DETERMINATION OF WATER CONCENTRATION IN WATER-IN-OIL EMULSIONS BY THE IMPEDANCE SPECTROSCOPY METHOD

Matheus Puttinati Casari
Faculty of Mechanical Engineering- University of Campinas
matheuscasari@gmail.com

Niederauer Mastelari
Faculty of Mechanical Engineering- University of Campinas
niede@fem.unicamp.br

Eugênio Spano Rosa
Faculty of Mechanical Engineering- University of Campinas
erosa@fem.unicamp.br

Vanessa Cristina Bizotto Guersoni
Center for Petroleum Studies – University of Campinas
vanessa@cepetro.unicamp.br

Fabiana de Assis Perrechil
Center for Petroleum Studies – University of Campinas
fabiana@cepetro.unicamp.br

Abstract. *The volumetric concentration of water in crude oil production is a parameter constantly monitored to access the ever changing reservoir properties as well as for economical purposes; after all what is needed is the net oil production. The measurement of water in oil is usually done over-the-bench (sampling the crude stream and screening in a chemistry lab) or by online instruments which continuously monitor the concentration. One of the techniques for online assessment of water concentration is the impedance spectroscopy. In fact, the dielectric property of the liquid phase is proportional to the electrical impedance. In the present analysis it was considered that the water phase is finely dispersed on the oil phase in the form of an emulsion. The objective of this work was to compare the measured water concentration against model's prediction based on the measured dielectric properties of the emulsion. The water in oil emulsions were synthesized in laboratory conditions. The water concentration range was 13.1% to 41.1% (v/v) at temperatures of 25ºC to 60ºC and water salinity of 0 (de-ionized water), 1kg/m³ and 10kg/m³ of NaCl. The emulsion dielectric constant was measured in a sensor made by two concentric cylinders whose height is of five cylinder diameters. This geometry favors to radial electric field lines and minimizes the end effects. The complex dielectric constant was measured by the Precision LCR Meter Agilent E4980A in a frequency range of 85 kHz to 250 kHz. The experimental data was found proportional to the volumetric concentration and follows Maxwell correlation within 3%. The experimental tests also disclosed that the dielectric constant, or the volumetric concentration, were almost insensitive to the changes in temperature and in salinity.*

Keywords: Impedance Spectroscopy, Water-in-Oil Emulsions, Water Concentration Measurement.

1. INTRODUCTION

During the oil production, it is common that the water appears in the form of droplets dispersed in oil and it is generally called as water-in-oil emulsions (W/O). Due to the water previously contained in the reservoirs and also due to the water injected in the oil wells by extraction and recuperation methods, the oil and water phases flow as a mixture inside the duct. The emulsion is generated due to the breakup action of the turbulent eddies. The volumetric concentration of water in crude oil production is a parameter constantly monitored to access the ever changing reservoir properties as well as for economical purposes; after all what is needed is the net oil production. Therefore it is important to know the water content in the oil production.

The field measurement techniques of volumetric concentration of water in crude oil emulsions are: capacitive based on the difference of permittivity values between water and petroleum, Near Infra Red (NIR) and gamma ray measurements. There are instruments that use gamma-ray attenuation to measure water concentration in crude oil, but they are very expensive, and they need governmental licenses and care with safety questions. The NIR is an accurate technique that uses the differences in infrared light absorption of hydrocarbons and water for measurement. However it requires sophisticated optical systems and pattern analysis to obtain good results. The capacitive sensors are simple and inexpensive, the probes are suitable for the demands of robustness in petroleum production and transportation and can be used on line to measure water fraction in fast and efficient way. This work objective is to study W/O emulsions

using impedance spectroscopy. It evaluates the relation between the water volumetric fraction and the electrical admittance of water-in-oil emulsions, the influence of salinity and temperature and the appropriate range of excitation frequency for the measurements.

The study is also a fundamental way to evaluate the use viability of online impedance sensors for the measurement of volumetric content of water in oil emulsions. Tests were conducted under controlled in laboratory conditions to understand, the electrical characteristics of the W/O emulsions and the relation between the water content and the complex permittivity of the mixture. The independent parameters analyzed were the volumetric fractions of the continuous and dispersed phases of oil and water respectively. Furthermore possible influences of temperature and water salinity were considered and analyzed on the measured results.

