Synthesis and Evaluation of Emulsions with Gallic Acid Derivatives

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ABSTRACT : The presence of heavy oil in the oil fields of Mexico presents a great challenge at a technological and scientific level. A line of research and technological alternative is to conceive chemical compounds capable of neutralizing the binding effects of asphaltenes in crude oil. In this work the synthesis of two molecules derived from gallic acid was carried out, then derivates were evaluated as stabilizers of heavy oil and congenital water emulsions. The affinity evaluation of these molecules with the emulsions was carried out through the bottle test method and demonstrated a great capacity of emulsion stabilization with 50% water retention. Scanning Electron Microscopy analysis with Dispersive Energy microanalysis (MEB-EDS) showed a fibrillar morphology.

KEYWORDS - gallic acid, emulsions, heavy crude, congenital water

I.   INTRODUCTION

Two immiscible liquids can form, when mechanically stirred, a dispersion of small drops of one, called internal or dispersed phase, in another, called external or continuous phase. This phenomenon produces a significant increase in the interfacial area and therefore the free energy. In the presence of a surfactant, the small drops dispersed are adsorbed in the liquid-liquid interface, reducing the interfacial tension and forming an electrical, steric and mechanical barrier around the drops [1]. The stability is a property of easy appreciation in the extreme cases in which the emulsion coalesces completely in a few minutes or, on the contrary, it remains apparently unaltered without any visible separation for several months. The only truly absolute measure of the stability of an emulsion is the variation in the number of drops present in an emulsion sample as a function of time. Such information cannot be obtained experimentally but by varying the distribution of the drop size over time, but this implies the disturbance or destruction of the sample. The speed of separation is directly related to the stability of the thin film of liquid that separates the scattered drops and the feasibility of delaying or preventing the drainage of the interdrop film (disjoining pressure), on which the London-Van der Waals forces, electrostatic forces and short-range forces contribute significantly [2,3]. The agitation of a mixture of crude oil and water can produce stable emulsions of water-in-oil that remains scattered for a long period of time. These emulsions can cause severe problems during production, transport and treatment processes, since they normally have a high stability and viscosity. In this work, organic molecules were synthesized from gallic acid capable of stabilizing the water-crude emulsions in order to modify the wettability of the mineral matrix of heavy mature fields.

II.   MATERIALS AND METHODS

2.1 Synthesis of gallic acid derivatives

2.1.1 Preparation of 3,4,5-tributoxy benzoic acid (1)

8.5 g of gallic acid (50 mmol), 20 ml of ethanol, 12.3 g of solid sodium hydroxide (NaOH) and 20 ml

of water were placed in a flat-bottomed flask, a pinch of powdered zinc was added to protect the carboxyl group during the reaction. The reagents were heated for 15 minutes with constant agitation. Then a mixture of 5.82 ml of butane bromide and 25 ml of ethanol was added dropwise to the flask, then heated with reflux for 5 hours. Subsequently the solution was left to cool at room temperature and poured into 100 ml of water, the pH was adjusted to 2 with 10% hydrochloric acid, obtaining two liquid phases which were separated with a rotary evaporator, recovering a dark liquid [4].
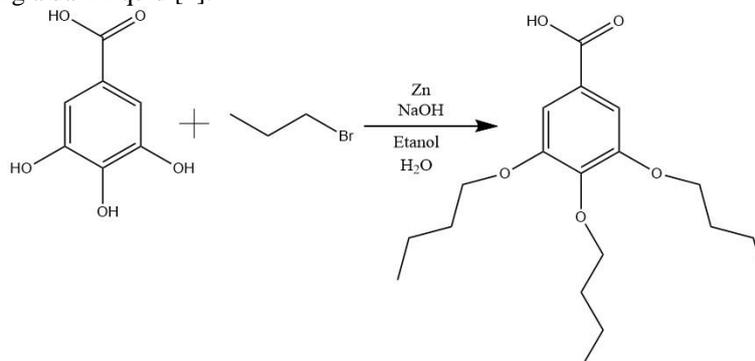
Fig. 1. Reaction of 3,4,5-tributoxy benzoic acid (1)

