Full Length Article

Synthesis and application of castor oil maleate and castor oil maleate-styrene copolymers as demulsifier for water-in-oil emulsions

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ABSTRACT

Oil industry has encountered a series of difficulties associated with flow assurance of petroleum fluids, especially those related with stable emulsion formation. Such emulsified systems could present problems during transportation, handling, and refining, because of their relation to operational factors, as follows: fluid viscosity, processing energy expenditure, and water coproduction. For this reason, the addition of interfacial active compounds, often polymers, is used in an attempt to phase separation in industrial processes. In this paper, five different chemical surfactants, referred to here as MACO 1, MACO 2, R1, R2, and R3, were synthesized based on castor oil. These additives were characterized by Fourier Transform Infrared (FTIR), Size-Exclusion Chromatography (SEC), and Thermogravimetrical Analyses (TGA). The demulsification activity was studied in synthetic emulsions by using two Brazilian crude oils and 30% (v/v) brine cut with 60 and 240 g/L NaCl, at neutral pH, and average droplet diameter of 10 μm. Bottle tests were carried out at 60 °C in graduated ASTM test tubes for 2 h, varying additive concentration from 100 to 5000 ppm. Interfacial tension measurements were performed to elucidate the demulsification activity in water-oil interface, at the same bottle test experimental conditions. These results were discussed on the basis of the oil characterization, mechanisms of demulsifying action, as well as interfacial tension data. Ward and Tordai equation was applied according to asymptotic approximations to evaluate additives diffusivity. The results show that demulsification is more significant for MACO 1, with maximum water resolution of around 90% for both emulsion systems.

1. Introduction

The problem of separating water from produced crude oil is as old as the petroleum industry [1]. Water coproduction occurs mainly because of the formation of stable water-in-oil emulsions (W/O). Crude oil and connate water can be submitted to extreme condition of shear stress, i.e., mixed under turbulence in the reservoir and production pipelines, making possible emulsion formation [1–3]. For instance, in the presence of natural interfacial active agents very stable emulsions can be formed, generating a costly operational problem [4–6].

Intimate contact between aqueous and oil phases lead to an accumulation surfactant agents in water-oil interface, triggering a tough viscoelastic barrier formation [7]. This strong and rigid film surrounds water droplets preventing the coalescence process, stabilizing the emulsions formed [8,9]. It is assumed that heavier molecules, such as asphaltenes, wax crystals, and oil soluble organic acids (e.g., naphthenic and carboxylic acids) could act as stabilizing agents [1,10–12]. Nevertheless, it is attributed to the aggregation state of asphaltenes the main mechanism of stabilization of emulsions [5,13–15].

Therefore, understanding the formation of W/O emulsions and how to mitigate it is an important achievement to the oil industry [11]. There are several methods used to induce phase separation in W/O emulsions, such as: mechanical, electrical, and chemicals techniques [16–18]. Otherwise, the chemical method appears as the most

economical and industrially applicable for dehydrating crude oils [19]. Chemical demulsification is based on the addition of synthetic surfactant actives (usually in a concentration ranging from 10 to 1000 ppm) with a great tendency to occupy the water-oil interface and increases phase separation rate [18,20]. Demulsification mechanism changes the elasticity or the interfacial viscosity of the viscoelastic barrier, resulting in a replacement of the natural surfactants [21,22].

Traditionally, oil industry uses petroleum-based non-ionic amphiphilic compounds as demulsifiers [23]. However, in the past decade, natural and less expensive components have been gained attention in the literature. Natural demulsifiers are favorable because of the lower production cost, high efficiency, low toxicity, and high biodegradability [24–27]. Several compounds could be applied, such as: ionic liquids [6,18,28,29], ethoxylate polymers and alkylphenols based on vegetable oils [5,30], among others.

In this context, castor oil could be present as an interesting raw material because of its chemical structure that has both unsaturation and nonconjugated hydroxyl. These structures provide several chemical reaction options in the synthesis domain, with a wide application range. Castor oil is nonedible and is attractive once it does not compete with food industry [31,32]. Demulsifiers with high hydrophilicity can be synthesized using castor oil, such as castor oil maleate (MACO), which can be further copolymerized with styrene to increase the hydrophilicity character of these compounds [32–34].

The present work aims to synthesize natural surfactant compounds on the basis of the use of castor oil to apply as demulsifiers for water-in-oil emulsions. Two surfactant classes were evaluated: castor oil maleate (MACO) and castor oil maleate-styrene (MACO-St) copolymer. This study is divided into three main steps. Firstly, demulsifying additives on the basis of castor oil have been synthetized by the following three different chemical routes, as follows: castor oil maleate using benzoyl peroxide (MACO 1); castor oil maleate using potassium persulfate (MACO 2); and, three copolymers with different levels of polymerization (R1, R2, and R3). Secondly, their performance as a demulsifier additive has been evaluated. Finally, the influence of these additives on the water-oil interfacial tension was determined, regarding separation behavior.

2. Experimental section

2.1. Materials

Castor oil was provided by Olveq Indústria e Comércio de Óleos Vegetais (Quixadá, Brazil). Maleic anhydride (99%) and tribasic anhydrous sodium phosphate (97%) were supplied by Vetec Química Fina (Rio de Janeiro, Brazil). Potassium persulfate (PSK, ≥99%), styrene (≥99%), benzoyl peroxide (BPO, 75%), N,N-dimethylaniline (DMA, 99%), toluene (≥99.3%), and inhibitor-free HPLC grade tetrahydrofuran (THF, ≥99.9%) were purchased from Sigma-Aldrich (Darmstadt, Germany). All the chemicals were used without any further purification process.

Two different Brazilian crude oils, referred to here as P1 and P2, have been supplied by Repsol Sinopec Brasil (Rio de Janeiro, Brazil), and they were used to emulsion formulation. The main characteristics of the crude oils are summarized in Table 1. Brine used for the formulation of emulsions was synthesized by using deionized water (conductivity of 18.2 ± 0.2 mΩcm, at 298.15 K) and sodium chloride (NaCl, Dinâmica Química Contemporânea, São Paulo, Brazil), with salt concentrations based on the natural reservoir composition of each crude oil. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were used to pH regulation of the synthesized brine, both supplied by Vetec Química Fina (Rio de Janeiro, Brazil).

Table 1
Crude oil properties.

Properties	P1	P2	Standard method
API gravity (deg)	19.56	29.78	ASTM D1298
Density at 60 °C (g.cm^{-3})	0.9083	0.8524	ASTM D7042
Viscosity at 60 °C (mPa.s)	39.580	7.6383	ASTM D7042
Saturate content (± 2, wt%)	44.30	51.71	ASTM D2007
Aromatic content (± 2, wt%)	30.74	26.62	ASTM D2007
Resins content (± 3, wt%)	22.60	21.09	ASTM D2007
Asphaltene content (± 0.05, wt%)	2.36	0.57	IP 143
Wax content (wt%)	0.42	2.06	UOP 46–64
WAT (± 1, °C)	24.46	15.69	ASTM D2500
Water content (wt%)	0.63	0.22	ASTM D6304
Total acid number (mg KOH/g)	2.52	0.23	ASTM D974
Salt content (mg of NaCl/dm^3)	33.43	28.85	IP 77

3. Synthesis and characterization of demulsifiers

3.1. Synthesis of castor oil maleate (MACO)

Maleic anhydride and castor oil (1:1 mol:mol) were added to a batch reactor (400 mL, Metalquim, Brazil). After that, initiators benzoyl peroxide (0.010 wt%) and potassium persulfate (0.010 wt%) were added to produce MACO 1 and MACO 2, respectively. The reaction mixture was heated up to 140 °C for 3 h with constant continuous stirring of 600 rpm. Synthesis of MACO could be carried out without using free radical initiators, however the use of free radical initiators increases the rate of reaction, productivity and allows the synthesis of MACO dimers and trimers, which are rare in conventional thermal reaction [35,36]. MACO was used without further purification.