2. METHODOLOGY

2.1. EMULSIONS

Emulsions are dispersions between two or more immiscible or partially miscible liquids in which its disperse phase consists on droplets with size ranging from $0.1\,\mu$ to $100\,\mu$. The most of emulsions have an aqueous and an oleaginous phase (Karcher, 2008). The dispersion which contains oil as continuous phase and water as disperse phase is called as water-in-oil emulsion (W/O); complementary, the dispersion which contains oil as disperse phase and water as continuous phase is called as oil-in-water emulsion (O/W). There are also emulsions in which water droplets are dispersed within oil droplets, which are dispersed in a continuous aqueous medium (W/O/W). The opposite also occurs in the case of O/W/O emulsions (Schramm, 2005).

This work regards to water-in-oil (W/O) emulsions. The water droplets are dispersed in the oil medium, producing interfaces between the two phases on each drop surface. According to Djuve *et al.* (2001), the interfaces generated by the dispersion of one phase in another causes the system free energy increases leading to a thermodynamically unstable state. Thus, a phase separation tendency is noted due to the droplets coalescence, which causes a decrease on the interfacial area and, therefore, a reduction in the system free energy.

To achieve the kinetic stability of the emulsion it is necessary to add a third component called emulsifier or surfactant. Surfactant is a chemical substance which, in low concentration, has the characteristic of adsorbing on the system interfaces and changes its interfacial tension (Adamson and Gast, 1997). According to Shaw (2003), the interfacial tension between oil and water phases tends to decrease in the presence of a surfactant. According to Adamson and Gast (1997), due to the interfacial energy decrease and assuming that emulsions consist of a large interfacial area, the forces responsible for the coalescence of the droplets are reduced promoting the system stability. Such components (natural surfactants as asphaltenes and resins) are found abundantly in the oil.

The presence of petroleum basins, composed mainly by heavy oils, can be seen in large areas in Brazil and around the world. The heavy oils consist of high molecular weight hydrocarbons and have densities near to the water density (920kg/m³ to 1000kg/m³) and viscosity of more than 100 mPa.s. By the fact, the oils have density close to the water, they end up forming stable emulsions (Karcher, 2008). Such emulsions are highly undesirable in the extraction and production processes due to the great increase of the viscosity compared to the pure oil, making the fluid flow within pipelines more difficult (de Oliveira, 1998). The water-in-oil emulsions may exhibit up to 75% of water volume, above this content an emulsion inversion could occur. The emulsion inversion is one of the techniques used to improve the extraction process by the fact that oil-in-water emulsions show a lower viscosity. And, the percentage of water volume must be reduced to at least 1% which is the maximum limit accept by the refineries (Melo, 2007). The breakdown of an emulsion involves gravitational, thermal, electrostatic and/or chemical (through surfactants) treatments. Thus, the knowledge of the water volume content in the mixture is important to make an emulsion inversion or to break a W/O emulsion (de Oliveira, 1998; Melo, 2007).

2.2. IMPEDANCE SPECTROSCOPY

The impedance spectroscopy, IS, is a relatively new and powerful method of characterizing many properties of materials and their interfaces with conducting or polarizing electrical charges. This technique is used to investigate the dynamics of the bounds or the charge mobility in the bulk or in interfacial regions of any kind of solid or liquid material: ionic, semiconducting, mixed semiconducting-ionic, and even dielectrics (MacDonald and Johnson, 2005). The measurements are usually made within cells in the form of a circular cylinder or rectangular parallelepiped.

The ost co on approach to IS is to apply a s all alternated voltage to cell, $V(j\omega) = V_0 \exp(j\omega t)$, $\omega = 2\pi f$, and measure the phase shift and amplitude, or the real and the imaginary parts, of resulting current at that single frequency, $I(j\omega)=I_0.\exp[j(\omega t + \theta)]$. In frequency domain voltage-current relations can be rearranged to for si ilar Oh s's law $I(j\omega)=V(j\omega)/Z(j\omega)$ where the complex quantity $Z(j\omega)$ is defined as the impedance function. The frequency spectrum is obtained by changing the base frequency as a function of the angular frequency ω. Several intrinsic factors, such as: the chemical composition, the molecular or the crystalline structures, the homogeneity, the presence of charge carriers and their types, may affect the spectrum response (Silveira, 2010). The impedance can be written as:

$$Z(\omega) = Z' + jZ''=R_s(\omega)+jX_s(\omega)\quad,\tag{1}$$

where $R_s(\omega)$, $X_s(\omega) = [\omega C_s(\omega)]^{-1}$ are respectively the resistive and reactive components. The subscript s stands for series. The impedance can be represented as a vector and represented by rectangular or polar coordinates on a plan.

