactant to reduce the interfacial tension and enhance the electrochemical properties (like dipole moments) of micelles. Therefore, the preparation of biodiesel-based microemulsions presents an alternative means for the use of analytical methods, avoiding the conductivity resistance hindrance of the medium of interest [7]. The microemulsions are clear, isotropic and thermodynamically stable interfacial systems, consisting mainly of three or more constituents, produced spontaneously by self-organization of surfactant and/or co-surfactant molecules in the oil–water interfaces, forming microstructures dispersed in a continuous medium [8].

Castro Dantas and collaborators, developed some diesel-based microemulsions with blends of diesel and vegetable oils, to investigate the influences of the nature of surfactant (Texapon HBN and Comperlan SCD), cosurfactant and oil phases, as well as the surfactant/co-surfactant mass ratio [9]. Although the current standards for biodiesel analysis do not include dielectric characterization, there have been an increasing number of works, that explore the use of electrochemical methods to assess the properties of biofuels [10,11]. Perini et al. evaluated the application of the electrochemical impedance spectroscopy technique for the characterization of contents of petroleum and water-in-oil emulsions of the refining production process at different stages [12].

Thus, electrochemical impedance spectroscopy (EIS) has been proposed as a simple and non-invasive way to characterize biodiesel, diesel and their mixture samples. The proposed technique allows us the determination of physical properties, i.e. dielectric constant, resistivity and relaxation time or frequency, which have been shown to be sensitive to the inherent characteristics of the fuel. This strongly recommended

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the implementation of EIS measurement of biodiesel and/or diesel samples, to evaluate and monitor the processes of production and quality of biofuel products [13,14].

The objective of this study is to evaluate the use of microemulsions, as a means of analysis by providing an easy and stable handling system and decrease the use of organometallic standards and carcinogenic solvents in the pretreatment of analytical samples, to measure the electrical properties through electrochemical impedance spectroscopy.

2. Materials and methods

2.1. Materials

The materials used for biodiesel synthesis were: refined babassu oil (commercial, purchased from a local market), methanol (99.5% purity), and sodium hydroxide (97.0% purity).

The materials used for the preparation of microemulsion systems were:

a) The ultrapure water with a specific resistivity of 18.2 MΩ cm, obtained from a Nanopure Master water purification system (Gehaka, USA).
b) The surfactant Triton® X-100 (Merck) and the alcohols (Merck): ethanol and isopropanol.
c) Biodiesel samples were produced in the laboratory, at the Federal University of Maranhão, São Luiz, Brazil.

2.2. Synthesis of biodiesel

For the production of biodiesel from babassu seed oil, a one step catalysed process was adopted [15]:

The crude oil, pre-dried at 100 °C in the oven for 2 h, was esterified with methyl alcohol, in the presence of sodium hydroxide as a catalyst, in a reactor at 60 °C with agitation for 1 h. After the completion of the reaction, the product mixture was poured into a separating funnel for the decantation of byproducts (glycerine), which subsequently separates the biodiesel from glycerol.

Subsequently, the biodiesel was washed with a dilute acid solution to neutralize it. After washings, pure biodiesel was kept in the oven at 100 °C, to reduce the moisture content, and finally, the dried biodiesel, identified, was stored in a closed flask.

2.3. Characterization of biodiesel

The confirmation of a transesterification reaction of alkyl ester babassu oil was performed through infrared spectroscopic analysis (1000 at 4000 cm^{-1}). To ensure the quality of the biodiesel, samples were characterized by a number of analytical methods: (A) methods to evaluate the production process, as an aspect, i.e. methanol content and flash point; (B) methods to evaluate the inherent properties of the molecular structures, such as density, viscosity and iodine index, and (C) methods for monitoring the storage stability of biodiesel, i.e. oxidative stability and acid index [16].

2.4. Construction of microemulsion systems

The babassu oil samples, after characterizing its parameters, as mentioned above, were used as one of the components for the construction of microemulsion systems. Besides biodiesel, water, surfactant (S) Triton® X-100, and ethanol as co-surfactant (CS) were used as constituents of diagrams. The construction of the phase diagram was made by preparing several samples of the above-mentioned constituents, weighted at different proportions. The samples were homogenized manually by stirring and then kept thermostatically in closed tubes, to avoid any loss of the component, at 25 °C for a few days. During this period, changes in their physical appearance (phase separation) were observed that ceased to reach chemical equilibrium. While in some cases, the differentiation in the phases took a week to occur.

2.5. Identification of biodiesel-based microemulsions regions in phase diagram

The identification of regions in the diagram was performed visually. Three regions comprising one phase, two phases and three phases, were being observed. The region of one phase, that has a clear appearance and transparent, is identified as the microemulsion region, depending on its location in the diagram, and can be distinguished as a microemulsion of water in oil (region of the diagram with more oil), or as an oil in water microemulsion (region of the diagram with more water). Other regions were of biphasic and triphasic systems, formed by an excess of one or more constituents of the system.

After characterizing the phase diagram, three microemulsions were selected for the electrochemical impedance spectroscopy measurement. The selection of the samples was realized by varying the composition of the microemulsion, particularly, based on the increase in the concentration of the biodiesel sample, and with a subsequent decrease in the amounts of water.

2.6. Electrochemical impedance spectroscopic measurements

The electrochemical impedance measurements were performed in an electrochemical cylindrical cell, containing two platinum electrodes of dimensions (1.2×0.4 cm^2), with a capacity of 1 mL of sample. To obtain the electrochemical experimental data, an Autolab Electrochemical Analyzer (Metrohm) PGSTAT 302 coupled to a computer for data logging, using the software program: FRA — Frequency Response Analyzer, was used. The EIS measurements were performed in the electrochemical cell containing 0.5 mL of methyl babassu biodiesel-based microemulsion sample, where the following parameters have been established: frequency range of 0.1 Hz to 10^5 Hz, amplitude of 15 mV rms, open circuit potential (OCP) time 20 s and 10 points per decade/frequency for each perturbation of AC potential. The electrical conductivity measurement was performed by using the conductivity of Digimed, Model DM 32.

3. Results and discussion

3.1. Synthesis and characterization of biodiesel

The production of methyl babassu biodiesel (MBB-100), through a methanol route, obtaining approximately 89% yield relative to the amount of crude babassu palm oil, was identified, from the presence

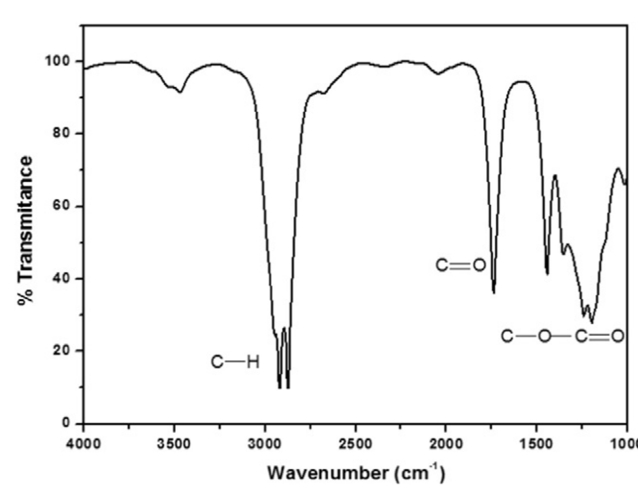

Fig. 1. Infrared spectra of the pure methylated biodiesel (MBB-100).