3.2. Synthesis of copolymer castor oil maleate/styrene (MACO-St copolymer)

For polymer synthesis, MACO 1 was mixed with styrene (St), benzoyl peroxide (BPO), and N,N-dimethylaniline (DMA) in different proportions. The R1 copolymer was produced using a St/MACO molar ratio of 2:1 and 0.10 wt% of BPO. The production of the R2 copolymer was carried out by using a St/MACO molar ratio of 2:1, 0.10 wt% of BPO, and 0.10 wt% of N,N-dimethylaniline (DMA). The synthesis of the R3 copolymer was done with a St/MACO molar ratio of 4:1, and 0.20 wt% of BPO. Water (50% of the weight of MACO) and anhydrous tribasic sodium phosphate (0.50 g) were added to all reactions. The suspension polymerization was carried out in batch reactor (400 mL). The mixture was stirred for 3 h at 100 °C. These conditions were based on a previous work [36] and were chosen to evaluate copolymers with different molecular weights (Mn and Mw) as demulsifiers. MACO-St copolymer was applied without further purification.

3.2.1. Characterization

The molecular structures of MACO and MACO-St copolymers were analyzed by Fourier Transform Infrared Spectroscopy (FTIR), carried out on an Agilent Cary 630 spectrometer. The FTIR spectrum was collected over the wavenumber range of 400–4000 cm^{-1} with a spectral resolution of 1 cm^{-1}.

The molecular weights of MACO and MACO-St copolymers were measured by Size-Exclusion Chromatography (SEC) with THF (flow rate: 1 mL/min), as mobile phase. These analyses were performed by intermediate of a Varian SEC system equipped a Pro Star 355 refractive index (IR) detector, an automated Rheodyne injector and a column heater (operating at 30 °C). A TSK Gel G2500HHR column (30 cm × 7.88 mm, 5 μm) was used. The molecular weight distribution of the copolymers was determined based on five polystyrene standards ranging from 266 to 45,500 g/mol.

The thermal stability of the demulsifiers were measured by using a SHIMADZU DTG-60 thermal analyzer. The samples were heated from
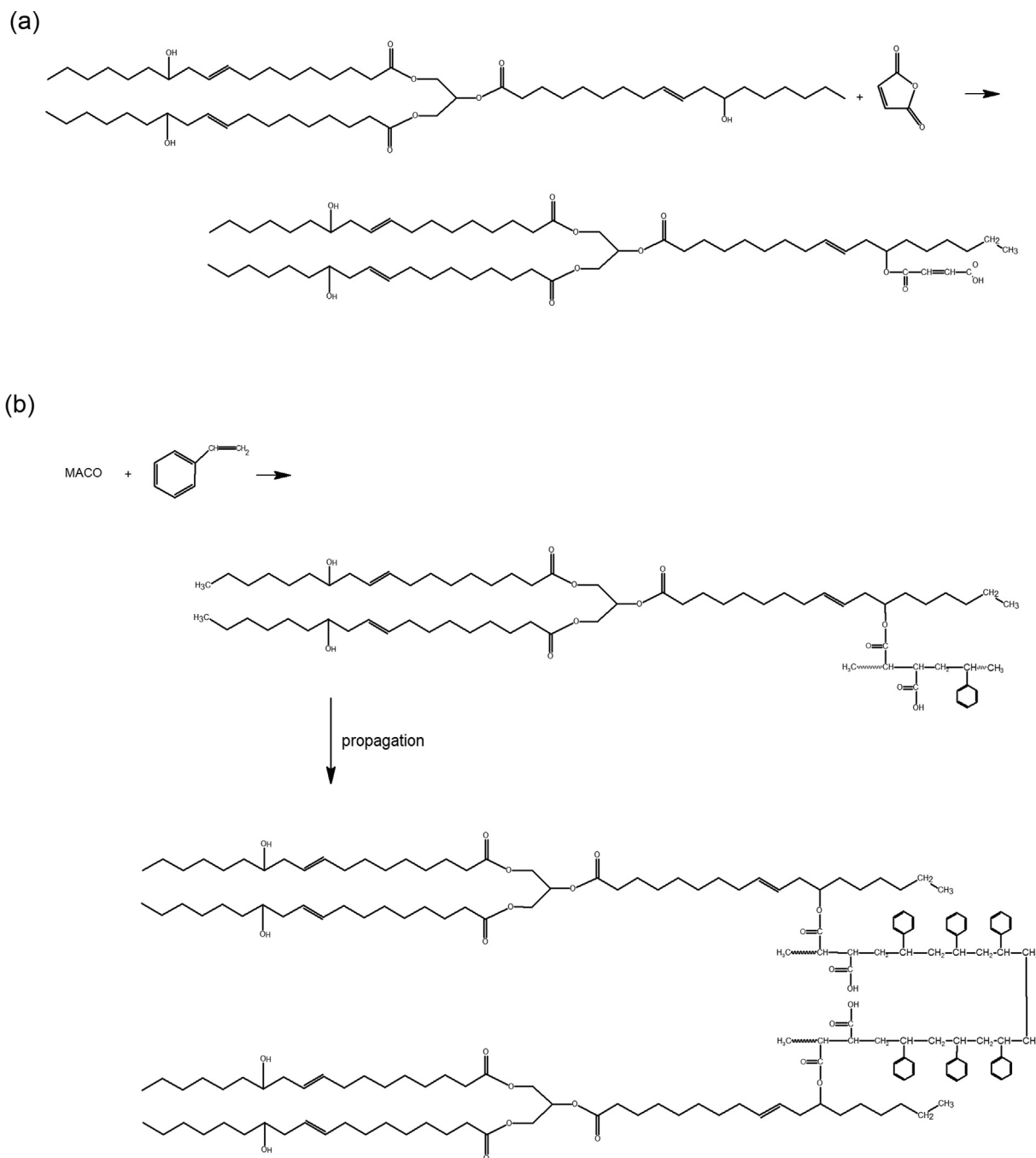
(a)

(b)

Fig. 1. Schematic synthesis routes for the obtention of the MACO (a) and MACO-St copolymer (b).

30 to 500 °C at a heating rate of 10 °C/min. The amount of 20 mg of the samples was used in all experiments. Nitrogen flow was set at 50 mL/min.