2.1.2 Preparation of 3,4,5-tributoxy ethyl ester benzoic acid (2)

2 g of ethyl gallate, 50 ml of dimethylformamide and 5 g of potassium carbonate (K_2CO_3) were preheated at 70 °C for 15 minutes. Then, 4 g of butyl bromide were added, keeping the temperature constant for 12 hours. After reaction time 300 ml of hydrochloric acid 1 M (HCl) were added, the organic phase was recovered with two 50 ml washes of chloroform and a third wash of 300 ml of distilled water. Once the solvent was removed, the molecule was precipitated in ethanol [5].
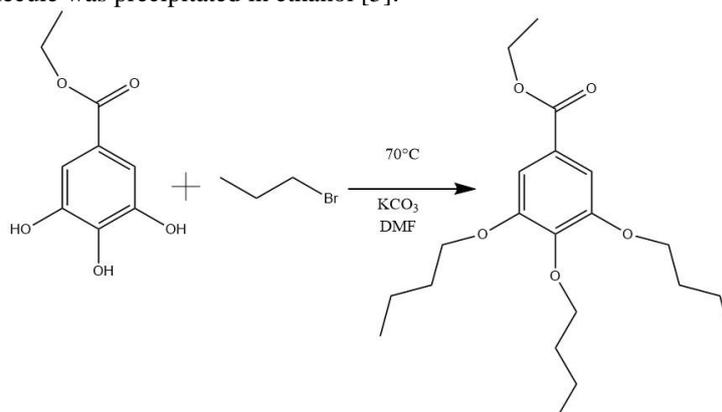
Fig. 2 Reaction of the 3,4,5-tributoxy ethyl ester benzoic acid (2)

2.2 NMR analysis

The ^{1}H and ^{13}C NMR data were acquired, at a temperature of 25 °C, on a Bruker 400 MHz Advance III HDspectrometer. Deuterated dimethyl sulfoxide was used as the solvent, chemical shifts are expressed in δ (ppm) values relative to tetramethylsilane (TMS) as an internal reference.

2.3 FTIR analysis

The analysis was performed by the Attenuated Total Reflectance (ATR) method on a Perkin Elmer Spectrum One FTIR Equipment, with 12 scans and a resolution of 4 cm^{-1} in a range of 4000 to 400 cm^{-1}.

2.4 UV-visible analysis

The characterization was carried out in a UV-Vis spectrophotometer Model GBC Cintra 303 using ethanol as solvent, samples of 3,4,5-trihydroxy, butyl ester, benzoic acid (2) 0.04M, 3,4,5-tributoxi benzoic acid (1) 0.03M, 0.05M gallic acid, 0.007M bromine butane were dissolved, 3,4,5- tributoxy ethyl benzoic acid (224) 0.02M was dissolved in distilled water and 1M butanol.

2.5 Preparation of emulsions with the ultrasonic sonicator

The sonifier is used as a homogenizer to generate the emulsions, an ultrasonic processor Hielscher

Up200Ht was used. It has a temperature sensor to control the emulsions since they can react at a temperature higher than 70ºC, sample was also deposited in a container with ice so that it wouldn't reach the temperature quickly and that it could be longer in the ultrasonic and show a good emulsion.

Once the equipment calibration has been done, the congenital water-heavy oil emulsions, which contained 15 ml of congenital water and 85 ml of heavy crude oil, were placed in two duplicate tests to determine the behavior of the molecules in the emulsion and if there was an improvement in the times with respect to the amount of sample poured into the mixtures made.

2.6 SEM analysis

Sample 2 was observed on a Carl Zeiss Evo HD-15 Scanning Electron Microscope with integrated X-ray energy dispersive microanalysis system using magnifications of 100X to 3000X acceleration voltage 2 and 1.3 kV at high vacuum.

III.   RESULTS AND DISCUSSION

3.1 Characterization by Nuclear Magnetic Resonance (RMN)

3.1.1 Molecule 3,4,5-tributoxy benzoic acid (1)

^{1}HNMR (DMSO-d_6, 400MHz): δ= 7.27 (s, 2H, ortho-H), 4.8 (s, 1H, OH), 4.3 (t, 4H, OCH$_2$), 4.2 (t, 2H, OCH$_2$), 1.78 (m, 6H, OCH$_2$CH$_2$), 1.45 (m, 6H, OCH$_2$CH$_2$CH$_2$), 0.95 (t, 9H, CH$_3$).

^{13}CNMR (DMSO-d_6, 400MHz): δ= 122 (1C, CCOOH), 108 (2C, C-H), 152 (2C, CO), 131 (1C, CO), 168 (1C, COOH), 69 (1C, OCH$_2$), 31.1 (1C, OCH$_2$CH$_2$), 19.3 (1C, OCH$_2$CH$_2$CH$_2$), 13.8 (1C, OCH$_2$CH$_2$CH$_2$).