The admittance, Eq. (2), is other correlated quantity which has an important hole in the IS analyses.

$$Y(\omega)=1/Z = Y + jY'' = G_p(\omega)+jB_p(\omega) \quad , \tag{2}$$

where the $G_p(\omega)$, $B_p(\omega)= \omega C_p$ are, respectively, the Conductance and the Susceptance. The subscript p stands for parallel. Commercial RLC bridges measures the impedance or admittance automatically in the frequency range of mHz to MHz giving lists of data of their components $R_s(\omega)$, $X_s(\omega);$ or $G_p(\omega)$, $B_p(\omega)$. The relationship among these parameters is given in Eq. (3).

$$G_p = \frac{R_s}{R_s^2 + X_s^2} \quad ; B_p = \frac{X_s}{R_s^2 + X_s^2} \tag{3}$$
$$R_s = \frac{G_p}{B_p^2 + G_p^2} \quad ; X_s = \frac{B_p}{B_p^2 + G_p^2}$$

The complex dielectric constant or dielectric permittivity, Eq. (4), can be calculated from the measure of the impedance or admittance. In this expression, C_0 is the capacitance of measuring cell when filled with air. The measurement and use of the complex $\varepsilon(\omega)$ function is particularly appropriate for dielectric materials.

$$\varepsilon(\omega)= \varepsilon' + j\, \varepsilon'' = Y(\omega)/j\omega C_0 \tag{4}$$

Any intrinsic property that influences the conductivity of an electrode-materials system can be studied by IS. When an electrical field is applied through the electrode into the W/O emulsion different effects occurs at different response time. There are an almost instantaneous polarization as electronic polarization, which due to the displacement of the electrons with respect to the nuclei and, atomic polarization, which due to the displacement of atoms of a molecule. They occur up to ultra violet and infrared regions of the spectrum respectively. A third kind of time constant is dependent on the polarization of permanent dipoles by the electric field, this effect happens up to about 10^{10} Hz. In fact, water molecules behave as dipoles. Furthermore, there is a kind of polarization due to the phenomena of mass transport of charged particles in dispersed conducting regions called ionic polarization. And, interface polarization on low frequencies which may be disregarded above 10^4 Hz (Feldman, et al, 2006; Kowalski, 2006). The Figure 1, by the Kowalski (2006) work, shows the polarization mechanisms and their respective response on the frequency domain.

The dielectric constant of the mixture, ε, is defined in term of polarization by:

$$\varepsilon(\omega)-1= \frac{P(\omega)}{\varepsilon_0 . E(\omega)} \quad , \tag{5}$$

where E is the electric field, P is the polarization of the dielectric material, and ε_o =8.854 10^{-12} F/m is the permittivity of free space.
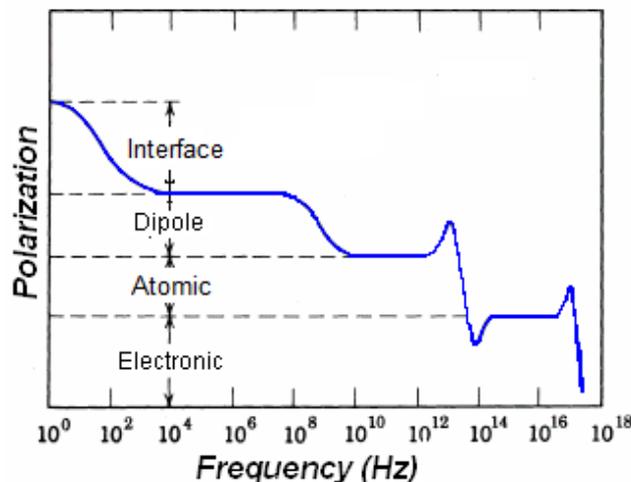
FIGURE 1. Polarization responses on the frequency domain
Source: Kowalski, 2006, p. 19.