3.3. Bottle test

Emulsion systems were prepared in a water/oil ratio of 30:70 (vol %) in total volume sample of 15 mL. Synthetic brine was used as the aqueous phase containing 60 g/L of NaCl for P1 sample and 240 g/L of NaCl for P2 sample, according to oil field information. All tests were performed with aqueous phase at neutral pH, controlled by the addition of NaOH and HCl solutions. All additives were diluted in toluene (1:99 vol%) and injected at different concentrations into oil phase, ranging from 100 to 5,000 ppm. Then, water and oil phases were subjected to shear in a Digital UltraTurrax IKA T-25 homogenizer, at room temperature, as follows: 2 min at 6,000 rpm for P1 sample and 4 min at 12,000 for P2. Those values have been determined by screening formulation tests to guarantee that no water resolution occurs on the first 2 h. For all tests, a similar mean droplet diameter (MDD) of 10 μm (± 1.5 μm) was applied, seeking to evaluate emulsions industrially described as problematic. Droplet diameter evaluation was carried out by using Alltion trinocular LED microscope, coupled with 5MP digital camera and ImageJ software, according to the methodology discussed in previous studies [5,12]. The blank experiments were performed by applying the same operating conditions. From emulsion formulation tests, it was calculated an overall average deviation of 1.5% (v/v). For all these tests, a minimum of three parallels test were performed.
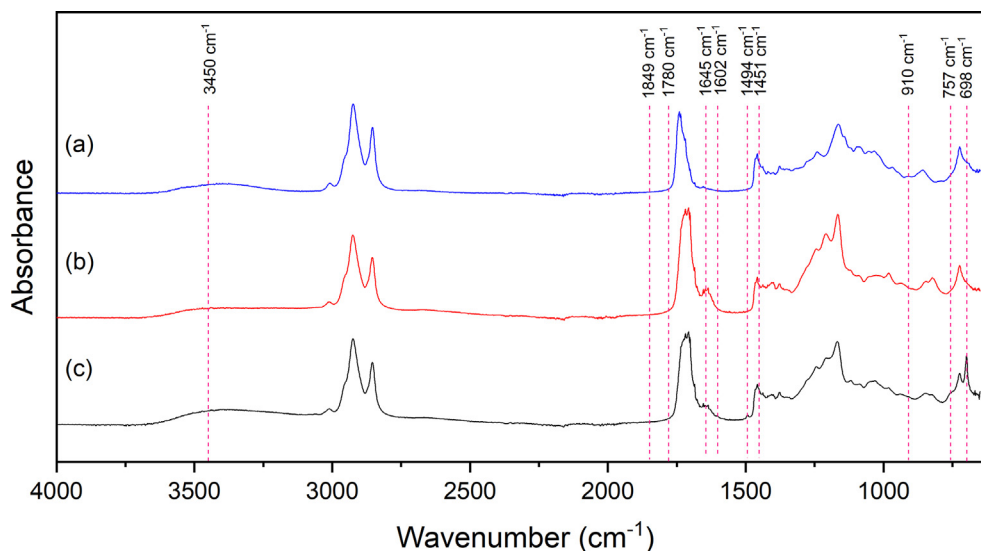
Fig. 2. FTIR spectra of castor oil (a), castor oil maleate (b), and MACO-St copolymer (c).

Gravitational water/oil separation was evaluated by using bottle test [9,37]. Emulsions were placed in graduated ASTM D-91 tubes and maintained in a transparent water bath at 60 °C. The volume of water separated was measured at 5 min intervals in the first half hour of the test, at 10 min in the second half hour, and at 20 min in the last hour, totalizing 2 h test [5]. After water separability, each emulsion was shifted to a falcon tube and centrifuged for 15 min at 5000 rpm, ensuring separation of free water [29]. The results were expressed in terms of separate water percentage (vol%) as a time function (min). Bottle tests were performed for concentrations between 100 and 5000 ppm for all additives tested. However, when a nonactivity demulsifier was observed, a different concentration range was applied. All bottle test has been initiated with a demulsifier concentration of 1000 ppm.

3.4. Interfacial tension measurements

A digital Kruss EasyDine K-20 tensiometer was employed for interfacial tension measurements, by using a Du Noüy ring methodology. This apparatus has a thermostat jacket coupled with a thermostatic bath (Julabo F25-ED) and a Pt-100 temperature sensor, for accurate temperature-controlled measurements, which allows us to take note of standard deviation, temperature, and time. Uncertainties associated with measurements are reported as 0.01 mN/m for interfacial tension and 0.1 °C for temperature. All analyzes were carried out at 60.0 °C and progressed for 2 h, approximate equilibrium time. Organic and aqueous phases used were equal as used in emulsions formulation, with a 20 mL sample. Furthermore, specific concentrations of additives were chosen for interfacial tension evaluation according to the demulsification process of each oil.

For demulsification process, the knowledge of the surfactant kinetic plays an important role in the emulsion breakdown. Ward and Tordai [38] equation is widely used to model adsorption kinetics limited only by diffusion towards an interface. This model explains how the molecules are being diffused and afterwards adsorbed, allowing the calculation of the diffusion coefficients based on the interfacial tension data (IFT). It is assumed there are any interaction between the adsorbed species and the monolayer adsorbed molecules. Thus, two associated mechanisms are addressed in this equation. Firstly, at short time, surfactants are adsorbed on an empty interface. Secondly, after the formation of a monolayer, surfactants reach the interface and return to the bulk [2,39,40]. Ward and Tordai equation in its regular form cannot be solved. Therefore, two asymptotic solutions could be useful for a better

understand of dynamic IFT behavior [41].

For short time approximation, Eq. (1) describes the relationship between solute diffusivity (D) and fresh bulk concentration (c_0), where, n is a constant dependent on the dissociation of the solute (n = 1, for non-ionic surfactants), R is the ideal gas constant, T is the absolute temperature, γ is the interfacial tension of pure solvent, and t is the analysis time.

$$\gamma_{t\to 0} = \gamma_0 - 2nRTc_0\sqrt{Dt/\pi} \tag{1}$$

Already for long time approximation, Eq. (2) should be used for correlate diffusivity (D) and concentration of surfactant in the bulk (c), where, γ_{eq} is the equilibrium interfacial tension and Γ_{eq} is the equilibrium surface excess of surfactant.

$$\gamma_{t\to\infty} = \gamma_{eq} + (nRT\Gamma_{eq}^2/c)\sqrt{Dt/\pi} \tag{2}$$

For both approximations π represents the difference in IFT between a clean and an occupied interface. Depending upon the adsorption isotherm, an equation of state could be used to establish a relationship between the interfacial tension and the amount of the adsorbed surfactant. In this work, Langmuir (Eq. (3)) and Szyszkowski (Eq. (4)) equations have been used, in accordance with literature [40,42,43].

$$\Gamma = \Gamma_\infty\left(\frac{K_L c}{1 + K_L c}\right) \tag{3}$$

$$\pi = \gamma_0 - \gamma = kRT\Gamma_\infty\ln(1 + K_L c) \tag{4}$$

where, Γ_∞ is the surface excess at saturation and K_L is known as the adsorption constant. These two parameters have been adjusted by intermediate of the square root minimization of the quadratic interfacial tension deviation as a function of concentration.

