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Synthesis and application of additives based on cardanol as demulsifier for water-in-oil emulsions

Filipe X. Feitosa, Raissa S. Alves, Hosiberto B. de Sant'Ana*

Grupo de Pesquisa em Termofluidodinâmica Aplicada, Departamento de Engenharia Química, Universidade Federal do Ceará, Campus do Pici, Bloco 709, 60455-760 Fortaleza, CE, Brazil

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ABSTRACT

Emulsion formation is one of the most important problems faced by petroleum companies to guarantee the flow of fluids during petroleum production, once its formation is often associated to the colloidal state of asphaltenes in petroleum. For this reason, chemical additives should be frequently used to stabilize the asphaltenes and reduce or prevent emulsion formation. Unfortunately, it does not exist any widespread chemical compound that could be used for petroleum reservoirs indistinctly. Consequently, scanning and screening analysis for new compounds should be performed with the purpose to find more efficient and eco-friendlier demulsifiers. In this paper, four different chemical routes (hydrogenation, ethoxylation, formaldehyde polycondensation, and ethoxylation of formaldehyde polycondensation) have been used to synthesize four new products from cardanol to evaluate their activity as demulsifier agents. These additives were characterized by FTIR and ^1H NMR analysis. The demulsification activity were studied in emulsions using three Brazilian crude oil produced with a 30% (v/v) brine cut, 60 and 240 g/L NaCl of salinity, at different pH (range from 3 to 10), under agitation (3200 rpm). Bottle test was carried out at 60 °C in graduated tubes for water separability tests, by adding a constant composition (200 ppm) of each chemical tested. The results show that demulsification is more significant for ethoxylated compounds, at neutral pH.

1. Introduction

Petroleum extraction is often associate to water (or brine) co-production [1,2]. During petroleum processing or refining there are many points of changes in speed, pressure and direction of flow, making possible the formation of emulsions [3]. These formation is frequently responsible for serious problems on petroleum field, such as: corrosion of pipelines and plant equipment; viscosity increase and subsequent high transportation costs; and, additional costs for water and oil separation, reducing the potential petroleum recover [4–6]. The main mechanism of emulsion stabilization is attributed to the colloidal aggregation of asphaltenes [7–9], acting as a natural surfactant at interface, creating a rigid and mechanically strong film around the water droplets, prevents them from coalescing [4,10,11].

Asphaltenes are the heaviest fraction of petroleum, with associative characteristics and high polarity [10]. Typically, they are defined as solubility class of crude oil, insoluble in *n*-alkanes (e.g., *n*-pentane and

n-heptane) and soluble in aromatic compounds (e.g., toluene) [12–14]. Due to broad definition, asphaltenes exhibit different properties and molecular weights, mainly dependent on the type of crude oil [15,16]. However, they present an interfacial behavior with a certain degree of uniformity [17].

Therefore, high investments are made to develop efficient strategies for separating or inhibiting the formation of W/O emulsions. Demulsification refers to process of breaking up emulsions to separate the water from crude oil. There are several methods that are used in petroleum industries, such as: mechanical, thermal, electrical, and chemicals techniques [18–21]. Nevertheless, chemical demulsifiers attracted great attention, because is the most economical and commonly applied method [22,23]. This technique consists of the addition of minimal amounts of surfactant (usually from 10 to 1000 ppm) to enhance phase separation rates [24]. Surfactant additives are common amphiphilic compounds used to break up emulsions. These compounds should have a great tendency to interfacial adsorption at oil-water

Abbreviations: ATR, attenuated total reflectance; CFR, cardanol formaldehyde resin; CNSL, cashew nut shell liquid; EC, ethoxylated cardanol; ECFR, ethoxylated cardanol formaldehyde resin; FTIR, Fourier transform infrared; ^1H NMR, proton nuclear magnetic resonance; PPh₃, triphenylphosphine; ppm, parts per million; W/O, water-in-oil

* Corresponding author.

E-mail address: hbs@ufc.br (H.B. de Sant'Ana).

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Table 1
Crude oil properties (PET-1, PET-2, and PET-3) used for emulsion preparation.

Properties	PET-1	PET-2	PET-3
Density at 60 °C (g.cm ⁻³)	0.8718	0.9224	0.9118
Viscosity at 60 °C (mPa.s)	15.795	108.400	56.119
Saturates (% wt)	42.5	30.1	43.0
Aromatics (% wt)	26.0	25.0	25.9
Resins (% wt)	31.5	38.4	29.6
Asphaltenes (% wt)	1.14	6.43	1.55

droplets to replace the stable asphaltene films, occupying quickly the water/oil interface [23,25], and promoting the coalescence and film drainage with high efficiency [26]. Traditionally, petroleum industry uses non-ionic surfactant mixtures based mainly in ethoxylate polymers and alkylphenols, but several compounds could be applied as demulsifiers [26–29].

In the last decades, petroleum industry is trying to replace petroleum-based surfactants for natural demulsifiers, as a result of their low biodegradability and toxicity that can cause hazardous risk to the ecosystem [25,30]. Natural demulsifiers are favorable due to lower production cost, when compared to petroleum-based surfactants, along with easy handling, high efficiency, and low toxicity [31,32]. Therefore, the development of new surfactant molecules remains still a challenge for petroleum industry.