2.3. MAXWELL MODEL

Maxwell, 1881, developed a model for the conductivity of a dispersion of spheres in a continuous medium. Maxwell Garnett, 1904, derived a si ilar expression applied to dielectric properties. Wagner, 1914, extended the Maxwell's model to the complex domain, Eq. (6), and thereafter this model has been known as the Maxwell-Wagner model (Bonanos, *et al*, 2005).

$$\varepsilon_m = \varepsilon_c . \frac{2.\varepsilon_c + \varepsilon_d - 2.\alpha(\varepsilon_c - \varepsilon_d)}{2.\varepsilon_c + \varepsilon_d + \alpha(\varepsilon_c - \varepsilon_d)} ; \quad ;if \quad \varepsilon_d >> \varepsilon_c \quad \varepsilon_m \cong \varepsilon_c \frac{1+2\alpha}{1-\alpha} \tag{6}$$

Where $\varepsilon_m, \varepsilon_d, \varepsilon_c$ are the dielectric constants of the mixture, dispersed phase and continuous phase respectively. α is the volume fraction of the dispersed phase.

2.4. TEST CELL

The test cell is made by three stainless steel concentric cylinders. The two innermost cylinders are the electrodes (Garis, 1996). The external cylinder acts as an electric shield and creates an external chamber where a thermostatic fluid can flow to assure a constant temperature during the tests. The cylinders are hold by a PVC base with o-rings which guarantees the sealing. On the cell top there is a PVC disc which seals the thermostatic fluid chamber. Lastly, there is a cell lid, with o-rings built-in, that covers the space destined to the test samples, Fig. 2. The empty cell capacitance, Eq. (8), can be calculated by the electric field distribution on Eq. (7).

$$V = \int_a^b \vec{E}.d\vec{r} = \frac{Q}{2\pi L\varepsilon_0} ln(\frac{b}{a}) \tag{7}$$

$$C_o = \frac{Q}{V} = \frac{2\pi L\varepsilon_0}{ln(\frac{b}{a})} \tag{8}$$

Where *a, b* and *L* are dimensions showed in Fig. 2.
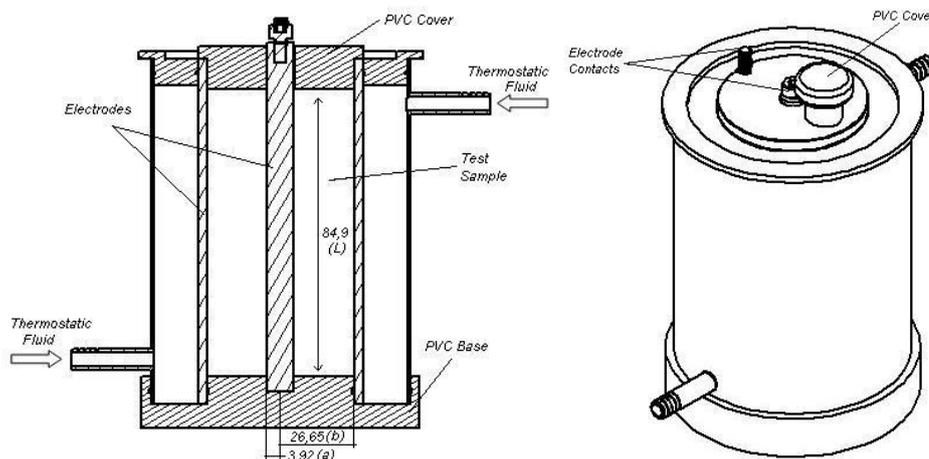
FIGURE 2. Test cell

3. EXPERIMENTAL PROCEDURE

The tests were realized using the test cell connected with a RLC bridge *Agilent E4980A*. The empty intrinsic capacitance of the cell was first measured disregarding the parts of PVC that constitute the cell and its value results in $C=2,85 \ 10^{-12}$ F. The emulsion tests procedures starts by fixing a mixture with water and oil in mass basis defined by an analytical scale. This mixture has been emulsified by the *Ultra Turrax T18 Basic* rotating homogenizer (IKA, Germany). This disperser device, as it is commonly known, is composed by a dispersion impeller and an electric motor with a speed control which allows the operation between 6000 and 24000rpm. The mixture was homogenized during 5 minutes and placed inside the test cell. Then the data were acquired. The E4980A device was setup for getting the admittance data within a logarithmic range with 201 frequency steps from 20Hz up to 1MHz with amplitude of 0,1V.

Experiments were realized considering emulsions with the respective water volume percentage: 13.1%, 19.8%, 26.8% e 41,1%. In addition, two NaCl aqueous solutions were evaluated at 1kg/m³ and 10kg/m³, and only deionized water (0kg/m³ NaCl). The temperature influence was also assessed on the measurement process of the dielectric constant of the mixtures. The dielectric constant of the samples with 19,8% and 26,8% (v/v) water content and salinity of 0kg/m³ and 10kg/m³ were analyzed under a temperature variation between 25°C and 62°C.