4. Results and discussion

4.1. Characterization of demulsifiers

Chemical synthesis routes for the obtention of castor oil maleate (MACO) and MACO-St copolymers have been shown in Fig. 1. The hydroxyl groups in the castor oil triglycerides reacts with maleic anhydride to produce MACO (Fig. 1a). The MACO-St copolymer was produced through suspension polymerization of styrene with MACO. The reaction of MACO and styrene occurs by free radical polymerization of styrene reacting with the carbon double bonds of the maleate group (Fig. 1b).
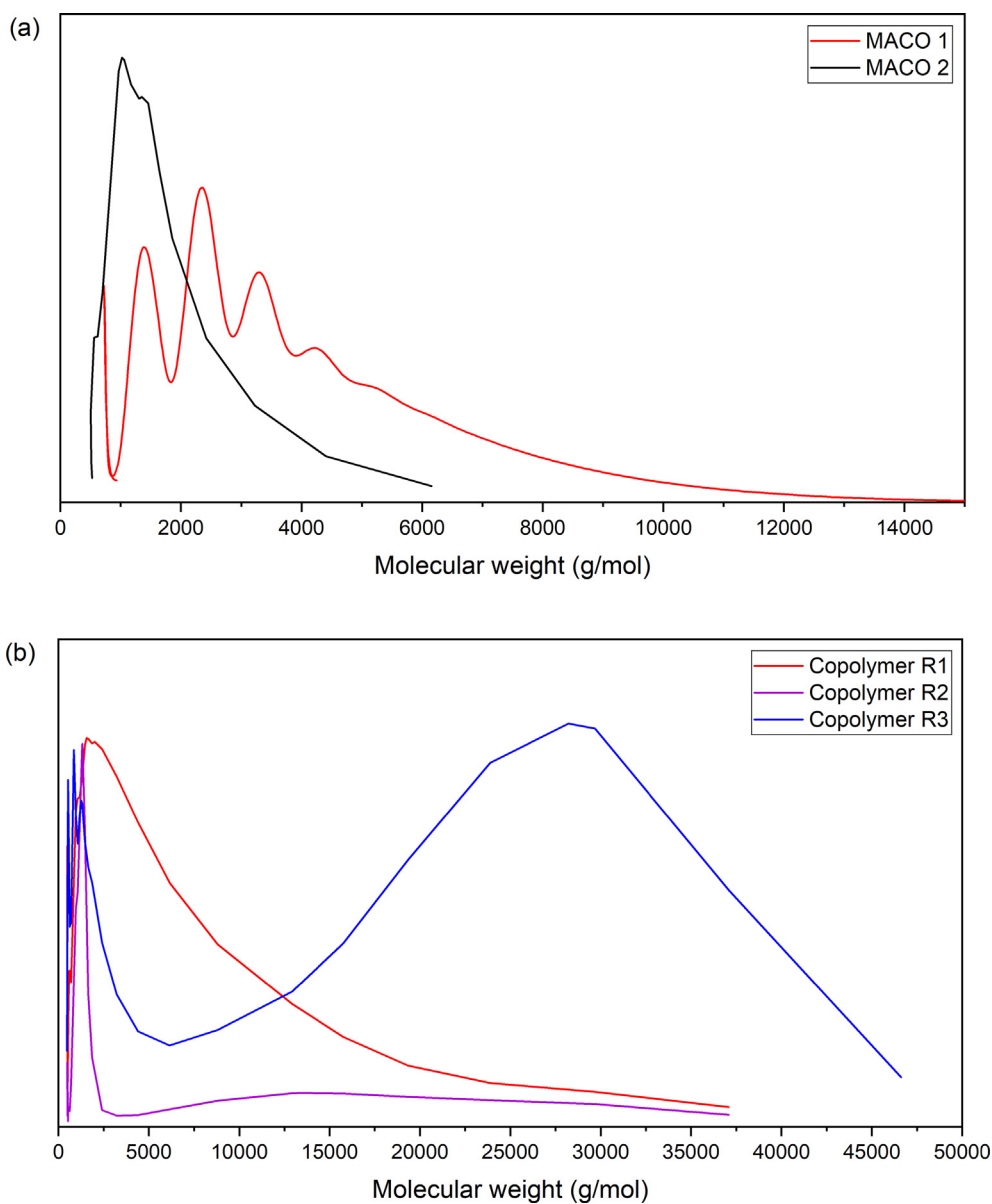
Fig. 3. Chromatographs of castor oil maleates (a) and MACO-St copolymers (b).

Table 2
Number average molecular weight (Mn), weight average molecular weight (Mw) and dispersity (Đ) of the demulsifiers.

Demulsifiers	Mn (g/mol)	Mw (g/mol)	Đ	$T_{5\%}$ (°C)
MACO 1	2255	4665	2.1	233
MACO 2	1439	1928	1.3	240
R1	3465	15,108	4.4	236
R2	11,565	28,817	2.5	244
R3	12,611	26,255	2.1	241

The FTIR spectra of castor oil, castor oil maleate (MACO 1), and MACO-St copolymer (Resin R3) are shown in Fig. 2. Similar FTIR behavior has been found for other components for the same synthetized class. Castor oil maleate was characterized by the band at 3450 cm^{-1}, which represents the hydroxyl groups, and by the band 1645 cm^{-1}, which corresponds to the carbon double bonds, as can be observed in Fig. 2b. The absence of absorption bands of cyclic anhydride (1780 and 1849 cm^{-1}) indicates total consumption of maleic anhydride in the reaction with castor oil.

MACO-St copolymer (Fig. 2c) was characterized by the band at 1643 cm^{-1}, which corresponds to stretching vibrations of carbon-carbon double bonds of both maleate and styrene. The disappearance of this band indicated that the reaction between MACO and styrene occurred [44]. The bands of carbon-carbon vibration of benzene rings appeared at 1602, 1494 and 1451 cm^{-1}. The band at 910 cm^{-1} was attributed to the CH=C−H out of plane bending vibrations of styrene. The bands at 757 and 698 cm^{-1} corresponds to the bending vibrations of monosubstituted benzene. The bands at 698 and 910 cm^{-1} confirmed the presence of benzene group in the chain of the copolymer [33].

Fig. 3 shows the chromatographs of the demulsifiers obtained by Size-Exclusion Chromatography (SEC). The peaks of the resins (R1, R2, and R3) were broader than those of MACO (MACO 1 and MACO 2), as expected for polymers. Average molecular weight number (Mn), average molecular weight (Mw), and dispersity (Đ) of the demulsifiers are presented in Table 2.

The MACOStyrene copolymer was produced through suspension polymerization of styrene with MACO. The reaction initiates with the formation of free radicals from BPO, which reacts with styrene. The
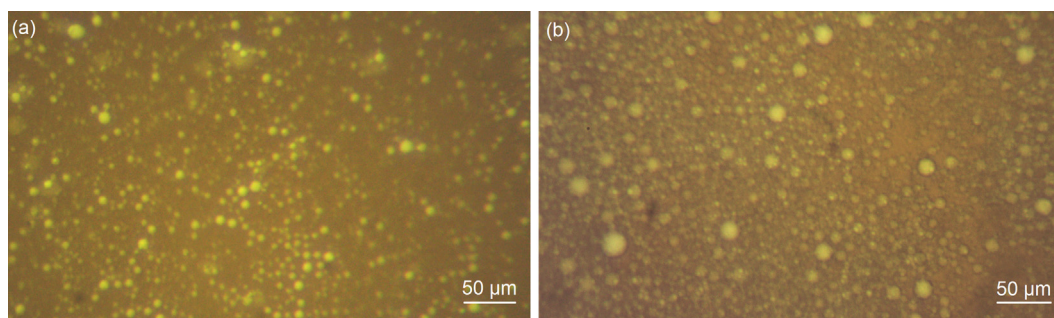
Fig. 4. Water-in-oil emulsions micrograph formulated in a ratio of 30:70 (vol %) with P1 (a) and P2 (b), after 2 h at 60 °C. Total magnification of 180×.
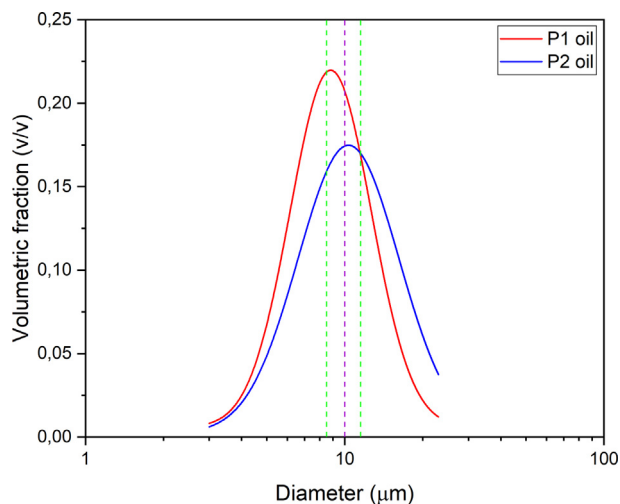

Fig. 5. Droplet size distribution for emulsions prepared with P1 and P2, after 2 h at 60 °C (MDD of 10 μm ± 1.5 μm).

reaction of MACO and styrene occurs by radical styrene reacting with the carbon double bonds of the maleate group. Addition polymerization continues by reactions with styrene or MACO molecules. Crosslinking can occur because MACO monomers may contain more than one anhydride in the molecule and may propagate by two ends increasing its molecular mass. Further information on the reaction mechanism can be found in [36].

