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Electrochemical Impedance Spectroscopy of Water-in-Crude Oil Emulsions

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ABSTRACT

We conducted a study of Electrochemical Impedance Spectroscopy on water-in-crude oil emulsions based on a heavy oil sample from the Orinoco Belt. Electric impedance measures were obtained by means of an HP 4192A impedance analyzer and a stainless steel coaxial cylinder capacitor; due to impedance coupling between the analyzer and the sensor, the frequency range was taken from 75 kHz to 4 MHz. Impedance modulus and phase angle of the studied samples showed that the composed system behaves like an ideal capacitor filled with dielectric. Overall, the dielectric permittivities of samples, real and imaginary part, increase with the water contained in emulsions. The electric conductivity of all emulsions increase with frequency. The experimental data was fitted to Wagner's theory and Hanai's theory, finding a good correlation with the high frequencies Hanai model at water concentrations lower than 30%.

KEYWORDS: Spectroscopy; Impedance; Dielectric; Water content.

INTRODUCTION

Reservoirs around the world contain a naturally occurring proportion of oil, water and gas. Oil and water are well differentiated in two phases which happen to mix due to drilling, extraction and transport processes, forming water-in-oil emulsions. Such emulsions are a constant problem for oil production and water content is a constantly monitored parameter in the industry (VELÁSQUEZ, PEREIRA, 2014).

During the last decade, Electrochemical Impedance Spectroscopy (EIS) has established as one of the most used analysis in material science, especially in corrosion studies, polymer properties, ionic and electric conduction, coatings and colloids. It is based on the application of an external alternate electric field of variable frequency to the studied sample and analysis of the — electric current — response (LVOVICH, 2012).

Another technique derived from EIS is Dielectric Spectroscopy (DS), in which properties like electric permittivity (ε) is obtained and analyzed through complex diagrams — also called Cole – Cole or Nyquist plots —. Electric conductivity (σ) is another obtained property. These properties are related to the capacity of a dielectric to store electric energy and transfer electrical carriers, both associated to molecular activity (LVOVICH, 2012).

Dielectric response is based on energy storage and resulting relaxation, the latter being the required time (τ) that polar molecules have to reversibly orientate in the alternate electric field. As frequency increases, the real part of permittivity decreases (ε') and dielectric loss increases (ε''), provided that polarized molecules are completely aligned with the electric field at low frequencies. At higher frequencies polarization can no longer follow the change of direction of the field, molecules relax and can't store more energy, thus increasing the loss factor ε''.

The materials' dielectric properties dependence of frequency is expressed through empirical relaxation models, such as the Debye model which considers a single relaxation time and applies mostly to highly insulating materials. For low electrical permittivity materials and higher molecular complexity, the Cole – Cole model is used given that it considers a distribution of relaxation times (LVOVICH, 2012). Crude oil is typically a highly insulating material with high impedance and low permittivity, thus following the Debye model; however, the proportion in which its fractions (saturated, aromatics, resins and asphaltenes) naturally distribute in the oil alters its electrical properties (PUNASE, PRAKOSO, HASCAKIR, 2016).

In this work we conducted an EIS and DS study on water-in-crude oil emulsions from a sample of heavy oil from the Orinoco Belt. Impedance measures were conducted in a frequency range from 75 kHz to 4 MHz; complex impedance, complex permittivity and electric conductivity were calculated. Experimental permittivity was fitted to Wagner's model and Hanai's model to estimate the water content in emulsions (OLIVA, 2019).

ELECTRIC PROPERTIES

According to Ohm's law, complex impedance (Z^*) of any material being stimulated by an alternating potential $V_{(t)} = V_0 exp(j\omega t)$ is expressed as:

$$Z^* = \frac{V_{(t)}}{I_{(t)}} = \frac{V_0 e^{-j\omega t}}{I_0 e^{-j(\omega t+\theta)}} = |Z|e^{j\theta}$$
$$= |Z|(\cos\theta + j\sin\theta) \quad (1)$$
$$= Z' + jZ''$$

where $\omega = 2\pi f$, ϑ the phase angle between current and voltage and $j = \sqrt{-1}$; Z' and Z'' are the real and imaginary part of impedance.