Cardanol is a compound extracted from cashew nut shell liquid (CNSL), widely available as an agricultural byproduct in Asia, Africa, and South America [33]. It is a phenolic compound with an aliphatic C15 chain meta-substituted, and less aggressive to the environment [34]. Considered a versatile raw material, cardanol presents itself an attractive molecular structure due to the phenolic ring functionalities and the presence of double bonds in the aliphatic chain, allowing several chemical modifications [10,35]. Many applications have been mentioned in the literature for cardanol and derivatives, acting as varnishes, paints, stabilizers, plasticizers, ion exchange resins, and surface treatment agents [35–38]. Furthermore, due to the similarity with the

chemical structure of the alkylphenols used as asphaltene stabilizers, it has also been studied for this purpose [25,39]. There are several modifications that may be proposed to improve the demulsification capacity of cardanol. Among the most frequent reactions are the synthesis of ethoxylated products [40] and alkylphenol formaldehyde resins [33], due to their known high performance as demulsifiers [41].

This work aims to develop natural surfactant compounds based on cardanol as an alternative to traditional petroleum based demulsifiers. This study is divided into two stages. Firstly, it consists on the synthesis and characterization of the surfactant additives based on cardanol, obtained from different chemical routes: hydrogenated cardanol (HC), ethoxylated cardanol (EC), cardanol formaldehyde resin (CFR) and ethoxylated cardanol formaldehyde resin (ECFR). Secondly, it has been evaluated the performance of these additives on emulsion separation capability.

2. Experimental section

2.1. Materials

Cardanol extracted to CNSL was obtained from Resibras – Brazilian Company of Resins Ltd. (Brazil). Hydrogen (grade 6.0) was supplied by Whyte Martins Industrial Gases Ltd. (Brazil). Citric acid (99.5% mass fraction) and methanol (99.8% mass fraction) were supplied by Vetec Química Fina Ltd. (Brazil), while formaldehyde (37% mass fraction) was purchase by Dinâmica Química Contemporânea Ltd. (Brazil). Cardanol, methanol, Raney-Nickel catalyst (Sigma-Aldrich, USA), and hydrogen were used to prepare hydrogenated cardanol. Ethoxylation and resins synthesis were based on hydrogenated cardanol. Triphenylphosphine (PPh₃, 99%) and ethylene carbonate (98% mass fraction) were used for ethoxylation, both from Sigma-Aldrich (USA). Citric acid, methanol, formaldehyde, and ethyl acetate (from Sigma-Aldrich, USA, 99.8% mass fraction) were used for resins synthesis. It is important to mention that all chemical used in this work were used without any further purification process.

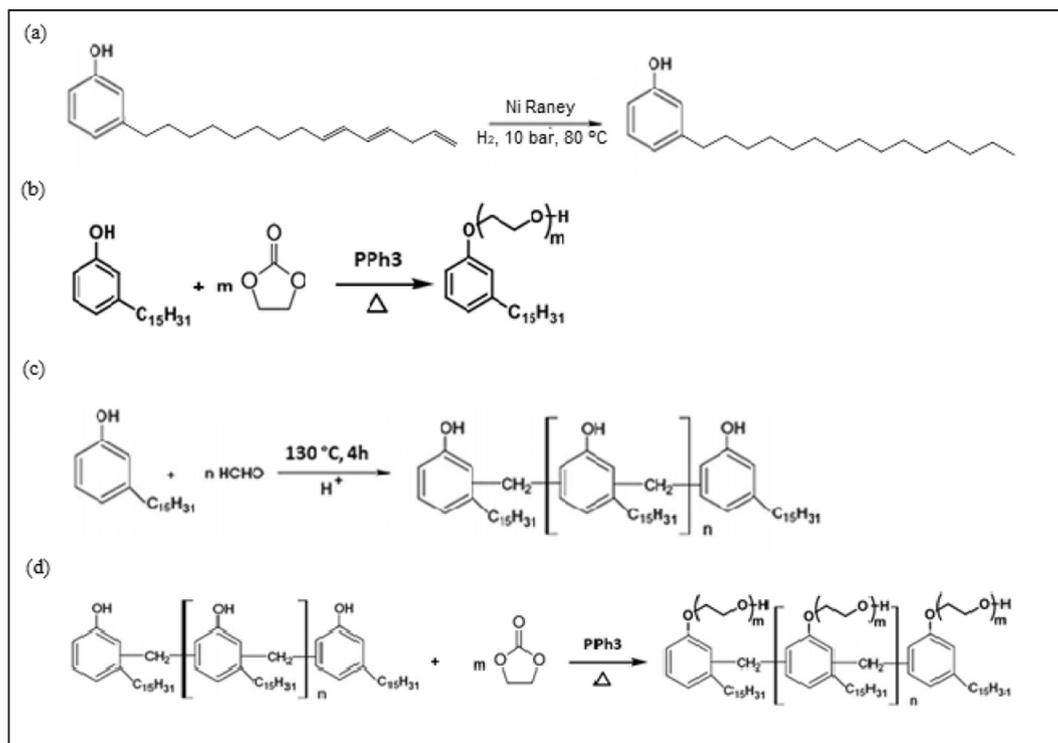


Fig. 1. Scheme of the cardanol reactions, forming: (a) hydrogenated cardanol, (b) ethoxylated cardanol, (c) cardanol formaldehyde resin, and (d) ethoxylated cardanol formaldehyde resin.