The thermal stability of the demulsifiers were determined by Thermogravimetrical Analyses (TGA). All demulsifiers are stable below 230 °C. The decomposition temperatures for 5% weight loss (T_5%) of the materials were observed in the range of 233 and 244 °C (Table 2). All demulsifiers had good thermal stability for the applicability range used in this work, as reported in the literature for castor oil based materials [45].

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

Emulsions micrographs (Fig. 4) show the formation of uniform water droplets with droplet sizes visually similar, such as confirmed on Fig. 5. It could be observed that the emulsions with both oils have a well-defined droplet sphericity. Nevertheless, a better definition of micrograph is clearly observed when P1 oil is used (Fig. 4a), probably because of the translucency of this sample.

Fig. 5 depicts droplet size distribution analysis. The emulsions prepared with the oils P1 and P2 presented a diameter variation in volumetric frequency ranging between 3 and 25 μm. Average diameters based on the volumetric fraction weight were 9.6 ± 1.5 μm for the emulsion prepared with the oil P1 and 10.9 ± 1.5 μm for the emulsion prepared with the oil P2. These values show that emulsions with an average droplet diameter (MDD) similar to that described as

problematic in the field (10 μm) were obtained.

The evaluation of castor oil as a demulsifier was performed and did not present phase separation, thus attesting any demulsifying activity to the molecular modifications carried out in this work. Figs. 6 and 7 show that none of the additives (for all concentration tested in this work) was able to reach 100% water resolution, which was not totally unexpected. It should be remembered that commercial chemical demulsifiers present a complex composition of additives with distinct functions, which is responsible for total water resolution [46]. From these figures, it could be observed that depends on the additive used and its concentration, a different separation behavior was found. A demulsification efficiency comparison among the five demulsifiers tested shows that water resolution increased by increasing demulsifier concentration, except for R2 (Fig. 7d) and R3 (Fig. 7e) used for P2 crude oil. These copolymers are characterized for having a greater molar mass. For this reason, emulsions formed by using them are more stable, reversing the demulsification process. This reversion may have occurred due to the water-oil interface alteration caused by the excess of surfactant [47].

Emulsions formulated with the P2 oil sample presented a better response to the demulsifiers, requiring lower concentrations for water separation (Fig. 7). However, all demulsifiers showed some level of water separation for both oils. In this context, MACO 1 presented better demulsifying activity for W/O emulsions, with maximum water resolution of 90% approximately (Figs. 6a and 7a). For MACO-St copolymers, R1 present similar water resolution observed for MACO 1 in P1 emulsions (Fig. 6c). On the other hand, R3 copolymer presented the worst performance, with a maximum of 11.1% and 44.4% water resolution for the P1 and P2 emulsions, respectively. These results indicate that MACO-St copolymers with high molecular mass have greater difficulty in in reaching the interface and provides a lower performance. Therefore, the relative hydrophilicity of the MACO molecules and the MACO-St copolymers should be balanced to the size of the final molecule. In this way, greater separation efficiency could be achieved.

Moreover, after 2 h tests, all emulsions formulated were centrifugated and analyzed qualitatively, as showed in Figs. 8 and 9. Possible due to transferring process to centrifuge vials, maximum water separation of 3.5 mL was observed. Centrifugation tests reveals demulsifier activity for concentrations that had not observed previously on bottle tests. Therefore, it can be identified that all demulsifiers studied in this works have W/O interface action leading to a emulsion softening, but not enough to obtain a complete coalescence process [48]. Probably the water resolution would occur with longer test periods, but the goal in the oil industry is to achieve a rapid separation. It is interesting to note that water translucid could be an indicative of the absence of oil in the water phase, as shown for P2 emulsions. It is interesting to notice that stains observed in the P1 vails could be associated to incrusted oil.

Table 3 shows a performance comparison among additives produced in this work (MACO 1, R1, and R3), and maleates/copolymers available in literature. Nevertheless, this comparison is a difficult task to be done, specially because of the non-uniformity of crude oils studied
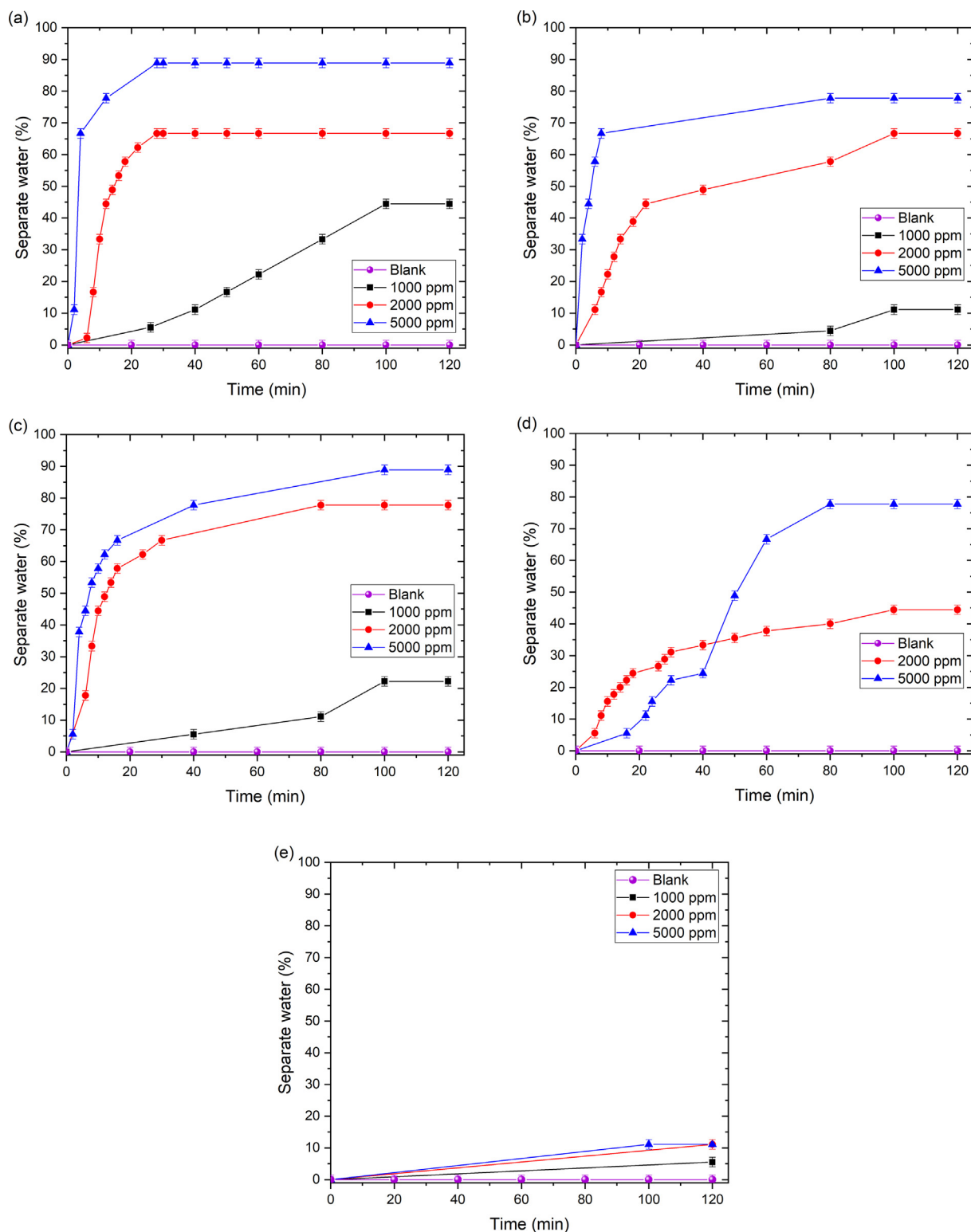
Fig. 6. Water resolution as a time function for emulsions prepared with P1 containing MACO 1 (a), MACO 2 (b), R1 (c), R2 (d), and R3 (e), for the experiments carried out at pH 7 and 60 °C.