Dielectric properties of the analyzed material are obtained from impedance measurements. Complex dielectric permittivity (ε^*) with its real (ε') and imaginary part (ε'') are calculated as:

$$\varepsilon^* = \frac{1}{j\omega C_0 Z^*} \quad (2)$$

$$\varepsilon' = \frac{-Z''}{|Z|^2 \omega C_0} \quad (3)$$

$$\varepsilon'' = \frac{Z'}{|Z|^2 \omega C_0} \quad (4)$$

where C_0 is the geometric capacitance of the capacitive sensor.

AC electric conductivity of dielectric materials has a dependence on permittivity, making it a complex function (σ^*) with its real (σ') and imaginary part (σ'') as it follows:

$$\sigma^* = j\omega\varepsilon_0\varepsilon^* \quad (5)$$

$$\sigma' = \omega\varepsilon_0\varepsilon'' \quad (6)$$

$$\sigma'' = \omega\varepsilon_0\varepsilon' \quad (7)$$

where ε_0 is the vacuum permittivity.

WATER-IN-CRUDE OIL EMULSIONS

Emulsions are a mixture of an immiscible liquid in the form of droplets, usually called dispersed phase, a second immiscible liquid called continuous phase and a surfactant that stabilizes the system preventing the droplets from coalescence.

An emulsion containing water droplets dispersed in oil is called water-in-oil (W/O) emulsion; when oil becomes the dispersed phase then the emulsion is called oil-in-water (O/W) emulsion (WONG, LIM, DOL, 2015; JORGE *et al*, 2018).

In W/O emulsions, water droplets disperse in the continuous medium, produce an interface, the free energy increases and the system turns to a thermodynamically unstable state. In order to stabilize the system, a surfactant must be added in small concentrations to lower surface tension between the two phases. In the oil industry, W/O emulsions are formed due to extraction, pumping and transport processes, thus making the water content in crude oil a constantly measured quantity.

The stability of such emulsions is due to natural surfactants, i.e. asphaltenes, resins and paraffin; other external surfactants help to stabilize the emulsion, for example: clay sediments, rust in the pipeline, chemicals used to extract the oil, etc. (OLIVA, 2019; JORGE *et al*, 2018).

WATER CONTENT

Electric properties of W/O emulsions such as dielectric permittivity (ε) and electric conductivity (σ) can be obtained from the electric properties of the dispersed phase, usually formed by spherical droplets of permittivity ε_p and conductivity σ_p, and the continuous phase of permittivity ε_m and conductivity σ_m and the water content (HANAI, KOIZUMI, 1975). According to Wagner's theory, the permittivity and conductivity at high (ε_h) and low (ε_l) frequencies are calculated following equations (8) – (11):

$$\frac{\varepsilon_h}{\varepsilon_m} = \frac{\varepsilon_p + 2\varepsilon_m + 2\phi(\varepsilon_p - \varepsilon_m)}{\varepsilon_p + 2\varepsilon_m - \phi(\varepsilon_p - \varepsilon_m)} \quad (8)$$

$$\frac{\varepsilon_l}{\varepsilon_m} = \frac{1 + 2\phi}{1 - \phi} \quad (9)$$

$$\frac{\sigma_h}{\sigma_m} = \left(\frac{3\varepsilon_m}{\varepsilon_p + 2\varepsilon_m - \phi(\varepsilon_p - \varepsilon_m)}\right)^2 \quad (10)$$

$$\frac{\sigma_l}{\sigma_m} = \frac{1 + 2\phi}{1 - \phi} \quad (11)$$

σ_h and σ_l are the conductivities of the system at high and low frequencies respectively, ϕ is the volumetric fraction of water. According to Hanai's theory, both permittivity and conductivity at limiting frequencies are calculated in equations (12) – (16):

$$\frac{\varepsilon_p - \varepsilon_h}{\varepsilon_p - \varepsilon_m}\left(\frac{\varepsilon_m}{\varepsilon_h}\right)^{1/3} = 1 - \phi \quad (12)$$