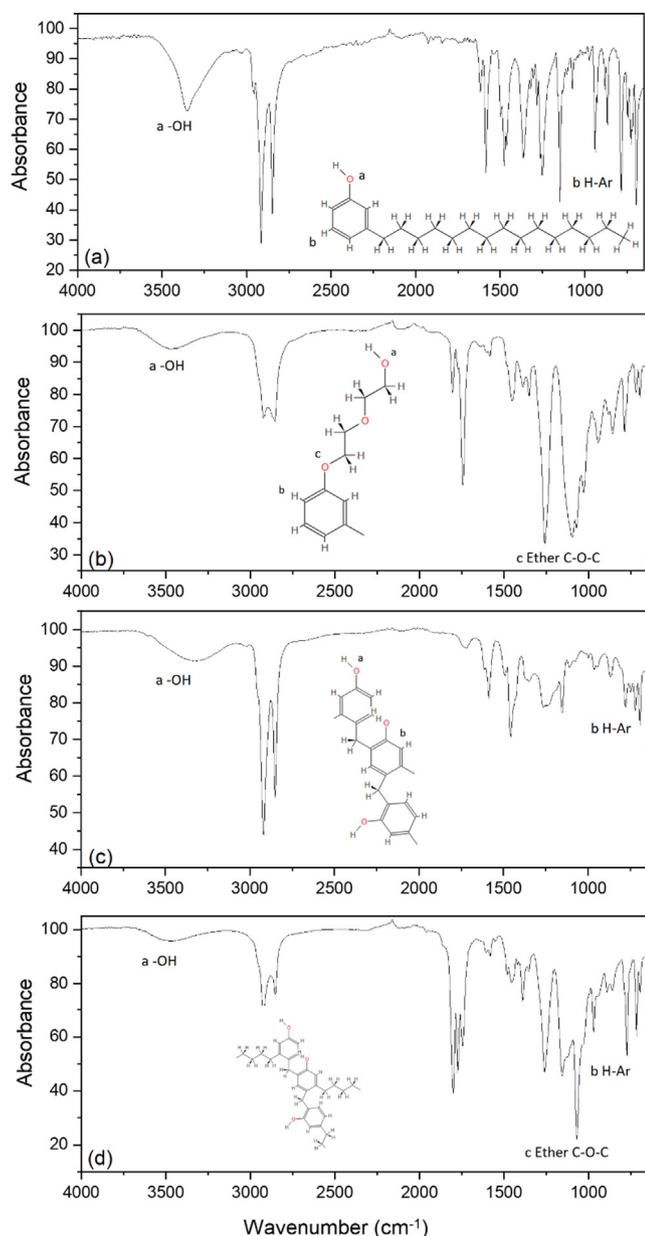


Fig. 2. FTIR spectra of (a) hydrogenated cardanol, (b) ethoxylated cardanol, (c) cardanol formaldehyde resin, and (d) ethoxylated cardanol formaldehyde resin.

Three Brazilian crude oils were used to formulate emulsions, here named as PET-1, PET-2, and PET-3 oils. Crude oils properties are summarized in Table 1. The water used for the formulation of emulsions was synthesized from deionized water (18.2 M Ω .cm at 25 °C) and sodium chloride (NaCl, Dinâmica Química Contemporânea Ltd.), with brine concentrations based on the natural reservoir composition of each oil. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used to pH regulation, both supplied by Vetec Química Fina Ltd.

2.2. Synthesis and characterization of demulsifiers

2.2.1. Hydrogenated cardanol

Cardanol (0.21 mol, 62.41 g), methanol (240 mL), and Raney-Nickel catalyst (5% wt/wt) were added to a reactor (Paar, 1 L capacity, with a maximum operation pressure of 300 bar, and a maximum temperature of 550 °C) and kept under stirring (250 rpm). After reach temperature of 80 °C, reactor was pressurized with hydrogen to 10 bar. The reaction occurs in 5 h. After that, reaction mixture was filtered and the solvent

removed by evaporation under reduced pressure (250 mbar). Hydrogenated cardanol is purified by distillation in a high vacuum glass oven (250 °C and 2 mbar), whereby a white solid is obtained at room temperature.

2.2.2. Ethoxylated cardanol (EC)

Hydrogenated cardanol (3.0 g) and PPh₃ (10% wt/wt) are mixed and heated (150 °C) in a three-necked flat bottom flask coupled to a condenser and a digital temperature thermocouple. The third inlet was used to add ethylene carbonate (20:1 mol/mol), by slow dripping. After the addition of ethylene carbonate, the temperature was adjusted to 190 °C and the reaction occurs for 5 h. The intense bubbling indicates the reaction progress.

2.2.3. Cardanol formaldehyde resin (CFR)

Citric acid (10% wt/wt) was dissolved in methanol (2 mL) under gentle heating and added to the hydrogenated cardanol (5 g) in a three-necked flat bottom flask, with a condenser and a digital thermocouple of temperature. A solution of formaldehyde (13 mmol) in methanol (3 mL) was prepared, and slowly added dropwise through the third inlet of the flask. At the end of the drip, temperature was controlled (130 °C) and the system stirred. After 4 h of reaction the product is cooled and purified by addition of ethyl acetate (20 mL) and deionized water (20 mL), with subsequent decanting and drying. Final product is a reddish and viscous liquid.

2.2.4. Ethoxylated cardanol formaldehyde resin (ECFR)

Previously produced, CFR (3.0 g) is mixed with PPh₃ (10% wt/wt) and heated (at 150 °C) in a three-necked flat bottom flask coupled to a condenser and a digital temperature thermocouple. This procedure is identical to that proposed for ethoxylated cardanol, with the addition of excess ethylene carbonate (20:1 mol/mol) at 190 °C, and reaction duration of 5 h. The intense bubbling also indicates the reaction progress.