The W/O emulsions have dielectric characteristic that can be seen by the admittance data. The conductance component, G_s, is one order of magnitude less than susceptance, B_s. Therefore complex dielectric constant is constituted mainly by the imaginary part of the admittance. So, only the real part of the complex dielectric constant was considered, ε', Eq. (8) deduced from Eq. (2).

$$\varepsilon' = \frac{B_s}{\omega C_0} \tag{8}$$

The dielectric permittivity is function of the polarization of the dipoles formed by water molecules, Eq. (5). Analyzing the spectrum between 83kHz to 245kHz this effect is predominant, therefore 21 points in this range were selected to calculi the dielectric constant.

4. RESULTS

The Figure 3 shows the emulsion dielectric constant, ε_m', dependency on the water volume concentration and also on the water salinity. It is important to remember that ε_m' utilizes the same method showed in the Eq. (3), therefore it refers to the dielectric constant of the W/O emulsion and, α is the water volume fraction.

(a)   (b)   (c)
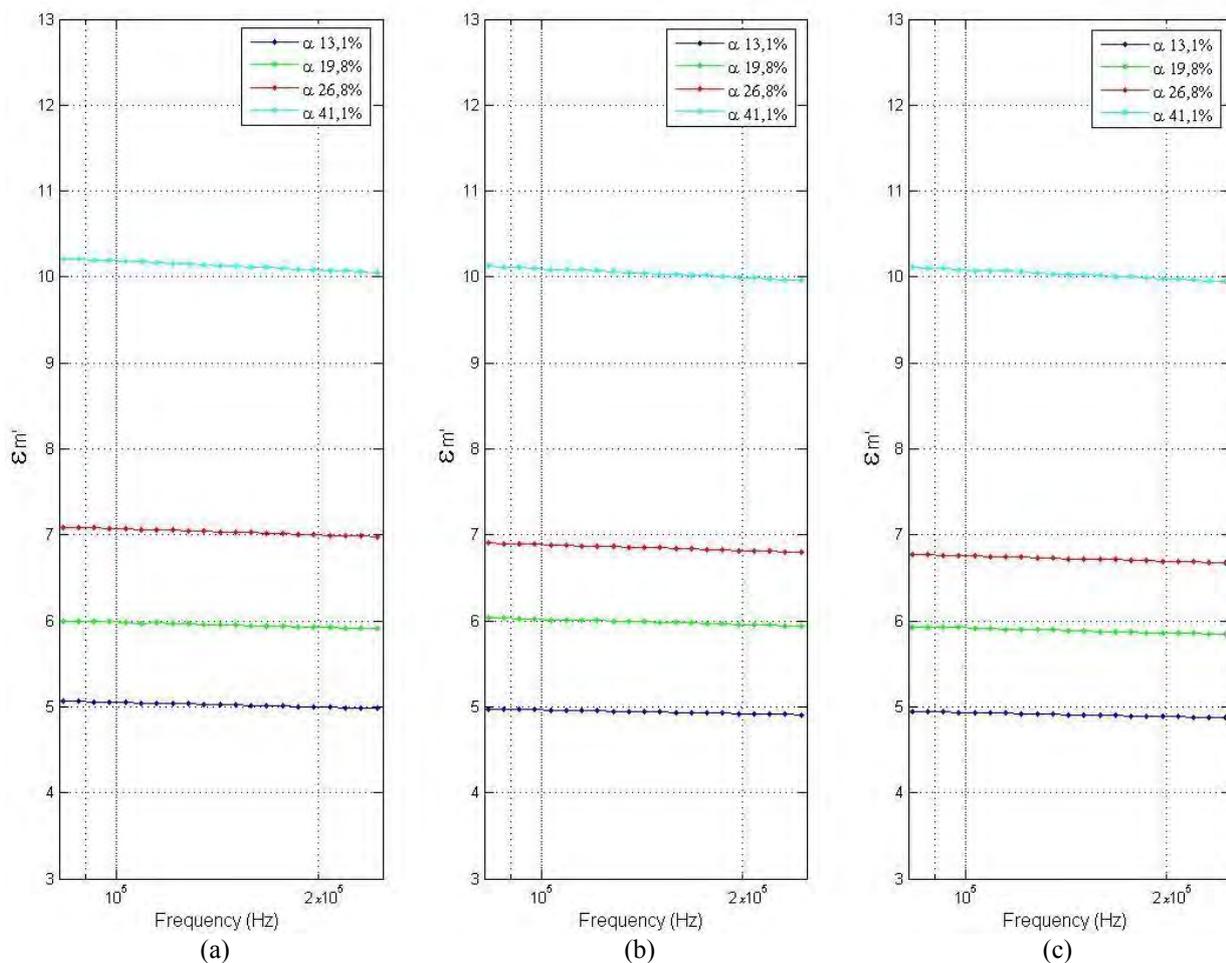
FIGURE 3. Emulsion dielectric constant (ε_m') of W/O emulsion with different water volume fraction and salinity of:
(a) De-ionized; (b) 1kg/m³; (c) 10kg/m³.