$$\frac{\varepsilon_l}{\varepsilon_m} = \frac{1}{(1 - \phi)^3} \quad (13)$$

$$\frac{\sigma_h}{\sigma_m} = \frac{3\varepsilon_h(\varepsilon_h - \varepsilon_m)}{(2\varepsilon_h + \varepsilon_p)(\varepsilon_p - \varepsilon_m)} \tag{14}$$

$$\frac{\sigma_l}{\sigma_m} = \frac{1}{(1-\phi)^3} \tag{15}$$

Knowing the parameters ε_h, ε_l, ε_m and ε_p from equations (8) and (9), the volumetric fraction of water using Wagner's theory is calculated as it follows:

$$\phi = \frac{\varepsilon_l - \varepsilon_m}{\varepsilon_l + 2\varepsilon_m} \tag{16}$$

$$\phi = \frac{(\varepsilon_p + 2\varepsilon_m)(\varepsilon_h - \varepsilon_m)}{(\varepsilon_h + 2\varepsilon_m)(\varepsilon_p - \varepsilon_m)} \tag{17}$$

From equations (12) and (13), the volumetric fraction of water according to Hanai's theory is calculated as:

$$\phi = 1 - \left(\frac{\varepsilon_m}{\varepsilon_l}\right)^{1/3} \tag{18}$$

$$\phi = 1 - \left(\frac{\varepsilon_p - \varepsilon_h}{\varepsilon_p - \varepsilon_m}\right)\left(\frac{\varepsilon_m}{\varepsilon_h}\right)^{1/3} \tag{19}$$

Equations (16) and (18) are used in measurements at low frequencies, equations (17) and (19) at high frequencies.

EXPERIMENTAL SECTION

A sample of extra heavy oil from the Orinoco Belt was used to synthesize water-in-crude oil emulsions, its physical properties are shown in **Table 1**.

Table 1 - Physical properties of crude oil

Physical properties	Result
Density at 50 °C (g/cm³)	0.9916
Viscosity at 50 °C (cP)	21590
API	8.10
% asphaltenes	7

Source: own authorship.

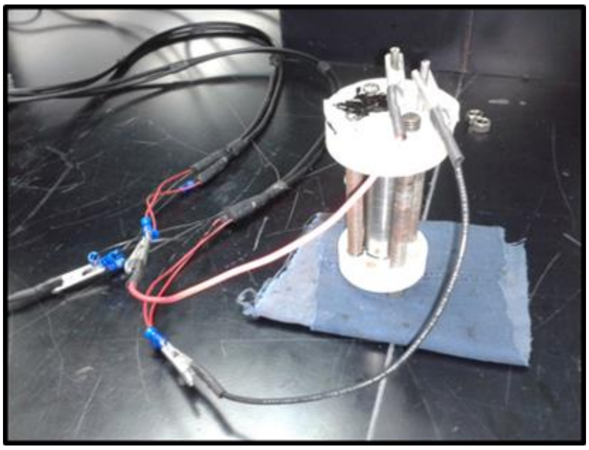
The crude oil was previously dehydrated. Emulsions were prepared by pouring 100 ml of crude oil in a beaker inside a water bath at 60°C, stirring the sample with a propeller mixer at 60 rpm and adding the necessary amount of distilled water to complete 9%, 25%, 35% and 45% of water content. The mixture was left in stir for 30 minutes.

Impedance measurements were conducted using a stainless steel coaxial cylinder of inner radius r_1 = (5.95 ± 0.05) mm, outer radius r_2 = (12.80 ± 0.05) mm and length l = (86.70 ± 0.05) mm. Geometric capacitance (C_0) was calculated following equation:

$$C_0 = \frac{2\pi l \varepsilon_0}{ln\left(\frac{r_2}{r_1}\right)} \quad (20)$$

where ε_0 is the vacuum permittivity. Calculated C_0 gave a result of 6.29 pF ± 0.01%. Test cell was connected to an HP 4192A LF impedance analyzer, as shown in **Figure 1** and **Figure 2**; values of impedance modulus and phase were displayed by the analyzer and used in equations (1) – (7). Values below 1 MHz have an accuracy of 4%, above 1 MHz between 5% - 7%.