2.2.5. Characterization

Qualitative analysis of the structures was conducted by Fourier-transform infrared spectroscopy (FTIR), carried out on an Agilent Cary 630 spectrometer coupled to a germanium attenuated total reflectance (ATR) element. Spectrum range was from 4000 to 400 cm⁻¹. Proton nuclear magnetic resonance (¹H NMR) was also applied to confirm the structures of the resulting products from proposed synthesis, by intermediate of a Bruker Avance III 500 spectrometer, at 300 MHz, at 28 °C, using deuterated chloroform as solvent.

2.3. Demulsification tests

Firstly, water-in-oil emulsions were prepared with synthetic brine as an aqueous phase containing 60 g/L of NaCl for PET-2 and PET-3 oils, from mature oil fields. Nevertheless, 240 g/L of NaCl was used for PET-1 oil, from a recent developed oil field. Aqueous phase pH control was done by the addition of NaOH and HCl solutions, to reach samples of 3, 7 and 10 pH, since stabilizing agents usually have ionizing groups that depend on the pH of the medium [42,43]. Organic phase was prepared with 35 mL of crude oil doped with 200 ppm (v/v) of additive in a 100 mL beaker, for each test. These emulsions were prepared in a water/oil ratio of 30:70 (% v/v), totalizing 50 mL. Then, these mixtures were subjected to shear in an IKA Turrax T-25 homogenizer, under rotation of 3200 rpm. The system was left under stirring for 5 min for PET-1 oil and for 15 min for PET-2 and PET-3 oils, at room temperature. Time required for emulsion formulation, from PET-1 and PET-2 oil, were determined by intermediate of a screening test made previously, in order to guarantee no water resolution on the first 2 h test and to obtain similar droplets distribution. It is interesting to state that blank tests were made following the same experimental procedure described here. From emulsion formulation tests, it was calculated an

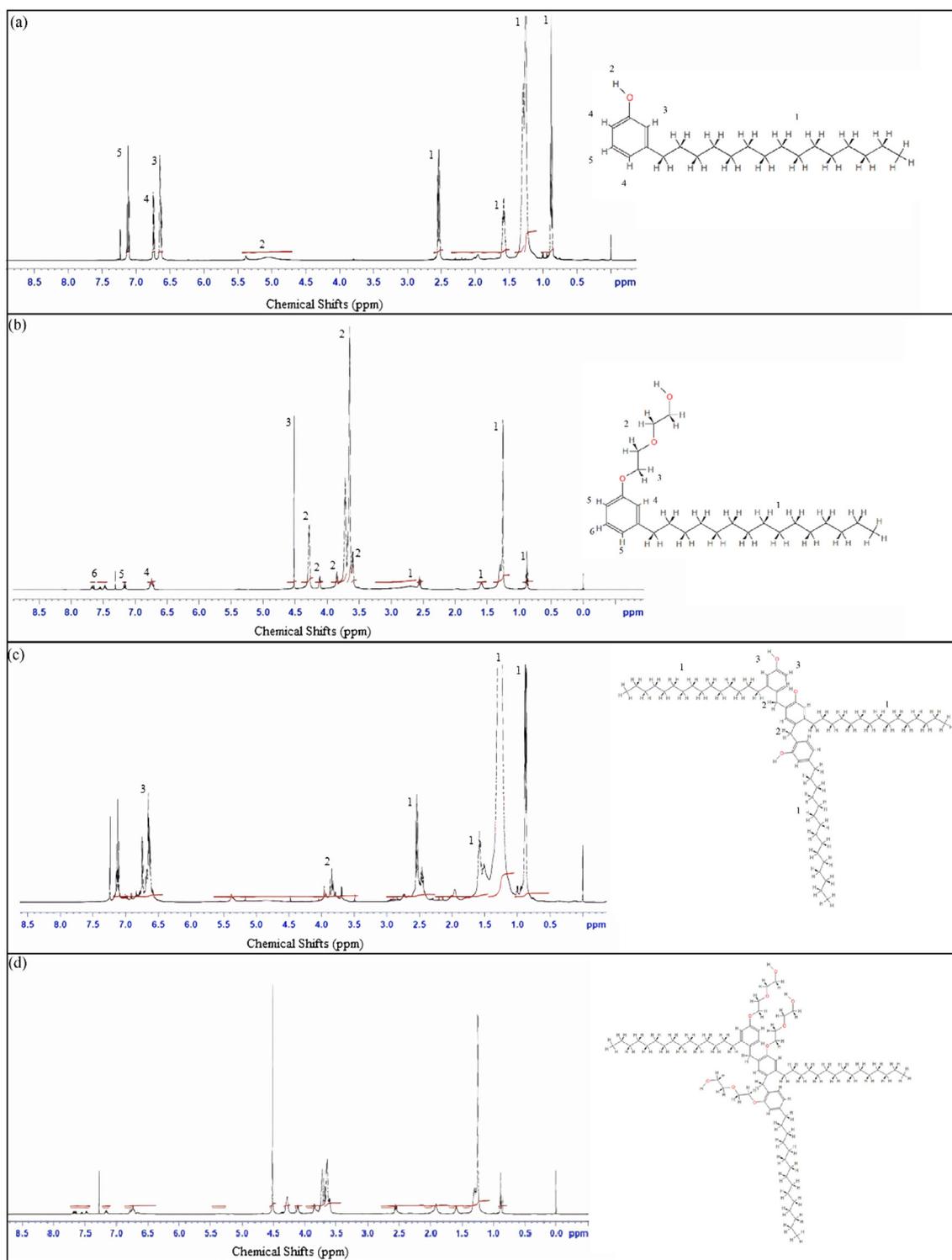


Fig. 3. ^1H NMR spectra of (a) hydrogenated cardanol, (b) ethoxylated cardanol, (c) cardanol formaldehyde resin, and (d) ethoxylated cardanol formaldehyde resin.

overall average deviation of 2% (v/v). For all these tests, a minimum of three parallels test were performed. It is important to notice that all molecules synthesized in this work were used as demulsifiers, i.e., additives were added after emulsification process.