3.1.2 Molecule 3,4,5-tributoxy ethyl ester benzoic acid (2)

^{1}HNMR (DMSO-d_6, 400MHz): δ= 7.26 (s, 2H, orto-H), 4.37 (t, 2H, COOCH$_2$), 4.17 (t, 2H, OCH$_2$), 4.03 (t, 4H, OCH$_2$), 1.86 (m, 6H, OCH$_2$CH$_2$), 1.75 (m, 2H, OCH$_2$CH$_2$CH$_2$), 1.55 (m, 4H, OCH$_2$CH$_2$CH$_2$), 1.39 (t, 3H, OCH$_2$CH$_3$).1.0 (t, 9H, CH$_3$).

^{13}CNMR (DMSO-d_6, 400MHz): δ= 125 (1C, CCOO), 108 (2C, C-H), 154 (2C, CO), 139 (1C, CO), 166 (1C, COO), 69 (1C, OCH$_2$), 61.5 (1C, COOCH$_2$), 31.1 (1C, OCH$_2$CH$_2$), 19.3 (1C, OCH$_2$CH$_2$CH$_2$), 14.1 (1C, COOCH$_2$CH$_3$), 13.9 (1C, OCH$_2$CH$_2$CH$_2$).

3.2 Characterization by Fourier Transform Infrared Spectroscopy (FTIR)

3.2.1 FTIR of 3,4,5-tributoxy benzoic acid (1)

An intense band at 3478 cm^{-1} can be observed corresponding to the O-H functional groups [6]. At 2962 and 2929 cm^{-1} vibrations corresponding to asymmetric stretches of CH$_3$ and CH$_2$ bonds respectively, at 2874 and 2857 cm^{-1} attributed to the symmetrical stretching of CH$_3$. An intense band at 1267 and 1087 cm^{-1} associated with the asymmetric stretching vibrations of the ether group C-O-C can be observed [7]. The bands of the carboxylic group appear at 1690 and 1388 cm^{-1} represent C = O and C-OH. The particular bands of the aromatic ring C = C appear at 1630, 1540 and 1453 cm^{-1} [8], and at 966 cm^{-1} attributed to the H-ring as shown in Figure 3.
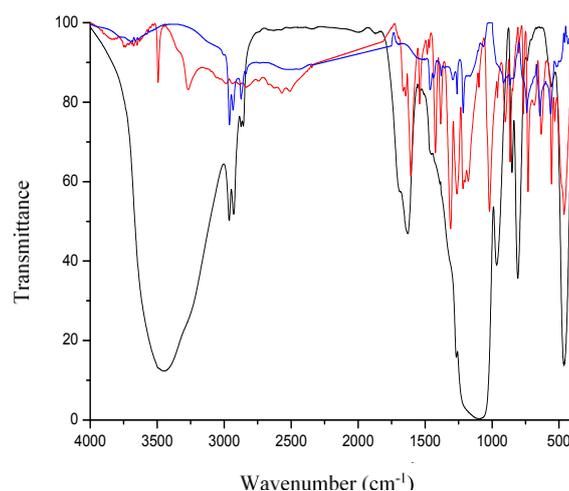
Fig. 3 FTIR spectra of 1 (black), gallic acid (red), bromobutane (blue)

3.2.2 FTIR of 3,4,5-tributoxy ethyl ester benzoic acid (2)

In Figure 4 the characteristic bands of the CH$_3$ and CH$_2$ groups at 2959, 2932 and 2872 cm^{-1}can be observed, confirming the etherification of ethyl gallate appearing at 1258 and 1092 cm^{-1} the vibrations of