Figure 1 - Test cell used for impedance measurements with connections to the analyzer



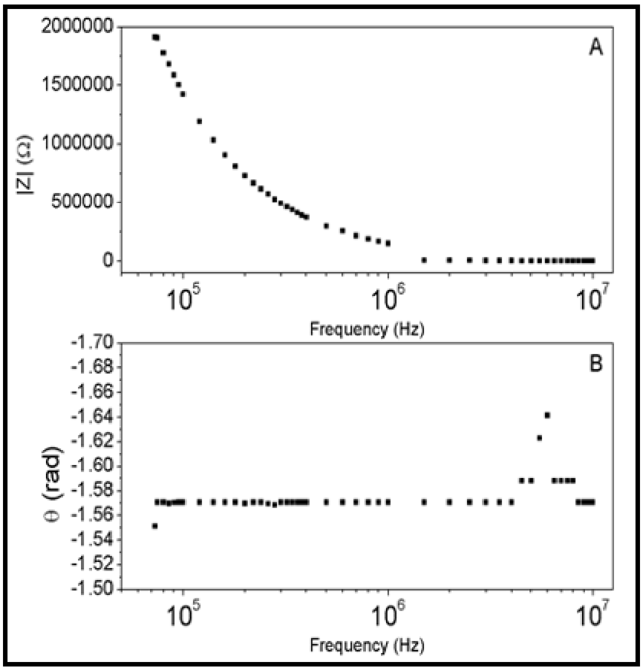
Source: own authorship.

RESULTS AND DISCUSSION

The coaxial cell's impedance modulus shown in **Figure 2A** decays as the potential function $1/\omega C_0$, behaving as an ideal capacitor filled with dielectric; in **Figure 2B**, the phase angle exhibits two limit values at 80 kHz and 6 MHz.

This effect can be attributed to a problem related to the impedance coupling between the cell and the analyzer in the mentioned range; however, between 75 kHz and 4 MHz the phase angle stabilizes in $-\pi/2$ and the cell behaves like an ideal capacitor.

Figure 2 - Impedance modulus (A) and phase angle (B) of empty test cell

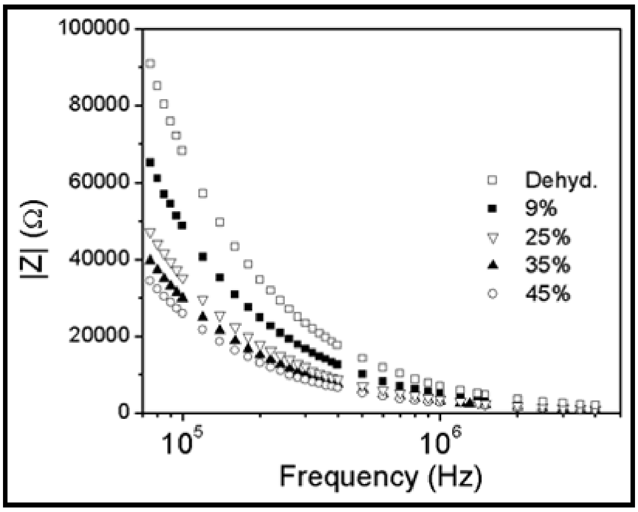


Source: own authorship.