Droplet size distribution were evaluated by using an Alltion trinocular LED microscope, coupled with 5MP digital camera and ImageJ software. From these images, it was carried out the following treatment procedure: i) the conversion of original image (16-bits, color) into a 8-bits image; ii) use of bandpass filter to contrast enhance; and, iii) image

binary transformation. Microscope calibration slide was used in order to convert pixels to micrometers. Droplets diameters were measure by pixel area that cover the droplet image (Waddel disk diameter). Diameter distributions were calculated by volume fraction of each diameter range. For that, at least three images were used to ensure that a minimum of one thousand particles are observed, providing confidence level of 95% for droplet size distribution.

Water/oil separation was done by using a bottle test [44]. Emulsion were placed in graduated tubes and maintained in a transparent water

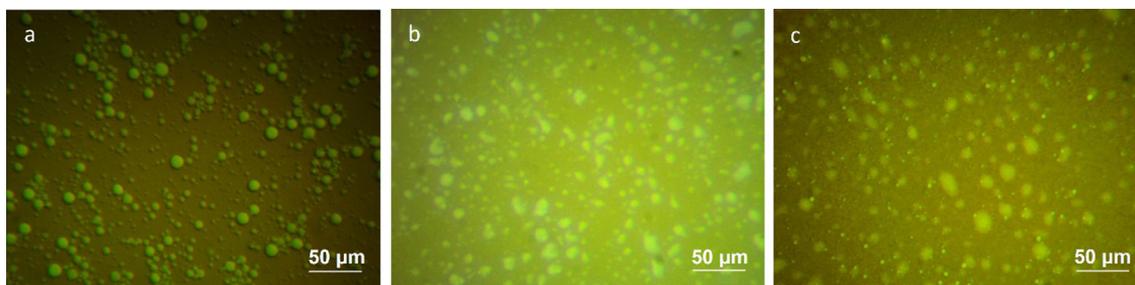


Fig. 4. Water-in-oil emulsions micrograph formulated in a ratio of 30:70 (% v/v) with PET-1 (a), PET-2 (b), and PET-3 (c) oils, under rotation of 3200 rpm, for 2 h at 60 °C. Total magnification of 180 ×.

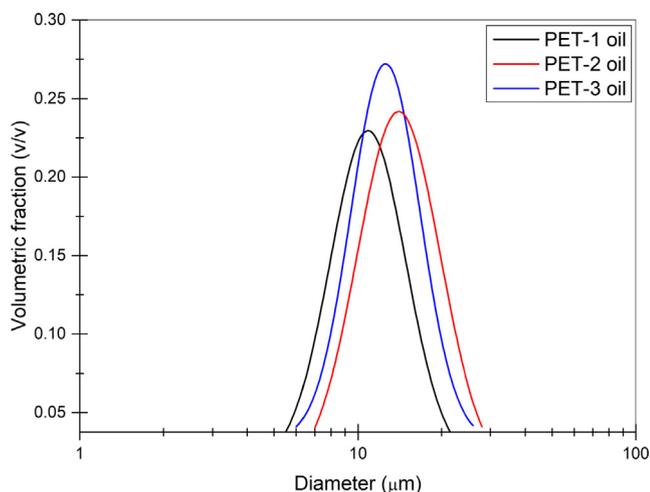


Fig. 5. Droplet size distribution for emulsions prepared with PET-1, PET-2 and PET-3 oils, after 2 h at 60 °C.

bath at 60 °C. Water resolution was measured at 5 min intervals in the first half hour of the test, 10 min intervals in the second half hour of the test, and at 20 min in the last hour, totalizing 2 h total test. The results were expressed in terms of water volume separated (mL) as a function of time (min).

3. Results and discussion

3.1. Synthesis and characterization of demulsifiers

Four additives were synthesized according to the schemes shown in Fig. 1. Hydrogenation reaction aims to complete saturation of the cardanol aliphatic side chain, giving a hydrogenated cardanol. This product has been used for subsequent reactions. Ethoxylation reaction occur on the hydroxyl group and consist in the addition and opening of the ethylene carbonate ring. Moreover, resin formation is a polymerization reaction through the cardanol aromatic ring.

Demulsifiers synthesized were characterized by FTIR spectrometry, as represented in Fig. 2. It is possible to observe that FTIR spectra confirm the synthesis proposed on Fig. 1. For hydrogenated cardanol (Fig. 2a) an intense band at 721 cm^{-1} was observed, related to out-of-plane angular deformation associated with four or more $-\text{CH}_2$ groups present in alkyl chain. Wavenumber 1459 cm^{-1} is associate to the asymmetric angular deformation related band of $-\text{CH}_3$, although wavenumber 1367 cm^{-1} is related to the symmetrical angular deformation. In 2922 cm^{-1} the band relative to asymmetric stretch of $-\text{CH}_2$ is found. In addition, with broad bands in the $\nu\text{ C-H}$ region of CH_2 and $\nu\text{ C-H}$ of CH_3 , the spectrum confirms the hydrogenation of the side chain of the cardanol.