worldwide, along with a lack of experimental data for the additives described here. Even though, it is important to compare and to contrast the phenomenological effect of additives on demulsification processes, showing to be valid and necessary. The additives synthetized in this paper could be characterized as a water dropper, i.e., they are responsible for breaking emulsified systems in a relative short time. This behavior could be advantageous, especially for the oil industry. For this

reason, at a glance, it could be erroneously concluded that additives synthetized it this paper could present a minor effect when compared to the literature. Nevertheless, the choice of industrial additive should be represented by a balanced effect on the relationship between the amount used, the required separation time, and the cost and raw material for creating this additive. In this case, components on the basis of the low-cost environmental liabilities, such as castor oil, could be
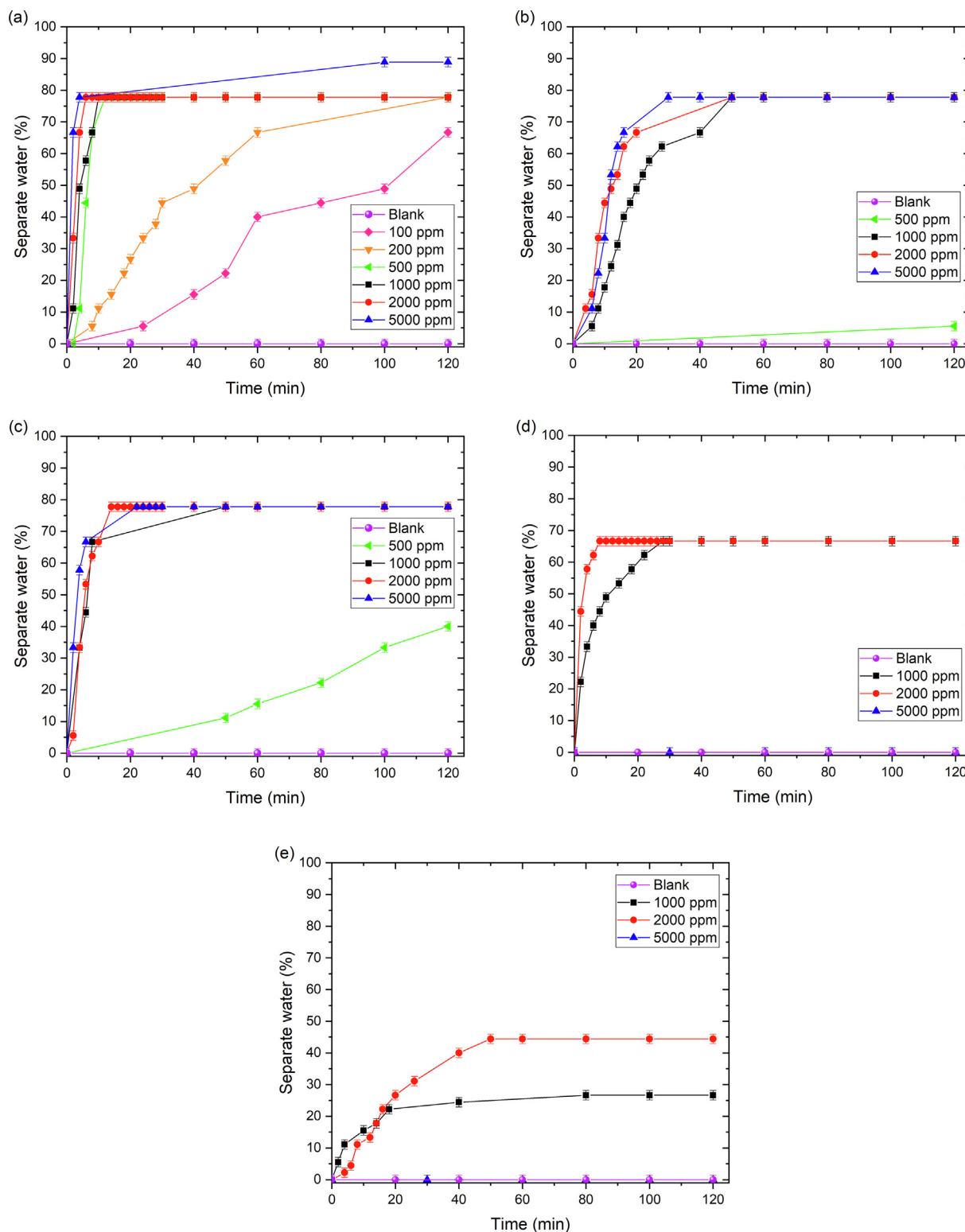
Fig. 7. Water resolution as a time function for emulsions prepared with P2 containing MACO 1 (a), MACO 2 (b), R1 (c), R2 (d), and R3 (e) for the experiments carried out at pH 7 and 60 °C.

promising. Furthermore, it was possible to observe that larger copolymers present lower efficiency when compared to shorter ones, as observed in our results.

4.3. Interfacial activity of additives

IFT equilibrium data of P1 (+ 60 g/L NaCl brine) and P2 (+ 240 g/L NaCl brine) oils are presented in Table 4. The conditions of interfacial tension evaluation were identical to those used for the bottle test, 60 °C for 2 h. Four concentrations of demulsifiers were analyzed for each oil, by using representative values for a better understanding of demulsifier action. Due to the limitation imposed by the equipment and method used, analyzes with low IFT values did not return numerical results. However, the influence of each demulsifier on the interfacial tension
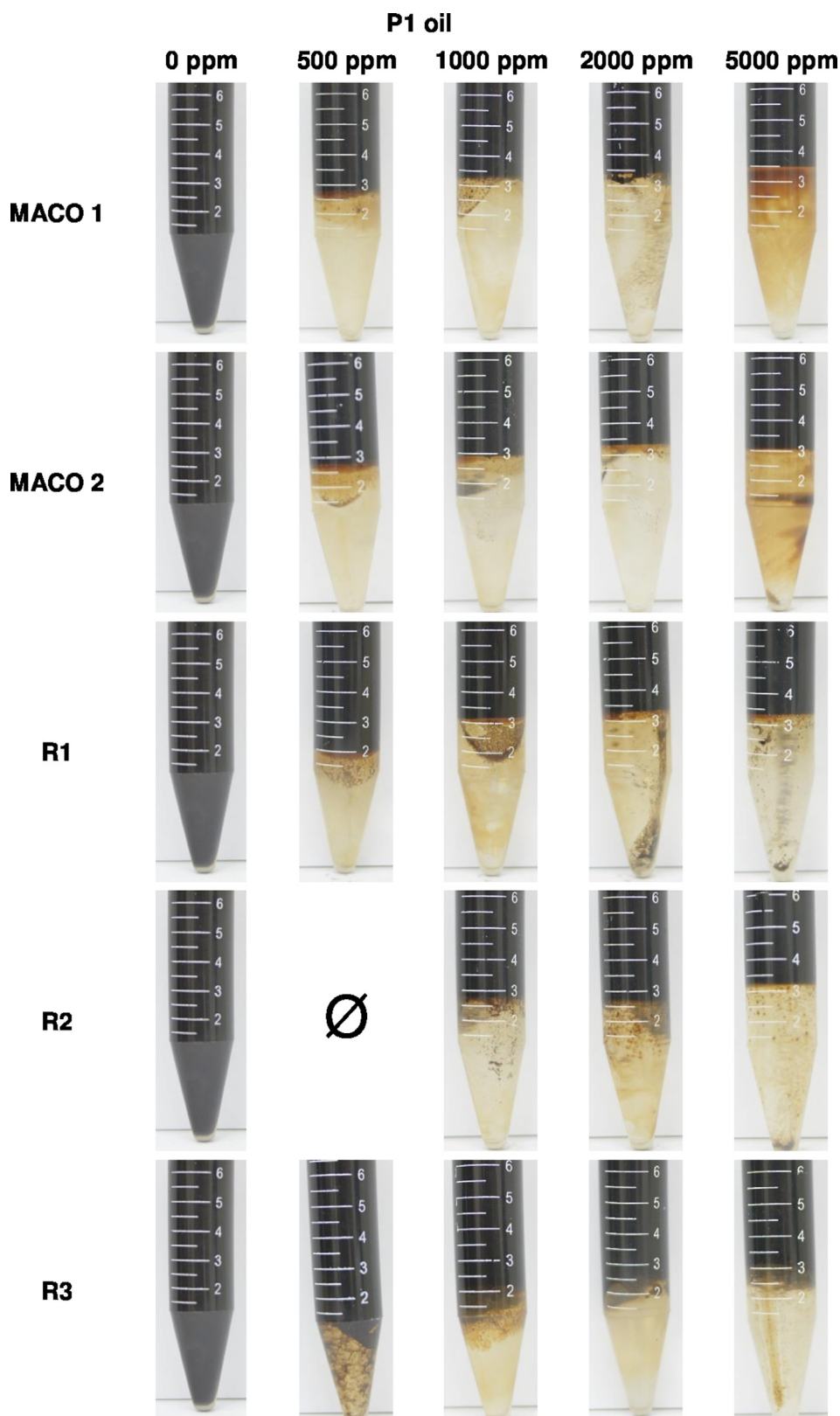
P1 oil