IMPEDANCE MODULUS AND PHASE ANGLE

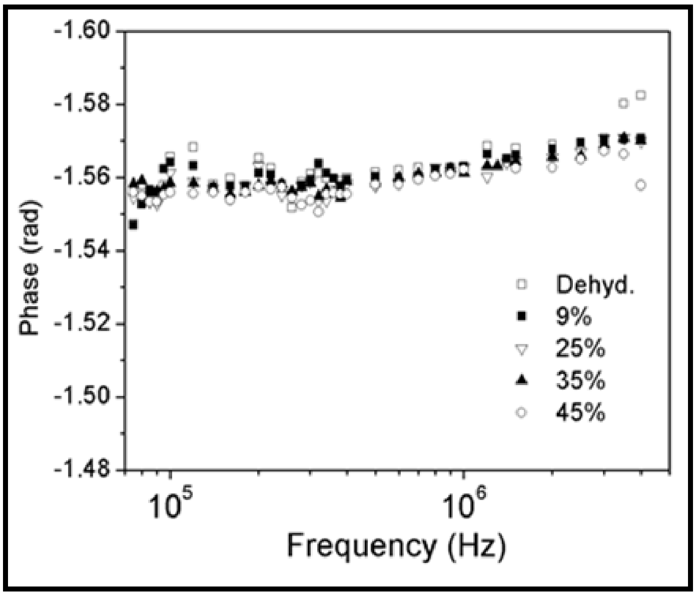
Impedance modulus ($|Z|$) of water-in-crude oil emulsions decrease as frequency increases. $|Z|$ decrease as water content increases, being the dehydrated sample with the highest impedance and the emulsion with 45% of water the lowest, as shown in **Figure 3**.

Figure 3 - Impedance modulus of water-in-crude oil emulsions and dehydrated sample



Source: own author

Figure 4 - Phase angle of water-in-crude oil emulsions and dehydrated sample



Source: own authorship.

In Figure 4, the phase angle (θ) of all samples increase from -88° to -90°, fluctuating between 200 kHz and 400 kHz, giving the cell-fluid system a capacitive behavior as |Z| decays as 1/ωC and θ tends to –π/2.

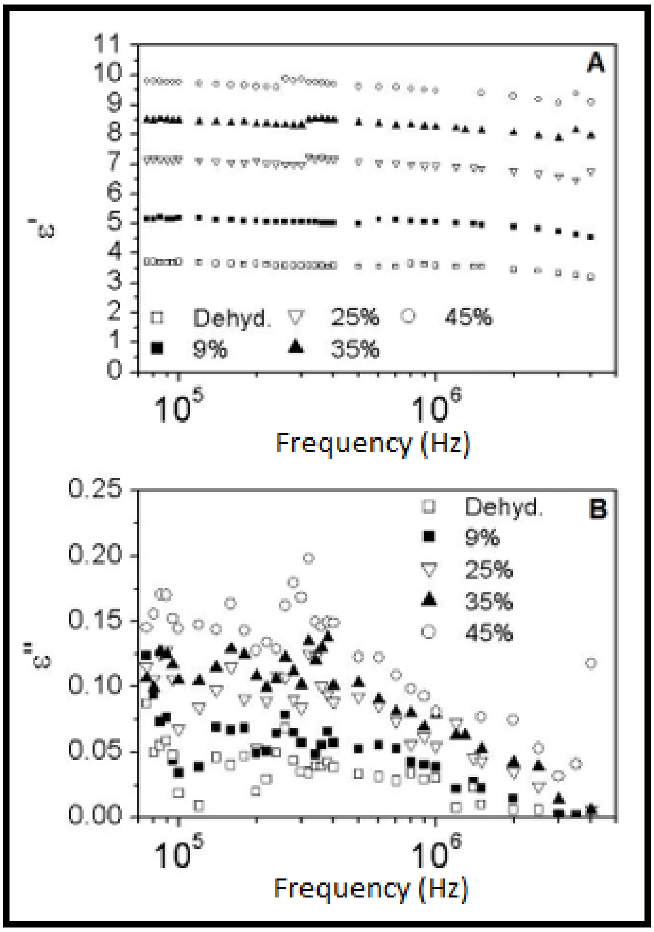
DIELECTRIC PERMITTIVITY

Real (*ε′*) and imaginary (*ε′′*) parts of dielectric permittivity were graphed in **Figure 5** according to equations (3) and (4).

ε′ displays a constant trend with a slight tilt in the experimental range of frequencies, as seen in **Figure 5A**.

ε′′ shows a decreasing trend as frequency increases and increasing value with water content, as it is shown in **Figure 5B**, the emulsion with 45% of water has the highest value of *ε′′*; likewise, the value of *ε′* increases with the water content in emulsions, as shown in **Table 2** where the values of *ε′* at 75 kHz and 4 MHz tend to increase as water content in emulsions increases.