Structural confirmation of the ethoxylation of cardanol and the formation of cardanol formaldehyde resin could be observed by the

significant increase of absorbance in the region of 1070 cm^{-1} (Fig. 2b and d), which appears associated with peaks in the $1275\text{--}1200\text{ cm}^{-1}$ region, due to the aromatic character of the ethers synthesized. The confirmation of formaldehyde resin formation is made by comparing region $770\text{--}730\text{ cm}^{-1}$ and $710\text{--}690\text{ cm}^{-1}$ of panels a, c, and d. This reduction observed is associated with a reduction of adjacent hydrogens in the aromatic ring, possibly caused by polycondensation synthesis.

Additionally, chemical structures of the synthesized in this paper were elucidated from $^1\text{H NMR}$, as represented in Fig. 3. According to the panel a (Fig. 3a) chemical shifts are evident in the aromatic region of the hydrogenated cardanol molecule, as: two narrow and partially overlapping duplets, at approximately 7.12 ppm; one singlet elongated at approximately 6.65 ppm and one duplet partially unfolded and overlaid on the singlet. These displacements are an indicative of the characteristic meta-substitution of cardanol. In addition, the hydroxyl group is indicated by the extended singlet in the region of 4.8–5.3 ppm. The insignificance in the displacement of region bound to presence of olefinic hydrogens (5.3–5.5 ppm) and elevation in the region of saturated hydrogens (0.5–4.0 ppm) indicates the efficiency of the hydrogenation. From this result, it could be observed, from peaks integration of chemical shift in the 5.3–5.5 ppm range, a almost complete hydrogenation process, with an olefinic hydrogen fraction of 0.4% (m/m).

The presence of peaks in chemical displacements of 3.3–4.7 ppm could be associated to the addition of ethoxylated groups (Fig. 3b e d). These panels also shows the presence of a 4.517 ppm displacement peak that could be associate to the hydrogen signal in the cyclic ring structure of ethylene carbonate [45]. Thus, confirming the ethoxylated structure. From these results, it could be stated, from the integration peaks of chemical shift between 3.5 and 4.5 ppm, that it was obtained a conversion of ethoxylated cardanol (EC) of 96.9% (m/m) during ethoxylation.

The synthesis of cardanol formaldehyde resin is associated with the appearance of $\text{Ph-CH}_2\text{-Ph}$ characteristic peaks in the region of 3.4–4.1 ppm, as observed in Fig. 3c. However, in the synthesis combining polymerization on the aromatic ring of cardanol for resin formation and ethylene carbonate ring aperture for ethoxylation, it was not possible to determine structural parameters characterizing the product formed by intermediate of $^1\text{H NMR}$ spectrum due to the overlapping of signals in the range of 3.5 and 4.5 ppm. Average number of phenolic units were calculated by the ratio of area for chemical shifts between 3.4 and 4.1 ppm (attributed to phenol- CH^2 -phenol bonds) and 6.4–7.2 ppm (attributed to aryl-H bonds) giving a number of 2 phenolic units, in other words, a mean of two cardanol molecules are condensed to form cardanol formaldehyde resin (CFR). Nevertheless, for ECFR product, it is important to mention that it was not possible to calculate both average number of phenolic units neither ethylene carbonate conversion, due to the superposition of characteristics chemical shifts.