Fig. 8. Demulsification photos for emulsions prepared with P1 after centrifugation for 15 min at 5000 rpm. (Ø – this test was not performed).

can be observed.

IFT measurements were used to describe the ability of MACO and MACO-St copolymers to adsorb at the water-crude oil interface and replace the viscoelastic film, acting as demulsifiers for W/O emulsion [52]. Molecules such as wax crystals, soluble organic acids, and asphaltenes are usually associated with emulsions stabilization [10,11]. In this work, the hypothesis of stabilization by paraffins is discarded due to the working temperature (60 °C) superior to WAT of both oils, in which the wax crystals formation is not expected. The emulsion stability by organic acids is still an unknown subject, because of the acidity
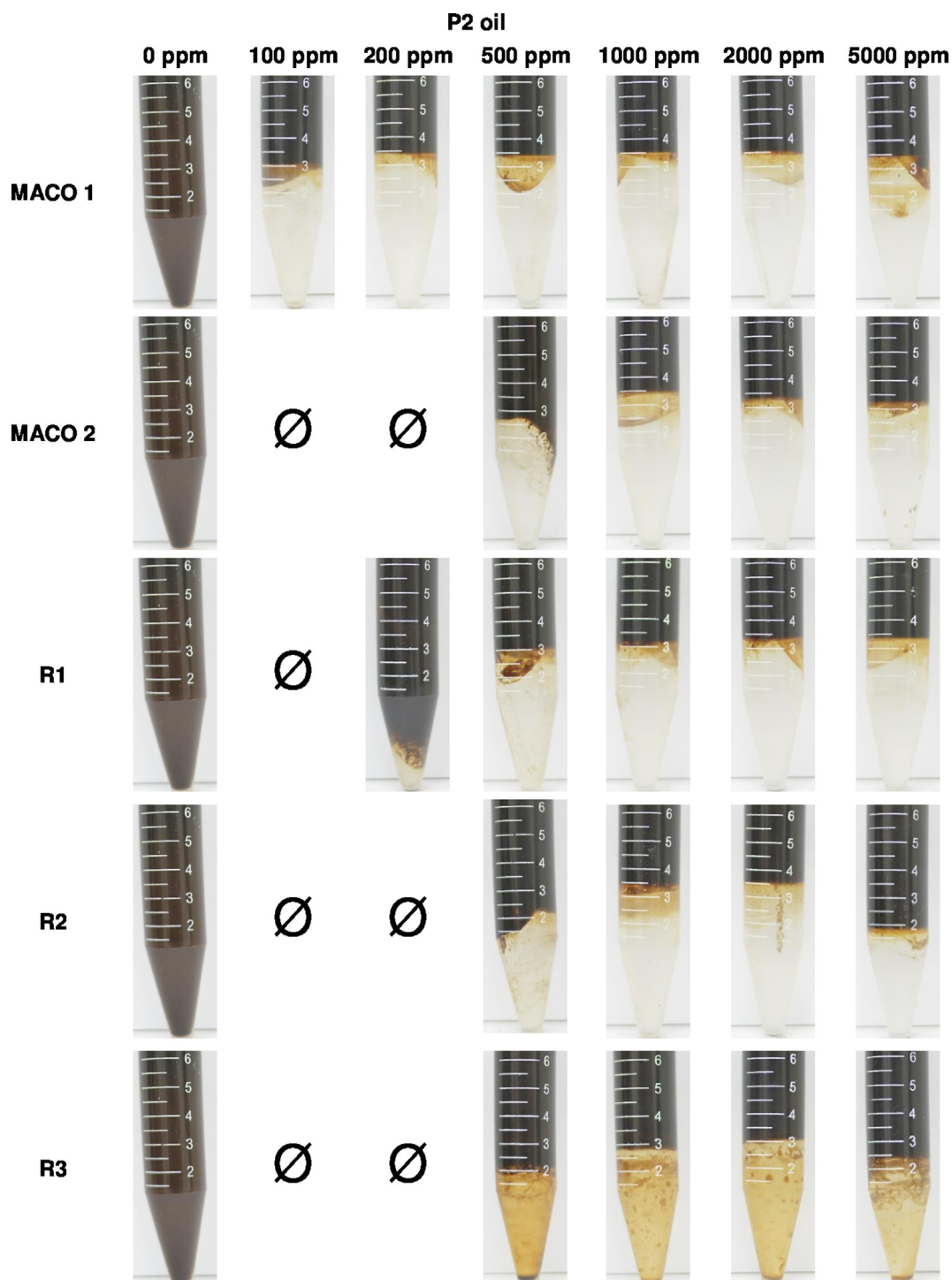
Fig. 9. Demulsification photos for emulsions prepared with P2 after centrifugation for 15 min at 5000 rpm. (Ø – this test was not performed).

of the crude oil by itself is not a sufficient criterion [1,11]. Therefore, asphaltene surfactant activity was assumed to be the cause for the stability of water-in-oil emulsions, as well as described by several studies in the literature [3,6,21,53].

For both crude oils studied in this work, reduce on interfacial tensions were observed by adding synthetized compounds (Table 4). The MACO and MACO-St copolymer classes have dentritic characteristics, that is, molecular branching. This type of structure, in the presence of hydrophilic groups such as hydroxyls, travel through the oil bed to water-oil interface. Then, the hydrophilic groups adsorb at interface, displacing the agglomerated asphaltenes. At the same time, their

ramifications prevent asphaltenes molecules approximation. Adsorption of the demulsifier at interface decreases the interfacial tension over time until equilibrium is achieved. This result could be associate to their superior surface activity when compared to the natural surfactants. For this reason, reduction of interfacial tension is not only the effective parameter in terms of the action of demulsifier but also can be considered as one of the important factors for breaking emulsions [34]. According to the results presented in the bottle test, MACO 1 presented greater reduction in IFT for P1 and P2 emulsions. The increase in demulsifiers concentration favored reduction of interfacial tension in most cases. IFT increment in tests with content of 5000 ppm of R2 and R3 for

Table 3

Performance of demulsifiers related on literature and this work. Description of test conditions: concentration, demulsifier efficiency (DE), time for maximum water separation, temperature, and water cut.