Figure 3 shows the mixture dielectric constant, ε_m', as a function of the frequency spectrum for deionized water (Fig. 3a), 1kg/m^3 of NaCl (Fig. 3b) and 10 kg/m^3 of NaCl (Fig. 3c). A visual inspection disclose a weak dependence of ε_m' with the frequency spectrum and a weak dependence on the water salinity. The dielectric constant is strongly related to the molecules polarization. The ionic dissociation due to water salinity was isolated by the oil and generates only ionic polarization effects and weak influence on the frequency range analyzed.

The tests data were compared to the Maxwell-Wagner model for mixtures, Fig. 4. To calculate the Maxwell's curve it was utilized the measured $\varepsilon_d' = 80.71$ for the dispersed medium's dielectric constant and, $\varepsilon_c' = 3.67$ for the continuous medium's dielectric constant, water and oil respectively.

The Figure 4 shows the mixture dielectric constant as a function of the water volumetric fraction for experimental points with different saline concentrations. The data set is in agreement with the Maxwell-Wagner model. Each point in this graphic represents the average of the 21 points in the range 83kHz to 245kHz. The calculated error was less 3%. It demonstrates experimentally the effectiveness of the dielectric constant measurement as a method for the quantification of the water volume fraction in water-in-oil emulsions.
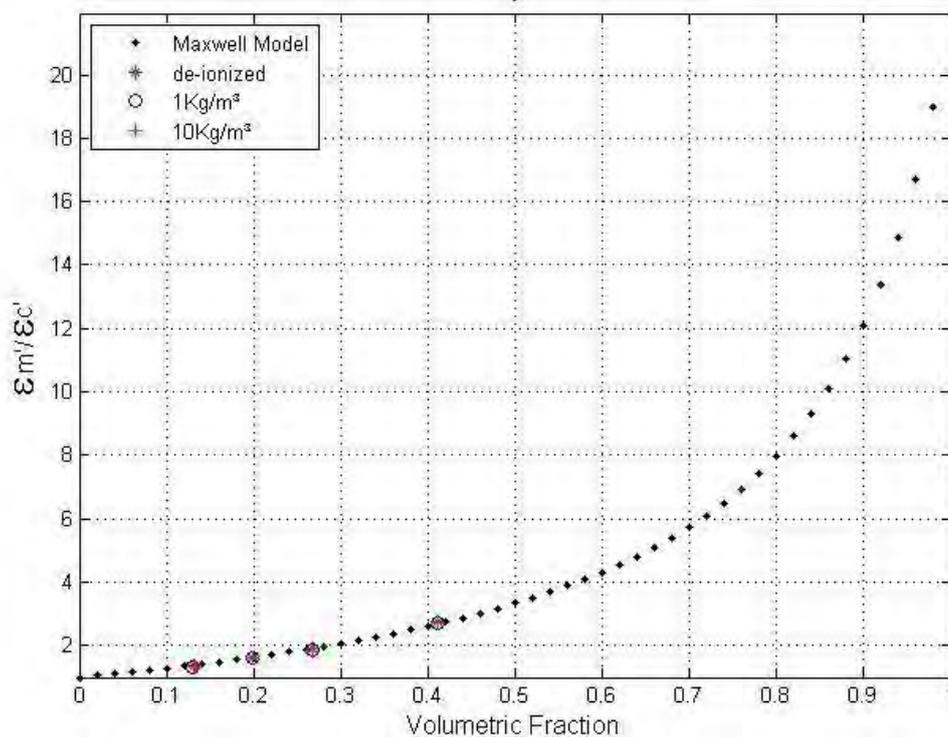
FIGURE 4. Comparison between Maxwell model and experimental data