3.2. Effects of additives in water-in-oil demulsification

Fig. 4 shows a comparative micrography for emulsions prepared by

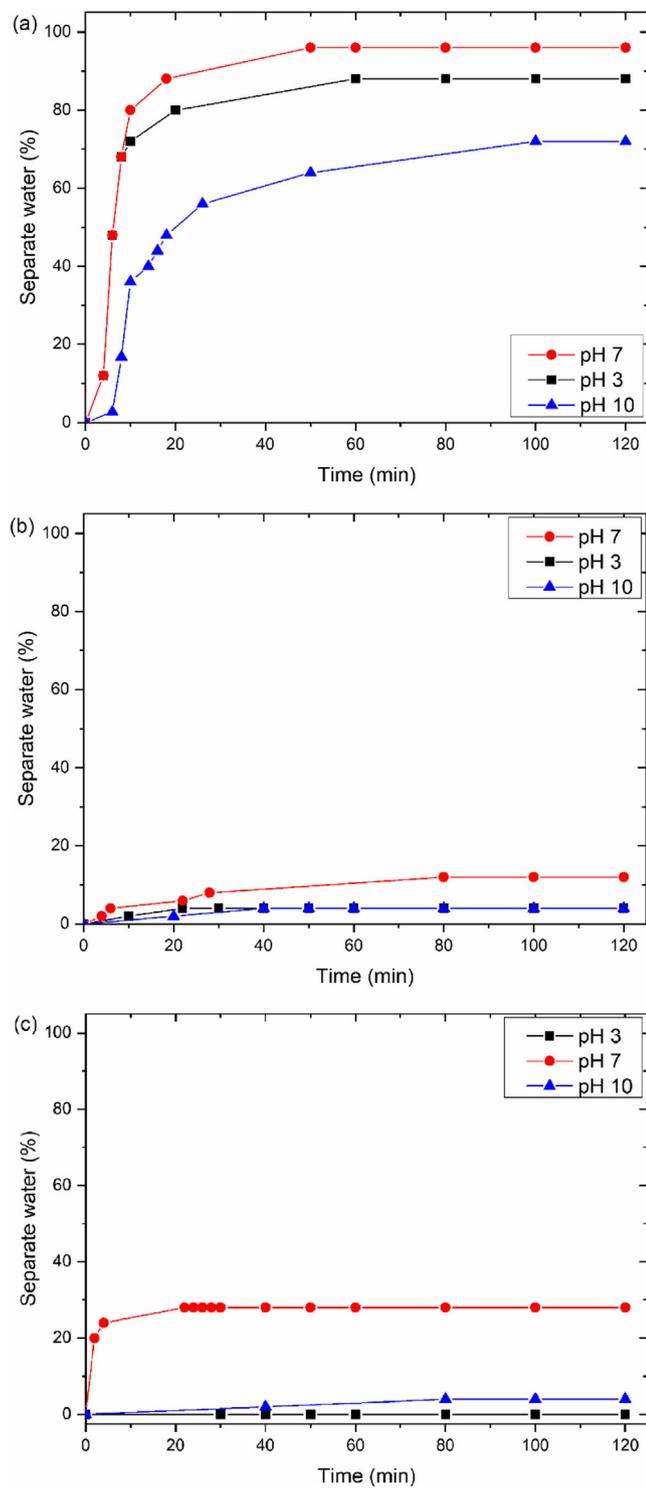


Fig. 6. Water resolution as a function of time for emulsions prepared with PET-1 (a), PET-2 (b) and PET-3 (c) oils, containing ethoxylated cardanol formaldehyde resin (ECFR). Test of 2 h, with pH variation and 60 °C.

using PET-1, PET-2, and PET-3 oils. It could be observed that there is a formation of stable emulsions with droplet sizes visually similar, confirmed on Fig. 5, discussed later. Nevertheless, there is two important points regarding these results: firstly, PET-1 emulsion presents a well-defined droplets sphericity; secondly, it is clearly observed a better micrograph definition when using PET-1 oil, probably due to the translucency of this sample.

Fig. 5 depicts droplet size distribution analysis by using ImageJ

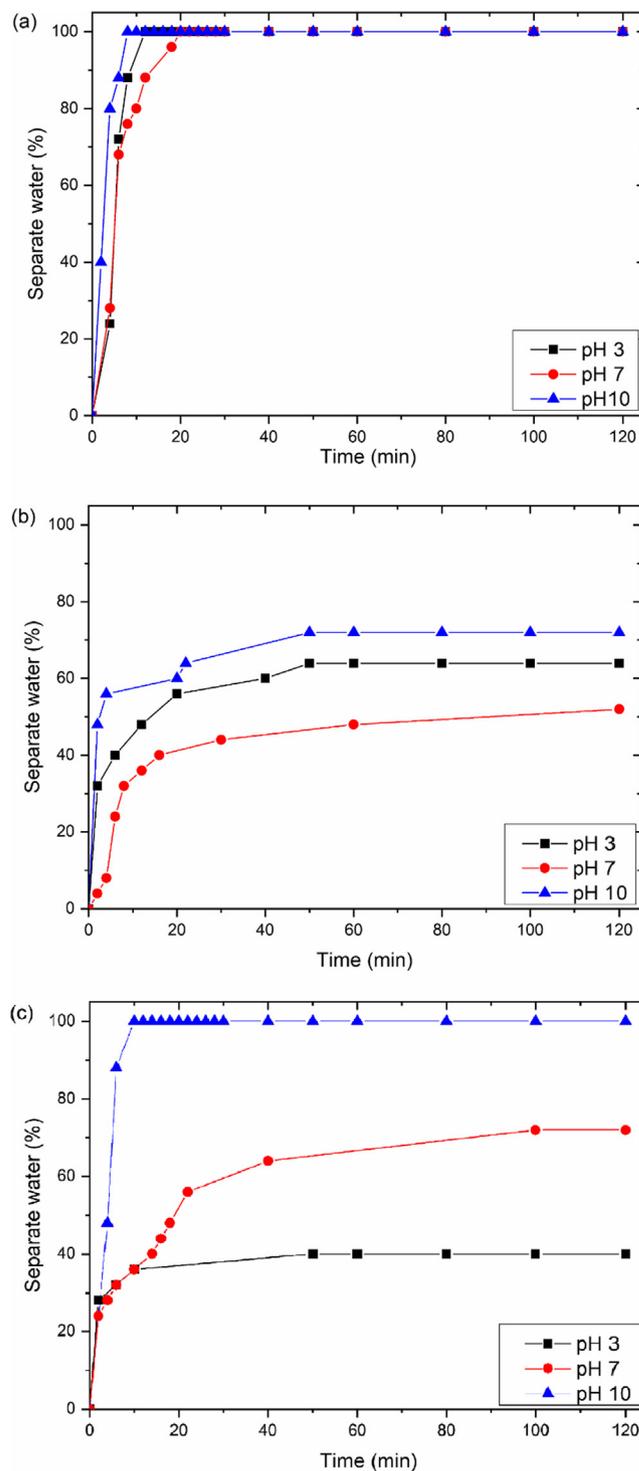


Fig. 7. Water resolution as a function of time for emulsions prepared with PET-1 (a), PET-2 (b) and PET-3 (c) oils, containing hydrogenated cardanol (HC). Test of 2 h, with pH variation and 60 °C.

software. From this analysis, it could be seen that the largest diameter in volumetric frequency was around 30 μm for emulsions prepared with PET-2 oil and the smallest one was near 5.5 μm for PET-1 oil. Average diameters based on the volumetric fraction weight were 11.2, 15.1 and 15.2 μm for emulsion prepared with PET-1, PET-2 and PET-3 oils, respectively. A 2 μm uncertainty was established for this technique. For this reason, average diameter measured for all emulsion presented the same value, i.e., 13 μm .

Water resolution test performed with hydrogenated cardanol (HC)

Table 2

Performance of chemical modification from Cardanol related on literature and this work and conditions of tests: concentration, demulsifier efficiency (DE), time, temperature, water cut.