Compound	Concentration (ppm)	DE (%)	Time (min)	Temperature (°C)	Water Cut (%)
OM [49]	200	100	160	60	30
MACO 1 [this study]	200	78	120	60	30
PEG400-PPG1-PEG400 [50]	500	100	120	60	30
PEG3000-PPG2-PEG3000 [50]	500	46	300	60	30
D1 [51]	100	73	150	60	30
D4 [51]	100	53	300	60	30
R1 [this study]	1000	78	50	60	30
R3 [this study]	1000	27	80	60	30

OM – Oleic acid maleate; MACO 1 – Castor oil maleate Mw = 4665 g/mol; PEG400-PPG1-PEG400 – Poly(ethylene oxide)-Block-Poly(propylene oxide)-Block-Poly (ethylene oxide) copolymer Mw = 1440 g/mol; PEG3000-PPG2-PEG3000 – Poly(ethylene oxide)-Block-Poly(propylene oxide)-Block-Poly(ethylene oxide) copolymer Mw = 9230 g/mol; D1 – Styrene/Maleic anhydride ester copolymers Mw = 2500 g/mol; D4 – Styrene/Maleic anhydride ester copolymers Mw = 8000 g/mol; R1 – Castor oil maleate/Styrene copolymer Mw = 15108 g/mol; R3 – Castor oil maleate/Styrene copolymer Mw = 26255 g/mol.

Table 4

IFT equilibrium data (IFT_{eq}) for P1 and P2 emulsions with different concentrations of additives, at 60 °C, and 2 h test. (NNR – This test not return a numerical result).

Additives concentration (ppm)	IFT_{eq} (mN m^{-1})				
	MACO 1	MACO 2	R1	R2	R3
P1 oil					
0	13.9	13.9	13.9	13.9	13.9
500	9.1	12.0	12.5	13.7	13.1
1000	8.1	11.9	11.1	12.0	11.6
2000	5.1	10.0	8.6	10.3	11.1
5000	3.0	6.5	5.7	7.3	10.5
P2 oil					
0	17.6	17.6	17.6	17.6	17.6
100	15.5	16.4	16.1	16.0	16.0
500	9.6	12.8	11.4	13.4	14.6
1000	5.1	9.1	8.4	10.5	12.2
5000	NNR	NNR	NNR	14.0	13.3

the oil P2, proved the inversion of copolymers action in these conditions. At this point, the additives may have stopped replacing the asphaltenes film and begun to agglomerate at interface stabilizing the emulsions. In addition, even the tests that did not return numerical results validated argument of excessive tension reduction by demulsifiers action.

Diffusion coefficient could be useful to better understand process related with demulsifiers transferring to water-oil interface. Ward and Tordai equation was used to determine demulsifiers diffusion coefficients according to asymptotic approximation [41]. In this work, demulsifiers concentrations used did not allow the short-time approximation application.

Table 5 shows values for diffusion coefficient calculated using long-time approximation. These values are less than D ~10^{-15} which leads to the conclusion that the adsorption process of all demulsifiers are no longer diffusion-controlled at long times [2,42]. This behavior may be related to the condition of the monolayer occupation model of the interface. For long periods of time, this interfacial occupation is partially complete. For this reason, demulsifier transfer to interface is probably more dependent on the rate of exchanging naturally interfacial active compounds and demulsifiers.

In addition, it can be observed that MACO compounds have the highest values of diffusion coefficients. The most polydisperse compound of this class (MACO 1) has high diffusion coefficient and demulsifier performance, as discussed previously. Although, MACO-St compounds present lowest values of diffusion coefficient, attributed to the higher value of molar mass, revealing an inversely proportion between diffusivity and molar mass.

Additionally, Table 5 shows that increasing concentration of demulsifiers reduces diffusion coefficient for all cases. This behavior could be associated with the greater availability of additives and consequently occupation of the interface in the first few instants of the test.

Finally, in this paper a new class of additives is proposed to act as a demulsifier from an environmental liability (castor oil), increasing its aggregate value by using it in an industrial application. Regarding the demulsifying activity of the MACO and MACO-St copolymer classes, it will be possible to evaluate how different structural modification on these molecules could better be used to reduce the amount needed for different oil samples, with different chemical composition. In this scenario, the production of MACO and MACO-St copolymer in an industrial plant are feasible, since a single reactor is needed to produce both, and no purification step is required. A batch of MACO can be produced in 3 h and further production of the copolymer can be achieved in 5 h. The same free radical catalyst can be used to product both and the operating conditions are similar [35,36]. MACO, which gave better results in demulsifying crude oil is produced by low cost

Table 5

Diffusion coefficient for demulsifiers at different concentrations using long-term approximation of the Ward-Tordai equation (D_{LT}). (NNR – No numerical result).

Additives concentration (ppm)	D_{LT} (m^2 s^{-1})				
	MACO 1	MACO 2	R1	R2	R3
P1 oil					
500	1.60×10^{-15}	1.50×10^{-15}	1.50×10^{-17}	1.40×10^{-21}	8.03×10^{-21}
1000	7.86×10^{-16}	6.26×10^{-16}	6.68×10^{-18}	1.07×10^{-21}	1.03×10^{-21}
2000	1.87×10^{-16}	1.09×10^{-16}	2.37×10^{-18}	2.41×10^{-22}	3.40×10^{-22}
5000	1.22×10^{-17}	2.08×10^{-17}	9.99×10^{-19}	1.11×10^{-22}	1.93×10^{-22}
P2 oil					
100	8.99×10^{-19}	1.31×10^{-18}	3.65×10^{-19}	7.44×10^{-21}	3.98×10^{-21}
500	5.86×10^{-19}	3.52×10^{-19}	4.95×10^{-20}	2.53×10^{-21}	1.79×10^{-21}
1000	2.34×10^{-19}	1.77×10^{-19}	1.60×10^{-20}	6.13×10^{-22}	4.74×10^{-22}
5000	NNR	NNR	NNR	5.44×10^{-22}	4.37×10^{-22}

materials (castor oil and maleic anhydride) at mild industrial operating conditions. Based on the raw materials, MACO would be produced for slight over US$ 1300.00/ton, while conventional demulsifier may cost between US$ 2000.00 and 3500.00/ton.

5. Conclusion

Five demulsifier additives obtained from castor oil have been synthetized in this work, as follows: two castor oil maleates (MACO 1 and MACO 2) and three castor oil maleate-styrene copolymers (R1, R2, and R3). All these synthetized compounds present some demulsifying activity. Nevertheless, MACO 1 presents the best results, with a maximum water resolution of approximately 90%. Showing that some effort should be done in order to obtain biodegradable demulsifiers with higher water resolution. From Interfacial Tension (IFT), the adsorption of demulsifiers at interface decreased the interfacial tension, except for 5000 ppm R2 and R3 additive content for P2 oil. These results could be attributed to an inversion of demulsifier action these copolymers, regarding their high molecular weight. Additionally, diffusion coefficient results corroborated both IFT and bottle test results. Emulsion breakdown is strongly dependent on the adsorption process at interface, i.e., higher interfacial diffusivity was directly associated with better demulsifier performance and the structure of demulsifiers plays an important role in a compromise solution between molar mass and interfacial activity.

CRediT authorship contribution statement

Raissa S. Alves: Methodology, Formal analysis, Validation, Investigation, Writing - original draft. **Dayanne L.H. Maia:** Methodology, Investigation, Writing - original draft. **Fabiano A.N. Fernandes:** Conceptualization, Writing - review & editing, Supervision. **Filipe X. Feitosa:** Conceptualization, Writing - original draft. **Hosiberto B. de Sant'Ana:** Conceptualization, Supervision, Funding acquisition, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fuel.2020.117429.

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