Figure 5 - Dielectric permittivity of emulsions and dehydrated sample. Real (A) and imaginary (B) part



Source: own authorship.

Table 2 - Real part of dielectric permittivity at 75 kHz and 4 MHz

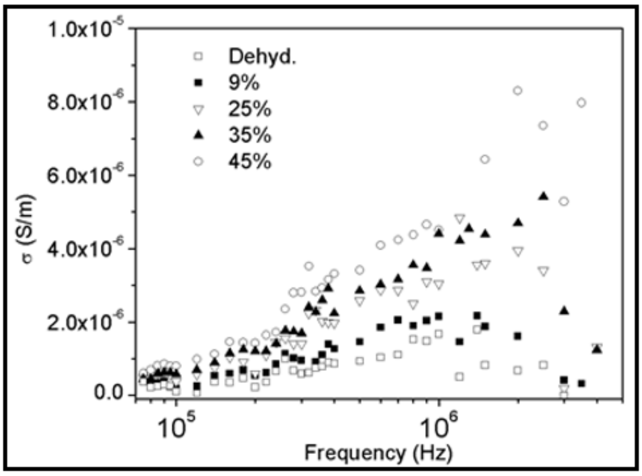
Sample	ε′ at 75 kHz	ε′ at 4 MHz
Dehydrated	3.71 ± 0.97 %	3.18 ± 1.00 %
9%	5.17 ± 0.97 %	4.55 ± 1.02 %
25%	7.15 ± 0.97 %	6.76 ± 1.06 %
35%	8.50 ± 0.97 %	7.97 ± 1.08 %
45%	9.79 ± 0.97 %	9.11 ± 1.10 %

Source: own authorship.

ELECTRIC CONDUCTIVITY

The electric conductivity (σ') of the emulsions, **Figure 6**, clearly increases as water content increases and has the highest values at high frequencies.

Figure 6 - Electric conductivity of emulsions and dehydrated sample



Source: own authorship.

The increase of σ' with water content is backed by the observations made in **Figure 5B** and equation (6). Conductivities at 75 kHz and 2 MHz are reported in **Table 3**.

Table 3 - Electric conductivity of emulsions and dehydrated sample at 75 kHz and 2 MHz

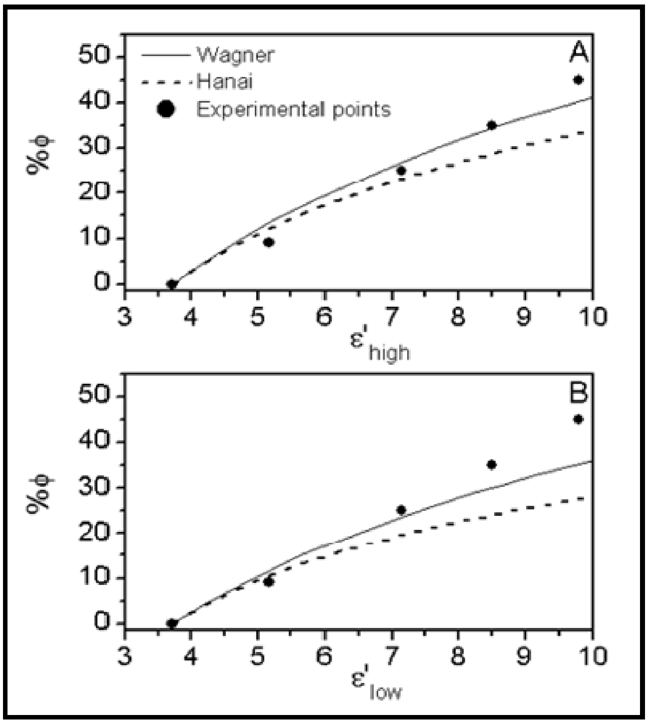
Sample	σ' (μS/m) at 75 kHz	σ' (μS/m) at 2 MHz
Dehydrated	0.365 ± 1.2 %	0.671 ± 11 %
9%	0.515 ± 1.2 %	1.614 ± 8%
25%	0.484 ± 1.4 %	3.950 ± 7%
35%	0.446 ± 1.7 %	4.695 ± 8%
45%	0.606 ± 1.5%	8.301 ± 9%

Source: own authorship.