asymmetric and symmetrical stretching respectively of the COC ether group. The bands at 1729 and 1319 cm^{-1} corresponding to the vibrations of the C (= O) -O esters can be observed. At 1606, 1567, 1488 and 1463 cm^{-1} aromatic groups are located.
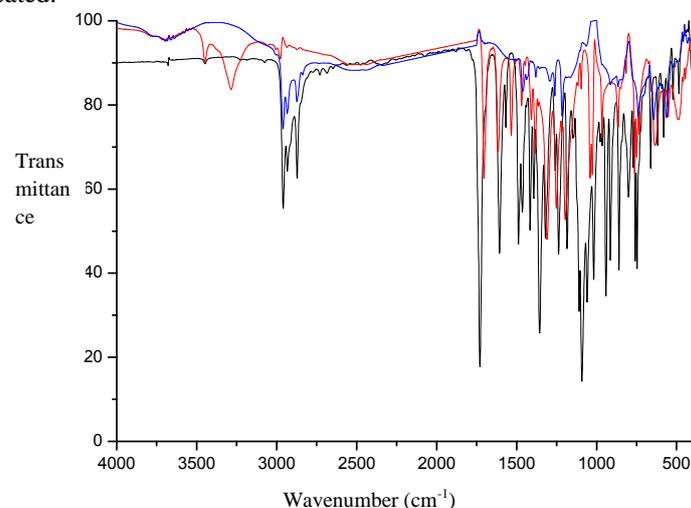
Fig. 4 FTIR spectra between 2 (black), ethyl gallate (red), bromobutane (blue)

3.3 Characterization by UV-Visible Spectroscopy (UV-Vis)
3.4.1 UV-vis of 3,4,5-tributoxy benzoic acid (1)

In 1spectra two bands attributed to the aromatic ring at 211 and 261 nm can be observed, the hypsochromic effect is observed in addition to a shoulder in the band at 261 nm suggesting etherification of the three hydroxyl groups of the ring (Figure 5).
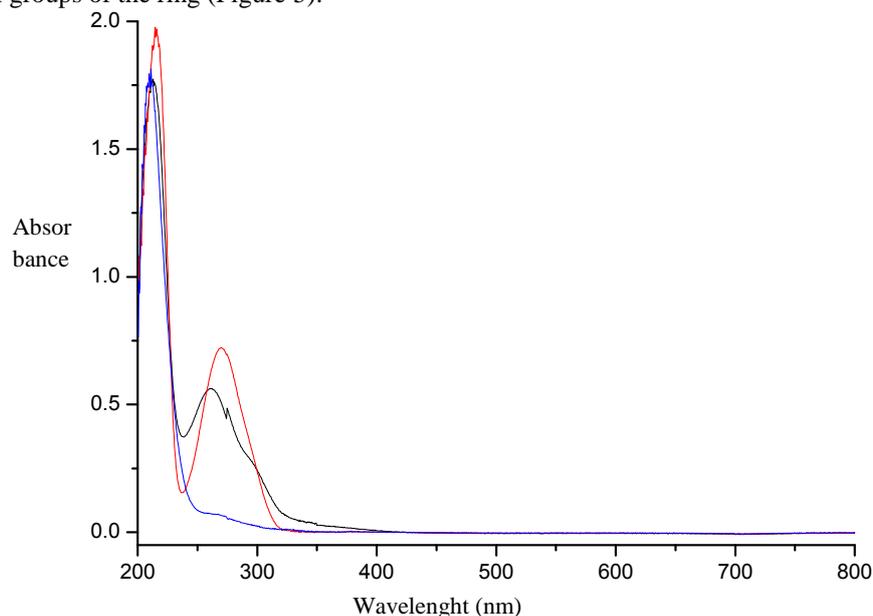
Fig. 5 UV-visible spectrum of 1 (black), gallic acid (red) and bromobutane (blue)