The influence of the temperature on the dielectric constant is shown in FIG. 5 for a mixture with water fraction of 19.8% in deionized water (Fig. 5a), and in salinity water solution with 10kg/m^3 of NaCl (Fig. 5b); Similarly to 26.8% in deionized water (Fig. 5c), and in salinity water solution with 10kg/m^3 of NaCl (Fig. 5d). The changes in temperature did not significantly influence the dielectric constant measurement for de-ionized water and for water solution with 10kg/m^3 of NaCl.
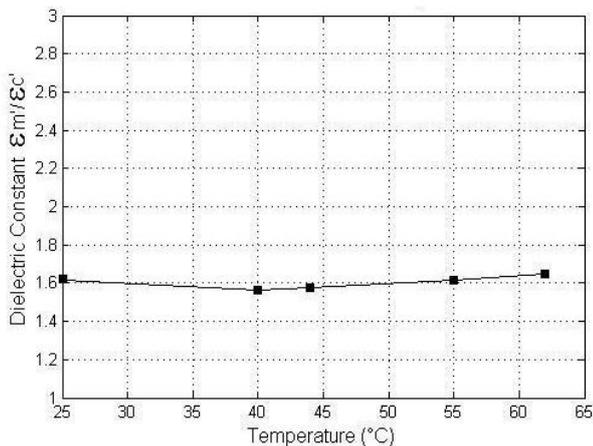
(a)
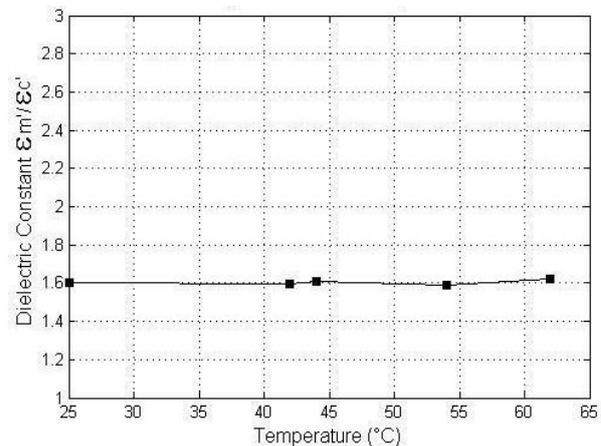
(b)
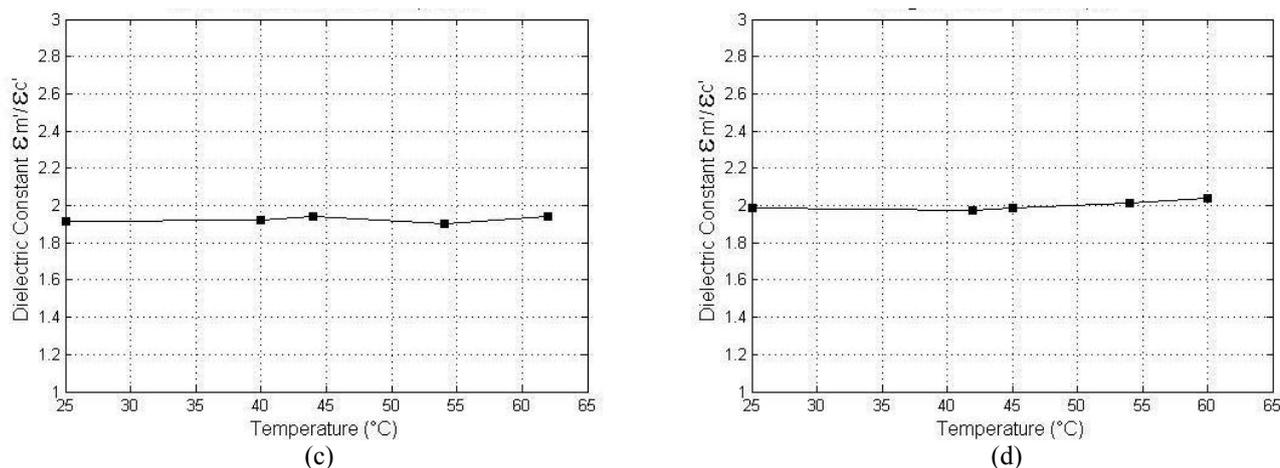
FIGURE 5. Dielectric constant of emulsions from 25°C to 62°C:
(a) De-ionized water-in-oil 19,8% v/v (b) 10kg/m³ water-in-oil 19,8% v/v
(c) De-ionized water-in-oil 26,8% v/v (d) 10kg/m³ water-in-oil 26,8% v/v