Compound	Concentration (mg.L ⁻¹)	DE (%)	Time (min)	Temperature (°C)	Water Cut (%)
DECA [31]	50	68	420	60	30
TECA [31]	100	60	600	60	30
QTECA [25]	10	90	180	60	30
QDECA [25]	10	100	60	60	30
CPEHA [48]	50	84	600	60	30
QCPEHA [48]	50	84	540	60	30
ECFR*	175	95	50	60	30
EC**	175	100	10	60	30

DECA – Di-etherified cardanoxo amine; TECA – Tri-etherified cardanoxo amine; QDECA – Quaternized Di-etherified cardanoxo amine; QTECA – Quaternized Tri-etherified cardanoxo amine; ECFR – Ethoxylated cardanol formaldehyde resin; EC – Ethoxylated cardanol.

* Results observed for PET-1 as depicted on Fig. 6(a).

** Results observed for PET-3 as depicted on Fig. 7(c).

and cardanol formaldehyde resin (CFR) additives do not show any water separation. These results demonstrate the absence of demulsifying activity for these additives, once it misses a strong polar group that could act as amphiphilic group that could increase this activity, as can be seen in Fig. 3(a) and (c). However, ethoxylated cardanol (EC) and ethoxylated cardanol formaldehyde resin (ECFR) showed some water separation under different conditions tested. This behavior indicates a possible ability of ethoxylated compound to stabilize asphaltene in the emulsion. Figs. 6 and 7 show water resolution kinetics plots that present demulsifier action of ECFR and EC additives, respectively. It is important to mention that it has been also performed a pH variation (pH 3, 7, and 10) studies also described in Figs. 6 and 7. From these results, it is possible to state that best performance was attained for emulsions prepared with PET-1 oil, for both additives, due to lower viscosity range, as described in Table 1. Additionally, it could be also observed that there is a complete water separation for all pH tested when used EC additive. Nevertheless, for ECFR additive, best results was obtained at neutral pH.

For emulsions prepared with PET-2 and PET-3 oils, it was not observed higher water resolution (less than 30% water resolution) when using ECFR additive, as seen in Fig. 6. This result could be directly associated to the low content of average number of phenolic units, as discussed previously. Likewise, it is clear that neutral pH presents best results for all emulsions tested. These results could be attributed to the smaller elastic compression modules for neutral pH, which may be an indicative of lower interfacial action of asphaltenes, thus lower emulsion stability [46]. Conversely, pH 10 was favorable when using ethoxylated cardanol (EC) additive, for all emulsion systems studied. This behavior runs away from expectation, once at basic pH (pH = 10) emulsions are less stable when using distilled water in their preparation, once no ionization effects occur [47]. Possible additive size plays an important role on water resolution when EC additive is used.

From literature data, it was possible to compare and contrast

Table 3

Properties of the crude oil used on this work and literature [31,35,48].

Crude oil	°API	Saturates (wt%)	Aromatics (wt%)	Resins (wt%)	Asphaltenes (wt%)
PET-1 [this work]	25.4	42.5	26.0	31.5	1.14
PET-2 [this work]	17.2	30.1	25.0	38.4	6.43
PET-3 [this work]	18.8	43.0	25.9	29.6	1.53
Arabian Heavy [25]	20.8	ni	ni	ni	6.0
Arabian Heavy [31]	19.8	ni	ni	ni	12.0
Arabian Heavy [48]	20.8	ni	ni	ni	8.3

ni – not informed.

cardanol chemical modification to produce demulsifier additives. Table 2 shows performance comparison between additives produced in this work (EC and ECFR) and those produced by Atta and coauthors (2018) [31,48] and Ezzat and coauthors (2018) [25], showing additive concentration used, best demulsifier efficiency (DE), and time required to reach DE. Table 3 shows a comparison between crude oils (PET-1, PET-2, and PET-3) used in this work with three different arabian heavy oils. It is important to stressed temperature (60 °C) and water cut (30%) were the for all selected data, in order to be able to compare all data. Additive produced by Ezzat and coauthors, a quaternized di-etherified cardanoxo amine (QDECA) show a complete water resolution, even using the lowest additive concentration (10 mg.L⁻¹). Ethoxylated cardanol (EC) produced in this work has obtained same DE value, but in a lower time. In spite of using a higher concentration (175 mg.L⁻¹). Also from Table 3, it could be observed that higher asphaltene content leads to a need of more complex structures of demulsifiers for a complete water separation. In this work, using more simple modification on cardanol than literature, the worst result of DE is observed by the PET-2, crude oil with the higher asphaltene content. It should be emphasized that there is an important commitment solution among additive concentration, demulsifier efficiency, complexity reaction chemical route to additive synthetize and time. This comparative analysis shows how difficult is the development of new chemical demulsifier additives for petroleum industry, once a large effort should be done on individual tests and chemical compatibility analysis for all additives used in the field.

4. Conclusion

Four different additives (hydrogenated cardanol, ethoxylated cardanol, cardanol formaldehyde resin and ethoxylated cardanol formaldehyde resin) have been synthesized based on cardanol, which structures have been characterized by FTIR and ¹H NMR. These additives have been tested for three Brazilian petroleum samples, at 60 °C, 30% water cut, 3200 rpm, and 200 ppm additive concentration, at different pH. Ethoxylated cardanol and ethoxylated cardanol formaldehyde resin present some demulsifier activity, probably due to ethoxylated compounds that are responsible for asphaltene stabilization. Nevertheless, best additive performance was obtained for ethoxylated cardanol with a complete water resolution in 10 min for a crude oil with low asphaltene content (1.14 wt%).

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Declarations of interest

The authors declare no competing financial interest.

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