3.4.2 UV-vis of 3,4,5-tributoxy ethyl ester benzoic acid (2)

In 2spectra, since the sample was dissolved in distilled water and considering the hypochromic effect of the solvent on the interaction with the molecule, two signals were observed, one at 196 nm assigned to the ester, a decrease in absorbance at 260 nm related to a hypsochromic effect presumably due to the absence of hydroxyl groups (Figure 6).
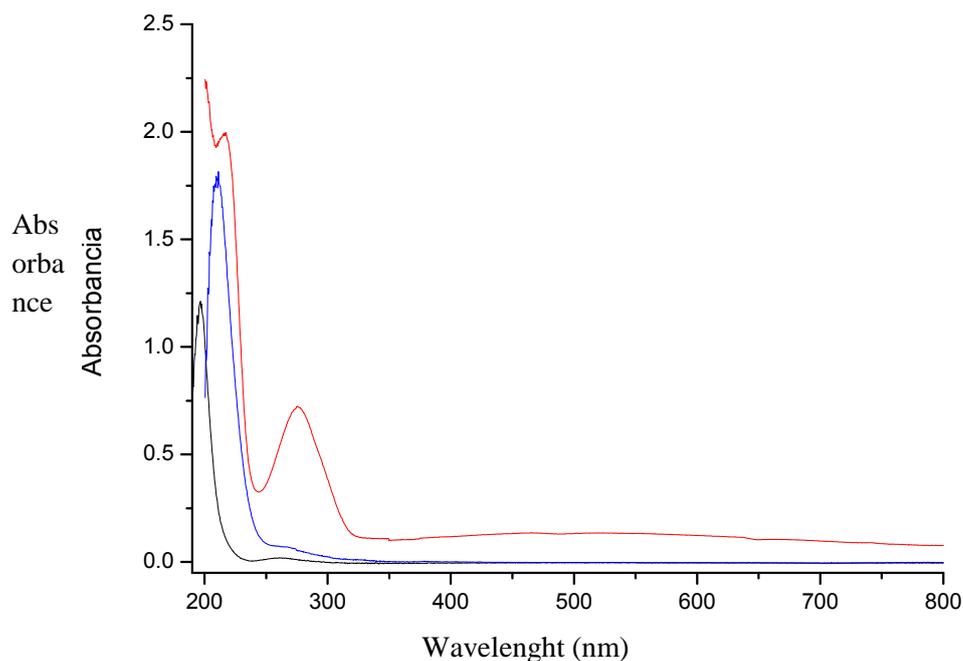
Fig. 6 UV-visible spectrum of 2(black), ethyl gallate (red) and bromine butane (blue)

3.5 Results of the emulsions

After 24 hours in both tests it was determined that the best results were presented by 2 when maintaining 50% of the volume of emulsified congenital water, 9 ml, and stabilized in the crude 40% volume of congenital water corresponding to 7.5 ml as shown in Table 1.

Table 1. Released water after 24 hrs by the bottle test

Emulsions	Crude oil	1	2
First test	15 ml	9 ml	7.5 ml
Second test	15 ml	10 ml	7.5 ml

3.6 Scanning Electron Microscopy (SEM)

Sample 2 presents nucleation and acicular growth with equiaxial growth, this growth mechanism confers a fibrillar morphology to the material and therefore a high contact surface area (Figure 7).
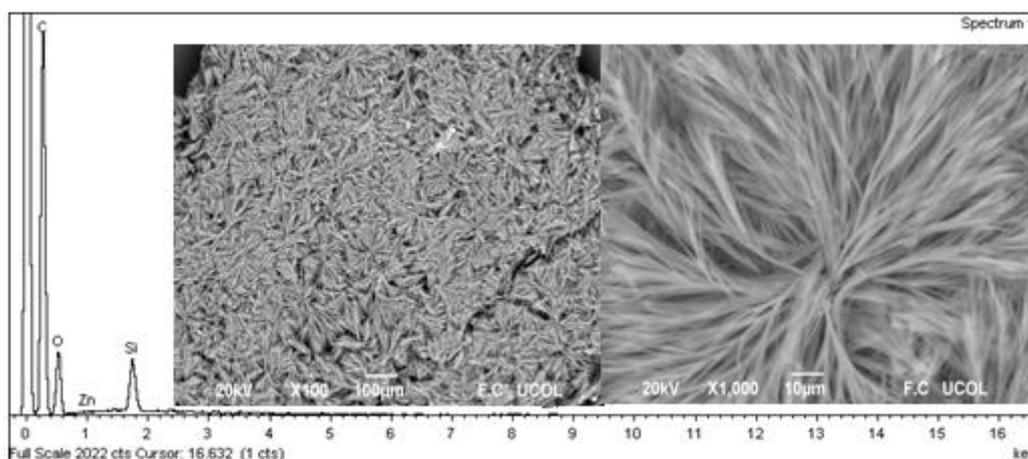
Fig. 7 Morphology of 3,4,5-tributoxy ethyl benzoic acid (2) by SEM-DS

IV.   CONCLUSION

The Nuclear Magnetic Resonance (NMR), Fourier Transform Infrared Spectroscopy (FTIR) and Visible Ultraviolet Spectroscopy (UV-vis) analyzes elucidated the desired chemical structures of the 3,4,5-tributoxy benzoic acid (1) and 3,4,5-tributoxy ethyl ester benzoic acid (2). The best results obtained from the

emulsions were observed by 2 maintaining 50% of the volume of congenital water emulsified and stabilized in the crude oil, where 1 only maintained 40%. Scanning Electron Microscopy (SEM) showed for molecule 3,4,5-tributoxy ethyl ester benzoic acid (2) a fibrillar morphology that favors the stabilization of the emulsion.

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