WATER CONTENT

In **Figure 7** the graphical representation of Wagner's theory and Hanai's theory to determine the water content (ϕ) in emulsions as function of real part of permittivity at high (ε'_{high}) and low (ε'_{low}) frequencies are shown, following equations (8), (9), (12) and (13) respectively.

Figure 7 - Water content as function of ε'low and ε'high, Wagner's theory (—) and Hanai's theory (---). ε'high (A) and ε'low (B)



Source: own authorship.

Experimental values of ε' at 75 kHz, shown in Table 2, were added to the plots. A notable dispersion between the curves dependant of ε'low and experimental points is seen, being more noticeable at water concentrations higher than 30%.

On the other hand, dispersion decreases between the Hanai's theory curve dependant of ε'high and experimental points, finding a good fit at lower concentrations than 30%. In previous works, it was found a good correlation between experimental data for synthetic W/O emulsions with low φ and their then new theory for low and high frequency (HANAI, KOIZUMI, 1975).

CONCLUSION

The combination of EIS and dielectric spectroscopy results in a quick and non destructive technique to characterize the electrical properties of crude oil samples, emulsified oil and water-in-crude oil emulsions. In the range between 75 kHz and 4 MHz, values of impedeance decrease as water content increases and the phase angle increase from -88° to -90°, indicating that samples have a capacitive behavior.

The dielectric permittivities of emulsions, real and imaginary part, increase with the concentration of water in them. The electric conductivity also increases with water content; in the dehydrated sample conductivity is attributed to dispersed metals, asphaltenes and salinity. The estimation of water content in emulsions from measured values of ε' at 75 kHz fit to Hanai's theory at high frequencies and a water content below 30%.

Espectroscopia de Impedância Eletroquímica de Emulsões de água em petróleo bruto

RESUMO

Realizamos um estudo de espectroscopia de impedância eletroquímica em emulsões de água em petróleo bruto de uma amostra de petróleo pesado do Cinturão de Orinoco. As medidas de impedância foram obtidas com um analisador de impedância HP 4192A e um capacitor de cilindro coaxial de aço inoxidável. Devido ao acoplamento de impedância entre o analisador e o sensor, a faixa de freqüência foi determinada entre 75 kHz e 4 MHz. O módulo de impedância e o ângulo de fase mostraram que o sistema se comporta como um capacitor ideal preenchido com dielétrico. As partes reais e imaginárias da permissividade dielétrica aumentam com o teor de água. A condutividade elétrica de todas as emulsões aumenta com a frequência. Os dados experimentais foram ajustados às teorias de Wagner e Hanai, encontrando uma boa correspondência com o modelo Hanai para altas frequências e em concentrações de água inferiores a 30%.

KEYWORDS: Espectroscopia; impedância; dieléctrico; teor de água.

Espectroscopía de impedancia electroquímica en emulsiones agua en petróleo crudo

RESUMEN

Realizamos un estudio de espectroscopía de impedancia electroquímica en emulsiones agua en crudo a partir de una muestra de crudo pesado de la Faja Petrolífera del Orinoco. Las medidas de impedancia se obtuvieron con un analizador de impedancia HP 4192A y un capacitor de cilíndros coaxiales de acero inoxidable. Debido al acople de impedancia entre el analizador y el sensor, el rango de frecuencias se tomó entre 75 kHz y 4 MHz. El módulo de impedancia y el ángulo de fase mostraron que el sistema se comporta como un capacitor ideal lleno de dieléctrico. Las partes real e imaginaria de la permitividad dieléctrica incrementan con el contenido de agua. La conductividad eléctrica de todas las emulsiones incrementa con la frecuencia. Los datos experimentales se ajustaron a las teorías de Wagner y Hanai, encontrándose una buena correspondencia con el modelo de Hanai para altas frecuencias y en concentraciones de agua menores al 30%.

PALABRAS CLAVE: Espectroscopía; impedancia; dieléctrico, contenido de agua.

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