5. CONCLUSIONS

The admittance of water in oil emulsion was experimentally measured in a capacitive cell probe for water fractions spanning from 13% to 41% under de-ionized water and water solutions with 1kg/m³ and 10kg/m³ of NaCl at temperatures ranging from 25°C to 62°C. The experimental tests have been done with average of 21 measures of admittance in the 83kHz to 245kHz frequency range using techniques of impedance spectroscopy. Within this frequency range, the effects of interfacial polarization were not observed. The electrical impedance of the W/O emulsion correlates with the water fraction through the Maxwell-Wagner model prediction with error less than 3%. The effects of temperature of the sample are negligible. And, the salinity of the water, which causes the ionic polarization, may be not considered on W/O emulsions due to the fact of its effect being very small compared with the dipole polarization effect. However, when the salinity concentration range is higher, the ionic polarization can show an influence on the sample total polarization. The method is promising to measure water volume fraction in W/O emulsions, however it is necessary that the equipment finely discriminates the amplitude and phase of the current passing through the sample related with the excitation voltage. About the case of an O/W emulsion, the sample becomes conductive and the factors as temperature, salinity and cell geometry would need to be treated more carefully.

6. ACKNOWLEDGEMENTS

7. REFERENCES

Adamson, A. W., & Gast, A. P.,1997. *Physical Chemistry of Surfaces.* John Wiley & Sons, New York.

Bonanos, N, Steele, B, Butler, E. *Applications of Impedance Spectroscopy.* In: E. Barsoukov and J. MacDonald, *Impedance Spectroscopy.* John Wiley & Sons, Inc, New Jersey.

Djuve, J., Yang, X., Fjellanger, I. J., Sjoblom, J., & Pelizzetti, E., 2001. *Chemical Destabilization of Crude Oil Based Emulsions and Asphaltene Stabilized Emulsions.* Colloid Polym Sci 279, 232-239.

Feldman, Y; Puzenko, A and Ryabov, Y. 2006. *Dielectric Relaxation Phenomena in Complex Materials*. In: Coffey, W. T. and Kalmykov, Y. P. *Fractals, Diffusion, and Relaxation in Disordered Complex Systems,* Advances in Chemical Physics, Part A, Volume 133. John Wiley & Sons, Inc.

Garis, E. J., Giordan, L. A., Magallane, C., Daruich, Y., Fornles, A., & Catenaccio, A., 1996. *Cell for the Measurement of the, Percentage of Polar Component in Polar-Nonpolar Emulsions*. IEEE Transactions on Instrumentation and Measurement, Vol. 4.5, n. 4, pp. 815-817.

Karcher, V., 2008. *Determinação da Energia Interfacial de Emulsões de Água em Óleo Pesado.* Dissertação de Mestrado, UNICAMP, Campinas-SP.

Kowalski, E. L., 2006. *Estudo da Borracha Natural por Meio de Técnicas de Caracterização de Dielétricos.* Tese de Doutorado, Universidade Federal do Paraná, Curitiba-PR.

MacDonald, J.R., Johnson, W. B., 2005. *Fundamentals of Impedance Spectroscopy.* In: E. Barsoukov and J. MacDonald, *Impedance Spectroscopy.* John Wiley & Sons, Inc., New Jersey.

Melo, E. M., 2007. *Estabilidade de Emulsões de Petróleo em Sistemas Pressurizados.* Universidade de Tiradentes – UNIT, Aracajú, Brasil.

de Oliveira, R. C. G., 1998. *Influência do tipo de Emulsão Sobre o Escoamento e o Processo de Deposição Orgânica de*

Petróleo. Centro de Pesquisa CENPES, Rio de Janeiro, Brasil.

Schramm, L. L., 2005. *Emulsions, Foams and Suspensions - Fundamentals and Applications.* WILEY-VCH Verlag GmbH & Co, Weinheim.

Shaw, D. J., 2003. *Colloid and Surface Chemistry.* Elsevier Science Ltd, Oxford.

Silveira, L.G.D., 2010. *Aplicação de espectroscopia de impedância no estudo de blendas de biodiesel/diesel.* Dissertação de Mestrado, Universidade Estadual de Maringá - Instituto de Física, Maringá-PR.

8. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.